Coagulation of suspensions in shear fields of different characters

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COAGULATION OF SUSPENSIONS IN SHEAR FIELDS OF DIFFERENT CHARACTERS

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ABSTRACT

Coagulation is effected in: (a) the space between two coaxial cylinders, both under laminar and Taylor vortex flow conditions; and (b) a cylindrical vessel in which a flow field is generated by stirring. The former geometry permits a theoretical calculation of shear rates, while the latter resembles more closely conditions met in practice. In this case, shear rates are calculated from a model based on Laser Doppler anemometry measurements of local velocities.

From the data, capture efficiencies (α_0) for the initial coagulation are calculated. At a given average shear rate, α_0 in laminar shear is larger than in Taylor vortex flow. This is ascribed to the partially elongational character of the latter type of flow stimulating breaking of aggregates.

Deviations from a smooth spherical shape lead to a lower mutual attraction between two approaching particles on the one hand, but to a lower hydrodynamic interaction on the other. The former leads to a lower coagulation rate for quartz particles than expected for spheres, while the latter could be responsible for larger α_0 values than predicted by the theory of spherical bodies as observed in the case of ZnO.

INTRODUCTION

The recent development of the theoretical understanding of some aspects of coagulation under shear which were hitherto not easily accessible has led to a revival of interest in this field [1–5].

Two theoretical advances predominate: the consideration of the hydrodynamic, attractive and electrostatic interactions during a collision between two suspended spherical particles [1–3], and the calculation of streamlines through a porous particle during flow [4, 5]. The former makes possible the use of realistic trajectories for two approaching particles. This is considered to be a substantial advance on earlier theories based on introducing the particle diameter as the “collision radius” into the von Smoluchowski theory of orthokinetic coagulation [6], which is equivalent to the hypothesis that the approach of two colliding particles is rectilinear. The calculation of streamlines through a porous floc provides insight into the erosion of flocs in a shear field. Floc erosion is one of the ways a floc can be degraded

with regard to the number of primary particles in it, the other being floc breakage [7-10].

In this situation we thought it interesting to investigate experimentally the influence of different types of flow on coagulation under the influence of shear, both because of its practical importance and because the theoretical developments mentioned above might provide a basis for understanding the phenomena. The types of flow we investigated were those in the gap between two coaxial cylinders of slightly different radii ("Couette geometry") with either the inner, or the outer cylinder rotating. The two flow types generated in the Couette geometry differ considerably, because Taylor vortices [11, 12] occur when the inner cylinder is rotating, while the flow remains laminar at much larger angular velocities when the outer cylinder is rotating [13]. Thus by comparing coagulation rates at the same average shear rate in laminar flow (outer cylinder rotating) and in Taylor vortex flow (inner cylinder rotating), the influence of the type of flow on the coagulation can be investigated. Such an influence is to be expected since Taylor vortex flow is partially elongational in character. The third type of flow, viz. that generated by stirring in a cylindrical vessel, is included here for comparison's sake and as a first step towards translating the results obtained in easily surveyable flow fields into situations met in practice.

This study is concerned both with initial coagulation rates, and with the final aggregate size. As suspensions, dispersions of quartz in water and of ZnO in water were employed; however, because of disturbance by sedimentation, the ZnO dispersions were studied only with regard to their initial coagulation rates.

EXPERIMENTAL

Materials

Quartz [14]: ex Merck pro analysis, ground in ethanol in an agate ball mill. After decanting and drying, the solid was heated for 8 h at 873 K.

TABLE 1

Equivalent hydraulic diameters (μm), smaller than which a given percentage is found to occur

Percentage	SiO ₂				ZnO
	1.5 μm (I)	1.5 μm (II)	3 μm	5 μm	
80%	1.60	1.78	3.94	6.76	0.93
50%	1.41	1.38	3.16	5.56	0.66
20%	1.29	1.17	2.82	4.80	0.46

Fig. 1. SEM of quartz 1.5 μm I. One side of the photograph is 20 μm .

Division into fractions with equivalent Stokes diameters 1.0–1.5; 2.75–3.25; and 4.75–5.25 μm , respectively, was effected by sedimentation in twice distilled water. The size distributions of the final quartz samples, as determined by a Micromeritics Sedigraph 5000 D particle size analyser, are shown in Table 1. The quartz suspensions were stored in quartz-glass vessels. Figure 1 shows a scanning electron micrograph (SEM) recording.

Zinc oxide [15, 16]: ex Merck pro analysis, surface area (BET, N_2 adsorption): $3.66 \text{ m}^2 \text{ g}^{-1}$. The particle size was determined in an aqueous solution of Vanidisperse CB (4 mg per 100 ml) see Table 1, last column). The ZnO contains 8.4 ± 0.3 hydroxyl groups per nm^2 surface area (determined by Morimoto and Naono's method [17]), and 1.7 carbonate groups per nm^2 surface area (determined in the Morimoto and Naono apparatus, with a 1 M HCl solution replacing the methyl magnesium iodide reagent). For an SEM photograph, see Fig. 2.

Apparatus and Methods

a. Couette geometry apparatus with inner cylinder rotating

The essential parts of the apparatus (see Fig. 3) are the two coaxial cylin-

Fig. 2. SEM of ZnO. One side of the photograph is 20 μm .

ders (pos. 9 and 10) made out of black nylon, with the following dimensions[14]:

	Inner cylinder	Outer cylinder
Radius (m)	$10.20 \cdot 10^{-3}$	$11.95 \cdot 10^{-3}$
Height (m)	$12.00 \cdot 10^{-3}$	$12.50 \cdot 10^{-3}$

The inner cylinder is rotated through the axis pos. 14, by a motor (at the top, not shown in Fig. 3). The angular velocities varied between 1.78 and 65.1 rad s^{-1} . By flow visualization, the onset of Taylor vortex flow at about the expected angular velocity (5.59 rad s^{-1}) was observed; no chaotic turbulence was observed, not even at the highest angular velocities realized.

Coagulation is followed by the extinction of light ($\lambda = 480 \text{ nm}$) passing the gap between the coaxial cylinders in the axial direction (entering at pos. 1, leaving at pos. 2). The light was passed afterwards to a photodetecting unit through a fiber optics scanner; the lamp, monochromator and photodetector were parts of a Canterbury SF—3A stopped flow spectrophotometer.

Fig. 3. Apparatus for coagulation in Couette geometry with inner cylinder rotating [14]. For explanation of numbers, see text.

At the start of an experiment, a dispersion of quartz in twice distilled water, of solid volume fraction $3.122 \cdot 10^{-4}$, was placed into the storage vessel (pos. 15) where it was stirred by a master and slave magnet system (pos. 7) in order to prevent sedimentation. It is separated by a rubber membrane (pos. 6) from water which fills a PTFE tube connecting pos. 5 with one of the pipettes of the stopped flow spectrophotometer. The other pipette is filled with 1 M NaCl solution and connected to pos. 3.

When the stopped flow spectrophotometer is operated, the quartz dispersion and the NaCl solution are mixed at pos. 16 in a ratio 1:1 by volume. Thus, the final solid volume fraction during coagulation is $1.561 \cdot 10^{-4}$, and the final NaCl concentration is 0.5 M. The mixture moves through the apparatus and excess leaves at pos. 4, until the flow through the apparatus is stopped by the stopped flow mechanism. The whole apparatus is submerged in water (298 ± 0.1 K).

b. Couette geometry with rotating outer cylinder

The apparatus described in the previous section was adapted for measure-

Fig. 4. Diagram of the apparatus for coagulation in Couette geometry with outer cylinder rotating. For explanation of numbers, see text.

ments with a rotating outer cylinder by replacing the two coaxial cylinders with the arrangement shown schematically in Fig. 4. Both inner cylinder (pos. 1) and outer cylinder (pos. 2) remain fixed but between them a hollow cylinder (pos. 3) is rotating. Light from a 5 mW HeNe-laser ($\lambda = 680$ nm; Spectra-Physics Nr. 105) enters the gap between the inner and the hollow cylinder at pos. 4 through one end of a two-way Fiber Optics Scanner. The light is reflected against a mirror attached to the bottom of the top part of the hollow cylinder (pos. 5) and leaves the apparatus again at pos. 4 through the other end of the two-way scanner; the light is conducted to a photodetector. The dimensions of the gap between the inner and the hollow cylinders are as follows:

	Inner cylinder	Outer cylinder
Radius (m)	$19.2 \cdot 10^{-3}$	$21.2 \cdot 10^{-3}$
Common axial length (m)	$20 \cdot 10^{-3}$	

The inner, outer and hollow cylinders are made out of aluminium anodized at 273 K; salt resistant bearings were used for the rotating axis.

The operation of the apparatus is similar to that described in the previous section.

c. Cylindrical vessel

A cylindrical cuvette (diameter 15 mm) was used which fitted into a Vitatron MPS spectrophotometer provided with a master magnet with adjustable stirring speed (200–1200 rpm) [15, 16]. The suspensions of ZnO in water were prepared in a glove box free of CO₂ as follows: An initial suspension was prepared by adding 0.4 g ZnO to 100 ml KCl solution (concentrations adjusted to the value finally required) of pH 8.70. The pH was adjusted by adding KOH or KCl if necessary. When changes in the pH became less than 0.001 pH unit per min, the suspension was dispersed by ultrasonic treat-

ment using a Sonicator SC-50-22 apparatus for 30 min. Afterwards, the pH of the suspension was corrected if necessary. This procedure was repeated until the pH did not change any more on sonication (usually four dispersion procedures were required). A 0.8-ml aliquot of this initial suspension was mixed with electrolyte solution and HCl or KOH solution, and the total volume was made up to 25 ml. A slave magnet was added, the flask was closed and the suspension was stirred vigorously. The flask was stored in the dark until measurement the next day. The pH was measured, and 10 ml of the suspension and the slave magnet were transferred to the cuvette. The suspension was then subjected to ultrasonic treatment, at 298 ± 0.1 K, for 30 min. The cuvette was placed into the spectrophotometer; stirring was started at a preselected speed, and the light extinction was registered as a function of time.

CALCULATION OF CAPTURE EFFICIENCIES

The capture efficiency for the initial coagulation stages can be defined by:

$$\alpha_0 = \frac{\left(\frac{d \ln n}{dt} \right)_{t \rightarrow 0, \text{ experimental}}}{\left(\frac{d \ln n}{dt} \right)_{t \rightarrow 0, \text{ rectilinear}}} \quad (1)$$

where n is the number of dispersed particles per unit volume. The experimental value of $\left(\frac{d \ln n}{dt} \right)_{t \rightarrow 0}$ is calculated from light extinction values by the formula [14] (valid for the geometrical optics region of particle size):

$$\left(\frac{d \ln n}{dt} \right)_{t \rightarrow 0} = 2.43 \left(\frac{d \ln E}{dt} \right)_{d \rightarrow 0} \quad (2)$$

The denominator in Eqn (1) is the value of $\left(\frac{d \ln n}{dt} \right)_{t \rightarrow 0}$ expected for rectilinear approach of two colliding particles. It can be calculated from [14]:

$$\left(\frac{d \ln n}{dt} \right)_{t \rightarrow 0, \text{ rectilinear}} = - \frac{4 \phi \bar{\dot{\gamma}}}{\pi \beta} \quad (3)$$

where ϕ is the solid volume fraction; $\bar{\dot{\gamma}}$ the average shear rate; and β the solid volume fraction within the aggregates ($\beta = 1$ in the initial stage of the coagulation).

Values for $\bar{\dot{\gamma}}$ were calculated as follows:

(a) For laminar Couette flow, an analytical expression is available:

$$\bar{\dot{\gamma}} = 4 \omega \frac{R_0^2 R_i^2}{(R_0^2 - R_i^2)^2} \ln \frac{R_0}{R_i} \quad (4)$$

where, R_0 is the radius of the outer cylinder (hollow cylinder in the arrangement of Fig. 4); R_i the radius of the inner cylinder; and ω the angular velocity of the rotating cylinder (rad s^{-1}).

(b) For Taylor vortex flow between two coaxial cylinders, $\bar{\gamma}$ was calculated by numerical averaging of

$$\bar{\gamma} = \left[\left(\frac{\partial |V|}{\partial r} - \frac{V_\theta}{r} \right)^2 + \frac{1}{r^2} \left(\frac{\partial |V|}{\partial \theta} \right)^2 + \frac{1}{r^2} \left(\frac{\partial |V|}{\partial z} \right)^2 \right]^{1/2} \quad (5)$$

where $|V| = (V_r^2 + V_\theta^2 + V_z^2)^{1/2}$, V_r , V_θ and V_z are the velocities in the radial, tangential and axial directions, respectively, calculated from Stuart's equations [12].

(c) The flow field generated by stirring in a cylindrical vessel was approximated [15, 16] by a model based on flow velocity measurements in dummy experiments with the same cuvette and stirring device by Laser Doppler Anemometry [18]. A DISA 55x Modular LDA system was used with a Spectra-Physics He-Ne Laser (632 nm, 35 mW) in conjunction with a DISA 55 L90a Counter Processor. The volume of the cuvette was considered to consist of three regions (Fig. 5):

(I) An inner core with diameter slightly increasing with increasing height. The shear rates here were very low, the core rotating approximately as a rigid body; collisions in this part of the cuvette were neglected;

(II) An outer region in which Taylor—Goertler-like vortices were formed (as shown by flow visualization). The average $\bar{\gamma}$ values were calculated from the Stuart equations [12] for the velocities in Taylor vortices between two coaxial cylinders, using the radius of the inner core as the radius of the inner cylinder in the equations. Thus, the latter varied slightly with increasing height;

(III) The space between the slave magnet and the cuvette wall. Here the

Fig. 5. Cylindrical cuvette with stirrer (schematic) I inner core, II outer region, III space between stirrer and cuvette wall [16].

Stuart equations were used with the length of the slave magnet as the radius of the inner cylinder.

An overall average of $\bar{\gamma}$ was then calculated through:

$$\langle \bar{\gamma} \rangle = \frac{\sum_i \gamma_i V_i}{\sum_i V_i} \quad (6)$$

The $\langle \bar{\gamma} \rangle$ values thus calculated were supported by two observations: (a) $\langle \bar{\gamma} \rangle$ is not critically dependent on the width of the inner core; and (b) the onset of Taylor–Goertler vortex-like disturbances of laminar flow was observed by flow visualization to occur near the rotation speed predicted from the model (150 rpm).

RESULTS AND DISCUSSION

a. An overall view on coagulation in Couette flow

Light extinction at different times at various angular velocities, measured during Couette flow in the absence and presence of Taylor vortices, is shown

Fig. 6. Extinction at various times after the start of the coagulation, as a function of rotating velocity (rpm). Couette geometry, inner cylinder rotating. The vertical dotted line denotes the onset of Taylor vortex flow. (x) 2 min; (o) 5 min; (+) 10 min; (Δ) 20 min; (□) 30 min; (∇) 50 min; (⊕) 100 min.

Fig. 7. Extinction at various times after the start of coagulation, as a function of rotation velocity (rpm). Couette geometry, outer cylinder rotating. The vertical bar denotes the onset of turbulence. (x) 1 min; (o) 5 min; (+) 15 min; (Δ) 25 min; ($\square$) 35 min; (∇) 60 min.

in Figs 6 and 7, respectively. In both cases, quartz $1.5\ \mu\text{m}$ (sample a) was employed. On the horizontal axis, $\ln \Omega$ (where Ω is the rotation speed of the inner cylinder in rpm) is plotted since this is the quantity directly observed. Figure 6 is obtained with the inner cylinder rotating (Fig. 3); Fig. 7 is obtained with the arrangement shown in Fig. 4.

Figure 6 shows the contours familiar from previous work [14]: with increasing angular velocities the light extinction measured after a certain time first decreases. This decrease corresponds to an increased coagulation rate with increasing shear rate during the first coagulation stages, as long as the flow is laminar. The onset of Taylor vortex flow (at an angular velocity indicated by the dotted vertical line) results in a decrease in the coagulation rate, because aggregates are then exposed to pronounced shear shortly after their formation.

A comparison with Fig. 7 shows that it is not only the partly elongational character of Taylor vortex flow but also the high $\bar{\gamma}$ value in the Taylor vortices, which is responsible for the slower growth of aggregates in the initial and intermediate stages of the coagulation. When the outer cylinder is rotating (i.e. the hollow cylinder is in the arrangement shown in Fig. 4), the flow remains laminar until turbulence starts at a certain Reynolds number

($Re = \omega R_0^2 \rho / \nu$), which is about 70,000 at the R_0/R_i value in the experiments concerned. This corresponds with $\Omega = 1488$ rpm (dotted vertical line in Fig. 7). Here, a turn towards lower initial and intermediate coagulation rates with increasing Ω is observed at $\ln \Omega \approx 5.8$ in the laminar region. A quantitative comparison shows that the type of flow definitely influences the initial coagulation rate at a given $\bar{\gamma}$ value (see following section b).

This turn toward smaller aggregates after a given coagulation time with increasing Ω is not found for the later coagulation stages (see following section c).

b. The initial coagulation rate

Figures 6 and 7 are not strictly comparable. The dimensions of the apparatus are such that, if laminar flow prevailed throughout, an equal angular

Fig. 8. Capture efficiency (α_0) for quartz $1.5 \mu\text{m}$ as a function of average shear rate. (+) Inner cylinder rotating; laminar flow, sample quartz $1.5 \mu\text{m}$ I; (o) inner cylinder rotating; Taylor vortex flow, sample quartz $1.5 \mu\text{m}$ I; (x) outer cylinder rotating; laminar flow, sample quartz $1.5 \mu\text{m}$ II; (□) theoretical values for spherical particles ($A = 4 \times 10^{-20}$ J; $b = 0.7 \times 10^{-6}$ m).

velocity would result in about equal $\bar{\gamma}$ values for rotating inner and outer cylinders, however, the onset of Taylor vortex flow invalidates this equality. In Fig. 8, we therefore plotted the initial capture efficiencies α_0 versus $\log_{10} \bar{\gamma}$, where $\bar{\gamma}$ had been calculated taking into account Taylor vortex formation.

In the $\bar{\gamma}$ region where both laminar and Taylor vortex flow can be realized, the α_0 values observed in laminar flow are systematically larger than those found in Taylor vortex flow. In view of the partly elongational character of Taylor vortex flow, this is not surprising. This elongational character will result in an additional pull on an aggregate at a given shear rate.

Figure 8 is qualitatively in agreement with theoretical predictions [3] that α_0 decreases with increasing $\bar{\gamma}$. However, quantitatively there are pronounced differences between theory and practice: the experimental α_0 values are much lower than those predicted by the theory. For comparison, some α_0 values calculated by the Van de Ven and Mason theory for spherical particles are included in Fig. 8. For the calculations, a particle radius of $0.7 \mu\text{m}$, a Hamaker constant of $4 \times 10^{-20} \text{ J}$, as expected for SiO_2 in water [19], and a London wavelength of 100 nm have been employed. This difference between theory and experiment should not surprise us, as the quartz particles are far from spherical (Fig. 1). Thus, the pronounced angular character of the quartz particles could be held responsible

Fig. 9. Quotient of the van der Waals attraction between cylinders, and that between spheres, at equal distances between the centers of mass [14].

Fig. 10. Capture efficiency versus average shear rate for quartz $5 \mu\text{m}$. Couette geometry, inner cylinder rotating. The vertical dotted line denotes the onset of Taylor vortex flow.

for a lower α_0 than expected for spherical particles, because the attraction energy at a given center-of-mass distance between non-spherical particles is lower than between spherical particles unless the mutual arrangement is particularly favourable for attraction (Fig. 9).

The decrease of α_0 with increasing shear rate shown in Fig. 8, is not found for larger quartz particles (Fig. 10), at least not in the laminar flow region. For $5\text{ }\mu\text{m}$ quartz particles at $\log_{10} \bar{\gamma} = 1.05$, no detectable coagulation was found; this can be ascribed to the combined action of the weakening of the Hamaker attraction by asymmetry (Fig. 9) and by retardation. With increasing $\bar{\gamma}$ in the laminar flow region, α_0 increases for these relatively large particles, due to inertia becoming important; calculation of the ratio between centrifugal pseudoforce and Hamaker attraction for spherical particles at different points in the trajectories of two approaching particles, confirm this view [14]. The onset of Taylor vortex flow results in a lowering of α_0 (Fig. 10); α_0 in this region is the net result of increasing importance of centrifugal pseudoforces, and increased disruption of newly formed pairs by shear and elongational stresses. The α_0 values, though low, increase in this region with increasing particle size (Fig. 11).

An increase of α_0 with increasing shear rate is also found for ZnO (Fig. 12). Experimental α_0 values are here combined with theoretical values for spherical particles with a Hamaker constant of 4×10^{-20} J, and a particle radius of $0.33\text{ }\mu\text{m}$. At relatively low shear rates ($\langle \bar{\gamma} \rangle \leq 200\text{ s}^{-1}$), α_0 is

Fig. 11. Capture efficiency versus average shear rate in the Taylor vortex region, for quartz samples of different sizes. (x) $1.5\text{ }\mu\text{m}$; (o) $3\text{ }\mu\text{m}$; (+) $5\text{ }\mu\text{m}$.

Fig. 12. Capture efficiency versus average shear rate for ZnO in cylindrical cuvette flow. (Δ) $\xi = -20.3$ mV; ($\circ$) $\xi = -27.3$ mV; ($\times$) $\xi = -29.7$ mV; (∇) $\xi = -30.8$ mV; ($\square$) $\xi = -32.5$ mV. (—) Theoretical values for spherical particles in absence of repulsion. ($A = 4 \times 10^{-20}$ J, $b = 0.33$ μm).

lower than the theoretical value, independent of the zeta potential; at low zeta potential, α_0 increases with increasing $\bar{\gamma}$, surpassing the theoretical value and approaching 1 for $\langle \bar{\gamma} \rangle = 400$ s^{-1} (thus, at this shear rate the initial coagulation rate is equal to that predicted by the von Smoluchowski theory for rectilinear approach). An increase in absolute value of the zeta potential (from 20 to 32 mV), however, can almost completely prevent this rise of α_0 .

The most interesting point about this graph is perhaps the importance of the centrifugal pseudoforces which it illustrates, for particles much smaller than those for which, with quartz as disperse phase, no distinct influence of inertia is found (cf. Fig. 8). Nor were pronounced influences of inertia found in calculations by the Van de Ven and Mason theory for spherical particles; in this theory, in addition to attraction and electrostatic repulsion, a third term for inertial pseudoforces had been incorporated [15, 16]. The fact that inertia is more important for irregular than for spherical particles, in itself can be understood: deviations from a smooth spherical shape lead to a decrease in hydrodynamic interaction between two approaching particles,

because the last liquid film between the two particles can be pierced by angular protrusions (it should be noted that two smooth spherical particles, in the absence of attraction and inertia, never come into direct contact [2], fundamentally because the last liquid between the particles takes an infinitely long time to flow away).

Thus, two counteracting effects of particle irregularity on α_0 should be discerned: (a) a decrease in attraction, and (b) a decrease in hydrodynamic interaction. Which of these effects predominates will depend on the Hamaker constant, the specific mass difference between the disperse and the continuous phase, the particles' dimensions, the shear rate and the absence or presence of electrostatic repulsion.

When comparing the results obtained for quartz dispersions with those for ZnO dispersions, differences in the Hamaker constant are not likely to play an important role: differences between the Hamaker constants of various oxides tend to remain within the range of accuracy [19]. The difference in specific mass between ZnO and water is certainly greater than that between quartz and water. Thus, it might qualitatively explain the shift of the particle diameter, at which inertial effects on the coagulation become important, towards lower values on going from SiO_2 to ZnO. Nevertheless, it is surprising that the relatively small difference in specific mass between SiO_2 and ZnO leads to a factor 10 in the particle dimension at which inertial effects appear. It should be kept in mind, however, that the quartz particles are characterized by sharp angular protrusions and irregular "shell-like" fracture surfaces, while the ZnO particles contain straight corners and straight faces (cf. Figs 1 and 2).

In addition, the $\bar{\gamma}$ values employed in the α_0 calculations for ZnO are rather uncertain, being calculated by a simplified model of the flow field. Uncertainties in $\bar{\gamma}$ lead, through Eqns (1), (3) and (6), to uncertainties in α_0 . However, the α_0 values are not likely to be uncertain to such a degree that the rise in α_0 shown in Fig. 12 for $\zeta = 20.3$ mV, with increasing $\langle \bar{\gamma} \rangle$, is uncertain. There clearly is a need for additional data.

c. The final coagulation stages

The final coagulation stages have only been investigated, until now, for quartz dispersions. Figure 13 shows b_∞/b_0 , where b_0 is the primary particle radius, and b_∞ the final aggregate radius. This ratio has been calculated through [14]:

$$\frac{b_\infty}{b_0} = \frac{1}{\beta} \frac{E_0}{E_\infty} \quad (7)$$

where for β , the solid volume fraction within a final aggregate, the value $1/2$ has been employed.

Fig. 13. Final aggregate size versus average shear rate in Couette flow. (Δ) 1.5 μm I, outer cylinder rotating; ($\circ$) 1.5 μm I, inner cylinder rotating; ($\times$) 3 μm , inner cylinder rotating; ($\square$) 5 μm , inner cylinder rotating.

As noted previously [14], for 3 and 5 μm particles the extinction becomes nearly constant after about 50 min coagulation. This means that the aggregates grow only very slowly beyond a certain size, which is indicated here by "final aggregate size". For 1.5 μm , the extinction only becomes constant within reasonable times if the flow is laminar. For Taylor vortex flow in 1.5 μm particle suspensions, the extinctions after 80 min of coagulation have been used to calculate b_∞/b_0 as closely as possible.

The use of the term "final aggregate size" does not imply that this same size will be approached on disruption of very large aggregates by shear.

At average shear rates lower than about 40 s^{-1} , the coagulation does not proceed beyond the very first stages ($b_\infty/b_0 \approx 4-6$) within the coagulation times realized in the present study. At these aggregate sizes, the two different mechanisms of floc degradation (breakage and erosion) cannot be clearly distinguished. With increasing $\bar{\gamma}$ values in laminar flow, b_∞/b_0 increases up to 30; there the final aggregate size tends to level off, though there is some slight increase with increasing $\bar{\gamma}$ values up to $b_\infty/b_0 \approx 40$. It appears from Adler's calculations [4, 5] that floc erosion tends to break down smaller aggregates more than large ones; thus the levelling-off of b_∞/b_0 between 30 and 40 can perhaps be best understood by assuming that here floc breakage becomes important.

At very large $\bar{\gamma}$ values, in the experiments with the outer cylinder rotating, b_{∞}/b_0 increases beyond the value of 40. This is only indicated schematically in Fig. 13, because here turbulence sets in which makes $\bar{\gamma}$ calculations very uncertain. A similar rise of b_{∞}/b_0 at very large $\bar{\gamma}$ values is observed in Taylor vortex flow; it can be understood on the assumption that floc collision at these large $\bar{\gamma}$ values is accompanied by considerable rearrangement of the primary particles leading to consolidation of the flocs.

In Taylor vortex flow, the levelling-off occurs at much lower b_{∞}/b_0 values than in laminar flow. This can be attributed to the partially elongational character of Taylor vortex flow, enhancing both floc erosion and floc breakage.

Floc erosion will be more pronounced in elongational rather than in laminar flow, because the fraction of the streamlines passing through an aggregate, which have a closed character, will be lower in elongational than in laminar flow. Thus the reattachment of eroded fines at the back of an aggregate is diminished. Floc breakage will be enhanced as well by the flow becoming elongational, because of larger tearing forces exerted on the aggregates.

The conclusion, that the final aggregate size increases with increasing $\bar{\gamma}$, is contrary to the findings of Hunter and Frayne [20]. However, in their experiments flocs were formed during ultrasonication preceding the shear application. The final aggregate size increased with increasing initial input of ultrasonic energy; this was attributed by Hunter and Frayne to an increasing floc density with increasing ultrasonic energy. If a floc of a given density is subjected to increasing $\bar{\gamma}$, a decreasing floc size should indeed be expected. However, in the present work the same shear rates were applied during the different stages of floc formation and breakage. Under these circumstances, the influence of the average shear rate during coagulation on floc structure becomes apparent, and this is evidenced by growing final floc dimensions with increasing shear rate.

CONCLUSIONS

The type of flow influences the coagulation rate, elongational flow leading to a lower coagulation rate than laminar flow at equal average shear rate values.

Initial capture efficiencies for the dispersions investigated are lower than those calculated theoretically for spherical particles, unless inertia becomes important. For ZnO this occurs at a smaller particle size than for SiO₂.

The results can be understood by assuming two counteracting effects of deviations of the particles from a spherical shape: a lowering of attraction, and a lowering of hydrodynamic attraction.

The final aggregate size obtained in laminar flow for 1.5 μm quartz particles is about 45–60 μm , but at very large shear rates larger aggregates are formed.

In Taylor vortex flow, the final aggregate size remains much smaller (15 μm) but at very large shear rates larger aggregates can again be formed. The ratio (radius of final aggregate)/(radius of primary particle) obtained in Taylor vortex flow is neither strongly dependent on the primary particle size nor on the shear rate.

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