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Coagulation of Aqueous Dispersions of Quartz in a Shear Field

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The coagulation of aqueous dispersions of quartz shows, with increasing particle radius (b) and increasing shear rate ($\dot{\gamma}$), a transition from coagulation under the predominant influence of Hamaker attraction, to coagulation caused in the main by centrifugal pseudoforces. For $b = 1.5 \mu\text{m}$, the transition is at $\dot{\gamma} \approx 20 \text{ sec}^{-1}$. For $\dot{\gamma} > 1000 \text{ sec}^{-1}$, the capture efficiency of collisions between the suspended particles, in the initial stages of the coagulation, is small (0.005–0.01) but not strongly dependent on $\dot{\gamma}$, due to most of the pairs breaking up shortly after their formation. The final aggregate size increases with increasing $\dot{\gamma}$ up to $\dot{\gamma} \approx 5000 \text{ sec}^{-1}$; this is ascribed to a smaller permeability of the aggregates formed at larger $\dot{\gamma}$. At $\dot{\gamma} > 5000 \text{ sec}^{-1}$, however, vortex formation after the aggregates retards their further growth.

INTRODUCTION

The influence of shear on coagulation has been studied intensively since von Smoluchowski (1) derived his well-known relation for J , the number of collisions experienced by one particle per unit of time:

$$J = \frac{4}{3} n \dot{\gamma} R_{ij}^3 \quad [1]$$

with n = the number of particles per unit of volume; $\dot{\gamma}$ = the shear rate; and R_{ij} = the "collision radius," i.e., that distance of shortest approach between the two passing particles which leads to pair formation.

During the last years, however, two important new theoretical developments make an experimental investigation of the influence of shear on coagulation again rewarding.

(a) van de Ven and Mason (2, 3) succeeded in taking into account the counteracting effects of hydrodynamic interaction and electrostatic repulsion on the one hand, and of Hamaker attraction on the other. They substituted $2b$ (b = particle radius) for R_{ij} , and in order to account for deviations from rectilinear approach of two particles

they introduced the "capture efficiency" α_0 . Thus

$$J = 32n\dot{\gamma}\alpha_0 b^3/3. \quad [2]$$

α_0 was calculated by numerical integration of the equations describing the mutual velocity of two approaching spherical particles; inertia forces were neglected. In the context of the present paper, the most important results of van de Ven and Mason's work are the following: (i) in the absence of repulsion, α_0 decreases with increasing $\dot{\gamma}$ ($\alpha_0 \sim \dot{\gamma}^{-0.18}$); (ii) α_0 remains significantly different from 0 ($\alpha_0 \approx 0.1$) even when the parameter $A/36\dot{\gamma}\eta b^3$ (with A = Hamaker constant) becomes as small as 10^{-5} .

(b) Adler (4, 5) calculated the streamlines through and around porous spherical particles. According to him, aggregates break up in simple shear at their periphery, but fragments drifting into closed streamlines will for the greater part be combined again with the aggregate from which they come, because of recirculation. The streamline separating closed from open ones moves outward with increasing $b/\sqrt{k}$, where b = the aggregate radius, k = the aggregate's permeability. Thus, at given k , small aggregates are broken down

effectively because their fragments mostly get into open streamlines, but large aggregates are broken down much less effectively because their fragments mostly get into closed streamlines.

In view of these new theoretical insights we thought it worthwhile to follow the coagulation of aqueous quartz dispersions at various shear rates, up to the final stages. In the latter respect, the aim of the present investigation differs from that of earlier ones (3, 6) which were predominantly directed at the early stages of the coagulation. An *in situ* determination of the degree of coagulation as a function of time was aspired to, in order to avoid disturbance of the flow through sampling.

Quartz was chosen as the disperse phase, because it offers a stable interface with aqueous solutions, and because quartz dispersions can easily be obtained stable and easily be destabilized. The irregular shape of the quartz particles (Fig. 1) must then be accepted. As a quality of this defect, however, it can be claimed that most coagulating suspensions met in practice involve irregularly shaped solid particles. A comparison of experimental results with the predictions of the theory developed for spherical particles (2) will be welcome.

EXPERIMENTAL

Materials

Quartz. Quartz, *ex Merck pro analysi*, specific mass 2648.5 kg m^{-3} , was ground in ethanol (*ex Merck pro analysi*), in an agate ball mill. Excess ethanol was decanted, and the remaining solid dried at 373°K and heated for 8 hr at 873°K . The quartz was dispersed in twice distilled water, and the fractions with equivalent Stokes diameter $1.0\text{--}1.5$, $2.75\text{--}3.25$, and $4.75\text{--}5.25 \mu\text{m}$ were isolated by sedimentation. Table I shows the size distributions of the final quartz preparations, as determined by a Micromeritics Sedigraph 5000D particle size analyzer. The

quartz suspensions were stored in quartz glass vessels.

NaCl. NaCl was *ex Merck pro analysi*.

Apparatus and Procedures

Coagulation experiments were carried out in the apparatus shown in Fig. 2. Its essential parts are two coaxial cylinders (pos. 9 and 10), made from black nylon; their dimensions are

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

The inner cylinder is screwed to an axis (pos. 14), which could be rotated at different speeds by a motor (at the top of Fig. 2; not shown). Rotation speeds could be varied between the limits 17 and 622 rpm; they were checked frequently by means of an Ono Sokki HT-430 digital tachometer.

The outer cylinder is closed at top and bottom by PMMA plates (pos. 12 and 13, respectively) with two windows: one (pos. 1) for leading light into the apparatus from a halogen lamp which had passed a monochromator, the other (pos. 2) for conducting the light away to a photodetecting unit, after it had passed through the gap between the coaxial cylinders in axial direction. Lamp, monochromator, and photodetecting unit are parts of a Canterbury SF-3A stopped flow spectrophotometer; the light was conducted from the monochromator to window 1, and from window 2 to the photodetecting unit through flexible light guides (composed of Jena B3 standard fibers; thickness of the light guides 3 mm, length 500 mm, with metal and PVC covers).

At the start of an experiment, a dispersion of quartz in twice distilled water (solid volume fraction 3.122×10^{-4}) was placed into storage vessel 15 (Fig. 2) where it is stirred by a master and slave magnet system (pos. 7) in order to prevent sedimentation. It is

FIG. 1. SEM of 5- μ m quartz particles. One side of the figure corresponds to 20 μ m.

separated by a silicon rubber membrane (pos. 6) from water which fills a PTFE tube connecting pos. 5 with one of the pipets of the stopped flow spectrophotometer. The other pipet is filled with 1 *M* NaCl solution and connected with pos. 3.

When the stopped flow spectrophotometer is operated, the quartz dispersion and the NaCl solution are mixed at pos. 16. The mixture moves through the apparatus; excess leaves at pos. 4. The mixing ratio of the quartz dispersions with the NaCl solutions is 1:1 by volume; thus the final solid volume fraction in the coagulation experiments is 1.561×10^{-4} .

The whole apparatus is submersed in water ($298 \pm 0.1^\circ\text{K}$). Normally, light with $\lambda = 480 \text{ nm}$ is used; light of other wavelengths was used to check the dependence of light extinction on λ/b .

During coagulation experiments, the output of the light-detecting unit is registered continuously by means of a BBC Goerz Servogor 320 recorder.

Flow visualization was performed in an exact copy of the measuring part of the apparatus shown in Fig. 2, with transparent walls. A suspension of 6.8 g of aluminium powder in 1 liter of 0.05 *M* sodium dodecyl sulfate solution was used.

The flow pattern in the apparatus is laminar at low rotation speeds; Taylor vortices form at higher rotation speeds. From the dimensions of the apparatus it follows that a critical Taylor number of 1708 (7) is surpassed at 53.3 rpm; Figs. 3a-e show, how-

TABLE I

Equivalent Hydraulic Diameters, Smaller Than Which a Given Percentage Is Found to Occur

Percentage	Sample designation		
	1.5 μm	3 μm	5 μm
80%	1.60 μm	3.94 μm	6.76 μm
50%	1.41 μm	3.16 μm	5.56 μm
20%	1.29 μm	2.82 μm	4.80 μm

ever, that end effects cause some Taylor vortex-like disturbances of laminar flow already at somewhat smaller rotation speeds. With increasing rotation speeds, the Taylor vortices become increasingly pronounced, but no wavy vortices were observed.

Flow visualization experiments were performed also with quartz as the disperse phase, at solid volume fractions of 1.561×10^{-4} and 1.561×10^{-3} . Taylor vortices were seen, but because of the less distinct particle alignment and poorer light reflection characteristics of the quartz particles employed when compared with Al, the ensuing photographs were less distinct than those shown in Fig. 3.

The calculation of shear rates in the laminar region was performed along traditional lines. In the Taylor vortex region, $\dot{\gamma}$ was calculated as

$$\dot{\gamma} = \left[\left(\frac{\partial|v|}{\partial r} - \frac{v_\theta}{r} \right)^2 + \frac{1}{r^2} \left(\frac{\partial|v|}{\partial \theta} \right)^2 + \left(\frac{\partial|v|}{\partial z} \right)^2 \right]^{1/2} \quad [3]$$

with

$$v = (v_r^2 + v_\theta^2 + v_z^2)^{1/2}. \quad [4]$$

v_r , v_θ , and v_z were calculated from Stuart's equations (7). These are approximate only, especially when the Taylor number greatly surpasses the critical one, by reason of Stuart's restriction to first harmonics. Inclusion of higher harmonics (8) appears, however, not to take away the approximate character of the description of the flow.

The average shear rate calculated from [3] is shown, as a function of rotation speed, in Fig. 4; Fig. 5 shows the spread of $\dot{\gamma}$ at three typical rotation speeds in the Taylor vortex region.

RESULTS AND DISCUSSION

The Initial Stages of the Coagulation

Calculation of α_0 from the experimental data (Fig. 6). The experimental data are light extinction E as a function of time. Following

FIG. 2. Sketch of apparatus used for coagulation experiments. For explanation of ciphers, see text.

La Mer (9) and Timasheff (10), this can be written as

$$E = l \sum_i n_i \pi b_i^2 Q_{scai} \quad [5]$$

with l = length of the path of the light through the suspension; n_i = number of aggregates with i primary particles; b_i = radius of aggregate of type i , considered as a sphere; and Q_{scai} = scattering cross-section/geometrical cross-section of aggregate of type i .

In general, Q_{scai} will be a function of λ/b_i :

$$Q_{scai} \sim (\lambda/b_i)^y \quad [6]$$

but for the suspensions employed in the present investigation, y was found to be ≈ 0 . This was checked both by measuring the light extinction of an aqueous quartz dispersion of solid volume fraction $= 1.561 \times 10^{-4}$, at different wavelengths, and by following coagulation experiments in turn at different wavelengths, by switching the monochromator

FIG. 3. Flow pattern in a replica of the apparatus shown in Fig. 2. Rotation speeds of the inner cylinder are indicated in the background (rpm). For the apparatus concerned, the theoretical Taylor vortex limit is at 53.3 rpm.

FIG. 3—Continued.

during the course of the coagulation. Thus, Eq. [5] can be written

$$E = \pi l Q_{scai} \sum_i n_i b_i^2. \quad [7]$$

In the initial stages of the coagulation we have predominantly primary particles and doublets. For the limit $t \rightarrow 0$ we have

$$E = K \times (n_1 + 1.587 \times n_2) \quad [8]$$

In addition

$$n_1 + n_2 = n \quad [9]$$

where n = the total number of particles, per unit volume, and

$$n_1 + 2n_2 = n_0 \quad [10]$$

with n_0 = the initial number of particles per unit volume. On eliminating n_1 and n_2 from [8]–[10], we obtain

$$E = K' \times (n/n_0 + 1.4236) \quad [11]$$

FIG. 4. Theoretical average shear rate vs ω_i .

FIG. 5. Distribution of shear rates for three typical rotation speeds: (1) $\omega_i = 8.90 \text{ rad sec}^{-1}$; (2) $\omega_i = 16.6 \text{ rad sec}^{-1}$; (3) $\omega_i = 48.2 \text{ rad sec}^{-1}$.

FIG. 6. $-(d \ln E/dt)_{t \rightarrow 0}$ vs ω_i for suspensions with 3- μm primary particles.

which leads to

$$d \ln (n/n_0) \simeq 2.43 \times d \ln E \quad (n/n_0 \rightarrow 1). \quad [12]$$

The number of collisions expected when all particles would approach each other along straight lines, would follow from

$$-\left(\frac{dn}{dt}\right)_{\text{rectilin.}} = \frac{1}{2} n \times J \quad [13]$$

where J is taken from [1] with $R_{ij} = 2b$. We take into account that the solid volume fraction $\phi = (4/3)\pi \bar{b}^3 \beta n$ ($\bar{b}$ = average particle, or aggregate radius; β = solid volume fraction within an aggregate) remains constant during a coagulation, and obtain

$$-\left(\frac{d \ln n}{dt}\right)_{\text{rectilin.}} = \frac{4\phi \bar{\gamma}}{\pi \beta}. \quad [14]$$

Thus

$$\alpha_0 = \frac{\left(\frac{d \ln n}{dt}\right)_{t \rightarrow 0, \text{experim.}}}{\left(\frac{d \ln n}{dt}\right)_{t \rightarrow 0, \text{rectilin.}}} = \frac{2.43 \left(\frac{d \ln E}{dt}\right)_{t \rightarrow 0}}{-\left(\frac{4\phi \bar{\gamma}}{\pi \beta}\right)}. \quad [15]$$

In the initial stages, β can be taken to be = 1.

α_0 vs $\bar{\gamma}$. The results obtained are shown in Fig. 7. For 1.5- μm primary quartz particles, α_0 behaves according to the predictions of the van de Ven and Mason theory, insofar as in the laminar region α_0 decreases with increasing $\bar{\gamma}$.

When we approach the Taylor vortex region, α_0 rises; this can, however, conveniently be ascribed to uncertainties of $\bar{\gamma}$ in this region (cf. Fig. 3). In the Taylor vortex region itself, α_0 decreases to about 0.005 which remains nearly independent of $\bar{\gamma}$ even when (at $\log_{10} \bar{\gamma} \simeq 3.7$) the extinction in the later coagulation stages shows a distinct transition (see later). This means of course that $(d \ln E/dt)_{t \rightarrow 0}$ in this region is in good approximation proportional to $\bar{\gamma}$ as calculated from the Stuart equations.

The agreement with the van de Ven and Mason theory is in quantitative respect not satisfactory, however. Thus, for $\log_{10} \bar{\gamma} = 1.05$ one would calculate, with a Hamaker constant of 11.5×10^{-13} erg, for α_0 a value of 0.75; if the experimental value of α_0 is used to calculate the Hamaker constant, we would come out a factor 500 too low. This discrepancy can be ascribed to the irregular shape of the quartz particles involved. Figure 8

FIG. 7. α_0 vs $\log_{10} \bar{\gamma}$ in the low $\bar{\gamma}$ region. The vertical dotted line indicates the theoretical Taylor vortex limit (Taylor number: 1708). +, 5- μm primary particles; O, 3- μm primary particles; X, 1.5- μm primary particles.

FIG. 8. $\log_{10}$ (attraction force between cylinders/attraction force between spheres) vs distance/ b (H = shortest distance between surfaces; AA = radius of a sphere with same surface area as the cylinders concerned).

shows, on a logarithmic scale, the quotient of the Hamaker attraction between cylinders (of various axial ratios, and in various orientations) on the one hand, and that between spheres of same surface on the other hand, as a function of the mutual distance between the centers of mass. In these calculations, the retardation of the attraction forces was taken into account by the Casimir and Polder equations (12). It is seen, that for a length/diameter ratio of 3.3 this quotient can be about 0.01 unless the orientation is particularly favorable: in the latter case it can rise to values exceeding 10. However, this case will occur only rarely in view of the tendency of anisometric particles to align themselves in a shear.

For larger primary particles, α_0 increases with increasing $\bar{\gamma}$ in the laminar region, even when we are still far away from the Taylor vortex region. This is especially clear for the suspensions with 5- μm -diameter primary particles (Fig. 7), where α_0 rises from 0 at $\log_{10} \bar{\gamma} = 1.05$ to 0.13 at $\log_{10} \bar{\gamma} = 1.32$. The absence of detectable coagulation at $\log_{10} \bar{\gamma} = 1.05$ for 5- μm particles must be ascribed to the combined action of weakening of the Hamaker attraction by anisometry (cf. Fig. 8) and by retardation. The increase of α_0 with $\bar{\gamma}$ for the larger primary particles is due to inertia becoming important. This follows

from calculations of the Hamaker attraction force and of the centrifugal pseudoforce operative when two particles approach each other.

The quotient of these two forces, for spherical particles at some values of the spherical polar coordinates r , θ , and ϕ , is shown in Table II; the values of the coordinates chosen for presentation in this table all correspond to the plane $\cos \theta / \sin \theta \cos \phi = 1$. Similar values were obtained for positions in the equatorial plane ($\theta = 90^\circ$). In these calculations, the centrifugal pseudoforce was calculated for particles following the Batchelor and Green trajectories (13), thus related to particles moving in the absence of inertia and interaction. This implies an approximation, but not an important one in view of the small values of both inertia effects and interaction forces when compared with the hydrodynamic friction force $6\pi\eta\bar{\gamma}b^2$. More important will be the effect of the nonspherical character of the quartz particles on the Hamaker attraction (cf. Fig. 8): thus, for the particles employed in the experiments, the quotient centrifugal pseudoforce/Hamaker attraction will be larger than the values mentioned in Table II.

In view of the large value of $6\pi\eta\bar{\gamma}b^2$ when compared with inertia or interaction forces, deviations from the Batchelor and Green trajectories become important only when the particles nearly touch.

In this case, however, the uncertainties caused by the nonspherical character of the particles become particularly important; thus more elaborate calculations of the trajectories, analogous to those performed by van de Ven and Mason, were considered not to be of much value. Nevertheless, Table II shows that centrifugal pseudoforces promote the approach of two particles as long as $|\phi|$ remains large, but that they counteract the approach when the two particles pass sideways. There is a transition from Hamaker attraction being important, to centrifugal pseudoforces being important, with increasing $\bar{\gamma}$ and b . The exact value of $\bar{\gamma}$ for which this

TABLE II
Centrifugal Pseudoforce/Hamaker Attraction for Spherical Particles^{a,b}

r/b	θ (°)	ϕ (°)	$b = 0.7 \mu\text{m}$			$b = 2.5 \mu\text{m}$		
			22.5°	1240°	8759°	22.5°	1240°	8759°
1.3064	45.0	0.0	-9.5×10^{-5}	-2.89×10^{-1}	-14.4×10^0	-1.94×10^{-1}	-5.91×10^2	-2.95×10^4
	60.0	-54.7	4.2×10^{-5}	1.28×10^{-1}	6.39×10^0	0.86×10^{-1}	2.62×10^2	1.31×10^4
	79.5	-79.3	1.2×10^{-5}	0.36×10^{-1}	1.77×10^0	0.24×10^{-1}	0.73×10^2	0.36×10^4
1.9596	45.0	0.0	-5.50×10^{-3}	-1.67×10^1	-8.33×10^2	-1.13×10^1	-3.45×10^4	-2.44×10^5
	60.0	-54.7	2.80×10^{-3}	0.85×10^1	4.24×10^2	0.58×10^1	1.76×10^4	1.24×10^5
	79.5	-79.3	0.55×10^{-3}	0.17×10^1	0.83×10^2	0.11×10^1	0.34×10^4	0.24×10^5

^a Spherical polar coordinate system, with r = distance of a particle to the center of mass which it has in common with an approaching particle; θ and ϕ as in Ref. (2) (see Fig. 9).

^b Negative values indicate centrifugal pseudoforce and Hamaker attraction force working in approximately opposite directions.

^c $\dot{\gamma}$ (sec^{-1}).

happens depends on r , but is for spherical particles with a radius between 0.7 and 2.5 μm situated in the vicinity of $\dot{\gamma} \approx 20 \text{ sec}^{-1}$. At about this value, α_0 shows a transition from a behavior dominated by Hamaker attraction to one dominated by centrifugal pseudoforces (Fig. 7).

In the typical Taylor vortex region, α_0 is low and not largely dependent on $\dot{\gamma}$. This justifies the employment in calculations, of average values of the shear rate, in spite of the rather large spread of $\dot{\gamma}$ about its average (cf. Fig. 5).

The low value of α_0 in this region may come as a surprise: after what has been said about the importance of centrifugal pseudoforces (cf. Table II), one would expect that α_0 in this region increases with increasing $\dot{\gamma}$, for all kinds of primary particles but most

distinctly for the 5- μm suspensions. However, a newly formed pair immediately after its formation is subject to considerable shear stress (e.g., for an encounter in the equatorial plane $\theta = 90^\circ$, $6\pi\eta\dot{\gamma}b \times \sin 2\phi$, see Fig. 9). Those newly formed doublets survive that "fit well" into each other, i.e., that have many contact points: only those parts of the two primary particles in a doublet adjacent to a contact point contribute significantly to the mutual attraction, because retardation weakens the attraction among the parts further away (cf. Fig. 8). Thus, α_0 in this region is the net result of increasing importance of centrifugal pseudoforces, and increased disruption of newly formed pairs by shear stresses. With increasing primary particle size, α_0 increases in this region; and especially for the largest particles a slight increase of α_0 with increasing $\dot{\gamma}$ is found (Fig. 10). Both effects indicate that centrifugal pseudoforces are important in this region; but in view of the uncertainties about both pair formation and disruption no more detailed opinion on this subject can be uttered with any confidence.

The Later Stages of the Coagulation

A survey of typical results for the later stages of the coagulation is given in Fig. 11. Four different regions can be discerned:

FIG. 9. Encounter between two particles in the equatorial plane ($\theta = 90^\circ$). In the inset is shown the coordinate system used.

FIG. 10. α_0 vs $\log_{10} \bar{\gamma}$ in the Taylor vortex region. +, 5- μ m primary particles; O, 3- μ m primary particles; x, 1.5- μ m primary particles.

(1) In the *laminar region* at low ω_i values E_t , the extinction reached after a certain time, decreases with increasing ω_i .

(2) In the *transition region* from laminar to Taylor vortex flow E_t increases with increasing ω_i .

(3) In the *Taylor vortex region* E_t decreases again with increasing ω_i .

(4) In the *high $\bar{\gamma}$ region* E_t increases with increasing ω_i .

Cases of (nearly) constant final extinction values. Especially interesting are those cases where at the end of the experiments E_t becomes nearly independent of that time. This was observed for 3- and 5- μ m primary particles in the laminar and Taylor vortex regions (1 and 3 in the above list). Thus, for the 3- μ m particle suspensions at $\ln \omega_i = 2.90$, it takes 30 min for E_t/E_0 to decrease from 1 to 0.222, while it takes 20 min more for a further decrease to 0.195. This situation did not arise for 1.5- μ m primary particles within the duration of our coagulation experiments (100 min).

When E_t reaches a nearly constant value, the aggregates apparently grow only slowly beyond a certain size. This size increases with increasing $\bar{\gamma}$. An estimate of the final size may be obtained as follows. From Eq. [7]

$$E = Q_{\text{sca}} \times \pi \bar{b}^2 n \quad [16]$$

with $\bar{b} = (\sum_i n_i b_i^2 / \sum_i n_i)^{1/2}$. If we assume that the average radius defined thus does not differ greatly from $\bar{b}' = (\sum_i n_i b_i^3 / \sum_i n_i)^{1/3}$, we can write

$$E \approx Q_{\text{sca}} \times \frac{3}{2} \frac{\phi}{\beta \bar{b}}. \quad [17]$$

Thus

$$\frac{E_\infty}{E_0} \approx \frac{\beta_0 b_0}{\beta_\infty \bar{b}_\infty}. \quad [18]$$

Assuming $\beta_0 = 1$, $\beta_\infty \approx 0.5$, we find the values shown in Fig. 12.

The course of this figure can be explained as follows. At not too large $\bar{\gamma}$, aggregates do not grow beyond $\bar{b}/b_0 \approx 3$ to 4. Then collisions occur between flocs rather than between primary particles or between primary particles and flocs. Because of the looser structure of flocs (as compared with primary particles), in a newly formed contact plane there will then be only a small amount of contact points. Thus, flocs formed on mutual collisions of flocs are, at least in the Taylor vortex region, prone to pronounced disruption unless there is considerable rearrangement of the primary particles within the colliding flocs during the collision. The prob-

FIG. 11. E_t/E_0 for various values of $\ln \omega_i$. Primary particles: 3 μ m. x, 2 min after mixing and subjecting to shear; O, 5 min after mixing and subjecting to shear; +, 10 min after mixing and subjecting to shear; Δ , 20 min after mixing and subjecting to shear; $\square$, 30 min after mixing and subjecting to shear; ∇ , 50 min after mixing and subjecting to shear.

FIG. 12. $\bar{b}_\infty/b_0$, calculated assuming $\beta_\infty = 0.50$, as a function of $\dot{\gamma}$.

ability for this to occur increases with increasing $\dot{\gamma}$. In Adler's terms (3, 4) this could be described by a decreasing permeability of flocs formed at increasing $\dot{\gamma}$, which makes the formation of larger flocs feasible.

This explanation makes of course the values of $\bar{b}_\infty/b_0$ shown in Fig. 12 subject to revision since β will increase with increasing $\bar{b}$. The increase of β with increasing $\bar{b}$, however, cannot invalidate the increasing character of $\bar{b}_\infty/b_0$ upon which the explanation was based.

The late coagulation stages in the high $\dot{\gamma}$ region. At $\dot{\gamma} > 5000 \text{ sec}^{-1}$ (approximately) the decreasing character of E_t/E_0 with increasing $\dot{\gamma}$ (at constant t) again turns into an increase. The explanation of this fact should take into account that the phenomenon is not observed for the formation of doublets from primary particles (cf. Figs. 7 and 10). Thus, the effect is related to the formation or degradation of larger flocs.

For these larger flocs, the Reynolds number for the motion of the liquid around them ($= 2b^2\dot{\gamma}/\nu$, where ν = the kinematic viscosity of the liquid) surpasses the value of 0.1. This is the limit at which, at least for impermeable spherical particles in a uniform flow field, the conditions for "creeping flow" cease: at larger Reynolds number, vortex formation downstream will occur (14). If this occurs the deg-

radation-recirculation-reattachment mechanism developed by Adler (3, 4) will be interfered with, and degradation becomes more pronounced.

The size for the aggregates, for which this will occur, can be indicated only roughly because we are dealing with permeable entities. For impermeable particles, b for the Reynolds number concerned at $\dot{\gamma} = 5000 \text{ sec}^{-1}$ would be about $3 \mu\text{m}$; but this will be an underestimate since the permeability of the particles will tend to suppress vortex formation. Nevertheless, the limit mentioned is of the right order of magnitude and gives us confidence that suppression of recirculation of aggregate fragments by vortex formation is the explanation of the increase of E_∞/E_0 with increasing $\dot{\gamma}$ in this region.

CONCLUSIONS

- (1) For large particles and large shear rates, orthokinetic coagulation is caused by inertia rather than by Hamaker attraction; though the latter is necessary to keep formed pairs together. The transition occurs for quartz particles of hydrodynamic diameter $3 \mu\text{m}$, at about $\dot{\gamma} = 20 \text{ sec}^{-1}$.
- (2) For the initial stages of the coagulation, the capture efficiency for $\dot{\gamma} > 1000 \text{ sec}^{-1}$ is small but $\neq 0$.
- (3) In the range $1000 \text{ sec}^{-1} < \dot{\gamma} < 5000 \text{ sec}^{-1}$, the final floc size increases with increasing $\dot{\gamma}$.
- (4) Vortex formation behind aggregates retards the formation of large aggregates.

APPENDIX: LIST OF SYMBOLS USED

A	Hamaker constant
b	Particle or aggregate radius (for non-spherical entities, equivalent hydrodynamic radius)
b_i	Radius of an aggregate with i primary particles
b_∞	Average aggregate radius for $t \rightarrow \infty$
E	Light extinction
E_t	Light extinction at time t
E_∞	Light extinction at time $t \rightarrow \infty$

J	Number of collisions experienced by one particle per unit of time	$\dot{\gamma}$	Shear rate
K_1 K'	Constants describing the proportionality between light extinction and number of particles per unit volume	θ	Coordinate (see Fig. 11)
k	Aggregate permeability	λ	Wavelength of light
l	Path length of light through the suspension	ν	Kinematic viscosity
n	Number of particles and aggregates per unit volume	Φ	Solid volume fraction in the suspension
n_i	Number of aggregates with i primary particles, per unit volume	ϕ	Coordinate (see Fig. 11)
n_0	Number of primary particles for $t = 0$	ω_i	Rotation speed of inner cylinder
Q_{scai}	Scattering factor (= scattering cross-section/geometrical cross-section) of an aggregate with i primary particles	ACKNOWLEDGMENT	
R_{ij}	Collision radius describing pair formation between aggregates with i and j primary particles, respectively		
r	Distance between a particle and the center of mass which it has in common with another, approaching particle	REFERENCES	
v	Velocity		
v_r, v_θ, v_ϕ	Velocity components in r, θ , or ϕ directions, respectively	1.	Overbeek, J. Th. G., in "Colloid Science I" (H. R. Kruyt, Ed., p. 290. Elsevier, Amsterdam, 1952).
y	Constant describing the dependence of Q_{scai} on λ/b_i	2.	van de Ven, T. G. M., and Mason, S. G., <i>J. Colloid Interface Sci.</i> 57 , 505 (1976).
α_0	Capture efficiency	3.	van de Ven, T. G. M., and Mason, S. G., <i>Colloid Polym. Sci.</i> 255 , 468 (1977).
β	Solid volume fraction in an aggregate	4.	Adler, P. M., and Mills, P. M., <i>J. Rheol.</i> 23 , 25 (1979).
β_∞	β for $t \rightarrow \infty$	5.	Adler, P. M., <i>J. Colloid Interface Sci.</i> 81 , 531 (1981).
		6.	Zeichner, G. R., and Schowalter, W. R., <i>J. Colloid Interface Sci.</i> 71 , 237 (1979).
		7.	Stuart, J., <i>J. Fluid Mech.</i> 4 , 1 (1958).
		8.	Davey, A., <i>J. Fluid Mech.</i> 14 , 336 (1962).
		9.	Ia Mer, V. K., <i>J. Phys. Colloid Chem.</i> 52 , 65 (1948).
		10.	Timasheff, S. M., <i>J. Colloid Interface Sci.</i> 21 , 489 (1966).
		11.	Visser, J., <i>Adv. Colloid Interface Sci.</i> 3 , 331 (1972).
		12.	Casimir, H. B. G., and Polder, D., <i>Phys. Rev.</i> 73 , 360 (1948).
		13.	Batchelor, G. K., and Green, J. T., <i>J. Fluid Mech.</i> 56 , 375 (1972).
		14.	Bird, R. B., Stewart, W. E., and Lightfoot, E. N., "Transport Phenomena," p. 57. Wiley, New York, 1960.