$\tau_w \qquad = t_0/\{(\varepsilon\rho_g C_{pg}+\gamma C_{ps})r/2h_0\}$ [—]

$\zeta \qquad$ = defined by Eq. (5) [—]

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TURBULENT COAGULATION OF PARTICLES DISPERSED IN A VISCOUS FLUID

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A kinetic equation for the turbulent coagulation of particles in a viscous fluid in which the hydrodynamic interaction between colliding particles is taken into account is proposed. The theoretical prediction of the time-dependent behavior of particle concentration is compared with results of experiments in which latex particles in KCl solutions are coagulated in a stirred tank. It is found that the effect of the hydrodynamic interaction is not negligible, and that changes of particle concentration under various experimental conditions are quantitatively predicted by the present theory. On the other hand, the Saffman-Turner theory is found to overestimate the coagulation rate considerably and to yield a systematic error in the dependence of coagulation rate on the dissipation energy.

Introduction

The coagulation of colloidal particles is found in many natural phenomena and industrial processes. In most situations the coagulation is caused by the flow of turbulence, where particles collide because of their relative motion induced by the velocity field of the medium. If there exists no repulsive surface force between particles, every collision leads to coagulation. This process, called rapid coagulation, in a turbulent viscous fluid is treated in this paper.

A theoretical treatment of turbulent coagulation was carried out approximately by Camp and Stein,[2] assuming that the collision mechanism of particles is analogous to that of the shear coagulation proposed by Smoluchowski.[12] Levich[7] also derived a kinetic equation of turbulent coagulation, assuming that the problem of coagulation of particles transported by turbulent eddies is reduced to a diffusion problem characterized by a turbulent diffusion coefficient. A theory developed by Saffman and Turner[11] is somewhat more rigorous. However, it is assumed in their analysis that particles encounter each other without interacting hydrodynamically; that is, each particle behaves as though the others were not present. This theory is approximately applicable to the collision in which the effect of inertia of particles is predominant, or the interparticle attractive force acts such that it cancels the effect of the hydrodynamic interaction. But it is unlikely that the theory is applicable to the collision between sufficiently small particles dispersed in a viscous fluid. The theories described above were developed to predict the coagulation process in which particles follow the fluid motion completely. There is another mechanism of turbulent coagulation in which the particle collision is attributed to the inertia of particles. This mechanism is not treated here because it is applicable to rather large particles in a vigorous turbulence.

Experimental investigations on turbulent coagulation have been carried out for aerosols,[1,10] but no rigorous measurements for colloidal dispersions in aqueous solutions are found.

In the present paper we propose a kinetic equation for the coagulation of particles in a viscous fluid of homogeneous isotropic turbulence in which the hydrodynamic interaction between particles is taken into account. And the theoretical prediction of the time-dependent behavior of particle concentration is compared with results of experiments in which latex particles are coagulated in a stirred tank using KCl solutions as the coagulant.

1. Kinetic Equation of Turbulent Coagulation

Consider a binary collision between particles of sizes i and j in a viscous fluid of homogeneous isotropic turbulence. Saffman and Turner[11] calculated the collision frequency per unit volume, J^0_{Tij}, by counting the number of particles flowing into the sphere of coagulation radius R_{ij} ($=a_i+a_j$, where a_i is the radius of particle of size i).

$$J^0_{Tij} = 1.294 R^3_{ij}(\varepsilon/\nu)^{1/2} n_i n_j \qquad (1)$$

where ε is the energy dissipation per unit mass of fluid, ν is the kinematic viscosity of the medium and n_i is the number concentration of particle i. Then the rate of change in concentration of particle k is given by taking a population balance.

$$\frac{dn_k}{dt} = \frac{1}{2} \sum_{\substack{i=1 \\ i+j=k}}^{i=k-1} 1.294 R^3_{ij}(\varepsilon/\nu)^{1/2} n_i n_j$$
$$- \sum_{i=1}^{\infty} 1.294 R^3_{ik}(\varepsilon/\nu)^{1/2} n_i n_k \quad (k=1,2,\cdots,\infty) \quad (2)$$

where t is the time. The first term on the right-hand side represents the rate of formation of particle k by coagulation of smaller particles and the second term the rate of disappearance due to coagulation of particle k with others.

In deriving this equation the following assumptions are required.

(1) R_{ij} is small in comparison with the smallest eddies of turbulence.

(2) Particles move with the fluid velocity.

(3) Effects of inertia and sedimentation of particles are negligible.

(4) The effect of the Brownian coagulation which proceeds simultaneously is negligible.

(5) Flocs never break up.

(6) There exists no interparticle force, and particles coagulate when they collide.

(7) The collision efficiency is unity, that is, the distortion of the particle trajectory by the hydrodynamic interaction between particles is neglected.

It is known[7] that assumptions (1), (3) and (4) are usually satisfied in the case of turbulent coagulation of aqueous colloidal dispersions. Assumption (5) is acceptable at a rather early stage of coagulation

where flocs are too small to break up. However, the other assumptions will not be satisfied when Eq. (2) is applied to the coagulation of aqueous dispersions. The theory is modified as follows.

Contrary to assumption (6), there exist interparticle forces between particles in an aqueous solution. Since it is conventional to assume that the van der Waals-London force is the only interparticle force in rapid coagulation, the other forces are not considered here. The retarded and unretarded van der Waals-London forces whose potentials are given in the previous paper[5] are employed in calculating the coagulation coefficient given below.

It was shown[5] that particles in a shear flow interact hydrodynamically when they are close to each other, and collide along a complicated trajectory. The collision frequency J_{Sij} is given by

$$J_{Sij} = \alpha_{Sij} J^0_{Sij} \qquad (3)$$

where α_{Sij} is the coagulation coefficient of shear coagulation by which the effects of the hydrodynamic interaction and the van der Waals-London force are represented, and J^0_{Sij} is the collision frequency given by the Smoluchowski theory of shear coagulation in which assumptions (2), (6) and (7) are assumed.[12] Since the collision of particles in a turbulent fluid is also attributed to the velocity gradient of the fluid, the effect of the hydrodynamic interaction will not be negligible. Then assumption (2) is invalid and assumption (7) may yield a considerable error. Since the definite flow field is not known in the case of turbulence, the hydrodynamic interaction cannot be evaluated exactly. However, it is plausible to expect that a flow field similar to the shear flow is found in the eddies of turbulence microscopically. Hence multiplying Eq. (1) by α_{Sij} suggests a first approximation for the collision frequency of turbulent coagulation. Since it was shown[5] that α_{Sij} is replaced by α_{S11} of initial particles without any serious error, α_{S11} may be regarded as the coagulation coefficient of turbulent coagulation α_{T11} ($\equiv \alpha_T$). Then Eq. (2) is rewritten in dimensionless form as

$$\frac{dn_k{}^*}{dt^*} = \frac{1}{2} \sum_{\substack{i=1 \\ i+j=k}}^{i=k-1} \left(\frac{R_{ij}}{a_1}\right)^3 n_i{}^* n_j{}^* - \sum_{i=1}^{\infty} \left(\frac{R_{ik}}{a_1}\right)^3 n_i{}^* n_k{}^*$$
$$(k=1,2,\cdots,\infty) \qquad (4)$$

where $t^* = 1.294 \alpha_T(\varepsilon/\nu)^{1/2} a_1{}^3 N_0 t$, $n_i{}^* = n_i/N_0$ and N_0 is the initial particle concentration. It is clear that this equation is reduced to Eq. (2) when $\alpha_T = 1$. The change of particle concentration is given by solving Eq. (4) for particles of all sizes simultaneously.

2. Experimental

Polystyrene latex (PSL) particles (0.85 μm) and

polyvinyltoluene latex (PVTL) particles (2.17 μm) were selected as the colloidal particles for the present study. Stable dispersions of these particles in water were prepared by a method reported elsewhere.[6] It was confirmed by the Coulter Counter and electron microscope that the size distribution of particles was nearly monodispersed and their shape was spherical. The effect of sedimentation and inertia of particles was regarded as negligible because the densities of PSL and PVTL particles were 1.05 and 1.02 respectively. KCl solutions were employed as the electrolyte solution. To prevent cavitation, air dissolved in colloidal dispersions and KCl solutions was eliminated by the pressure reduction method before experiments.

The experimental apparatus is shown in **Fig. 1**. The colloidal dispersion and KCl solution were fed into a mixing cell with the same flow rate, and then into a stirred tank with 4 baffles. As soon as the tank was filled, the impeller, an 8-flat-blade paddle, was rotated. Small volumes of the dispersion was sampled periodically using syringes with a needle of 1.5 mm diameter and the particle concentration was determined by the Coulter Counter. The manner of sampling, the location of sampling and the deposition of particles on the tank wall were found not to influence the result. All the experiments were carried out in the rapid coagulation region, that is, in 0.75 ± 0.1 mol/l KCl solutions at room temperature where the effect of the interparticle repulsion force due to the electrochemical double layer was avoided.[6]

Measuring the torque on the impeller T, the experimental value of energy dissipation ε_0 was evaluated by the following equation, where all the input energy was assumed to be dissipated in the bulk of the tank.

$$\varepsilon_0 = 2\pi N_I T / W \qquad (5)$$

where N_I is the rotational impeller speed and W is the mass of fluid in the tank.

3. Experimental Results

The change of reduced total particle concentration N_t/N_0 is examined for various experimental conditions. **Figure 2** shows the change of N_t/N_0 for dispersions of 0.85 μm particles of different initial concentrations. It is found that the relation N_t/N_0 vs. t depends on N_0 and that the coagulation rate increases rapidly with N_0. The dependence of the coagulation rate on N_0 is examined in **Fig. 3**. We define the coagulation time T_c as the elapsed time when N_t is reduced to half of N_0. Then $1/T_c$ may be regarded as a measure of coagulation rate. It is found that $1/T_c$ is proportional to about $N_0^{1.49}$. **Figure 4** shows the change of N_t/N_0 of dispersions of 0.85 μm particles for various impeller speeds in which N_0 is about the same.
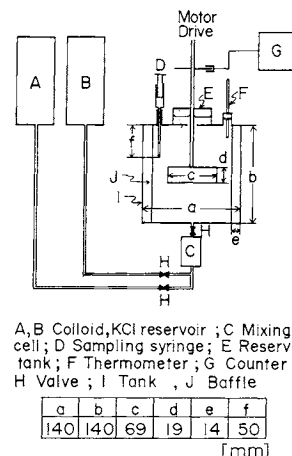

A,B Colloid,KCl reservoir ;C Mixing cell; D Sampling syringe; E Reserve tank; F Thermometer; G Counter; H Valve ; I Tank , J Baffle

a	b	c	d	e	f
140	140	69	19	14	50

[mm]

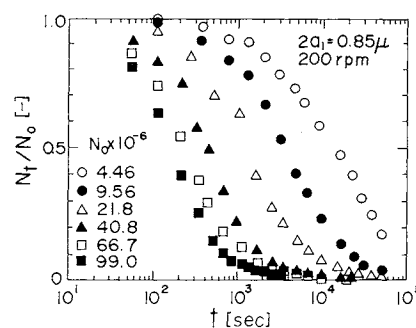**Fig. 1.** Experimental apparatus.

Fig. 2. Change of N_t/N_0 for various initial concentrations of particles.
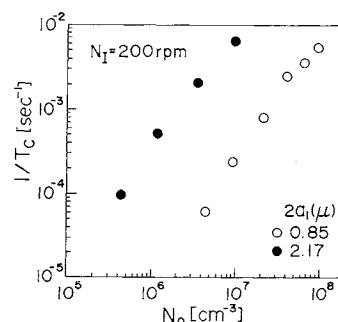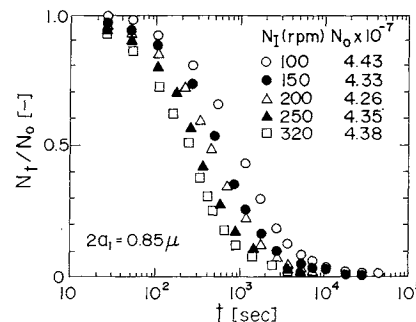

Fig. 3. Dependence of $1/T_c$ on N_0.

Fig. 4. Change of N_t/N_0 for various impeller speeds.

The dependence of $1/T_c$ on N_I is examined in **Fig. 5**. These figures indicate that relations N_t/N_0 vs. t are similar in shape and that $1/T_c$ is proportional to about
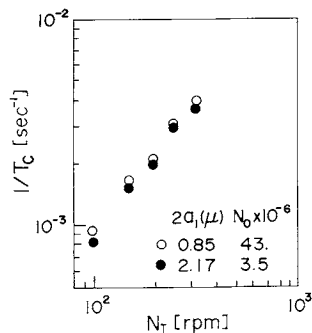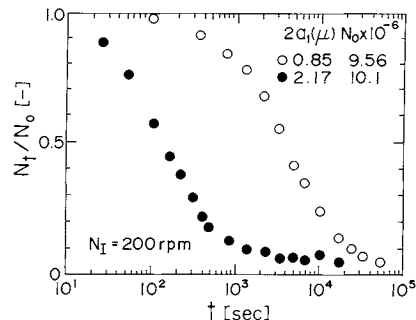
Fig. 5. Dependence of $1/T_c$ on N_I.

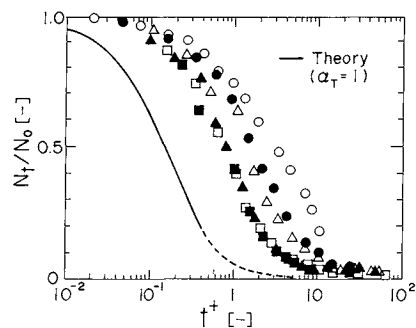Fig. 6. Change of N_t/N_0 for particles of different sizes.

Fig. 7. Comparison of data in Fig. 2 with Saffman-Turner theory. (Key for symbols is as in Fig. 2.)

$N_I^{1.27}$. Similar features are also found for dispersions of 2.17 μm particles. To examine the effect of particle size, the change of N_t/N_0 is plotted in **Fig. 6** for dispersions in which particles are of about the same concentration but differ in size. It is clear that particle size has a profound influence on the coagulation rate.

When coagulation proceeds for a sufficiently long time, N_t/N_0 is reduced to a constant value where the rate of coagulation is equal to the rate of floc break-up. Since this equilibrium value is quite small in this experiment, it is plausible to assume that the effect of floc break-up is negligible. This assumption is confirmed by a separate experiment in which it is examined whether flocs are redispersed by strong agitation.

4. Discussion

An isotropic and homogeneous turbulence is assumed in the theory. It was shown experimentally[9] that the assumption is acceptable as a first approximation for flows in a stirred tank, although the turbulence in the impeller stream deviates from isotropy and homogeneity. Hence it is plausible to compare the theoretical prediction with the experimental results given above.

The theoretical prediction of the change of particle concentration is obtained by solving Eq. (4) by a procedure described elsewhere,[5] assuming 200-fold particles are the largest. Dashed lines in the succeeding figures except Fig. 10 indicate the regions where the error in total volume of particles, due to the appearance of over 200-fold particles, exceeds 5%.

Experimental results are, first of all, compared with the Saffman-Turner theory in which α_T in Eq. (4) is unity, assuming that the effective energy dissipation ε is given by ε_0 defined by Eq. (5). By taking a dimensionless time t^+ ($\equiv 1.294(\varepsilon/\nu)^{1/2}a_1{}^3 N_0 t$) as the abscissa, the theoretical value of N_t/N_0 is given by a single curve independently of N_0, ε and a_1. **Figure 7** is the replot of the data in Fig. 2 against t^+. It is found that the data for N_0 greater than 4.08×10^7 cm^{-3}, which is called critical concentration N_c, fall on a single curve as predicted theoretically, while the data of $N_0 < N_c$ deviate from the curve with decreasing of

N_0. A similar feature is also found for dispersions of 2.17 μm particles for which N_c is equal to 1.26×10^6 cm^{-3}. No theories proposed so far can explain this deviation. It is possibly due to the failure of assumption (1) given in § 1, because R_{ij} becomes comparable with the eddy size of turbulence as N_0 decreases. But more detailed experiments are required to clarify the reason completely. We leave this problem to further study, and the data of $N_0 \geq N_c$ are employed in the following arguments. Figure 7 indicates that the relation N_t/N_0 vs. t is essentially the same in shape between theory and experiment but differs greatly in magnitude.

The data in Fig. 4 are replotted against t^+ in **Fig. 8**. It appears as if all the data fall on a single curve independently of N_I within experimental error. However, these curves shift from left to right with increasing of N_I when watched carefully. This shift, which is also found for dispersions of 2.17 μm particles, cannot be explained by the Saffman-Turner theory but explained by the present theory, as discussed later. **Figure 9** shows the replot of N_t/N_0 in Fig. 6 against t^+. Here the data of $N_0 = 4.08 \times 10^7$ cm^{-3} are used instead of those of $N_0 = 9.56 \times 10^6$ cm^{-3} for 0.85 μm particles, because the latter concentration is less than N_c as shown in Fig. 7. The dependence of N_t/N_0 on particle size predicted by the theory is satisfactory. The comparison made in these figures implies that the Saffman-Turner theory overestimates the magnitude of coagulation rate too much to use in estimating the
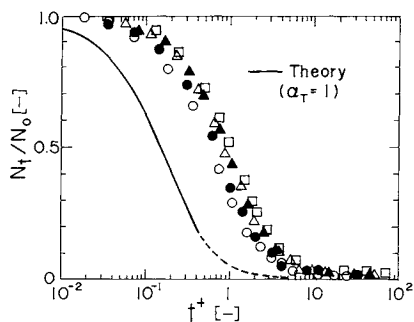
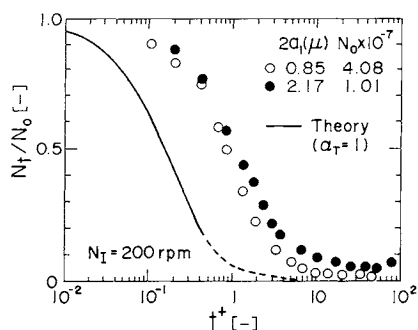**Fig. 8.** Comparison of data in Fig. 4 with Saffman-Turner theory. (Key for symbols is as in Fig. 4.)

Fig. 9. Comparison of data of N_t/N_0 change for particles of different sizes with Saffman-Turner theory.
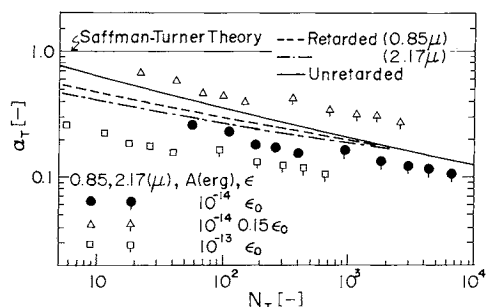

Fig. 10. Theoretical and experimental values of α_T.

Fig. 11. Comparison of data in Fig. 2 with present theory. (Key for symbols is as in Fig. 2.)

Fig. 12. Comparison of data in Fig. 4 with present theory. (Key for symbols is as in Fig. 4.)
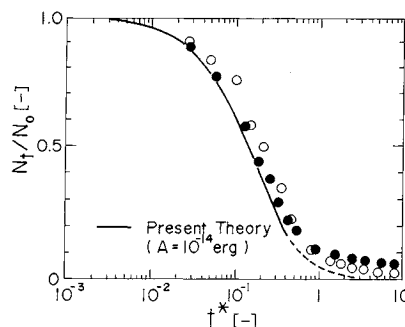
Fig. 13. Comparison of data in Fig. 9 with present theory. (Key for symbols is as in Fig. 9.)
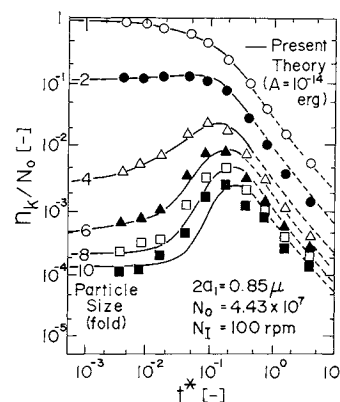
Fig. 14. Comparison of concentration change of particles of each size with theoretical prediction.

process of turbulent coagulation of aqueous dispersions in a stirred tank.

Now the experimental results are compared with prediction by the present theory. Relations between α_T and N_T $(=6\pi\mu a_1{}^3\dot{\gamma}/A)$, obtained by repeating a manipulation described elsewhere,[5] are drawn in **Fig. 10** for the retarded and unretarded van der Waals-London interparticle potentials. Assuming that (i) the Hamaker constant A for latex particles is 10^{-14} erg, (ii) the interparticle force is given by the retarded potential and (iii) the deformation rate $\dot{\gamma}$ $(=\overline{dU_x/dy})$ is given by $\dot{\gamma}=(4\varepsilon/15\pi\nu)^{1/2}$,[11,13] the theoretical values of α_T for these dispersions are obtainable from Fig. 10. Substituting α_T into t^*, the data in Figs. 2, 4 and 6 are replotted against t^* in **Figs. 11, 12** and **13** respectively. It is clear the agreement between theory and experiment is improved considerably; that is, the difference in magnitude of N_t/N_0 is reduced and the shift of the
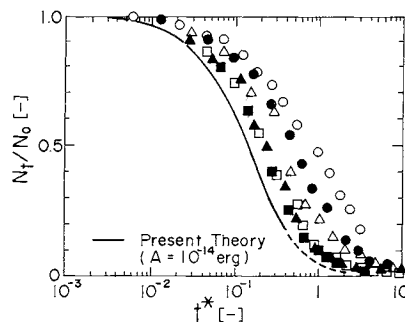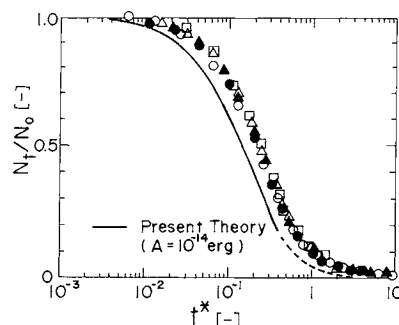
relation N_t/N_0 vs. t in Fig. 8 disappears in Fig. 12. **Figure 14** shows a typical change of concentration of particles of each size. It is confirmed that prediction

by this theory is satisfactory, especially in the case of small particles.

Experimental values of α_T may be evaluated by fitting Eq. (4) to the data of $N_t/N_0 \geq 0.2$ in Fig. 4 and the data for 2.17 μm particles, such that the sum of squared errors is minimized by the Simplex method. As expected from the good coincidence in Fig. 12, the dependence of α_T on N_T coincides fairly well with the theoretical relation as shown in Fig. 10. In this treatment it is assumed that A is 10^{-14} erg and that the power input to the impeller is dissipated completely in the bulk of the tank. However, it is known that the definite value of A for latex particles is uncertain but is somewhere between 10^{-14} and 10^{-13} erg,[8] and that some of the power input may be dissipated in the impeller or at the wall surface. It is difficult to estimate what proportion of the input energy is dissipated as the effective energy. Investigations on the turbulence in a stirred tank[3,4,14,15] imply that the value of ε is somewhere between $0.15\varepsilon_0$ and ε_0. Experimental values of α_T for various combinations of the extreme values of A and ε are shown in Fig. 10. It is important to find that they are placed around the theoretical curve and that the slope of the relation α_T vs. N_T is similar between theory and experiment. This means that α_T in the coagulation of common aqueous dispersions will also be placed around the theoretical curve. On the other hand, it is clear that the Saffman-Turner theory yields a considerable error even when $\varepsilon = 0.15\varepsilon_0$ is assumed.

These results suggest that it is necessary to introduce the hydrodynamic interaction between particles into the kinetic equation. It is important to note that this conclusion is consistent with that drawn previously for the Brownian coagulation.[6]

Conclusions

1) A kinetic equation of turbulent coagulation for dispersions of colloidal particles in a viscous fluid in which the hydrodynamic interaction between particles is taken into account is formulated.

2) Changes of particle concentration for the coagulation of latex particles in a stirred tank are successfully explained by the newly proposed theory.

3) The Saffman-Turner theory overestimates the coagulation rate considerably and yields a systematic error in the dependence of coagulation rate on energy dissipation when the theory is applied to the turbulent coagulation of common aqueous dispersions in a stirred tank.

Nomenclature

A	= Hamaker constant	[J]
a_i	= radius of particle of size i	[m]
$\overline{dU_x/dy}$	= mean shear rate in turbulence	[1/s]
J_{Sij}	= collision frequency per unit volume in a shear flow	[1/(s·m³)]
$J_{Sij}{}^0$	= J_{Sij} at $\alpha_{Sij} = 1$	[1/(s·m³)]
$J_{Tij}{}^0$	= collision frequency per unit volume in a turbulent flow defined by Eq. (1)	[1/(s·m³)]
N_I	= rotational impeller speed	[1/s]
N_T	= $6\pi\mu a_1{}^3\dot{\gamma}/A$	[—]
N_c	= critical particle concentration	[1/m³]
N_t	= total particle concentration	[1/m³]
N_0	= initial particle concentration	[1/m³]
n_i	= concentration of particle of size i	[1/m³]
$n_i{}^*$	= n_i/N_0	[—]
R_{ij}	= coagulation radius	[m]
T	= torque on impeller	[N·m]
T_c	= coagulation time	[s]
t	= time	[s]
t^*	= $1.294\alpha_T(\varepsilon/\nu)^{1/2}a_1{}^3N_0t$	[—]
t^+	= t^* at $\alpha_T = 1$	[—]
W	= mass of fluid in tank	[kg]
α_{Sij}	= coagulation coefficient for shear coagulation	[—]
α_{Tij}	= coagulation coefficient for turbulent coagulation	[—]
α_T	= α_{T11}	[—]
ε	= energy dissipation per unit mass of fluid	[m²/s³]
ε_0	= energy dissipation defined by Eq. (5)	[m²/s³]
$\dot{\gamma}$	= deformation rate	[1/s]
μ	= viscosity of medium	[Pa·s]
ν	= kinematic viscosity of medium	[m²/s]

⟨Subscript⟩

ij	= subscript indicating correlation between particles of sizes i and j	

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