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

Tomonori Fukasawa, Yasuhisa Adachi *

Graduate School of Life and Environmental Sciences, University of Tsukuba, Tennoudai 1-1-1, Tsukuba-shi, Ibaraki 305-8572, Japan

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 [Fukasawa and Adachi, J. Colloid Interface Sci. 304 (2006) 115].

Preprint submitted to Elsevier Science *28 October 2009*

Key words: Brownian coagulation, Floc structure, Restructuring, Critical coagulation concentration, Coagulation rate, Polystyrene latex

* Corresponding author.
Email address: yas@sakura.cc.tsukuba.ac.jp (Yasuhisa Adachi).

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 slow 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 slow 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 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]. That is, 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 $i \leq 5$, 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). That is,

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

where $n_{\mathrm{u},i}$ 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].

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 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,

$$K_{ij} = \alpha_{\mathrm{B}} \beta_{ij} W^{-1} \tag{5}$$

where α_{B} is the coagulation coefficient, β_{ij} is the coagulation kernel determined by the collision mechanism between i-fold flocs and j-fold flocs. W is called stability ratio describing the ratio of the rate of rapid (collision limited) coagulation to that of slow coagulation.

When collisions are induced by Brownian motion of colloidal particles, β_{ij} is derived by the evaluation of diffusion flux of particles to the reference particle. The derived expression for β_{ij} is,

$$\begin{aligned}\beta_{ij} &= 4\pi(R_{\mathrm{c},i} + R_{\mathrm{c},j})\left(\frac{k_{\mathrm{B}}T}{6\pi\mu R_{\mathrm{h},i}} + \frac{k_{\mathrm{B}}T}{6\pi\mu R_{\mathrm{h},j}}\right) \\ &= \frac{2k_B T}{3\mu}(R_{\mathrm{c},i} + R_{\mathrm{c},j})\left(\frac{1}{R_{\mathrm{h},i}} + \frac{1}{R_{\mathrm{h},j}}\right). \end{aligned} \tag{6}$$

k_{B} is the Boltzmann constant, T is the absolute temperature, μ is the viscosity of the solvent, $R_{\mathrm{c},i}$ is the collision radius of i-fold floc and $R_{\mathrm{h},i}$ is its hydrodynamic radius.

The coagulation coefficient, $\alpha_{\rm B}$, is empirically introduced to fit theoretical prediction by Smoluchowski to experimental data of rapid coagulation. The value of this coefficient was explained by taking into account the hydrodynamic interaction between colloidal particles [21,22]. However, there are some cases this correction is not valid [23,24]. In the present study, we use the value which is determined in the measurement of previous investigation.

The stability ratio, W, is introduced to describe the ratio of rate of rapid coagulation to that of slow coagulation. The prediction of W is the classical problem of colloidal dispersion. Fucks introduced the concept to the collision between two colloidal particles by the analogy of the rate theory of chemical reaction involving the DLVO theory [25]. Many experimental results qualitatively confirmed the validity of this prediction [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

$$n \longrightarrow n \times \left(\frac{1}{1-V_e}\right). \tag{7}$$

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

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} n_i n_j \left(\frac{1}{1 - V_e} \right)^2 - n_k \sum_{j=1}^{\infty} K_{kj} n_j \left(\frac{1}{1 - V_e} \right)^2 . \tag{8}$$

This means the rtes 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

$$V_e = \sum_{j=1}^{N} \frac{\pi}{6} d_{fj}^3 = \sum_{j=1}^{N} \frac{\pi}{6} \left(d_0 \left(\frac{i_j}{k} \right)^{1/D} \right)^3 . \tag{9}$$

Meakin and Jullien reported the increase of fractal dimension in the regime of slow coagulation due to the restructuring using three-dimensional off-lattice models [27]. The increase of fractal dimension means the floc has compact structure. That is, the effect of excluded volume is expected to decrease in the regime of slow 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 on the kinetics of Brownian coagulation. We observed and counted the number of flocs together with their size one by one in the frame of video tape recorded in each elapsed time of coagulation. Although this method is time consuming, this is the only way to obtain the reliable data of absolute number concentration of flocs with extremely fragile and irregular structure.

In the present study, we extended the region of analysis from that of the rapid coagulation to the region where the salt concentration corresponds to slightly below the critical coagulation concentration. In the case of rapid coagulation, we can realize the condition which is free from gravitational sedimentation by simply adjusting the concentration of electrolyte to that of latex particles. However, we need to apply D_2O for the analysis near CCC for density matching.

3.1 Materials

Monodispersed polystyrene latex (PSL) particles with a diameter of 1.6μm purchased from Interfacial Dynamic Corporation were used in the coagulation experiment. The number concentration of PSL particles was adjusted to 3.0 $\times$ 10^8 cm^{-3}. PSL dispersions were coagulated in KCl solution.

Fig.2 provides a plot of stability ratio against KCl concentration for this PSL dispersions. On the basis of this result, two different KCl concentrations, i. e., 1.12 M and 0.112M were chosen as a representative concentration. The concentration of former corresponds to the region of rapid coagulation; the rate of coagulation is plateau maximum. Coagulation is limited by the collision. Hereinafter, we term this regime as rapid coagulation. The latter corresponds to the point which is slightly below CCC and has characteristics of slow coagulation. The rate of coagulation is declined by the presence of electrostatic repulsion. Hereinafter, we term this regime as slow coagulation in this paper.

To avoid problem of differential sedimentation, we controlled the density of the solvent by using deuterium oxide (D_2O). In order to check whether or not the addition of D_2O have an influence upon surface property of PSL, we measured electrophoretic mobility of PSL particles which were dispersed in KCl solution or mixed solution (KCl solution and D_2O). The results of electrophoretic mobility are compared in Fig. 3. In this figure, electrophoretic mobility is corrected by the relative viscosity of solvent which measured by capillary viscometer. As indicated in the figure, a reasonably good agreements was confirmed implying that the addition of D_2O does not affect surface property of PSL.

3.2 Procedure

A certain volume of PSL suspension was mixed with an equal volume of KCl solution in a flask. The dispersion was sucked up gently into the square microslide with inside pass length of 500 μm and left to stand to induce coagulation by Brownian motion on the stage of a microscope mounted with a CCD camera. Monitoring of the progress of coagulation was simply done by microscopic observation. After certain period of time, predetermined volume of suspension was scanned to capture images of suspending flocs. The scanned data were recorded on videotape. All experiments were conducted in an air-conditioned room with temperature of 20 ℃.

The recorded data was used for the analysis of structure, the size distribution and number concentration of flocs. The length of major axis of the best-fit ellipse of respective floc was adopted as d_f obtained from the image analysis using the software of Scion Image. The number of flocs in a specific volume was also counted through the microscope to obtain the number concentration of flocs. In addition, the value of p_i was determined by the direct observation. Flocs with i ranging from $i = 3$ to $i = 5$ were arbitrarily chosen.

4 Results and discussion

Typical snapshots of the state of coagulation for slow and rapid coagulation are shown in Fig.4. As can be seen easily, flocs which are formed under the condition of slow coagulation (a,b) have more compact structure than those of rapid coagulation (c,d).

The evidence of restructuring for the slow coagulation can be confirmed also for the structure of small flocs. In Fig.5, the obtained values of p_i for rapid and slow coagulation are plotted for floc up to $i = 5$. The ratio of unbranched flocs which were formed under the condition of slow coagulation was found to be remarkably reduced as compared with that of rapid coagulation. In the slow coagulation, the unbranched floc was not detected for $i \geq 5$. These results were clear evidences that the floc restructuring started already at the beginning stage of coagulation in the regime of slow coagulation. That is, the lateral slipping or rolling motion can be induced by Brownian motion instead of rigid fixation at the point of first contact.

Cumulative size distributions of flocs for the slow coagulation (120min after the onset coagulation) and the rapid coagulation (60min) were plotted in Fig.6. The progress degrees of coagulation in these two samples are almost same, in other words, the values of $N(t)$ are close each other. The values of fractal dimension, D, are calculated using Eq.(2) based on results of size distributions of flocs. The value of D for the state of slow coagulation($D = 2.17$) was higher than that for rapid coagulation($D = 1.78$). This means that the flocs formed under the condition of slow coagulation have compact structures as compared to those formed under rapid coagulation. The obtained values of D for each rapid and slow coagulation are in agreement with previous results reported by means of light scattering [28].

In Fig.7, measured values of $1/N(t)$ are plotted against t. Solid and dashed lines are drawn numerically based on Eqs.(8) and (4), respectively. The values of $\alpha_{\rm B}$ and W for each sample are experimentally determined from the slope of measured values at the early stage of coagulation where the effect of excluded volume are negligibly small. In the regime of rapid coagulation (KCl = 1.12M), the slope of measured values i.e., the rate of coagulation was gradually increased according as the progress of coagulation. This result is consistent with the result we reported previously. On the other hand, in the regime of slow coagulation (KCl = 0.112M), the rate of coagulation was constant until later stage. The increment of coagulation rate coincided with the prediction reflecting the increment of excluded volume of formed flocs. As indicated in the figure, each predictions on the basis of Eq.(8) by using the obtained fractal dimensions agreed each other with the experimental results. This agreement between the predictions based on the equation taking into account the effect of excluded volume and experimental results also verifies the validity of the proposed theory and the adequacy of the method for estimation of excluded volume.

5 Conclusions

Careful and direct observations of floc structure, floc size distribution and the number of flocs subjected to Brownian coagulation were performed under optical microscope. Observations were focused on the formed structure of flocs and their effects on the rate of coagulation near the crossover region from rapid coagulation to slow coagulation. From the result obtained for slow coagulation, it was confirmed that restructuring of flocs is induced by Brownian motion at early stage of coagulation. Additionally, the obtained rate of coagulation in the regime of slow coagulation was constant regardless of the progress of coagulation.

Acknowledgements

This investigation was funded partially by a Grant-in-Aid for Scientific Research (Project No.16208023) from the Japanese Society for the Promotion of Science (JSPS). A suggestive discussion on the importance of excluded volume of coagulated suspension done in JSPS Core-to-Core Program (No.18004) is also acknowledged.

References

[1] T. Fukasawa, Y. Adachi, J. Colloid Interface Sci. 304 (2006) 115.

[2] T. Fukasawa, Y. Adachi, KAGAKU KOGAKU RONBUNSHU 35 (2009) 70 (in Japanese with English abstract).

[3] M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, P. Meakin, Nature 339 (1989) 360.

[4] Y. Adachi, S. Ooi, J. Colloid Interface Sci. 135 (1989) 374.

[5] Q. Jiang, B. E. Logan, Environ. Sci. Technol. 25 (1991) 2031.

[6] Y. Adachi, M. Kobayashi, T. Yanagibashi, Trans. JSIDRE 233 (2004) 49.

[7] R. H. Ottewill and J. N. Shaw, Disc. Faraday Soc. 42 (1966) 154.

[8] H. Sonntag, V. Shilov, H. Gedan, H. Lichtenfeld, C. Dürr, Colloids Surf. 20 (1986) 303.

[9] M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, P. Meakin, Phys. Rev. A 41 (1990) 2005.

[10] T. G. M. van de Ven, Colloidal Hydrodynamics, Academic Press, London, 1989.

[11] W. B. Russel, D. A. Saville, W. R. Schowalter, Colloidal Dispersions, Cambridge University Press, Cambridge, 1989.

[12] D. Sato, M. Kobayashi, Y. Adachi, J. Colloid Interface Sci. 272 (2004) 345.

[13] D. Sato, M. Kobayashi, Y. Adachi, Colloids Surf. A. 266 (2005) 150.

[14] Y. Adachi, S. Ooi, Proc. World Cong Chem. Eng. 3 (1986) 156.

[15] P. Sandkühler, M. Lattuada, H. Wu, J. Sefcik, M. Morbidelli, Adv. Colloid Interface Sci. 113 (2005) 65.

[16] A. M. Brasil, T. L. Farias, M. G. Garvalho, J. Aerosol Sci. 30 (1999) 1379.

[17] Y. Adachi, M. Kamiko, Powder Technology 78 (1994) 129.

[18] D. N. Sutherland, Nature 226 (1970) 1240.

[19] Y. Adachi, K. Aoki, Colloids Surf. A. 342 (2009) 24.

[20] M. von Smoluchowski, Z. Phys. Chem. 92 (1917) 129.

[21] L. A. Spielman, J. Colloid Interface Sci. 33 (1970) 562.

[22] K. Higashitani, M. Kondo, S. Hatade, J. Colloid Interface Sci. 142 (1991) 204.

[23] Y. Adachi, Adv. Colloid Interface Sci. 56 (1995) 1.

[24] M. Kobayashi, F. Juillerat, P. Galletto, P. Bowen, M. Borkovec, Langmuir 21 (2005) 5761.

[25] N. Z. Fuchs, Z. Phys. 89 (1934) 736.

[26] S. H. Behrens, M. Semmler, M. Borkovec, Prog. Colloid Polym. Sci. 110 (1998) 66.

[27] P. Meakin, R. Jullien, J. Chem. Phys. 89 (1988) 246.

[28] S. Tang, Colloids Surf. A. 157 (1999) 185.

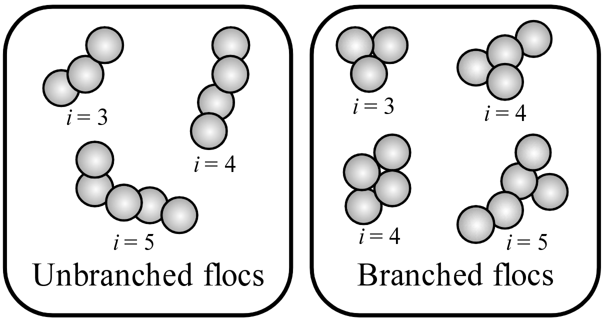

Fig. 1. Samples of unbranched and branched flocs.

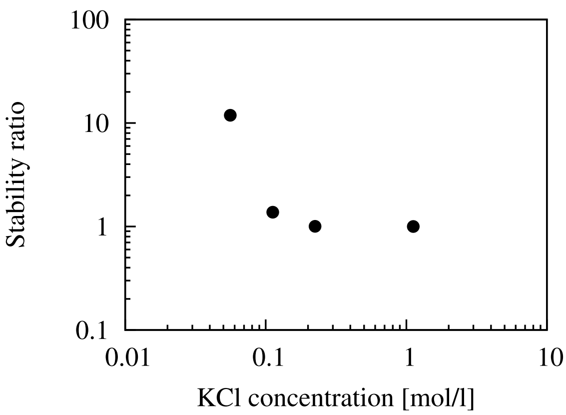

Fig. 2. Stability ratio as a function of KCl concentration for polystyrene latex particles $d_0 = 1.6\ \mu$m.

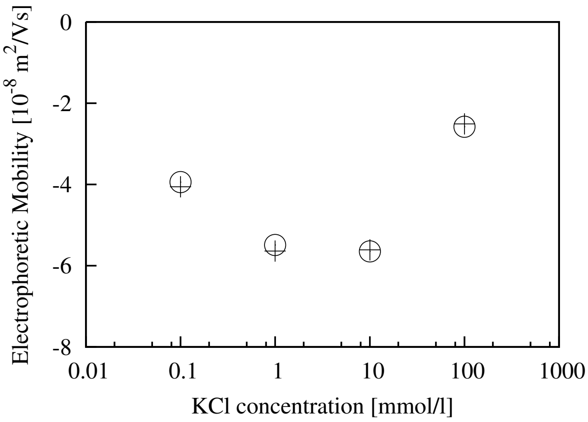

Fig. 3. Electrophoretic mobility of PSL particles which were dispersed in KCl solution (○) and mixed (KCl solution and D_2O) solution (+).

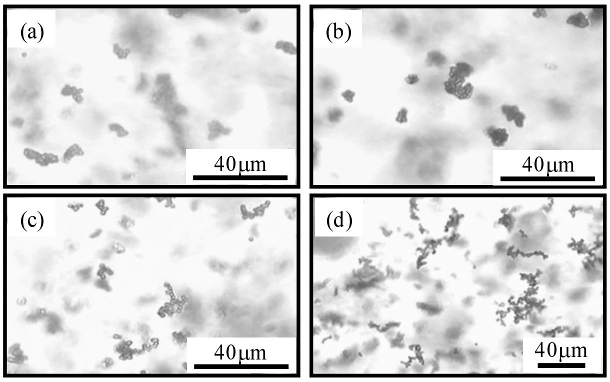

Fig. 4. Typical snapshot of the state of coagulation for slow coagulation (0.112 M KCl) (a,b) and rapid coagulation (1.12 M) (c,d). (a) 80 min, (b) 120 min, (c) 40 min and (d) 60 min after the onset of coagulation.

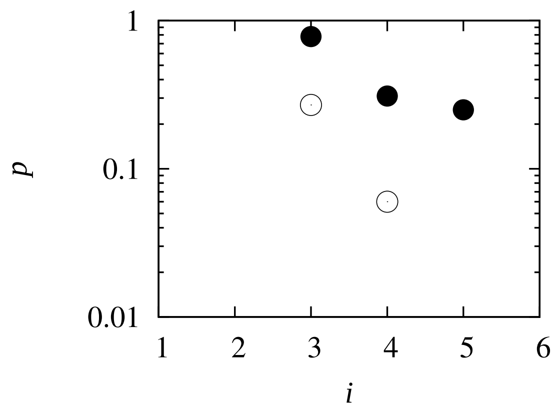

Fig. 5. Ratio of the number of unbranched flocs to the total number of flocs for each i. (●) 1.12 M KCl and (○) 0.112 M.

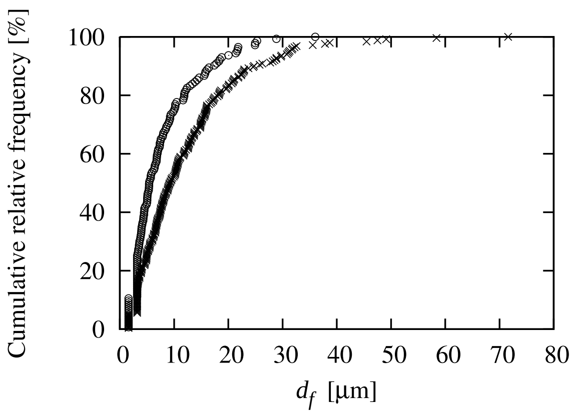

Fig. 6. Cumulative size distribution of flocs for (×) 1.12 M KCl (60 min after the on set of coagulation) and (○) 0.112 M (120 min).

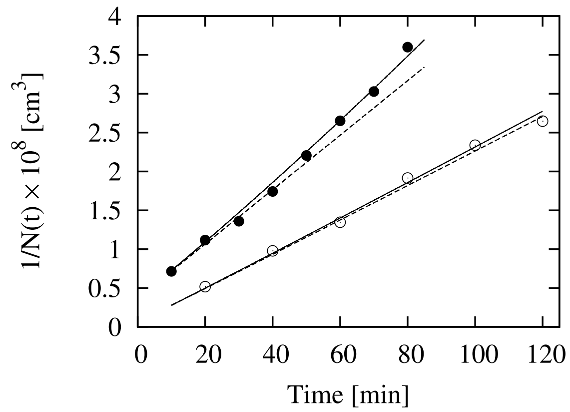

Fig. 7. Relation between $1/N$ and t. (•) 1.12 M KCl, (∘) 0.112 M. Solid lines represent curve calculated using Eq. (8), and dashed lines indicate evaluated values using Eq. (4).