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Aggregation kinetics of small particles in agitated vessels

Karl A. Kusters,* Johan G. Wijers and Dirk Thoenes

Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands

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Abstract—Rapid coagulation by turbulence in stirred tanks was studied for particles and aggregates smaller than the Kolmogorov microscale. The coagulation kinetics are determined by the floc structure and by the hydrodynamic and colloidal interactions between the colliding particles. The collision efficiency for doublet formation in the heterogeneous shear field of a stirred tank follows from particle trajectory analysis of solid particles in simple shear flow, provided the simple shear rate is made to correspond to the residence time weighted turbulent shear rate. Experimentally, the resulting aggregates proved to be fractal-like with their porosity increasing with aggregate size. Porosity within the aggregates results in penetration of the floc surface by the fluid flow, giving rise to enhanced collision efficiencies compared to solid particles. The collision efficiencies between porous flocs may be estimated by a model that pictures a porous floc as consisting of an impermeable core and a completely permeable shell. With the collision efficiencies from this shell-core model the aggregate growth could be described adequately. Copyright © 1996 Published by Elsevier Science Ltd

Keywords: Turbulent coagulation; collision efficiency; fractal aggregates; stirred tank.

INTRODUCTION

Many solid products from the chemical industries are produced by precipitation from reactive solutions. Typical examples of these products are ceramics, catalysts, fine chemicals, pharmaceuticals, non-ferrous oxides and halides, etc. Precipitation involves a sequence of steps, ranging in size scale from the molecular to the macroscopic and comprising chemical reaction, nucleation, crystal growth and aggregation processes. The latter process, wherein the particles stick together to form flocs, is thought to be highly decisive for the final size distribution and morphology of the solids that determine the properties of both suspension and dried product. Therefore, an understanding of the aggregation mechanism is of primary importance with regard to the behaviour, handling and treatment of suspension and product. Precipitation processes are usually carried out in stirred tanks where the different reactants are brought into contact. In stirred tanks in which turbulent conditions normally prevail, the flow patterns are complex and the shear field is far from uniform, thereby complicating adequate tests of theoretical predictions to be made. Unfortunately, results from experimental studies in ideal systems with a nearly uniform shear rate throughout the suspension, such as in a Couette-type apparatus, are generally not directly applicable to a stirred tank. One reason for

this may be that the size and structure of the aggregates are dependent upon the flow field in which they are produced. In this study the stirred tank has therefore been selected for the purpose of practical application. The objective of this work was to gain insight into the effects of operating variables on the aggregation kinetics, the final size distribution and morphology (structure) of the aggregates. This article discusses the aggregation kinetics in stirred tanks.

AGGREGATION THEORY

Collision frequency

Aggregation occurs when two or more particles collide and adhere. Except for very dense suspensions, simultaneous encounters between three or more particles can be ignored. In order that two particles aggregate (coagulate), they must first be brought into close proximity by a transport mechanism. The transport mechanisms give neighbouring particles different velocities and cause 'collisions'. Whether or not the particles remain attached to each other after a collision is dependent on the net interparticle forces. These may be attractive or repulsive.

The differences in the velocities of neighbouring particles may result from Brownian motion, spatial velocity variations in the fluid or different particle inertia. If the particles are submicron in size, Brownian motion is appreciable. However, as the particles grow larger, Brownian coagulation becomes less important and the other aggregation mechanisms take over (Levich, 1962). In turbulent solid-liquid

* Corresponding author.

Present address: Shell Research and Technology Centre,
P.O. Box 38000, 1030 BN Amsterdam, The Netherlands.

systems, the particles follow the fluid flow closely when they are contained in the smallest eddies, i.e. in the viscous subrange of turbulence. Therefore, collisions due to the particle inertia are less important than those caused by spatial differences in the fluid flow velocities as long as the particles are smaller than the length scale of the smallest eddies (see the Appendix). The length scale of the smallest eddies is given by the Kolmogorov microscale:

$$\eta = \left(\frac{\nu^3}{\varepsilon} \right)^{1/4} \quad (1)$$

At a characteristic value of energy dissipation rate ε of 0.1 W kg^{-1} , η amounts to $56 \mu\text{m}$ in water. Hence, for particles in the size range from about 1 to $100 \mu\text{m}$, the binary collision frequency per unit volume, J_{ij}^0 , of particles with collision radii R_i and R_j and number concentrations n_i and n_j , respectively, can be approximated by the expression derived by Saffman and Turner (1956):

$$J_{ij}^0 = \beta_{ij}^0 n_i n_j = 1.294 \left(\frac{\varepsilon}{\nu} \right)^{1/2} (R_i + R_j)^3 n_i n_j \quad (2)$$

where β_{ij}^0 is the collision frequency function.

For highly porous aggregates whose density approaches that of the liquid, the application of eq. (2) can be extended even up to 6η , i.e. about $300 \mu\text{m}$ for $\varepsilon = 0.1 \text{ W kg}^{-1}$ in water. The Kolmogorov microscale denotes the eddy scale where viscous forces begin to have a noticeable effect on the motion of the fluid. Particles that are contained within the smallest eddies experience almost laminar flow conditions. Camp and Stein (1943) obtained a result similar to eq. (2) by assuming simple shear flow within the smallest eddies and substituting $(\varepsilon/\nu)^{1/2}$ for the shear rate in the corresponding collision frequency expression, which is given by

$$J_{ij}^0 = 3/4 G (R_i + R_j)^3 n_i n_j \quad (3)$$

where G denotes the shear rate.

Substituting $G = (\varepsilon/\nu)^{1/2}$ into eq. (3) gives an equation for the orthokinetic collision rate in the smallest eddies with the numerical constant $4/3 = 1.33$ instead of 1.29 of Saffman and Turner's more exact solution.

Influence of aggregate structure

Neglecting hydrodynamic and colloidal interactions, shear coagulation can be modelled by substituting eq. (2) into the population balance developed by van Smoluchowski (1917):

$$\frac{dn_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} \beta_{i,j}^0 n_i n_{i-j} - n_i \sum_{j=1}^{\infty} \beta_{ij}^0 n_j \quad (4)$$

In order to solve eq. (4), the collision radii have to be related to the aggregate solid volumes. If the primary particles are evenly spaced and uniformly distributed in spherical aggregates, the collision radius, R , is given by

$$R_i = a(1/\varphi_0)^{1/3} \quad (5)$$

where φ_0 = packing density.

However, experiments (Tambo and Watanabe, 1979; Klimpel and Hogg, 1986; Oles, 1992) have shown that the aggregates formed by shear coagulation are usually 'fractal-like' (Schmidt-Ott *et al.*, 1990) with floc density ($= 1 - \text{porosity}$) decreasing with floc size according to a power law:

$$\varphi_i = \varphi_0 (R_i/a)^{D_f - 3} \quad (6)$$

where the fractal dimension, D_f , is less than the dimension of space, 3. Substituting $\varphi_i = i(a/R_i)^3$ into eq. (6) yields for the collision radius

$$R_i = a(i/\varphi_0)^{1/D_f} \quad (7)$$

From a comparison of eqs (5) and (7) it follows that fractal particles collide more frequently than aggregates for which $D_f = 3$ (Jiang and Logan, 1991). This is because the collision radius of the fractal aggregates increases faster during coagulation than for aggregates of constant density. For smaller fractal dimensions, the collision frequency function, β_{ij}^0 , increases more rapidly with aggregate growth.

For decreasing D_f this results in a faster decay of the total number concentration (n_{tot}) and a faster increase in average aggregate size. This is shown in Figs 1 and 2 where the total number concentration and the volume geometric mean floc size, d_g , are plotted vs the dimensionless coagulation time, τ , respectively. Starting from an initially monodisperse distribution, the evolution of n_{tot} and d_g was computed by solving the population balance, eq. (4), over the various aggregate sizes for different values of the fractal dimension. The maximum aggregate size in the computations was set to $i = 700$. Initially, n_{tot} decreases according to (Koh *et al.*, 1984)

$$n_{\text{tot}} = n_0 \exp(-\frac{16}{3} \tau) \quad (8)$$

As soon as an appreciable fraction of doublets, triplets and larger aggregates is formed, the number concentration starts to deviate from the curve corresponding to eq. (8). This deviation occurs at smaller values of τ for decreasing D_f . This is a consequence of the

Fig. 1. Simulated decay of total number concentration by shear coagulation for various values of the fractal dimension D_f and $\alpha_{ij} = 1$.

Fig. 2. Calculated evolution of d_g for various values of the fractal dimension D_f and $\alpha_{ij} = 1$. The geometric diameter is normalized by the primary particle diameter.

Fig. 3. Calculated evolution of geometric spread, σ_g , of aggregate volume distribution for various values of the fractal dimension D_f and $\alpha_{ij} = 1$.

particle size distribution becoming more rapidly poly-disperse for lower values of D_f . Figure 3 shows the geometric spread, σ , of the volume distribution as a function of τ . These calculations show that the geometric spread increases indefinitely with turbulent aggregation. Hence, no self-preserving state is obtained in agreement with the findings of Pulvermacher and Ruckenstein (1974).

Hydrodynamic interaction

When the particles come close together they will not pursue their approach along rectilinear paths as has been assumed in the derivation of eq. (2). Hydrodynamic and colloidal forces modify the trajectories of the colliding particles. The hydrodynamic interaction arises mainly from the distortion of the fluid flow due to the presence of the particles. The hydrodynamic interaction tends to inhibit encounters between particle pairs. The collision efficiency, which is defined as the ratio of the actual coagulation frequency and the collision frequency given by eq. (2), is then less than unity. In the case of an unstable suspension, the interparticle colloidal force is attractive and will enhance the collision efficiency.

At present no rigorous analysis accounting for hydrodynamic interactions between particles in turbulent orthokinetic encounters has been carried out. However, since the collisions between small particles in the smallest eddies can be considered as collisions in simple shear flow, multiplying eq. (2) by the collision efficiency computed for simple shear with $G = (\epsilon/\nu)^{1/2}$ is suggested as a first approximation for homogeneous turbulence.

Solid particles and impermeable porous flocs

The collision efficiencies for spherical particles in simple shear flow can be derived from calculations of the relative particle trajectories. Both Adler (1981b) and Higashitani *et al.* (1982) presented computations of the coagulation frequency of solid particles in simple shear flow as a function of the shear rate in the form of the flow number $Fl_{sp} [= 6\pi\mu(R_i + R_j)^3 G/8A]$ and the ratio of particle sizes $\lambda (= R_j/R_i)$. The flow number, Fl , represents the ratio of hydrodynamic shear forces to van der Waals forces between colliding particles. For completely destabilized suspensions, the collision efficiency was found to decrease monotonically with increase of Fl . For collisions between equally sized particles (homocoagulation), $\alpha \sim Fl^{-0.18}$ (van de Ven and Mason, 1977). Furthermore, homocoagulation turned out to be more favourable than coagulation between unequal particle sizes (heterocoagulation).

The values for the collision efficiency computed by Adler (1981b) and Higashitani *et al.* (1982) are applicable to encounters between solid rigid spheres, i.e. to the formation of doublets in the early stages of coagulation. They can, however, also be made to correspond to the collision efficiency of impermeable porous flocs by correcting the flow number for the fact that the attractive force between porous flocs is smaller than between solid particles. The only attractive interaction between two porous flocs which needs to be considered is that between the two nearest primary particles since the other particles in the two flocs are separated by too large a distance for the interaction forces to be effective (Firth and Hunter, 1976). Thus, the van der Waals attraction between porous flocs may be estimated by the force between two primary particles:

$$F_f = \frac{Aa}{12H^2} \quad (9)$$

whereas the attractive force between solid particles (formed by the coalescence of primary particles) is given by

$$F_{sp} = \frac{AR_i R_j}{6H^2(R_i + R_j)} = \frac{AR_i \lambda}{6H^2(1 + \lambda)}. \quad (10)$$

Equation (10) reduces to eq. (9) when $\lambda = 1$ and $R_i = R_j = a$. Note that the van der Waals attraction force between solid particles increases with increasing particle size (R_i) whereas the one between impermeable porous flocs remains constant.

In order to obtain the flow number corresponding to impermeable porous flocs (Fl_{if}), the flow number for solid particles (Fl_{sp}) has to be multiplied by the ratio of the attractive forces of solid particles and porous flocs, respectively:

$$Fl_{if} = Fl_{sp} \left[\frac{2\lambda R_i}{a(1+\lambda)} \right] = \frac{6\pi\mu R_i^3(1+\lambda)^3 G}{8A} \times \left[\frac{2\lambda R_i}{a(1+\lambda)} \right]. \quad (11)$$

For $\lambda = 1$, eq. (11) reduces to

$$Fl_{if} = Fl_{sp} \left(\frac{R_i}{a} \right) = \frac{6\pi\mu R_i^4 G}{Aa}. \quad (12)$$

Since $R_i/a > 1$, Fl_{if} is always larger than Fl_{sp} . As the collision efficiency decreases with increasing flow number Fl (either Fl_{if} or Fl_{sp}), it follows from eq. (12) that the efficiency for collisions between impermeable flocs decreases more rapidly with increasing particle size than the collision efficiency of solid particles.

Permeable porous flocs

If the fluid flow is able to penetrate the aggregates that are formed in the coagulation process, the hydrodynamic interactions will be far less pronounced than for solid rigid spheres, resulting in enhanced collision efficiencies for the porous multiplets. Fluid flow penetration in a uniformly porous floc has been studied in simple shear flow by Adler (1981a). The calculated streamlines in and around the porous floc can be considered as the relative trajectories between the aggregate and a much smaller (primary) particle. Here the influence of the interparticle attractive force on the relative trajectories is neglected. Values of the drainage cross-section as presented by Adler (1981a) can be interpreted as values for the capture cross-section due to penetration of fluid flow within the floc. The collision efficiency, α , can be readily obtained from this capture cross-section, σ_c (Arp and Mason, 1976):

$$\alpha = \left(\frac{\sigma_c}{\pi R^2} \right)^{3/2}. \quad (13)$$

The resulting values are representative for collisions where $\lambda \leq 0.1$. They are given as a function of the Debye's shielding ratio, ξ , in Table 1. The Debye's shielding ratio is defined as

$$\xi = \frac{R}{\sqrt{\kappa}} \quad (14)$$

where R denotes the collision or outer radius of the floc and κ is the floc permeability. Because of the neglecting of van der Waals attraction in the calculations, the collision efficiency becomes zero when fluid flow penetration stops, i.e. when ξ equals 10.89 (Adler, 1981a). Similar rigorous computations of capture cross-sections for $\lambda > 0.1$ have not been carried out.

Torres *et al.* (1991a) and Kusters (1991), however, presented an approximate method to derive the efficiencies for collisions between more equally sized

Table 1. Numerical values of the ratio of hydrodynamic and collision radii and the corresponding collision efficiency for $\lambda \leq 0.1$ as a function of the Debye's shielding ratio of the large floc

ξ_i	R_H/R	$\alpha_{ij} (\lambda \leq 0.1)$
∞	1	0
70	0.984	0
40	0.971	0
15	0.909	0
10.89	0.865	0
10	0.850	0.009
8	0.802	0.068
6	0.722	0.192
5	0.662	0.290
4	0.581	0.420
3	0.474	0.584
2	0.336	0.771
1	0.175	0.933

porous flocs ($\lambda \rightarrow 1$). They designated their approach as the two-radius model and shell-core model, respectively. This approximate method envisions the porous floc as a spherical body with an impermeable core and a completely permeable shell. The outer collision radius, R , of the floc represents the distance within which another floc must approach for coagulation to occur. The smaller core radius describes the drag the floc experiences in the flow field and corresponds to the hydrodynamic radius, R_H , of the floc. Starting from known hydrodynamic functions for hard spheres (Arp and Mason, 1976; Adler, 1981b), the trajectories of two colliding impermeable cores of porous flocs are calculated and the outer radius is used to determine the point of contact (see Fig. 4). In this way, the influence of fluid flow penetration in a porous floc is accommodated in the collision efficiencies that follow from the trajectory analysis.

The approaches by Torres *et al.* (1991a) and by Kusters (1991) differ in the way they related the hydrodynamic radius to the outer radius of a porous floc. Torres *et al.* (1991a) assumed a constant ratio between the hydrodynamic radius and radius of gyration, R_G . Since for a fractal aggregate

$$R^2 = \frac{D_f + 2}{D_f} R_G^2 \quad (15)$$

Fig. 4. Shell-core model.

it follows that the hydrodynamic radius is also proportional to the outer radius of the floc. This assumption corresponds to a constant Debye's shielding ratio, ξ , for all aggregate sizes. Kusters (1991) related the hydrodynamic radius and the collision efficiency directly to the Debye's shielding ratio. The approach by Kusters (1991) is briefly outlined below.

In analogy with van Saarloos (1987), Kusters (1991) approximated the fractal aggregates as being uniformly porous in the outer regions where fluid penetration occurs. Then, for $\xi > 20$ the ratio of hydrodynamic radius and outer radius can be approximated by (Jones, 1978)

$$\frac{R_H}{R} = \frac{1 - \xi^{-1} \tanh(\xi)}{1 + \frac{3}{2}\xi^{-2} - \frac{3}{2}\xi^{-3} \tanh(\xi)}. \quad (16)$$

For values of R_H/R for $\xi \leq 20$, see Table 1.

Figure 5 shows the values for α_{ij} that follow from the shell-core model for both $\lambda \leq 0.1$ and $\lambda = 1$ using the hydrodynamic radius that follows from eq. (16) and Table 1. The agreement with the values from Adler's rigorous analysis for $\lambda \leq 0.1$ is quite satisfactory. Modelling the porous floc as an impermeable core with a completely permeable shell seems to be a valid approach.

The collision efficiency for encounters between equally sized porous flocs is larger than for encounters where $\lambda \leq 0.1$. Furthermore the collision efficiency does not reduce to zero at $\xi = 10.89$ but remains at a fairly high level for ξ ranging from 10 to 100. This is because similarly sized impermeable cores are able to approach each other much closer than cores of largely different sizes.

The collision efficiencies for values of $\lambda \geq 0.2$ are expected to approximate the values calculated for $\lambda = 1$, since the trajectories of the impermeable cores are relatively similar to those with encounters between equally sized particles (Adler, 1981c). The region $0.1 \leq \lambda < 0.2$ is the transition range where the collision efficiency is intermediate between the values corresponding to $\lambda \leq 0.1$ and $\lambda = 1$, respectively.

Fig. 5. Values for collision efficiency α_{ij} as follows from the shell-core model for both $\lambda \leq 0.1$ and $\lambda = 1$ as a function of ξ .

The Debye's shielding ratio, ξ , is related to the outer floc radius through eq. (14). The permeability of a floc with solids density φ is estimated by

$$\kappa = \frac{3 - \frac{9}{2}\varphi^{1/3} + \frac{9}{2}\varphi^{5/3} - 3\varphi^2}{9\varphi(3 + 2\varphi^{5/3})C_S} 2a^2 \quad (17)$$

where φ is given by eq. (6) for a fractal floc. The original expression for the permeability has been derived by Happel (1958) and applies to random assemblies of non-contacting spheres. The requirement of no contact between the particles is not met in the floc since primary particles are bound to one or more neighbours. These short-range interactions are accommodated through the coefficient C_S . An average value of 0.5 for C_S seems to be a good estimate for all aggregate sizes except for the doublets where C_S equals 0.724 (Sonntag and Russel, 1986, 1987).

Values for ξ have been computed for fractal flocs using eqs (6), (7),[†] (17) and (14). Figure 6 shows ξ as a function of aggregate size for different values of the fractal dimension D_f . The relationship between the Debye's shielding ratio and actual floc radius makes it possible to couple the coagulation efficiencies presented in Fig. 6 directly to the aggregate sizes. For values of the fractal dimension near 2, ξ is almost constant over a wide range of aggregate sizes. This validates the assumption of a constant ratio between the hydrodynamic and outer radii by Torres *et al.* (1991a) for $D_f = 1.8$. For this value of the fractal dimension, $\xi = 8$ and $\alpha_{ij} = 0.8$ for $3 \leq i \leq 1000$, in agreement with the value Torres *et al.* (1991a) presented for the stability ratio $W_{ii} = \alpha_{ii}^{-1} = 1.2$.

Fig. 6. Debye's shielding ratio, ξ , as a function of normalized aggregate size $d_i/(2a)$ for different values of the fractal dimension. Packing density φ_0 in eqs (6) and (7) is set to unity.

[†] The power-law relationships (6) and (7) may be applied to aggregates consisting of more than two primary particles but it is not applicable to doublets. A doublet of two primary particles is uniquely defined and cannot be described by different values of D_f . For the doublets we assumed $\varphi = 0.8$ in analogy with Treweek and Morgan (1977).

Fig. 7. Values for the collision efficiency α_{ij} for porous flocs, for solid spheres of equal cross-section and for porous impermeable flocs as a function of collision diameter d_i . Primary particle diameter = 1 μm .

Figure 7 shows the collision efficiency α_{ii} for porous flocs derived from the shell-core model and the collision efficiencies for solid spheres and impermeable porous flocs of equal cross-section as a function of collision diameter. The flocs consist of primary particles of 1 μm and are assumed to have a fractal structure with D_f equal to 2.5. The collision efficiencies computed for solid spheres and impermeable porous flocs decrease very rapidly with increasing size. The collision efficiency derived from the shell-core model, however, increases rapidly to a maximum value of 0.36. After this peak value, it decreases only slowly with increasing aggregate size. Since with a smaller fractal dimension the flocs are more porous at a comparable aggregate size, the collision efficiency for permeable porous flocs increases with decreasing fractal dimension.

On the basis of their analysis of encounters between equally sized fractal flocs with $D_f = 1.8$, Torres *et al.* (1991a) concluded that hydrodynamic interactions can be neglected in kinetic calculations of coagulation. This is equivalent to setting α_{ij} equal to unity for all possible encounters. The above presented analysis by Kusters (1991) shows that α_{ij} is clearly smaller than unity for $D_f > 2$. Irrespective of the value of D_f , α_{ij} approaches zero for encounters between flocs with size ratio λ smaller than 0.1 when $\xi_i > 10.89$. For these values of the Debye's shielding ratio, a small particle is not able to approach the larger porous floc close enough for coagulation to take place. Since the present shell-core model does not take into account the van der Waals attraction between flocs, the resulting collision efficiency equals zero. Hence, for these encounters the collision efficiency follows from the values computed for encounters between impermeable flocs. It is advised to use these latter values whenever they are larger than the collision efficiencies calculated with the shell-core model.

Influence of heterogeneous shear field

If the turbulence in the stirred tank is homogeneous, the mean specific turbulent energy dissipation

rate, ε , can be used for calculating the coagulation rate. ε is derived from the power input, P (Laufhütte and Mersmann, 1985):

$$\varepsilon = \frac{P}{\rho_l V} = \frac{N_p N^3 D^5}{V}. \quad (18)$$

For large impeller Reynolds numbers, $Re = ND^2/\nu \geq 10^4$, the power number N_p is a constant. Usually the shear rate field is far from uniform in a stirred tank and instead of the shear rate obtained from the power input per unit mass, the residence time weighted shear rate, G_T , or 'Camp number' (Gregory, 1981), $G_T t$, should be used to calculate the extent of coagulation in a stirred tank. Koh *et al.* (1984) argued that G_T can be approximated by the volume average shear rate, G_V , since the circulation rates within stirred tanks are normally high compared to the coagulation rate. Values of the shear rate ratio, $G_V/(\varepsilon/\nu)^{1/2}$, were presented for a variety of stirred tank configurations. Kusters *et al.* (1991) calculated G_T for a stirred tank of standard configuration by numerical particle tracking. The movement of an aggregate within the vessel was simulated. During the particle's track, the residence time in zones of different energy dissipation rate was recorded, resulting in a residence time distribution as a function of the local energy dissipation rate. From this residence time distribution, G_T was calculated and found to be almost equal to G_V , validating the approach by Koh *et al.* (1984).

Thus, the coagulation rate in a stirred tank is given by

$$\begin{aligned} J_{ij} &= 1.294 \alpha_{ij} G_T (R_i + R_j)^3 n_i n_j \\ &\cong 1.294 \alpha_{ij} G_V (R_i + R_j)^3 n_i n_j. \end{aligned} \quad (19)$$

EXPERIMENTAL

Destabilizer

Sodium chloride was used to induce coagulation of polystyrene particles. The concentration of sodium chloride was chosen well above the critical coagulation concentration to ensure complete destabilization of the suspension. Above the critical coagulation concentration, the electrostatic double layer is compressed to such an extent that the net interaction energy is always attractive, independent of separation between the colliding particles. The coagulation is 'rapid' relative to 'slow' coagulation in the presence of weak interparticle repulsions (Schowalter, 1984).

Particulate system

Aqueous suspensions of monosized spherical polystyrene particles with a characteristic diameter of about 1 μm were used for studying coagulation. The polystyrene particles were prepared by polymerization without the addition of an emulsifying agent. The polymerization was based on the method as described by de Boer (1987). The residual reactants and product impurities, both inorganic and organic, were removed by dialysis against distilled water. Dialysis was carried out using a Visking dialysis tube.

The size of the primary particles was determined by scanning electron microscopy (SEM). The solids concentration of the final polystyrene latex was determined by evaporation of the fluid. The main reason for selecting polystyrene latex was the specific density of polystyrene ($\sim 1050 \text{ kg m}^{-3}$) being almost equal to the density of the sodium chloride solution. The density of the sodium chloride solution varies from 1020 to 1120 kg m^{-3} for the NaCl concentration range of 0.5–3 M. Sedimentation of solids could thus be avoided, even in quiescent flows.

Experimental procedure

The coagulation experiments were carried out in a stirred tank of standard configuration, i.e. with a flat bottom, a flat cover, four vertical baffles and a height equal to the tank diameter ($= 20 \text{ cm}$). The stirrer, a standard six-bladed Rushton disc turbine impeller, had a diameter of one-third the tank diameter and was located midway between top and bottom. The corresponding power number, N_p , amounted to 4.5 for $Re \geq 10^4$ (Kusters *et al.*, 1991a).

First, the tank was completely filled with the sodium chloride solution. Next, the electric motor that drives the impeller was started and the proper amount of the polystyrene latex was injected into the electrolyte solution to obtain the desired solids concentration. The polystyrene latex was concentrated by vacuum evaporation to limit the volume that had to be injected. Prior to addition, ultrasonics were applied to the concentrated latex to break up any doublets that might have been formed during the evaporation process. A siphon vessel was used for level control in order to avoid flooding upon addition of the latex and also to ensure that no bubbles were introduced into the stirred tank upon withdrawal of samples from the contents of the tank. The siphon vessel was filled with a sodium chloride solution of equal concentration to that in the stirred tank. Samples were withdrawn from the bulk of the tank. This was done gently with a pipet of large orifice and internal diameter, 5 and 8 mm, respectively, in order to avoid breakage of formed aggregates by sampling. Characteristic shear rates during sampling were of the order of 10 s^{-1} which is at least 3 times smaller than the shear rate experienced in the bulk of the stirred tank.

The later stages of coagulation that are affected by aggregate breakup had to be excluded from the analysis. These later stages could be discriminated by adding a steric stabilizing agent (polyvinyl alcohol) to the suspension after the steady state was reached. Polyvinyl alcohol adsorbs onto the surface of the primary particles and precludes coagulation and recombination of aggregate fragments due to steric hindrance. Hence only breakup remains (de Boer, 1987).

Particle sizing

The evolution of the aggregate size distribution was measured by taking samples which were analysed by laser diffraction spectrometry (Malvern 2600 Particle

Sizer). This technique is based on the measurement of the first diffraction lobe in the forward scattering by particles larger than the wavelength of light ($\lambda_w = 0.475 \mu\text{m}$ for He–Ne laser light in aqueous solutions). To avoid multiple scattering effects (Gorni, 1986) that arise from light rays being diffracted by more than one particle, the samples were diluted with the corresponding sodium chloride solution. Gentle mixing of sample and sodium chloride solution was performed with a magnetic stirrer at the bottom of the optical cell. Applied shear rates were less than 10 s^{-1} . The obscuration (also referred to as extinction) of the undiffracted laser beam was adjusted to values corresponding to particle concentrations where multiple scattering is negligible.

The interpretation of the forward scattering patterns is based on the assumption that the scatterers are spherical and homogeneous, which is not true for aggregates. From optical microscopic observations, it could be concluded that the deviation from spherical shape is not great. The aggregates show most resemblance to prolate spheroids. The aspect ratio of the agglomerates was normally less than 1.5. Shape effects on the forward diffracted lobe can therefore be neglected (Bohren and Koh, 1985).

The inhomogeneous composition of the aggregates only affects the refraction part of the forward scattering and is therefore less important. The diffraction part is equivalent to that arising from a spherical particle with the same mean projected area (Latimer, 1985; West, 1991). For aggregates consisting of primary particles with a radius larger than the wavelength of light, i.e. with a size parameter $x = 2\pi a/\lambda_w > 1$, the extinction efficiency approximates that of a sphere of equal projected area. Since, by definition, average projected area and collision cross-section are equal, the size distribution that is obtained by laser diffraction spectrometry corresponds to the collision diameter of the flocs. Because the diffraction part of the forward scattered intensity is proportional to the square of the projected floc area, it follows that it is the volume distribution which is determined most accurately by this technique. The Malvern Particle Sizer provides estimates of the volume fractions, Q_k , of 15, almost geometrical, size classes over a size range spanning two decades of collision diameter (Kusters *et al.*, 1991b). The lower limit of the size range can be varied from 1.2 to 20 μm . Characteristic average sizes that are determined are the volume and surface (Sauter) mean diameters:

$$\text{VMD} = 2 \sum \frac{Q_k}{R_k} \quad (20)$$

$$\text{SMD} = \frac{2}{\sum Q_k/R_k} \quad (21)$$

Apart from aggregate size, laser diffraction can also be used to determine the average floc density $\bar{\varphi}$ in a sample (Kusters, 1991; Oles, 1992). $\bar{\varphi}$ is defined as the ratio of the primary particle volume concentration, C_p , and the volume concentration of the flocs, C_f , in

the sample. The floc volume concentration C_F comprises the sum of individual particle and interstitial volumes.

The concentration C_P of the sample in the measuring cell is obtained by dividing the primary particle concentration in the stirred tank with the dilution factor that has been applied to avoid multiple scattering effects in the sizing analysis. The volume concentration of the aggregates, C_F , follows from the obscuration, OB, of the laser beam:

$$C_F = -\frac{4 \ln(1 - OB)}{3L \sum \gamma_k Q_k / R_k} \quad (22)$$

where L is the path length of the laser light in the optical cell ($= 14.3$ mm) and γ_k denotes the extinction efficiency of the particles in the k th size class. The extinction efficiency of flocs can be estimated by the extinction efficiency of polystyrene spherical particles (van der Hulst, 1981):

$$\gamma = 2 - \frac{4}{\rho} \sin \rho + \frac{4}{\rho^2} (1 - \cos \rho) \quad (23)$$

where $\rho = 4\pi(m-1)R/\lambda_w$ and m denotes the ratio of the refractive indices of polystyrene and water ($m = 1.16$). For $\rho \gg 1$, $\gamma = 2$ and eq. (22) reduces to Lambert-Beer's law:

$$C_F = -\frac{SMD \ln(1 - OB)}{3L} \quad (24)$$

The obscuration follows from the extinction measurement of the undiffracted laser light beam and the Sauter mean diameter is obtained from the measurement of the scattering pattern of the flocs.

RESULTS

The evolution of the VMD during coagulation in a stirred tank is shown in Fig. 8. De Boer *et al.* (1989b) discerned four different stages in the course of the coagulation process. The first stage (I) is the formation of doublets from the collisions between primary particles. As can be inferred from Fig. 1, this stage lasts only up to $\tau = 0.1$. Then, larger aggregates start to be formed, resulting in a deviation of the number concentration decay according to eq. (8). Stage I is followed by an exponential type of growth designated as stage II. The coagulation rate diminishes during stage III of the process because of aggregate breakup and finally a steady state is reached (IV). This article deals with stages I and II of the coagulation process. The evolution of VMD upon addition of polyvinyl alcohol is also shown in Fig. 8. From such plots, the aggregate size at which breakup becomes significant was determined. This aggregate size corresponds approximately to the deflection point in the growth curve. The size evolution prior to this deflection point has been used in the analysis to determine the dependence of the coagulation rate on the various process variables.

Fig. 8. Evolution of VMD during batch coagulation in a stirred tank. Addition of polyvinyl alcohol at steady state. PS particles, $0.48 \mu\text{m}$ in diameter. Process conditions: $N = 6 \text{ s}^{-1}$, $C_P = 3 \times 10^{-5} \text{ m}^3 \text{ m}^{-3}$, $c_{\text{NaCl}} = 0.48 \text{ M}$.

Stage I: doublet formation

It was discussed that the residence time weighted shear rate should be used to compute the theoretical collision frequencies rather than the shear rate calculated from the power input per unit mass in the stirred tank. Starting from this principle, collision efficiencies for the initial stages of the coagulation process as presented in the literature are replotted in Fig. 9 vs the flow number corresponding to the residence time weighted shear rate. De Boer *et al.* (1989a) performed their coagulation experiments with polystyrene (PS) primary particles in a stirred tank of similar configuration as used in our experiments, so $G_T = 0.66 (\varepsilon/v)^{1/2}$ (Kusters *et al.*, 1991a). Higashitani *et al.* (1983) conducted their experiments with polystyrene (PS) and polyvinyl toluene (PVT) primary particles in a stirred tank agitated by an eight-flat-blade paddle with its diameter equal to half the tank diameter. For such an impeller-tank diameter ratio, Koh *et al.* (1984) showed that the volume average shear rate G_V equals $0.83 (\varepsilon/v)^{1/2}$. Assuming that the equality between the residence time weighted and volume average shear rate also exists for this stirred tank configuration, the data of Higashitani *et al.* (1983) were plotted vs $Fl_{sp} = 6\pi\mu a^3 G_V/A$. The Hamaker constant, A , was set equal to $3.5 \times 10^{-21} \text{ J}$, corresponding to polystyrene particles (Visser, 1972).

For comparison, theoretical predictions for α_{ij} are also included in Fig. 9. The collision efficiencies for encounters between equally sized particles in simple shear flow are obtained from the values of the stability ratio as a function of Fl_{sp} presented by Feke and Schowalter (1983). The stability ratio is the reciprocal of the collision efficiency. Additional Brownian coagulation of particles may enhance the collision efficiency at small flow numbers. Two limiting cases of the influence of Brownian motion on shear coagulation are displayed in Fig. 9. Swift and Friedlander (1964) considered Brownian (perikinetic) and shear (orthokinetic) coagulation as additive processes. Feke and Schowalter (1983) showed that for small Peclet

Fig. 9. Values for the initial collision efficiency α_{11} vs Fl_{sp} for $A = 3.5 \times 10^{-21}$ J.

numbers, $Pe = 3\pi\mu a^3 G_T / k_B T$, larger collision efficiencies are obtained in simple shear flow than would be expected from a linear combination of the peri- and orthokinetic coagulation expressions.

Overall, the agreement between the replotted experimental data and theoretical values for simple shear flow is reasonable. This implies that the collision efficiency for primary particles smaller than the Kolmogorov microscale may indeed be calculated from particle interception trajectories in simple shear flow provided the correct equivalent shear rate is used. It also follows that the influence of Brownian motion on turbulent coagulation is not as strong as predicted by Feke and Schowalter (1983). The assumption of additivity seems to be in better agreement with the experimental data. The reason for this discrepancy may be that the enhanced collision efficiency is a distinct feature of pure simple shear flow. For instance, the influence of Brownian motion on orthokinetic coagulation in uniaxial extension (pure strain) flow is more along the lines of simple additivity. Since the laminar flow conditions for particles smaller than the Kolmogorov microscale comprise both shear and strain, the presence of the latter may reduce the perikinetic effect to simple additivity.

The collision efficiencies that follow from the experiments with polyvinyl toluene are systematically larger than the theoretical predictions. This may be attributed to a different Hamaker constant for polyvinyl toluene than for polystyrene. With a Hamaker constant of 7×10^{-21} J, the values would collapse onto the theoretical curve for simple shear flow.

Stage II: aggregate growth

The accelerated growth in stage II of the coagulation process is in disagreement with computations of coagulation assuming a uniform porosity within the flocs. With a constant collision efficiency an almost linear increase of the volume mean diameter with time is predicted (de Boer *et al.*, 1989b). The evolution of the VMD is similar to that of the volume average geometric diameter which is displayed for $\alpha_{ij} = 1$ in Fig. 2. From this figure it is apparent that the

Fig. 10. Variation of average floc density $\bar{\phi}$ in samples as a function of volume mean diameter. PS particles, $0.56 \mu\text{m}$ in diameter. Process conditions: $C_P = 8 \times 10^{-6} \text{ m}^3 \text{ m}^{-3}$, $c_{\text{NaCl}} = 0.48 \text{ M}$.

Fig. 11. Evolution of VMD as determined experimentally and also as obtained by solving the population balances over the various aggregate sizes with the appropriate values for the coagulation efficiency α_{ij} for permeable and impermeable flocs. PS particles, $0.56 \mu\text{m}$ in diameter. Process conditions: $N = 2 \text{ s}^{-1}$, $C_P = 8 \times 10^{-6} \text{ m}^3 \text{ m}^{-3}$, $c_{\text{NaCl}} = 0.48 \text{ M}$. In both simulations, $D_f = 2.5$.

observed exponential type of growth may stem from fractal dimensions less than 3. This hypothesis was verified by measurements of the floc density by LDS during coagulation. Figure 10 is a representative example of the variation of the average floc density $\bar{\phi}$ ($= C_P / C_F$) as a function of VMD. The average floc density in a sample is related to the floc density ϕ as a function of floc size, i.e. eq. (6) through the measured aggregate size distributions:

$$\bar{\phi} = \sum Q_k \phi_k = \phi_0 \sum Q_k \left(\frac{R_k}{a} \right)^{D_f - 3} \quad (25)$$

where ϕ_k denotes the floc density corresponding to size R_k . The variation in $\bar{\phi}$ with VMD has also been calculated with eq. (25). A good fit between measured and calculated values of $\bar{\phi}$ was obtained using values for ϕ_0 and D_f of 0.8 ± 0.2 and 2.5 ± 0.1 , respectively. The curves for $\bar{\phi}$ at $N = 4$ and 6 s^{-1} tend to drop below the curve at $N = 2 \text{ s}^{-1}$ as soon as breakup affects the aggregate growth. This is because the aggregate size distribution becomes narrower as it approaches its final steady-state form. In Fig. 11 the

evolution of the volume average aggregate size in stages I and II of the coagulation process is shown as determined experimentally and computed by solving the population balance, eq. (4), with the appropriate values substituted for the collision efficiency for the various aggregate sizes. In order to extend the computations to larger aggregate sizes, the discrete population balances have been replaced by sectional ones according to the Batterham scheme (Koh *et al.*, 1987). In the simulation, the computed number distributions were converted to volume size distributions similar to those that were obtained experimentally by LDS. The theoretical VMD values that are shown in Fig. 11 have been calculated from these simulated volume size distributions using eq. (20). Given the limited accuracy in the value for the fractal dimension, the agreement between the experimental results and the data computed with the collision efficiencies from the shell-core model is quite satisfactory. In Fig. 11 also the aggregate growth is depicted that follows from the computations where the porous aggregates are assumed to be impermeable. Clearly, this assumption underestimates the aggregate growth and should not be used for predictions of the coagulation process.

In Fig. 12 the experimental and simulated (cumulative) volume size distributions are shown at comparable values for the volume mean diameter. Increase in average aggregate size is accompanied by a considerable broadening of the floc size distribution. This increase in spread of the size distribution is predicted accurately by the simulations.

Dependency of coagulation rate on process variables

The growth rate is strongly dependent on the fractal dimension the aggregates attain as is shown in Fig. 2. Therefore, the fractal dimension was determined as a function of the process variables in order to verify whether changes in coagulation rates are to be attributed to different values of D_f . The fractal dimension proved to be independent of impeller speed and of concentration of solids, in agreement with the

findings of Tambo and Watanabe (1979) and Oles (1992). However, it was found to be slightly different for the various polystyrene lattices that were used in the course of the aggregation experiments. D_f varied from 2.3 to 2.6.

This dependency of fractal dimension on the polystyrene latex is to be attributed to a limited reproducibility of the surface properties of the primary particles giving rise to a different strength and flexibility of the bonds between them. The amount of restructuring after aggregate formation by collision may depend on the strength and flexibility of these bonds (Mühle, 1993). Torres *et al.* (1991b) showed that, in shear flow, cluster-cluster aggregation, i.e. coagulation by collisions between flocs of similar size and without restructuring, results in the formation of aggregate structures with $D_f = 1.8$. Particle-cluster aggregation, i.e. coagulation by collisions between dissimilar sizes, yields D_f values close to 3. The contribution of particle-cluster aggregation to shear coagulation, however, is small (Torres *et al.* 1991a) and is not expected to raise the fractal dimension above a value of 2. In fact, values between 1.7 and 2 are usually found in flocculation experiments, where the binding between primary particles results from strong aluminium hydroxide or polymer bridges (Klimpel and Hogg, 1986; Tambo, 1991). These bridges prevent aggregate restructuring. In coagulation experiments, where the binding is by the weaker van der Waals forces, restructuring to a more compact packing of primary particles within the flocs is not entirely hindered, and values for D_f larger than 2 are obtained. Following this line of reasoning, a dependency of D_f on salt concentration is also expected since an increase in destabilizer concentration reduces the electrostatic repulsion to a larger extent and maximizes the binding force between primary particles.

In the following sections, the dependency of the coagulation rate on impeller speed, on solids concentration and on concentration of destabilizer is discussed.

Effect of impeller speed

The impeller speed N affects the mean energy dissipation rate in the stirred tank through eq. (18). The residence time weighted shear rate, G_T , which controls the coagulation rate is proportional to the square root of the mean energy dissipation rate, ϵ . It follows from eq. (18) that G_T is proportional to $N^{3/2}$.

Figure 13 shows the experimentally determined and simulated aggregate growth at various impeller speeds, $N = 2, 4$ and 6 s^{-1} . Corresponding residence time weighted shear rates are 58, 163 and 299 s^{-1} . The initial aggregate growth has been simulated with and without (additive) Brownian coagulation. The simulation results corresponding to aggregate growth by shear and Brownian coagulation are in closer agreement with the experimental data than those neglecting Brownian coagulation. The influence of the Brownian motion of the primary particles and small clusters on the coagulation process is appreciable for

Fig. 12. Comparison of experimental and simulated cumulative volume distributions of the aggregate collision diameter, for $D_f = 2.5$.

Fig. 13. Evolution of VMD for various impeller speeds at $C_P = 8 \times 10^{-6} \text{ m}^3 \text{ m}^{-3}$ and $c_{\text{NaCl}} = 0.48 \text{ M}$. PS particles, $0.56 \mu\text{m}$ in diameter. Simulation: $D_f = 2.5$.

Fig. 14. VMD vs dimensionless coagulation time, τ , for various impeller speeds at $C_P = 6.2 \times 10^{-5} \text{ m}^3 \text{ m}^{-3}$ and $c_{\text{NaCl}} = 0.4 \text{ M}$. PS particles, $0.8 \mu\text{m}$ in diameter.

$N = 2 \text{ s}^{-1}$ ($Pe = 3$). The influence diminishes as the impeller speed is increased to 4 and 6 s^{-1} ($Pe = 8.3$ and 15.2 , respectively).

Because of the declining enhancement by Brownian coagulation, the initial parts of the growth curves (where breakup is absent) do not overlap each other perfectly when the volume mean diameter is plotted vs the dimensionless coagulation time, $\tau \sim N^{1.5}$. Figure 14 shows the respective plot for results from coagulation experiments carried out with larger primary particles, $0.8 \mu\text{m}$ in size. Here the influence of Brownian coagulation on the aggregate growth is negligible. However, again the initial parts of the growth curves do not overlap each other perfectly. A better match is obtained when VMD is plotted vs $N^{1.3}t$. The exponent is less than 1.5 because the collision efficiency in the initial stages of coagulation decreases with the impeller speed according to $N^{-0.4}$ as can be deduced from the dependency of α_{11} on shear rate as depicted in Fig. 9. This results in an initial dependency of the coagulation rate on impeller speed equal to $N^{1.1}$.

Since the collisions between the larger porous flocs are brought about by the penetration of fluid flow within the flocs, the collision efficiencies of the larger porous flocs are expected to be independent of stirrer speed. The corresponding collision rate, therefore, increases proportional to the shear rate G_T , which is proportional to $N^{1.5}$. The dependency determined experimentally is intermediate between $N^{1.1}$ and $N^{1.5}$.

Effect of solids concentration

In Fig. 15 results are shown from experiments in which the solids concentration, C_P , was varied. The initial parts of the growth curves overlap each other approximately when plotted vs the dimensionless coagulation time, τ . Hence, the evolution of the aggregate size (growth rate) is first-order with respect to C_P in agreement with the binary collision assumption. This assumption is expected to hold up to a solids concentration of $10 \text{ vol}\%$ (Brakalov, 1987). Of course, the simulation result that is shown in Fig. 15 for comparison is also based on this binary collision principle.

De Boer *et al.* (1989b) reported a proportionality of the growth rate with $C_P^{1.72}$. This large exponent, however, resulted from an analysis that also included parts of growth curves that were clearly affected by breakup. For instance, the deviation between experiments and simulations in Fig. 15 for $\tau > 2$ is due to breakup. It is clear that parts of the experimental growth curves for $\tau > 2$ should not be included in the determination of the coagulation kinetics.

Effect of salt concentration

Figure 16 shows the aggregate growth as a function of the concentration of the destabilizer (NaCl) for a specific polystyrene latex. At a salt concentration of 0.5 M the growth rate seems to be slightly smaller than for the larger concentrations. This may be caused by a larger value for the fractal dimension of the aggregates formed at $c_{\text{NaCl}} = 0.5 \text{ M}$. Better agreement with the experimental data at $c_{\text{NaCl}} = 0.5 \text{ M}$ is obtained for simulations with $D_f = 2.45$ instead of 2.4 .

Fig. 15. Variation of solids concentration C_P . PS particles, $0.8 \mu\text{m}$ in diameter. Process conditions: $N = 4 \text{ s}^{-1}$, $c_{\text{NaCl}} = 0.4 \text{ M}$. Simulation: $D_f = 2.55$.

Fig. 16. Variation of salt concentration c_{NaCl} . PS particles, $0.48 \mu\text{m}$ in diameter. Process conditions: $N = 6 \text{ s}^{-1}$, $C_P = 2.9 \times 10^{-5} \text{ m}^3 \text{ m}^{-3}$. Simulation: $D_f = 2.4$.

Such a small difference in fractal dimension cannot be detected experimentally due to the larger error in the D_f value (± 0.1) obtained from the floc density measurements. Nevertheless, a larger D_f value at smaller salt concentrations seems plausible as it may result from stronger restructuring with decreasing salt concentration as discussed previously.

DISCUSSION

The experimental results show that the collision frequency for turbulent aggregation in stirred tanks can be estimated by eq. (19) where α_{ij} can be obtained according to the calculation scheme depicted in Fig. 17.

In the present article, the trajectory analysis for hard spheres (Arp and Mason, 1976; Adler, 1981b) has been used to estimate the collision efficiency of permeable porous flocs, thereby neglecting any van der

Fig. 17. Calculation scheme for collision efficiency of porous flocs in a stirred tank.

Waals interaction between the colliding flocs. In that case, the collision efficiency only depends on the values of ξ_i and λ . Estimates of α_{ij} for $\lambda \geq 0.2$ and $\lambda < 0.2$ can be obtained as a function of ξ_i from the curves in Fig. 5 corresponding to $\lambda = 1$ and $\lambda \leq 0.1$, respectively. Neglecting the van der Waals interaction makes the collision efficiency of permeable flocs independent of the shear rate and of the corresponding flow number for permeable flocs, Fl_{pf} , which is defined as

$$Fl_{pf} = \frac{6\pi\mu R_{H,i}^3(1 + \lambda_H)^3 G}{8A} \left[\frac{2\lambda_H R_{H,i}}{a(1 + \lambda_H)} \right] \quad (26)$$

where $\lambda_H = R_{H,j}/R_{H,i}$. Incorporation of the influence of the van der Waals attraction in the trajectory analysis is optional. This is why the box with Fl_{pf} and the arrow emitting from G_V to the trajectory analysis for permeable flocs are indicated with dotted lines in Fig. 17. It should be noted also that electrostatic and/or steric repulsion between the colliding particles can be included in Fig. 17 in order to describe slow aggregation resulting from a sticking efficiency less than unity. This, however, is beyond the scope of this article.

CONCLUSIONS

The collision efficiency of encounters between primary particles smaller than the Kolmogorov microscale may be approximated by the theoretical values derived from trajectory analysis in simple shear flow provided the correct equivalent simple shear rate is used.

The accelerated growth of the aggregates in the stages following the doublet formation of primary particles is to be attributed to the fractal-like structure of the formed aggregates. In a fractal-like structure less primary particles are required to build up an aggregate of a certain size than in a uniformly closed packed structure. Due to the large porosities the aggregates attain, the fluid flow is able to penetrate the aggregates, resulting in enhanced collision efficiencies. Values for these collision efficiencies between porous flocs have been estimated by the shell-core model. The application of these values in the description of the aggregate growth yielded results in agreement with experimental findings.

The dependency of the coagulation rate on solids concentration and on impeller speed was found to be in agreement with the orthokinetic turbulent binary collision mechanism for aggregates smaller than the Kolmogorov microscale.

NOTATION

a	primary particle radius, m
A	Hamaker constant, J
C_S	shielding coefficient
C_P	solids concentration, $m^3 m^{-3}$
C_F	floc concentration, $m^3 m^{-3}$
d_g	volume average geometric diameter [$\ln d_g = \sum n_i d_i^3 \ln(d_i) / \sum n_i d_i^3$], m

d_i	diameter of aggregate consisting of i primary particles
D	impeller diameter, m
D_f	fractal dimension
F	van der Waals attractive force, N
Fl	flow number
G	shear rate, s^{-1}
H	binding distance, m
J_{ij}^0	collision frequency per unit volume of suspension, $m^{-3} s^{-1}$
J_{ij}	coagulation frequency per unit volume of suspension ($= \alpha_{ij} J_{ij}^0$), $m^{-3} s^{-1}$
k_B	Boltzmann constant, $1.38 \times 10^{-23} J K^{-1}$
L	path length of light passing through LDS measuring cell ($= 14.3$ mm)
m	refractive index ratio
n_i	number concentration of aggregates consisting of i primary particles
n_{tot}	total number concentration, m^{-3}
n_0	initial total number concentration, m^{-3}
N	rotational speed of impeller, s^{-1}
N_P	power number of impeller
OB	obscuration of laser light in LDS ($1 -$ transmission ratio)
P	power input, W
Pe	Peclet number ($= 3\pi\mu a^3 G_V / k_B T$)
Q_k	volume concentration of size class k of particle sizer, $m^3 m^{-3}$
R	outer (collision) radius of particle, m
R_G	radius of gyration, m
R_H	hydrodynamic radius of particle, m
SMD	surface or Sauter mean diameter, m
t	time, s
T	absolute temperature, K
V	volume of suspension, m^3
VMD	volume mean diameter, m
W	stability ratio
x	size parameter ($= 2\pi a / \lambda_w$)

Greek letters

α_{ij}	collision efficiency for encounters between aggregates consisting of i and j primary particles, respectively
β_{ij}^0	collision frequency function, $m^3 s^{-1}$
γ	extinction efficiency
ε	mean energy dissipation rate, $W kg^{-1}$
η	Kolmogorov microscale, m
κ	floc permeability, m^2
λ	particle size ratio
λ_w	wavelength for He-Ne laser light in aqueous solutions, m
μ	dynamic viscosity of suspension, $kg m^{-1} s^{-1}$
ν	kinematic viscosity of suspension, $m^2 s^{-1}$
ξ	Debye's shielding ratio
ρ_t	density of suspension, $kg m^{-3}$
ρ_p	particle density, $kg m^{-3}$
σ_c	capture cross-section of particle, m^2
σ_g	geometric spread of volumetric size distribution [$\ln^2 \sigma_g = \sum n_i d_i^3 \ln^2(d_i/d_g) / \sum n_i d_i^3$]

τ	dimensionless coagulation time [$(\epsilon/v)^{1/2} a^3 n_0 t = (3/4\pi)(\epsilon/v)^{1/2} C_p t$]
τ_{pi}	particle relaxation time, s
ϕ	floc density (1 – porosity)
ϕ_0	packing density (1 – minimum porosity)

Subscripts

f	floc
if	impermeable flocs
i, j	number of primary particles in floc
k	number of size class in particle size
pf	permeable flocs
sp	solid particles
T	residence time weighted
V	volume weighted

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APPENDIX

There are two ways in which turbulence causes particles in a suspension to approach one another. Mutual approach results from local velocity gradient in the vicinity of the particles and differing inertial response of particles to the fluid motion. Here we evaluate the contributions of these mechanisms to the aggregation of particles smaller than the Kolmogorov microscale.

If the distortion of the flow field due to the presence of the particles and the interparticle forces are neglected, the collision rate per unit volume J in the viscous subrange of turbulence is given by (Saffman and Turner, 1956; Kusters, 1991)

$$J_{ij}^0 = (8\pi)^{1/2} (R_i + R_j)^2 n_i n_j \left\{ 1.16 \left[\frac{2(\rho_p - \rho_l)}{2\rho_p + \rho_l} \right]^2 \times (\tau_{pi} - \tau_{pj})^2 v^{-1/2} \varepsilon^{3/2} + \frac{1}{15} (R_i + R_j)^2 \frac{\varepsilon}{v} \right\}^{1/2}. \quad (\text{A1})$$

This expression comprises both the collisions due to the inertia of the particles (first term between braces) and the collisions brought about by the fluid flow (second term between braces). In deriving this equation the densities of the two colliding particles were assumed to be equal, i.e. $\rho_{pi} = \rho_{pj} = \rho_p$. With collisions between aggregates of different sizes this may not be the case because of the variations in porosity, but the assumption of equal particle densities enables us to evaluate the relative importance of the collisions brought about by the different inertia of the particles and those brought about by the fluid flow more easily.

The first term between the braces on the right-hand side of eq. (A1) is zero when relaxation times, τ_{pi} and τ_{pj} , are zero or equal, or when $\rho_p = \rho_l$. The ratio of the first term to the second in eq. (A1) is equal to and larger than unity if

$$\frac{2R_i}{\eta} \geq 2.15 \frac{\rho_l}{\rho_p - \rho_l} \frac{1}{1 - \lambda}. \quad (\text{A2})$$

With $\lambda = 0$, eq. (A2) reduces to

$$\frac{2R_i}{\eta} \geq 2.15 \left(\frac{\rho_l}{\rho_p - \rho_l} \right). \quad (\text{A3})$$

Hence we can conclude that with liquid suspensions, the particles have to be at least of the size of the Kolmogorov microscale η , for the collisions due to the inertia to become important relative to those caused by differences in the velocities in the fluid flow. In liquid suspensions, the collision rate between particles that are smaller than the Kolmogorov microscale can therefore be obtained from the equation that only takes into account the collisions brought about by the fluid flow.