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THE EFFECTS OF PARTICLE SIZE ON BREAKUP OF POLYSTYRENE LATEX FLOCS IN A TURBULENT FLOW

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SYNOPSIS

In our recent paper (*Langmuir* Vol. 15, pp. 4351-4356, 1999), we proposed a simple model of floc strength expressed as the product of the cohesive force between primary particles (f) and the number of contacts (N_c) between clusters (small flocs) in the floc. This model was verified by the experiment of floc breakup, where N_c was controlled. In this study, to confirm the effectiveness of the model including the former effect, i.e., floc strength is proportional to f, we performed a series of floc breakup experiment in the turbulent flow generated with a mixing vessel. In these experiments, the magnitude of the cohesive force was controlled by changing diameters of primary particles composing flocs. The obtained relationships, maximum diameter of floc versus turbulent shear stress as well as the mean number of particles composing a floc versus turbulent shear stress, showed good agreement with the prediction based on the model.

INTRODUCTION

An understanding of the physical properties (size, structure and strength) of flocs (aggregates of colloidal particles) is very important factor in predicting and controlling the transport of cohesive sediment in water environment (1-3).

Thus far, the Smoluchowski's equation (4) and the fractal geometry (5) have given us the framework to treat the growth kinetics of flocs and the structure of formed flocs. However, the backbone of floc breakup, which reduces floc size, is insufficient because the theoretical expression of floc strength against fluid force is unclear.

It is indicated that floc strength depends on both the cohesive force between primary particles composing a floc and the structure of a floc. With regard to the former, Sonntag & Russel (6) broke up flocs which were formed with monodisperse polystyrene latex colloidal spheres in various concentrations of electrolyte solutions in a simple shear flow and obtained relationships between the average number of primary particles composing a broken floc and the shear stress at each salt concentration. They demonstrated that differences in relationships between the average number of primary particles composing a floc and the shear stress can be normalized by the cohesive forces between two colloidal spheres predicted by the so-called Derjaguin-Landau-Verwey-Overbeek theory (6, 17). This finding indicates that the cohesive force between primary particles directly controls the floc strength. On the other hand, Tambo, Yamada & Hozumi (7) pointed out the significance of the floc structure and derived floc strength as a function of floc density, which decreases with increasing floc size. They concluded that floc strength is proportional to the floc diameter. Recently, however, the Tambo's model has been opposed by Yeung & Pelton (8), who measured directly floc strength

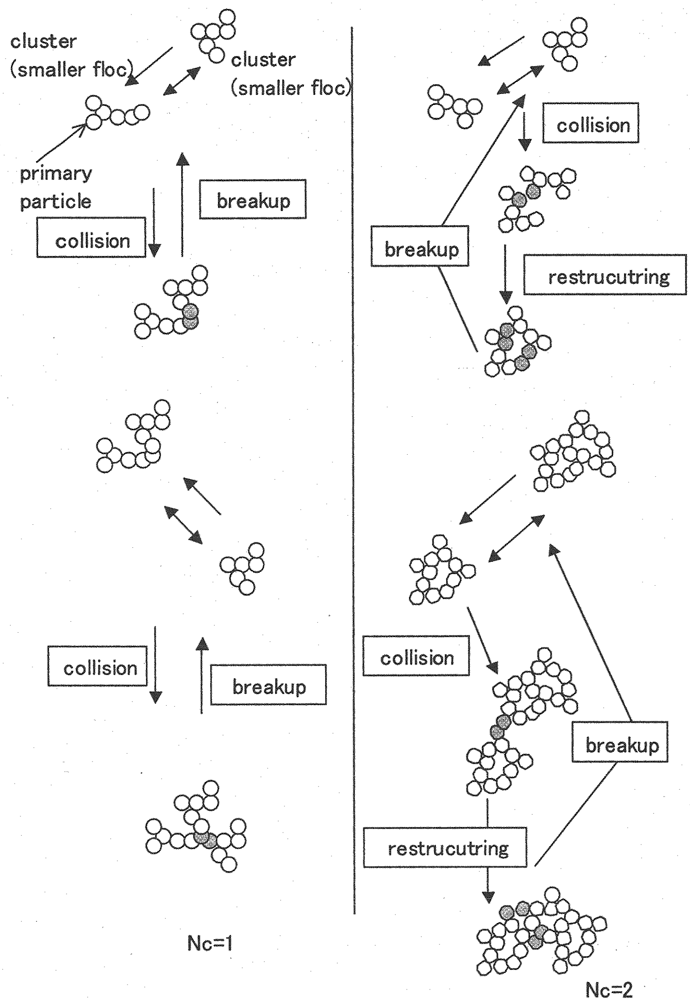

Fig. 1 Schematic illustration of formation and breakup of flocs.

from the distortion of two micropipettes rupturing a floc. From the measurement, they found that floc strength does not change with floc size but change with fractal dimension of flocs.

It is well known that flocs are fractal (self-similar) objects (5, 9, 10) reflecting the sequence of binary collision between clusters (Fig. 1). Fractal dimension (D) of a floc increases with increasing the number of contacts between the two colliding clusters (N_c) when the floc is formed (9, 10). Thus, it can be expected that the increase of fractal dimension will increase floc strength as a result of the increase of the number of contacts between clusters (N_c).

Very recently, on the basis of these findings (6, 8, 10), we (11) proposed a simple model of floc strength (F_{floc}) expressed as the product of the cohesive force between primary particles (f) and the number of contacts between clusters (N_c) (Fig. 1):

$$F_{floc} = f \cdot N_c \qquad (1)$$

The latter effect of the model, F_{floc} is proportional to N_c, was validated by the experiment where we broke up three types of flocs with different values of N_c in a turbulent flow (11). In our experiment, flocs were formed by the coagulation of monodisperse polystyrene latex (PSL) model spheres in KCl solution. However, the effect of the former is not examined. Thus, to complete the expression of eq. (1), it is also necessary to obtain the experimental proof that F_{floc} is proportional to f. For this purpose, we planned the experiment to break up flocs formed with different sizes of PSL spheres because f is proportional to the diameter of a primary particle.

THEORETICAL MODEL OF FLOC BREAKUP

Brief Description of Model

The analogy of breakup of droplets in a locally isotropic turbulent flow (12) indicates that a floc is broken up when the hydrodynamic force acting on the floc exceeds the floc strength (F_{floc}) given by eq. (1). On the basis of this criteria, we derived the following equations for the maximum value of floc diameter ($d_{f,max}$) in a certain turbulent flow field (11).

$$d_{f,\max} \propto \left(\frac{\mu G}{f \cdot N_c} \right)^{-1/2} \quad \text{for } d_f < \eta \qquad (2)$$

$$d_{f,\max} \propto \left(\frac{\rho \varepsilon^{2/3}}{f \cdot N_c} \right)^{-3/8} \quad \text{for } d_f >> \eta \qquad (3)$$

where $G=(\varepsilon/\nu)^{1/2}$ and $\eta=(\varepsilon/\nu^3)^{-1/4}$ are local shear rate and Kolmogorov microscale of turbulence, respectively. Other symbols, μ, ε, ν and ρ denote viscosity of fluid, rate of energy dissipation per unit mass, kinematic viscosity of fluid and density of fluid, respectively. These equations show that the size of flocs decreases as ε increases. Eq. (2) was validated in the previous paper (11).

Effect of Particle Size

If coagulation is induced under the condition of sufficiently high ionic strength, the electrical repulsive force between particles is negligible. In this case, f is written as the following equation based on the van der Waals attractive forces between two spheres with an equal diameter of d_0.(6, 17):

$$f = \frac{A d_0}{24 h^2} \qquad (4)$$

where A is the Hamaker constant and h is the minimum distance of separation between particle surfaces. A and h are considered to be material properties. Thus, supposing A and h are constants, one can derive the following equations from eqs. (2-4).

$$d_{f,\max} \propto \left(\frac{\mu G}{d_0 \cdot N_c} \right)^{-1/2} \quad \text{for } d_f < \eta \qquad (5)$$

$$d_{f,\max} \propto \left(\frac{\rho \varepsilon^{2/3}}{d_0 \cdot N_c} \right)^{-3/8} \quad \text{for } d_f >> \eta \qquad (6)$$

When a floc is a fractal object, the relationship between the number of primary particles composing the floc (i) and the diameter of the floc (d_f) is written as the following equation (13):

$$i = \left(\frac{d_f}{d_0} \right)^{D} \qquad (7)$$

where D is so-called fractal dimension and is in the range of $1 \leq D \leq 3$. Substituting eq. (7) into eqs. (5, 6), one can derive the following equations for the relationship between i and ε.

$$i_{\max} \propto \left(\frac{\mu G d_0}{N_c} \right)^{-D/2} \quad \text{for } d_f < \eta \qquad (8)$$

$$i_{\max} \propto \left(\frac{\rho \varepsilon^{2/3} d_0^{5/3}}{N_c} \right)^{-3D/8} \quad \text{for } d_f >> \eta \tag{9}$$

To verify these equations, which take into account d_0, we carried out the following experiment, where flocs formed with different d_0 of PSL spheres were broken up in a turbulent flow.

EXPERIMENTS

Materials

In this experiment, flocs were formed by the coagulation of monodisperse PSL spheres in the solution of KCl. To form flocs with different *f*, we adapted PSL spheres with three different diameters (480, 1356 and 1956 nm). All these spheres were synthesized by aqueous polymerization without surfactant. Henceforth, we denote the flocs using the value of particle diameters; "480 floc" is the floc that consists of particles with d_0 = 480 nm. Before the experiment was carried out, all distilled waters and KCl solutions were filtered by using the Millipore filter with a 0.22 μm mesh size.

Floc Formation

The formation of flocs was induced by mixing 1 mL of 2.236 mol/L KCl solution to 1 mL of the PSL suspension, whose volume fractions (ϕ_0, volume of particles/volume of suspension) were 0.00162, 0.0182, 0.00182, 0.0891 and 0.00101 for 480 floc, 1356 A floc, 1356 B floc, 1356 C floc and 1956 floc, respectively. After mixing, the mixed suspension was sucked up into a sampler (a syringe with a glass tube) and left over three days to be fully coagulated. The KCl concentration of the mixed suspension was adjusted to have the equivalent density of PSL spheres and is higher than critical coagulation concentration (14). Thus, the van der Waals attractive force is the dominant force between particles.

Agitation Apparatus to Generate Turbulent flow

Turbulent flows to break up flocs were generated with an agitation apparatus composed of a Rushton type stirrer installed in the cylindrical vessel with equally placed four baffles. To evaluate hydrodynamic force and Kolmogorov microscale (η), we evaluated ε from the measurement of the rate of coagulation of PSL spheres in the vessel (15). The reason for doing this is that the rate of coagulation is a function of ε. The evaluated values of ε were consistent with the rate of energy input per unit mass (ε_i) measured by using a torque meter (15) with the equation, $\varepsilon_i = 2\pi N_r T_r / w$, where N_r, T_r and w are rotational speed of stirrer, torque needed to rotate the stirrer at N_r and mass of solution in the vessel. The schematic illustration of the vessel and the values of ε are described elsewhere (11, 15).

Procedure

The prescribed volume of coagulated suspension in the sampler was carefully poured into the vessel filled with 1.118 mol/L KCl solution (Fig. 2). During this process, volume fractions of PSL in the vessel (ϕ_b) were adjusted to 5.84×10^{-7}, 5.25×10^{-7}, 5.25×10^{-7}, 5.14×10^{-7} and 4.67×10^{-7} for 480 floc, 1356 A floc, 1356 B floc, 1356 C floc and 1956 floc, respectively. These values are so low that the effect of the regrowth of broken flocs can be regarded negligible (11). After agitation for 90 minutes, which is sufficient time for the size distribution of broken flocs to reach steady-state (11), a small amount of suspension containing broken flocs was carefully extracted by means of a microslide (glass tube with rectangular cross section). Suspended flocs in the slide were photographed by means of a microscope and the maximum lengths of the projected flocs (D_m) were measured as an index of d_f one by one. To determine the value of N_c, we evaluated the value of the fractal dimension of flocs (D) by solving the mass conservation equation of primary particles (11, 13)

$$N(0) \cdot V_s = \sum_{n=1}^{N_f} i_n = \sum_{n=1}^{N_f} \left(\frac{D_{m,n}}{d_0} \right)^D \tag{10}$$

on the assumption that all monitored flocs in the prescribed volume (V_s) have the same D, where $N(0)$ and N_f are the number concentration of primary particles and the number of flocs in V_s, respectively.

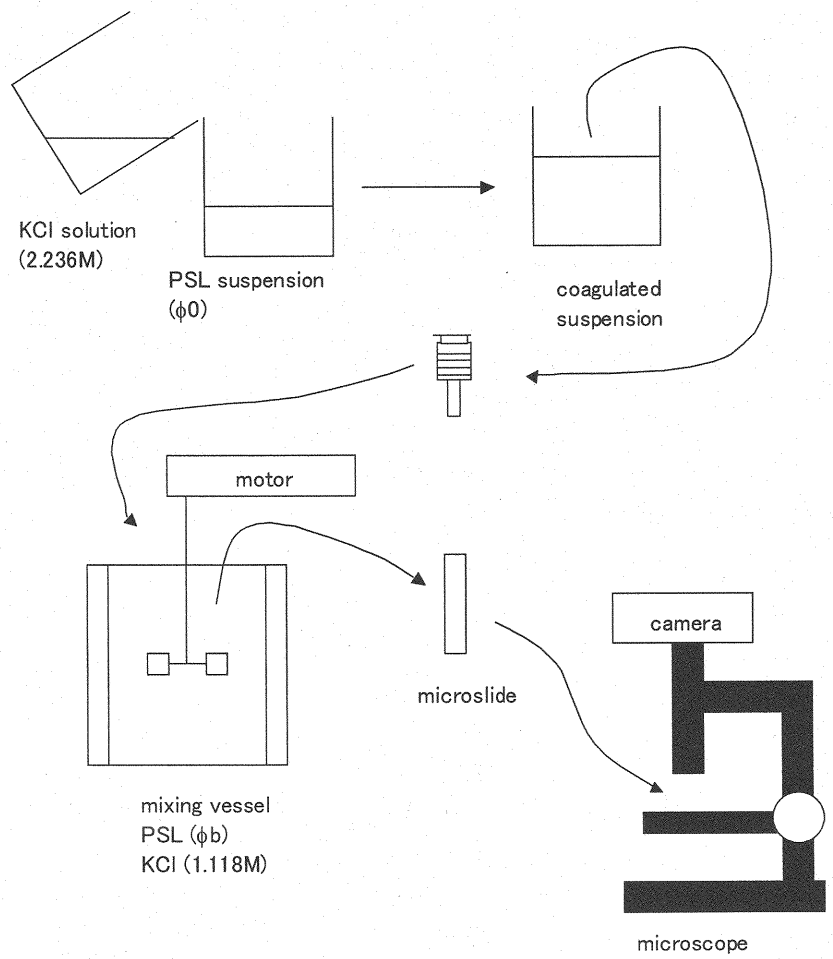

Fig. 2 Schematic illustration of experimental procedure.

From the experiment described above, D_m, <*i*>, and D were obtained. The value of N_c is deduced from D.

RESULTS AND DISCUSSION

In Fig. 3, the 95 percentile D_m of the size distribution ($D_{m,95}$) of broken flocs used as $d_{f,max}$ (18), is plotted against turbulent shear stress (μG). This figure indicates that floc size decreases as μG increases and floc breakup occurs in the region smaller than η represented by a solid line. A similar tendency is revealed in the relationships between the mean number of particles composing a floc (<*i*>) and μG (Fig. 4). Fractal dimension (D) is plotted against <*i*> in Fig. 5. This figure indicated that D decreases sharply with the decrease of <*i*> in <*i*> ≤ 70 as previously reported (11,16). This is due to the lower cut-off limit of scaling relation (16). That is, flocs composed with smaller *i* have the smaller values of D even if flocs have the same N_c value (16).

Mean values of D in <*i*> ≥ 70 are 1.91 (480 floc), 1.82 (1956 floc), 1.79 (1356 A floc), 1.68 (1356 B floc) and 1.91 (1356 C floc). Comparing these values to those of simulated flocs (9, 10) as done in the previous study (11), we determine that $N_c = 3$ (480 floc, 1356 C floc), 2 (1356 A floc, 1956 floc), 1 (1356 B floc) (11).

According to the model (eqs. (5, 8)) with N_c values determined above, we replotted $D_{m,95}$ and <*i*> against $\mu G/(N_c d_0)$ and $\mu G d_0/N_c$ in Figs. 6 and 7, respectively. As indicated in these figures, differences shown in Figs. 3 and 4 are normalized. Further, the power relation, $D_{m,95} \propto (\mu G/(N_c d_0))^{-0.511}$ agrees well with the model.

In Fig. 7, four solid lines are drawn for guide. These slopes, *dlog*<*i*>*/dlog*$(\mu G d_0/N_c)$, are -2.5/2, -2/2, -1.5/2, and -1/2, from steep to gradual. In the present model, the value of *dlog*<*i*>*/dlog*$(\mu G d_0/N_c)$ is given by $-D/2$;

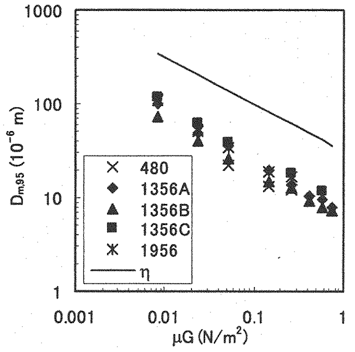

Fig. 3 The 95 % D_m, $D_{m,95}$ (used as the maximum diameter of flocs) vs. turbulent shear stress, μG. Solid line denotes Kolmogorov microscale, η.

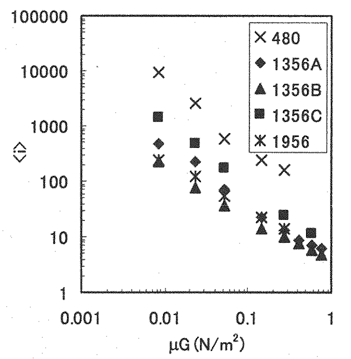

Fig. 4 The mean number of particles composing a floc, $<i>$ vs. turbulent shear stress, μG.

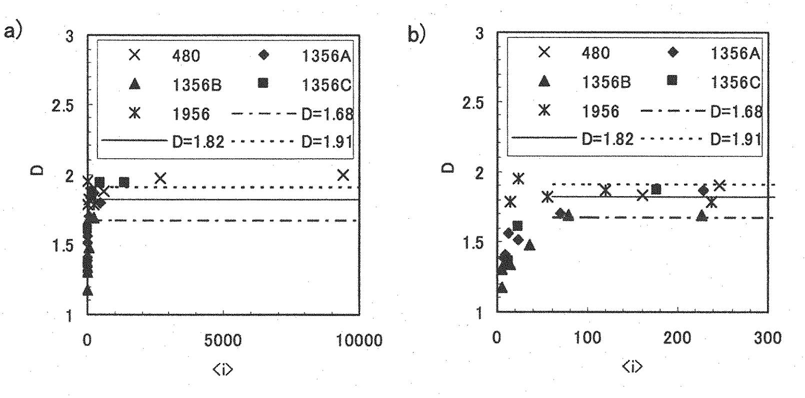

Fig.5 Fractal dimension, D vs. the mean number of particles composing a floc, $<i>$. a) all data. b) magnification.

$d\log<i>/d\log(\mu G d_0/N_c) = -1.5/2$ for $D = 1.5$, for example. As shown in Fig. 7, experimental data obey one of lines whose slopes are $-1/2>-D/2>-2.5/2$. The range of D from $d\log<i>/d\log(\mu G d_0/N_c)$ in Fig. 7 shows

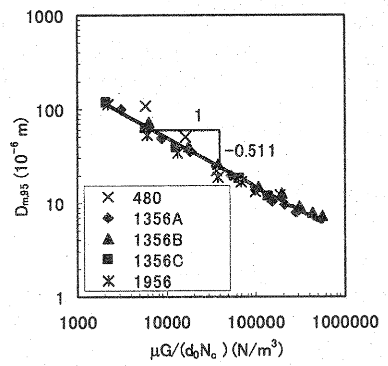

Fig. 6 The 95 % D_m, $D_{m,95}$ (used as the maximum diameter of flocs) vs. scaled turbulent shear stress, $\mu G/(d_0N_c)$.

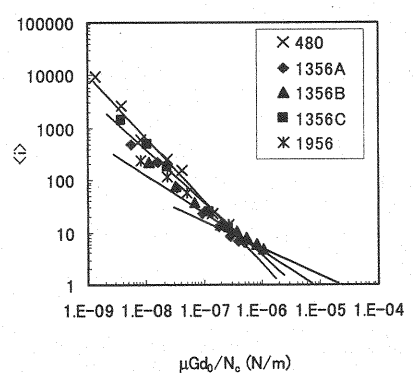

Fig. 7 The mean number of particles composing a floc, $<i>$ vs. scaled turbulent shear stress, $\mu Gd_0/N_c$. Four solid lines, whose slopes are -2.5/2, -2/2, -1.5/2, and -1/2, from steep to gradual, are drawn for guide.

reasonable agreement with that in Fig. 5. This provides evidence of the validity of the present model.

From the extrapolation of $<i>$ vs $\mu Gd_0/N_c$ for $N_c = 1$ (1356 B floc), the value of μGd_0 is expected to be between 6×10^{-6} (for $D = 1.5$) and 2×10^{-5} (for $D = 1$) at $<i> = 1$. The meaning of $i = 1$ is that doublets even break at $\mu Gd_0 = 6\times 10^{-6}$ - 2×10^{-5}. From the criteria of doublet breakup in a laminar flow (17), the following relation is obtained for $i = 1$.

$$\mu Gd_0 = \frac{A}{36\pi h^2} \tag{11}$$

The values of μGd_0 for $i = 1$expected from the present experiment, 6×10^{-6} - 2×10^{-5}, can be obtained by substituting reasonable values of A and h, e.g. $A = 1.0\times 10^{-21}$ J and h= 0.7-1.2 nm, into eq. (11). This agreement between experiment and calculation also substantiates the validity of the present experiment and analysis.

CONCLUSIONS

To extend the applicability of the previously proposed model of floc strength, flocs formed with three different diameters of monodisperse PSL spheres were broken up in the turbulent flow generated in an agitation vessel. Experimental results show that floc strength is proportional to the cohesive force between primary particles. The result showed good agreement with the prediction based on the model. All findings including previously reported results indicate that floc strength is expressed as the product of the cohesive force between primary particles and the number of contacts between clusters when the floc is formed.

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REFERENCES

1. Ashida, K. and K. Sawai : Nenchakusei dosya no shinshoku to taiseki, Ryusa no Suirigaku, Kikkawa, H. eds., Maruzen, pp.249-271, 1985, in Japanese.
2. Okuda, S. : Kancho kasen ni okeru taiseki kankyo, Kasen Kancho Iki, Saijo, Y. and Okuda, S. eds., Nagoya Daigaku Shuppan Kai, pp.85-105, 1997, in Japanese.
3. Winterwerp J.C. : A simple model for turbulent flocculation of cohesive sediment, J. Hydraulic Res., Vol. 36, pp.309-326, 1998.
4. Smoluchowski, M. von : Versuch einer mathematichen theorie der koagulation kinetik kolloider loesungen, Z. Phys. Chem., Vol.92, pp.129-168, 1917.
5. Lin, M.Y., H.M. Lindsay, D.A. Weitz, R.C. Ball, R. Klein and P. Meakin : Universality in colloid aggregation, Nature, Vol.339, pp.360-362, 1989.
6. Sonntag, R.C. and W.B. Russel : Structure and breakup of flocs subjected to fluid stress : I. Shear experiment, J. Colloid Interface Sci , Vol.113, pp.399-413, 1986.
7. Tambo, N., K. Yamada and H. Hozumi : Furokku kyodo ni kansuru kenkyu, Suido Kyokai Zasshi, Vol. 427, pp.4-15, 1970, in Japanese.
8. Yeung, A.K.C. and R. Pelton : Micromechnics: A new approach to studying the strength and breakup of flocs, J. Colloid Interface Sci., Vol.184, pp.579-585, 1996.
9. Adachi, Y. and S. Ooi: Structure of a floc Proc. World Congress Chem. Eng., Vol.3, pp.156-159, 1986.
10. Adachi, Y. and S. Ooi : Geometrical structure of a floc, J. Colloid Interface Sci, Vol.135, pp.374-384, 1990.
11. Kobayashi, M., Y. Adachi and S. Ooi : Breakup of fractal flocs in a turbulent flow, Langmuir, Vol.15, pp. 4351-4356, 1999.
12. Shinnar R. : On the behavior of liquid dispersions in mixing vessels, J. Fluid Mech., Vol.10, pp. 259-275, 1961.
13. Adachi, Y. and M. Kamiko : Sedimentation of a polystyrene latex floc, Powder Technol., Vol.78, pp. 129-135, 1994.
14. Adachi, Y. and S. Ooi : Sediment volume of flocculated material studied with polystyrene latex spheres, J. Chem. Eng. Japan, Vol.32, pp.45-50, 1999.
15. Kobayashi, M. and Y. Adachi : Ranryu chu ni okeru moderu koroido ryusi no gyoshu katei ni kansuru kenkyu, Nogyo Doboku Gakkai Ronbunshu, Vol.191, pp.111-115, 1997, in Japanese with English abstract.
16. Adachi, Y., M. Kobayashi and S. Ooi : Applicability of fractal to the analysis of the projection of small flocs, J. Colloid Interface Sci., Vol.208, pp.353-355, 1998.
17. Russel, W.B., D.A. Saville and W.R. Schowalter : Colloidal Dispersions, Cambridge Univ. Press, Cambridge, 1991.
18. Sherman, P. : Emulsion Science, Academic Press, New York, 1968.

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