Journal of Colloid and Interface Science 344 (2010) 343–347

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Direct observation on the Brownian coagulation of PSL particles through optical microscope in the regime near critical coagulation concentration (CCC)

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ARTICLE INFO

Article history:
Received 29 October 2009
Accepted 30 December 2009
Available online 11 January 2010

Keywords:
Brownian coagulation
Floc structure
Restructuring
Critical coagulation concentration
Coagulation rate
Polystyrene latex

ABSTRACT

Microscopic monitoring of floc structure, floc size distribution and the rate of coagulation was carried out for Brownian coagulation of PSL particles. Experiments were designed for the condition of salt concentration that is slightly below critical coagulation concentration (CCC). The density of the solvent was controlled by using deuterium oxide (D_2O) to avoid sedimentation. Results are summarized as follows: (i) Near CCC, floc restructuring from the beginning stage of coagulation was evidenced, i.e., the ratio of linear triplet is found to be remarkably reduced as compared with the result obtained for the case of rapid coagulation which was implemented under sufficiently high salt concentration. (ii) The increase of fractal dimension from 1.8 in the case of rapid coagulation to 2.2 was confirmed by the analysis of mass balance using size distribution of flocs. This increment resulted in the decrease of effective excluded volume of flocs. (iii) The rate of coagulation was constant until later stage. This result contrasts to the result of rapid coagulation [T. Fukasawa, Y. Adachi, J. Colloid Interface Sci. 304 (2006) 115].

1. Introduction

In the previous study, we proposed a modification of Smoluchowski rate equation of Brownian coagulation taking into account the effect of excluded volume of formed flocs with fractal structure [1]. The validity of the modified equation was tested by the rapid coagulation of polystyrene latex particles (PSL) with simple salt. The rate of coagulation was carefully measured by means of the direct counting of flocs or single particles through an optical microscope. The obtained data demonstrated the increment of the rate of coagulation in the later stage. This increment was successfully explained by the modified equation. Additional data obtained for different diameter of initial particles also confirmed the validity of modified equation, which is expressed as functions of fractal dimension, the diameter of flocs and the diameter of initial particles [2].

Although the condition of rapid Brownian coagulation realizes an ideal situation of the diffusion limited aggregation (DLA) which is characterized the formation of bulky flocs; every collision between two colloidal particles or flocs resulted in the formation of a new floc, two colloidal flocs are being fixed each other at their first point of meet, it is not always the case in practice in many engineering application or natural environments [3–6]. In this sense, it is necessary to extend the region of analysis to the regime of reaction limited coagulation [7–9] or the system controlled by hydrodynamic motion [10–13]. In both cases, restructuring of flocs can be considered to take place frequently, due to the decrease of bond strength by the effect of electrical double layers or the increase of internal stress at the point of cluster-to-cluster contact generated by the hydrodynamic forces exerted on the floc. Although the significance of such process was pointed out in our earlier studies [14,4], the onset mechanism of restructuring and its effect on the kinetics of coagulation has not been analyzed yet. In the present study, we focus our attention to the crossover from the regime of rapid coagulation to that of reaction limited coagulation where the restructuring can be expected due to the emergence of electrostatic repulsion.

Sandkühler et al. pointed out the importance of gravitational settling and internal cluster dynamics in the process of slow coagulation [15]. Since the magnitude of gravitational force exerted on the floc will increase with the growth of floc, the restructuring becomes significant in large floc. However, the information on the onset of restructuring, i.e., at which stage of coagulation and the way of restructuring taking place are still unclear. This situation avoids the quantitative analysis of the effect of restructuring floc on the kinetics of coagulation.

In the section of experiment, we examined the onset of restructuring of flocs based on the careful observation of the resulted floc structure under the condition of near critical coagulation concentration and that of rapid coagulation. The comparison of structure of flocs which are formed under the salt condition of rapid coagulation clearly demonstrates the onset of restructuring at beginning stage of coagulation. Additional measurement of floc

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doi:10.1016/j.jcis.2009.12.066

size distribution for the coagulated dispersion with restructured flocs revealed the remarkable reduction of excluded volume from that of rapid coagulation. The increment of the rate of coagulation in the later stage of coagulation which was obviously detected for the case of rapid coagulation was not critically detected in the case of slow coagulation. That is, the rate of coagulation in the regime of near critical coagulation concentration was kept constant throughout the period of measurement. In this respect, the effect of excluded volume on the rate of coagulation in the later stage is expected to be less than that of rapid coagulation.

2. Structure of a flocs and kinetics of Brownian coagulation

2.1. Evaluation of floc structure and restructuring

The structure of flocs has been characterized in the scheme of fractal geometry using the following relations.

$$i = k\left(\frac{d_f}{d_0}\right)^D \tag{1}$$

where i is the number of particles contained in a floc of diameter d_f. The diameter of the primary particles is d_0, k is a dimensionless proportionality constant (the value of k depends on the definition of d_f used [16]) and D is the fractal dimension.

The fractal dimension, D, of flocs was determined by the method of mass balance using their size distribution and the number concentration of flocs [17]. If we suppose that all flocs have the same fractal dimension, the value of D can be obtained by solving the following equation of mass conservation:

$$N(0) = \sum_{i=1}^{N} k\left(\frac{d_{fi}}{d_0}\right)^D \tag{2}$$

where $N(0)$ and N denote the number of primary particles and flocs in the specific volume, respectively. In this study, we used $k = 0.78$ obtained in the previous study [2].

The value of D can be used as an index of degree of densification of large flocs, however it is not sufficient to evaluate the restructuring of small flocs which are formed in the early stage of coagulation. For the evaluation of floc structure especially for $i \leqslant 5$, we adopted the concept of unbranched chain formation, which is quantified by p_i the ratio of the unbranched flocs (flocs without any branch as depicted in Fig. 1).

$$p_i = \frac{n_{u,i}}{n_i} \tag{3}$$

where $n_{u,i}$ and n_i are the number of unbranched flocs and the total number of flocs, respectively. The concept of unbranched chain was introduced by Sutherland for theoretical description of the geometrical structure of flocs [18]. The validity was confirmed in their computer simulation and also our result of table-tennis-ball simulation of one-point-contact model [4]. Recently, Adachi and Aoki used this index to evaluate floc restructuring which is induced by the application of polyelectrolyte flocculants [19].

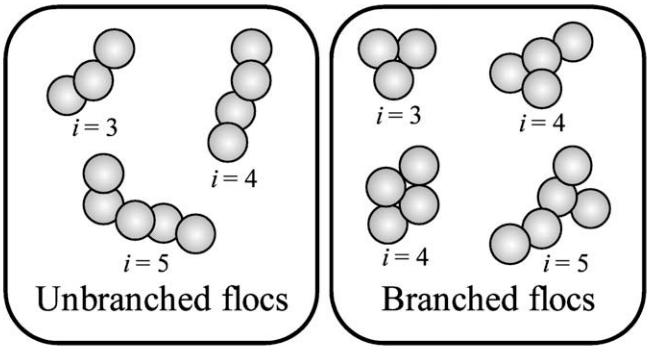

Fig. 1. Samples of unbranched and branched flocs.

2.2. The rate of Brownian coagulation taking into account the effect of floc structure

The framework for the mathematical theory on the kinetics of coagulation was worked out by von Smoluchowski [20] taking a population balance of the size distribution of coagulating flocs,

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} K_{ij} n_i n_j - n_k \sum_{j=1}^{\infty} K_{kj} n_j \tag{4}$$

where n_i is the concentration of i-fold flocs (flocs composed of i primary particles). K_{ij} is the coagulation rate constant and can be expressed by the following equation,

$$K_{ij} = \alpha_B \beta_{ij} W^{-1} \tag{5}$$

where α_B is the coagulation coefficient [21–24], β_{ij} is the coagulation kernel determined by the collision mechanism between i-fold flocs and j-fold flocs. W is the stability ratio describing the ratio of the rate of rapid (collision limited) coagulation to that of reaction limited coagulation [25,7,26]. In this paper, we restrict our attention to the restructuring of flocs and the effect of excluded volume. Therefore, the values of W for each sample are experimentally determined from the measurement of the early stage.

In our previous investigation, we proposed an expression for the temporal evolution of the concentration of flocs due to Brownian coagulation taking into account growth effect of floc structure [1]. The effect of structure formation is expressed as a decrease of free volume in accordance with the progress of coagulation. Due to this, the number concentration of flocs is increased substantially as

$$n \rightarrow n \times \left(\frac{1}{1 - V_e}\right) \tag{6}$$

where V_e is the excluded volume of flocs. Therefore, Smoluchowski theory is modified as follows:

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} K_{ij} n_i n_j \left(\frac{1}{1 - V_e}\right)^2 - n_k \sum_{j=1}^{\infty} K_{kj} n_j \left(\frac{1}{1 - V_e}\right)^2 \tag{7}$$

This means the rate of coagulation will increase with an increase of V_e. The value of V_e can be obtained by the sam of floc volume characterized by size distribution and fractal dimension. That is

$$V_e = \sum_{j=1}^{N} \frac{\pi}{6} d_{fj}^3 = \sum_{j=1}^{N} \frac{\pi}{6}\left(d_0\left(\frac{i_j}{k}\right)^{1/D}\right)^3 \tag{8}$$

Meakin and Jullien reported the increase of fractal dimension in the regime of reaction limited coagulation due to the restructuring using three-dimensional off-lattice models [27]. The increase of fractal dimension means the floc has compact structure; the effect of excluded volume is expected to decrease in the regime of reaction limited coagulation. In order to verify this prediction, we need the simultaneous measurement of the rate of coagulation, the structure of flocs and their size distribution. For this purpose, following experiments were designed.

3. Experiments

In our previous studies, we carried out the direct observation through optical microscope to analyze the effect of floc structure