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by

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COAGULATION IN TURBULENT FLOW - THEORY AND EXPERIMENT

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Abstract

The coagulation of colloidal particles in turbulent flows is investigated theoretically and experimentally. A coagulation model is developed for destabilized particles in an isotropic turbulent flow. Simple binary collision mean free path concepts are employed and for monodisperse systems coagulation rate relations are derived for particle sizes less than and larger than the Kolmogorov microscale of turbulence. Polydisperse systems are also considered and some general results concerning their behavior are obtained. Also discussed are the effects of interparticle repulsion on the coagulation rates.

Coagulation experiments are reported on inside fully developed turbulent pipe flows using an approximately monodisperse UCAR latex dispersion in which the particle sizes are less than the Kolmogorov microscale. The flow rate, destabilizer concentration and volume fraction of the dispersed phase were varied in these experiments. The experimental results for destabilized particles are shown to agree very well with the theoretical predictions. Brownian motion coagulation experiments for partially destabilized systems are compared with the corresponding turbulent motion experiments and the results indicate that the coagulation efficiency does not appear to depend on the particle transport mode.

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NOMENCLATURE

$A(t)$	dimensionless coefficient characterizing polydispersity, Eq. [15]
c_f	turbulent friction coefficient, Eq. [29] (dimensionless)
d	particle diameter (cm)
D	pipe diameter (cm)
$f(v,t)$	particle volume probability density (cm^{-6})
L	Eulerian macroscale of turbulence (cm)
n	particle number density (cm^{-3})
n_v	cumulative particle number density (cm^{-3})
Q	flow rate in pipe (gal/min)
Re	Reynolds number, UD/ν (dimensionless)
t	time (sec)
u_*	turbulent friction velocity, Eq. [27] (cm/sec)
u_i	induced relative velocity between particles due to repulsive effects (cm/sec)
u_r	relative particle velocity during collision (cm/sec)
$(u_r)_{eff}$	effective collision velocity for partially destabilized particles (cm/sec)
U	average pipe velocity (cm/sec)
v	particle volume (cm^3)
V	characteristic potential energy of interaction between particles (ergs)
x	distance along pipe measured from first sampling station (cm)
W_{Br}	Brownian coagulation stability factor (dimensionless)
W_{turb}	turbulent coagulation stability factor (dimensionless)

Greek

ε	rate of turbulent energy dissipation per unit mass (ergs/g · sec)
η	Debye length (cm)
λ	Kolmogorov microscale, $(\nu^3/\varepsilon)^{1/4}$ (cm)
μ	viscosity of continuous phase (g/cm · sec)
ν	kinematic viscosity of continuous phase (cm^2/sec)
ξ	dimensionless particle volume, nv/ϕ
τ	Kolmogorov time scale, $(\nu/\varepsilon)^{1/2}$ (sec)
ϕ	volume fraction of dispersed phase (dimensionless)
ϕ_D	volumetric concentration of destabilizer (dimensionless)
$\psi(\xi,t)$	dimensionless particle volume probability density, Eq. [13a]
ω	particle coagulation (collision) rate (sec^{-1})
ω_*	retarded coagulation rate (sec^{-1})
$\tilde{\omega}(v,v)$	volume swept by each particle per unit time during collision (cm^3/sec)
$\tilde{\tilde{\omega}}(\xi,\xi')$	dimensionless collision frequency function, Eq. [13c]

Subscripts

1,2	reference to two monodisperse systems 1 and 2 with different particle volume fractions, diameters and number densities

Superscript

'	reference to particles of diameter d' and volume v'

INTRODUCTION

Coagulation of particles in turbulent flows is a phenomenon which arises in many engineering systems. In particular, an understanding of the coagulation mechanism is of primary importance with regard to the behavior, handling and treatment of dispersions.

Particles dispersed in a liquid medium generally acquire an electrical charge, usually negative. As a result of the potential field surrounding each particle, coagulation is inhibited at short interparticle distances by the repulsive action between the particles. It follows that coagulation may be considered as a two-step process (1): a) kinetic transport of particles; b) actual particle aggregation after the interparticle repulsion is overcome. Particle transport may take place as a consequence of Brownian motion, shear flow or turbulent motion. The repulsive interparticle forces can be neutralized, that is, the dispersion can be destabilized, by the addition of appropriate chemicals usually called coagulants or coagulant aids (1).

It was Camp and Stein (2) who first suggested that the coagulation rate in turbulent flows inside agitator tanks can be estimated using the theory developed by Smoluchowski (3) for shear flow coagulation. In deriving their result for the coagulation rate they replaced the rate of strain in Smoluchowski's expression by an effective turbulent rate of strain equal to $(\varepsilon/\nu)^{1/2}$, where ε is the average turbulent energy dissipation rate per unit mass inside the agitator tank and ν is the kinematic viscosity of the continuous phase [see also (1)].

Later Saffman and Turner (4) proposed a theory to estimate the coagulation rate of drops in turbulent clouds in which they considered the nature of the flow field around a drop. The drop sizes in their

theory were smaller than the Kolmogorov microscale of turbulence. The form of their results for the collision rate, which they identified with the coagulation rate, agreed with the equation proposed by Camp and Stein to within a constant factor.

Finally Levich (5) developed a coagulation model based on a diffusion equation for the relative particle motion, and estimated the coagulation rate for particles of a size less than the Kolmogorov microscale. His model led to the same functional form for the coagulation rate as the one obtained by the previously mentioned authors but with a value larger by approximately an order of magnitude. This discrepancy may be attributed to the inability of a steady diffusion model to correctly describe the relative motion of particles in turbulent flows due to the non-Markovian nature of the turbulent dispersion process.

Experiments carried out in agitator tanks [see Birkner and Morgan (6)] have verified the functional form for the coagulation rate predicted by the various theories but were unable to establish which of the proportionality constants was correct among the different values predicted. The main reason for the uncertainty is that the turbulent conditions in an agitator tank are far from isotropic (7), so that the use of average turbulent properties in correlating the experimental results (6) introduces an error.

In this work a new model is developed for destabilized systems based on simple binary collision mean free path concepts for noninteracting particles. For monodisperse systems coagulation rate relations are obtained for particle sizes less than and larger than the Kolmogorov microscale of turbulence. Polydisperse systems of unequal size spherical particles are also considered and some general results concerning their

behavior are obtained. Also discussed are the effects of interparticle repulsion on the rate of coagulation between particles. The theoretical results are compared with coagulation rate experiments carried out inside fully developed turbulent pipe flows. Fully developed turbulent pipe flow was selected because its characteristics are well known and because the flow is nearly isotropic at the core of the pipe (8). A further reason for carrying out these experiments was that no coagulation measurements in turbulent pipe flows have been reported previously in the literature.

KINETIC MODEL FOR COAGULATION IN TURBULENT FLOW

In what follows the particles are considered to be sufficiently small that we may neglect inertial effects so that the particles can be assumed to follow the turbulent motion, which in our analysis we take to be isotropic. Particle-particle interactions, gravitational forces and any breakup of particles due to turbulent forces are neglected. The particle volume fraction is taken sufficiently small ($\phi \lesssim 3\%$) that only binary collisions need be considered. At first we examine a destabilized system in which the interparticle repulsion has been reduced to zero by the addition of appropriate chemicals (1).

Under the assumptions outlined we may apply simple binary collision mean free path concepts for noninteracting particles to calculate the coagulation frequency associated with the statistical nature of a turbulent flow. Thus for a monodisperse system, consisting of equal size spherical particles, the volume swept out by each particle per unit time during collision will be

$$\mathcal{J}(v,v) = \pi d^2 u_r \qquad [1]$$

Here v is the particle volume, d its diameter, πd^2 the effective collision cross section and u_r the relative particle velocity during collision.

It follows that the coagulation rate, equal in effect to the particle collision rate, is given by

$$\omega = \frac{1}{2} n \tilde{\omega}(v,v) = \frac{1}{2} n \pi d^2 u_r \qquad [2]$$

where n is the particle number density and the factor 1/2 ensures that each collision of two equal size particles is counted only once.

The decrease of particle number density with time due to coagulation will be

$$\frac{dn}{dt} = - \omega n \qquad [3]$$

The relative particle velocity appearing in Eq. [1] is approximately equal to the root mean square relative turbulent velocity between two points at a distance of a particle diameter apart. From the Kolmogorov theory of isotropic turbulence the relative velocity depends on the turbulent scale and its magnitude is given by the relations (9)

$$u_r = \sqrt{\frac{1}{15}} \left(\frac{\varepsilon}{\nu}\right)^{1/2} d \qquad d < \lambda \qquad [4a]$$

$$u_r = 1.37 (\varepsilon d)^{1/3} \qquad d > \lambda \qquad [4b]$$

$$u_r \approx (\varepsilon L)^{1/3} \qquad d \sim L \qquad [4c]$$

Here, L is the Eulerian macroscale of turbulence and λ is the Kolmogorov

microscale defined by the relation

$$\lambda = (\nu^3/\varepsilon)^{1/4} \qquad [5]$$

where ε is the rate of turbulent energy dissipation per unit mass and ν is the kinematic viscosity of the continuous phase. We note that Eq. [4b] is applicable only when an inertial subrange of turbulence exists, that is, for sufficiently large Reynolds numbers where $L >> \lambda$ (9). Furthermore, it is assumed here that the macroscale is of a size which could be acquired by a dispersed particle (e.g., $L \sim 0.1$ cm).

Using the appropriate value for the relative velocity u_r in Eq. [2], we get after some rearrangements

$$\frac{\omega\tau}{\phi} = 0.77 \qquad d < \lambda \qquad [6a]$$

$$\frac{\omega\tau}{\phi} = 4.11 \left(\frac{\lambda}{d}\right)^{2/3} \qquad d > \lambda \qquad [6b]$$

$$\frac{\omega\tau}{\phi} \approx 3\left(\frac{L}{\lambda}\right)^{1/3} \frac{\lambda}{d} \qquad d \sim L \qquad [6c]$$

In these equations τ is the Kolmogorov time scale defined by

$$\tau = (\nu/\varepsilon)^{1/2} \qquad [7]$$

and ϕ is the volume fraction of the dispersed phase,

$$\phi = \frac{1}{6}\, n\, \pi d^3 \qquad [8]$$

We have plotted in Fig. 1 the dimensionless coagulation rates $\omega\tau/\phi$ given by Eqs. [6] as a function of d/λ. In plotting Eq. [6c] we have assumed by way of example that $L/\lambda = 10^3$, which implies sufficiently large Reynolds numbers that there exists an inertial subrange of turbulence. In Table I the theoretical dimensionless coagulation rate of Eq. [6a] derived for particle sizes less than the Kolmogorov microscale is compared with the comparable results of previous authors. The value of 9.24 attributed to Levich was obtained by taking the constant of proportionality in his effective turbulent diffusion coefficient to be equal to $\sqrt{1/15}$, consistent with the Kolmogorov result (cf. Eq. [4a]).

TABLE I

THEORETICAL COAGULATION RATES FOR PARTICLE SIZES SMALLER THAN THE KOLMOGOROV MICROSCALE

Author	$\omega\tau/\phi$
Camp and Stein (2)	1.27
Saffman and Turner (4)	1.23
Levich (5)	9.24
Present study (Eq. [6a])	0.77

For a spatially homogeneous polydisperse system, consisting of unequal spherical particles of volume v, it is necessary to introduce the particle volume probability density f(v,t) at a time t. The kinetic equation governing the temporal evolution of f or population balance is then written (10)

$$\frac{df(v,t)}{dt} = \frac{1}{2}\int_0^v \tilde{\omega}(v',v-v')\ f(v',t)\ f(v-v',t)\ dv'$$

$$- \int_0^\infty \tilde{\omega}(v,v')\ f(v,t)\ f(v',t)\ dv' \qquad [9]$$

where $\tilde{\omega}(v,v')$ is the volume swept per unit time by each of the particles with volumes v and v'. According to our simple collision model,

$$\tilde{\omega}(v,v') = \pi\left(\frac{d+d'}{2}\right)^2 u_r \qquad [10]$$

where d,d' are the diameters of particles of volume v and v' respectively, and the relative velocity u_r is equal to the root mean square velocity between two points at a distance $(d + d')/2$ in an isotropic turbulent flow [see (9)].

Integrating Eq. [9] with respect to v over all volumes and introducing the definitions of the particle number density n and volume fraction ϕ

$$n = \int_0^\infty f(v,t)\ dv \qquad [11a]$$

$$\phi = \int_0^\infty vf(v,t)\ dv \qquad [11b]$$

leads to the kinetic equation

$$\frac{dn}{dt} = -\omega n \left[\int_0^\infty \int_0^\infty \tilde{\tilde{\omega}}(\xi,\xi')\ \psi(\xi,t)\ \psi(\xi',t)\ d\xi\ d\xi'\right] \qquad [12]$$

in terms of the dimensionless variables (10)

$$\psi(\xi,t) = \frac{\phi}{n^2} f(v,t) \qquad [13a]$$

$$\xi = \frac{nv}{\phi} \qquad [13b]$$

$$\mathfrak{K}(\xi,\xi') = \frac{1}{2}\frac{n}{\omega}\,\mathfrak{B}(v,v') \qquad [13c]$$

We note that for a monodisperse system with the same volume fraction ϕ, ω in Eq. [12] is the coagulation rate defined in Eqs. [2] and [6], if we assume that no more than one value of u_r in Eq. [4] is applicable for the entire spectrum of particle sizes in evaluating the volume swept per unit time by Eq. [10].

For dispersed systems where the particle sizes are less than the Kolmogorov microscale we can readily show from Eqs. [4a] and [10] that

$$\tilde{\mathfrak{B}}(\xi,\xi') = \frac{1}{8}\,(\xi^{1/3} + \xi'^{1/3})^3 \qquad [14]$$

It follows that we may write Eq. [12] in the form

$$\frac{dn}{dt} = -\,\omega n\, A(t) \qquad [15a]$$

with A(t) a coefficient characterizing the polydisperseness of the system defined by

$$A(t) = \frac{1}{8}\int_0^\infty\int_0^\infty (\xi^{1/3} + \xi'^{1/3})^3\, \psi(\xi,t)\, \psi(\xi',t)\, d\xi\, d\xi' \qquad [15b]$$

and with ω given by Eq. [6a].

The coefficient A(t) will be time dependent since as recently shown by Pulvermacher and Ruckenstein (11) a self similar solution for $\psi(\xi,t)$ independent of time cannot exist for the collision frequency function of Eq. [14].

Another important result we can derive is that A(t) satisfies the inequalities

$$0.25 \leq A(t) \leq 1 \qquad [16]$$

The above result may be derived from the definition of A(t) in Eq. [15b] through the use of the algebraic inequalities

$$(\xi + \xi') < (\xi^{1/3} + \xi'^{1/3})^3 \leq 4(\xi + \xi') \qquad [17]$$

and the conditions obtained from introducing the dimensionless variables of Eq. [13] into the definitions of Eq. [11],

$$\int_0^\infty \psi(\xi,t)\, d\xi = 1 \qquad [18a]$$

$$\int_0^\infty \xi\psi(\xi,t)\, d\xi = 1 \qquad [18b]$$

The coefficient A(t) can be shown to take on the value of 1 for a monodisperse system, and the minimum value of 0.25 for a system consisting of two monodisperse systems with widely differing volume fractions ($\phi_1 << \phi_2$) where the number densities are also widely different but in the inverse order ($n_1 >> n_2$). The derivation of this result is outlined in the Appendix.

EFFECTS OF INTERPARTICLE REPULSION

In the analysis so far it has been assumed that charge repulsion effects between particles could be neutralized by the addition of appropriate chemicals (1). Colloidal particles usually acquire a negative surface charge in solution so that they tend to repel each other upon collision. Thus coagulation between particles is retarded or totally inhibited, when the particle surface potential (zeta potential) is different from zero.

Due to the complex character of turbulent flows it is not feasible to describe analytically the retarding effects on coagulation of interparticle potentials. In this regard, the use of the turbulent diffusion model suggested by Levich (5), in which potential effects would be incorporated as was done by Fuchs (12) for Brownian motion, is not justified because of the non-Markovian nature of turbulent flows.

In what follows a rather qualitative description of the effects of interparticle repulsion is proposed for particles of a size less than the Kolmogorov microscale. The characteristic potential energy of interaction between the particles is designated by V and typically may be taken equal to the maximum interparticle potential energy. The range over which this potential energy is effective is characterized by the Debye length η which is the characteristic thickness of the double layer surrounding the colloidal particles (13). In general, the particle size is large compared to the Debye length η, which typically is like 50 $\mathring{A}$.

The other force acting on the particles is fluid dynamic in origin and, for particle sizes less than the Kolmogorov microscale, is the low Reynolds number Stokes drag

$$F \approx 3 \pi \mu u_r d \qquad [19]$$

where u_r is the relative particle velocity during collision (cf. Eq. [1]) and μ is the viscosity of the continuous phase. The approximately equal sign has been used here because the drag force will be somewhat smaller than indicated as a result of the fluid dynamic interactions between the particles as they approach each other.

Comparing the electrostatic potential force to the fluid dynamic drag force, it can be seen from dimensional arguments that the retarded coagulation rate ω_* is expressible through the functional relation

$$\omega_* = \omega \text{ fcn } \left(\frac{V}{\mu u_r d \eta}\right) \qquad [20]$$

Here ω is the coagulation rate for the fully destabilized system and the function represents a coagulation efficiency which tends to 1 as $V \to 0$ and to 0 as $V \to \infty$.

The motion of a particle of a size less than the Kolmogorov microscale in the potential field of another particle is characterized by three time scales, the particle motion characteristic relaxation time ($d^2/18\nu$), the characteristic Kolmogorov eddy time scale [$(\nu/\varepsilon)^{1/2}$], and the time required for the particle to move a distance equal to the Debye length (η/u_r). We may estimate that the relaxation time for micron size particles is much less than the time required for the particle to move a Debye length, while the characteristic turbulent eddy time is much larger. It follows that the change in turbulent velocity

during the time the particles interact can be neglected. The amount by which the coagulation frequency is reduced when the interparticle potential energy V is small may then be estimated in the following way. At a distance of the order of a Debye length η, the repulsive potential energy between the particles induces a relative particle velocity of the order of

$$u_i \sim \frac{V}{3\pi\mu\, d \cdot \eta} \qquad [21]$$

Therefore at short interparticle distances the instantaneous relative turbulent particle velocity will be reduced by an amount given by u_i.

The effective collision velocity between the particles can be found from the requirement that the *instantaneous relative turbulent* velocity must be absolutely larger than the induced velocity in order for a collision to lead to actual particle coagulation. For small values of the induced velocity in comparison with the root mean square velocity difference u_r (cf. Eq. [1]), the effective collision velocity may be approximated by

$$(u_r)_{eff} = u_r - u_i \qquad [22]$$

Using the same simple mean free path model defined through Eq. [2], with an interparticle velocity $(u_r)_{eff}$, we obtain the following expression for the reduced coagulation rate

$$\omega_* \sim \omega[1 - \frac{V}{3\pi\mu\, u_r\, d\eta}] \qquad [23]$$

where we have used the value of u_i given by Eq. [21] and have assumed $n/d << 1$.

EXPERIMENTS

Experiments were carried out to measure the coagulation rate of colloidal particles inside a fully developed turbulent pipe flow. The principal advantage of this configuration in contrast to say a stirred tank, is that the turbulent characteristics of such a flow are well known [see, e.g., (8)]. Furthermore, in a fully developed flow the turbulence is nearly isotropic in the pipe core. Commercial latex particles having a narrow size distribution were dispersed in water. The particle sizes and the number of particles per unit volume were measured using a Coulter counter [see, e.g., (14)].

Figure 2 shows a diagram of the experimental setup. The flow is established by means of a centrifugal pump. The flow rate is measured by a rotameter and controlled by the overflow arrangement shown in the figure. Two honeycomb filters are used in the feed line to filter the supply water. The stable latex emulsion was released, at a measured rate, at station I into the pipe flow from a pressurized tank, through a solenoid valve controlled by an electric timer. Destabilizer is injected, at a measured rate, at station II, where the latex particles are known to be completely mixed with the turbulent flow. This injection system is similar to that for the emulsion.

Latex particles manufactured by Union Carbide (878 UCAR) with an average size of 0.6 μm were used in these experiments. A mixture of 1 mol/liter of HCl and 5.6 mol/liter of $CaCl_2$ was used as the destabilizer. A special construction for the injection port at station

II ensured complete mixing of the destabilizer with the flow in a short distance. Sufficient pipe length is provided after each bend, so that fully developed turbulent flow prevails.

After steady flow conditions are established (for the present experiments, approximately 10 sec after the release of the latex emulsion) samples are withdrawn at five stations along the pipe. The sample at each station is withdrawn automatically by a solenoid valve, through a 1/4 inch I.D. pipette in the wall of the pipe. The velocity through the pipette was much larger ($\sim$ 500 cm/sec) than the average pipe velocity ($\sim$ 180 cm/sec), so that the withdrawn sample is representative of the conditions at the core of the pipe flow. The coagulation inside this pipette was estimated to amount to less than 2% of the total particle number density. As shown in Fig. 1 each sample is diluted directly in a 1 liter flask containing distilled water. The dilution is sufficient to ensure that Brownian coagulation effects are negligible, prior to the time at which the actual analysis of each sample is carried out.

Prior to carrying out the measurements, each sample is further diluted by a known amount in a pure aqueous solution of 1% sodium chloride. These samples are then analyzed using the Coulter counter. The theory behind the operation of the Coulter counter is quite simple. The dispersed particles suspended in the 1% aqueous solution of sodium chloride are forced to flow through a small aperture which has an immersed electrode on each side. As each particle passes through the aperture it replaces a volume of electrolyte equal to its own value

within the aperture, thus momentarily changing the resistance between the electrodes. This produces a voltage pulse of short duration which has a magnitude proportional to the particle volume. The resulting series of pulses is electronically amplified, rated and counted. Thus for each sample not only is the total number of particles in a measured volume counted, but the particle size distribution is also measured. Apertures of different sizes can be used for different ranges of particle size. Detailed information on this measurement technique may be found in the previously cited paper of Wachtel and La Mer (14).

Calibration of the counter was done using latex particles of a known size. Sufficiently diluted samples ($\phi \approx 10^{-7}$) were used for the analysis so that corrections due to coincidental passing of two or more particles through the aperture were unnecessary. Aperture sizes of 19 μm, 50 μm and 200 μm were used in the present experiments.

Additional details of the apparatus, including dimensions of the various components, may be found in (15).

RESULTS

Prior to carrying out detailed measurements in the turbulent pipe flow system described, the Brownian coagulation rate was measured for different destabilizer concentrations for the latex dispersion to be used in the pipe flow experiments. Samples from a dilute dispersion ($\phi = 10^{-3}$ to 10^{-4}) were taken from a beaker at specified time intervals and analyzed with the Coulter counter. The purpose of these tests was to determine the destabilizer concentration required for the dispersion to be fully destabilized.

Figure 3 shows the experimental results. In this figure the stability factor W_{Br} is plotted as a function of the volumetric destabilizer concentration ϕ_D. The stability factor is the ratio of the coagulation rate for a fully destabilized system to the coagulation rate for a partially destabilized system (13) (cf. Eq. [20]). From this figure we conclude that the destabilizer concentration necessary for complete destabilization of the present dispersion is approximately 4.5%. The experimental linear fit for destabilizer concentrations less than 4.5% has been drawn consistent with previous results (16).

Experiments in the turbulent flow system shown in Fig. 2 were carried out in which the flow rate through the pipe, the volume fraction of the dispersed phase and the destabilizer volume concentration were varied. The flow rates Q ranged between 5 and 15 gal/min for which the corresponding Reynolds number based on pipe diameter ran between 17,000 and 51,000. The volume fraction ϕ of the latex particles was varied between 10^{-3} and 6×10^{-3} while the volumetric fraction of the destabilizer ϕ_D was controlled between 1 and 10%. Brownian coagulation was always negligible compared to turbulent coagulation and the particle size in these experiments was always less than the Kolmogorov microscale.

In each experiment the particle size distribution was measured at every sampling station along the pipe (see Fig. 2). A typical set of results is shown in Fig. 4 for a pipe flow rate of 15 gal/min. In this figure the cumulative particle number density n_v is plotted as a function of the particle volume at different sampling stations. The cumulative particle number density gives the number of particles per unit volume of the continuous phase with volumes larger than a certain

volume v. It is defined by (cf. Eq. [11a])

$$n_v = \int_v^\infty f(v,t)\, dv \qquad [24]$$

From Fig. 4 it can be seen that the total particle number density decreases along the pipe due to coagulation.

Figure 5 shows the same experimental points as in Fig. 4 plotted in the reduced dimensionless similarity variables suggested by Eqs. [13]. This figure would seem to indicate that over the length of pipe in which the experiments were conducted the cumulative particle size distribution at each sampling station remains approximately similar to the initial particle size distribution at the first station. A best fit curve through these points is drawn in Fig. 5. Using this curve the coefficient A(t), which was introduced in Eq. [15] to characterize the polydisperseness of the system, is found to be

$$A(t) = 0.90 \qquad [25]$$

where any time dependence has been suppressed through the use of the "best fit similarity curve."

Due to the limited length of the pipe in the present setup, no experiments could be run for times much larger than the characteristic coagulation time, in order to test whether the particle size distribution was or was not self similar. However, as we have discussed previously, a self similar solution independent of time cannot exist

for the collision frequency function consistent with the present theoretical model (Eq. [14]).

Figure 6 is a typical log-linear plot of the total particle number density as a function of distance along the pipe. The ordinate in this figure is the ratio of the total particle number density at a sampling station to the total particle number density at station one. The abscissa is the time required for the dispersion to flow to the sampling station

$$t = x/U \qquad [26]$$

where x is the distance along the pipe measured from the first sampling station and U is the average pipe velocity.

For the same degree of destabilization, the experimental points lie on a straight line in agreement with the theoretical Eq. [3] for a constant coagulation rate ω. As may be seen in the figure, the slope of the lines which define the coagulation rate increases absolutely with an increase in the volumetric destabilizer concentration ϕ_D.

In Fig. 7 we have shown a typical set of results for the measured coagulation rates as a function of destabilizer concentration ϕ_D. The Kolmogorov time scale (Eq. [7]) was calculated from the characteristics of turbulent pipe flow. Experiments by Laufer (8) have shown that fully developed turbulent pipe flow is very close to homogeneous and isotropic to within about 90% of the pipe radius. As previously described, the sampling stations in the experiment were designed in such

a way that the sample withdrawn from the pipe is representative of the conditions at the core of the pipe flow. It follows that in calculating the Kolmogorov time scale, the turbulent characteristics representative of the core of the pipe flow are the ones to be used.

From the experimental work of Laufer (8) the rate of energy dissipation per unit mass corresponding to the core of the pipe flow is

$$\varepsilon = 4 \frac{u_*^3}{D} \qquad [27]$$

Here D is the pipe diameter and u_* the pipe friction velocity, which may be found from the relation (17)

$$u_* = U \sqrt{c_f/8} \qquad [28]$$

where c_f is the turbulent friction coefficient. Measurements of the pressure drop in the piping system of the experiments gave values of c_f equal to those obtained from the standard friction coefficient for turbulent flow in smooth pipes (17),

$$c_f = \frac{0.316}{Re^{1/4}} \qquad [29]$$

where Re is the pipe flow Reynolds number ($Re = UD/\nu$).

It can be seen from Fig. 7 that for $\phi_D \sim 5\%$ the reduced coagulation rate $\omega\tau/\phi \approx 0.78$ and thereafter remains essentially constant with increasing destabilizer concentration. This indicates that the dispersion is effectively fully destabilized for destabilizer

concentrations larger than 5%. Taking into account the correction factor characterizing the polydispersity of the system (Eq. [25]) the reduced coagulation rate for a monodisperse system becomes (see Eq. [15a]),

$$\frac{\omega\tau}{\phi} = \frac{0.78}{0.90} = 0.86 \qquad [30]$$

It can be seen that this value agrees very well with the theoretical result of Eq. [6a].

For destabilizer concentrations less than 5% a linear fit has been drawn through the experimental points of Fig. 7, in analogy with the behavior observed in Brownian coagulation. However, we note that this behavior is in agreement with the predicted dependence shown in Eq. [23]. This follows from the fact that near the critical destabilizer concentration for full destabilization of the dispersion the potential energy V is linear in ln ϕ_D [see (18)].

In Fig. 8 we have plotted the turbulent stability factor W_{turb} as a function of destabilizer concentration for different flow rates. The stability factor is the ratio of the coagulation rate for the fully destabilized system to the coagulation rate for the partially destabilized system and is just the inverse of the "coagulation efficiency" function defined in Eq. [20]. We may make the following remarks concerning the results of Fig. 8:

a. The slope of the linear fit for partially destabilized systems ($\phi_D \gtrsim 5\%$) is independent of the flow rate and hence of the turbulent rate of energy dissipation per unit mass (Eq. [27]). This does not agree with the approximate result represented by Eq. [23],

where the relative velocity u_r is a function of the energy dissipation ε (see Eq. [4a]).

b. The slope of the linear fit in Fig. 8 is almost the same as the slope for the Brownian stability factor in Fig. 3, although we might expect that turbulent motion would lead to higher relative rates of coagulation when compared with Brownian motion. This same behavior has been observed by other investigators in experiments conducted in agitator tanks [see (19)].

c. The experimental value of the destabilizer concentration for full destabilization of the dispersion is approximately the same for Brownian coagulation (4.5%) and turbulent coagulation (5%).

In the course of the present study experiments were carried out with particles larger than the Kolmogorov microscale. For this purpose the UCAR latex emulsion was allowed to coagulate in the emulsion tank (see Fig. 2) to the required degree by the addition of small amounts of destabilizer. The same procedure, as described in the previous section, was used to carry out an experimental run. Unfortunately, the results could not be intelligently interpreted because breakup of the particles took place simultaneously with coagulation. A comprehensive study and understanding of the breakup rate of particles in turbulent flows is not available at this time to enable the proper interpretation of the results of turbulent pipe flow coagulation experiments with particles larger than the Kolmogorov microscale.

CONCLUSIONS

A model based on simple binary collision mean free path concepts

was developed for the prediction of the coagulation rates in isotropic turbulent flows of destabilized monodisperse particles less than and larger than the Kolmogorov microscale. The same simple mean free path concepts were applied to the description of the temporal evolution of the particle volume probability density in coagulating polydisperse systems. It was shown that polydisperseness of the system resulted in a decrease in the total particle number density coagulation rate in comparison with the rate for a monodisperse system of the same volume fraction. For particles of a size less than the Kolmogorov microscale an estimate was made of the reduction in the coagulation rate as a result of the interparticle repulsion associated with charged particles in a partially destabilized system. This estimate was based on comparison of the fluid mechanical (Stokes drag) forces to the electrostatic potential forces.

Experimental results on coagulation of destabilized particles in fully developed turbulent pipe flows, where the particle sizes are small compared to the Kolmogorov microscale, showed excellent agreement with the theoretical prediction of the coagulation rate. The coagulation efficiency for partially destabilized systems appeared to be independent of the particle transport mode, that is, Brownian or turbulent, as has been observed by previous investigators (19). Experiments in which the dispersed particle sizes were larger than the Kolmogorov microscale could not be successfully analyzed because of simultaneous breakup of the particles in the flow.

APPENDIX

In a monodisperse system the dimensionless particle size distribution defined by Eq. [13a] is a delta function centered at 1. It follows directly from Eq. [15b] that for a monodisperse system at the onset of coagulation the coefficient $A(t) = 1$.

In a system consisting of two monodisperse systems with particle volume fractions, diameters and number densities ϕ_1, d_1, n_1 and ϕ_2, d_2, n_2 respectively, the evolution of the total particle density with time at the onset of coagulation is given by

$$\frac{d(n_1 + n_2)}{dt} = -\frac{1}{2}\omega_{11} n_1^2 - \omega_{12} n_1 n_2 - \frac{1}{2}\omega_{22} n_2^2 \qquad [A.1]$$

Here the symmetric tensor $\omega_{ij}(i,j = 1,2)$ represents the volume swept per unit time by particles with diameters d_i and d_j during collision and can be found from Eq. [10]. For particle sizes less than the Kolmogorov microscale

$$\omega_{ij} = \alpha\left(\frac{d_i + d_j}{2}\right)^3 \qquad [A.2]$$

where the proportionality coefficient

$$\alpha = \pi \sqrt{\frac{1}{15}} \left(\frac{\varepsilon}{\nu}\right)^{1/2} \qquad [A.3]$$

Then Eq. [A.1] can be rewritten in the following form

$$\frac{1}{(n_1 + n_2)} \frac{d(n_1 + n_2)}{dt} = - \omega \frac{4(n_1^2 d_1^3 + n_2^2 d_2^3) + (d_1 + d_2)^3 n_1 n_2}{4(n_1 + n_2)(n_1 d_1^3 + n_2 d_2^3)} \qquad [A.4]$$

wherein Eqs. [A.2] and [A.3] have been used and ω is the coagulation rate of a monodisperse system of volume fraction $(\phi_1 + \phi_2)$ (cf. Eq. [15a]).

It follows that the coefficient A(t=0) (cf. Eq. [15a] at the onset of coagulation) will be equal to

$$A(t=0) = \frac{4(n_1^2 d_1^3 + n_2^2 d_2^3) + (d_1 + d_2)^3 n_1 n_2}{4(n_1 + n_2)(n_1 d_1^3 + n_2 d_2^3)} \qquad [A.5]$$

After some rearrangements it is found that

$$A(t=0) = 1 - \frac{3}{4} \frac{(d_1 - d_2)^2 (d_1 + d_2) n_1 n_2}{(n_1 + n_2)(n_1 d_1^3 + n_2 d_2^3)} \qquad [A.6]$$

For the special case of two widely differing volume fractions $(\phi_1 << \phi_2)$ and widely differing number densities in the inverse order $(n_1 >> n_2)$ we have using Eq. [8]

$$1 << \frac{n_1}{n_2} << \left(\frac{d_2}{d_1}\right)^3 \qquad [A.7]$$

and the value of the coefficient A(t) becomes

$$A(t=0) = 0.25 \qquad [A.8]$$

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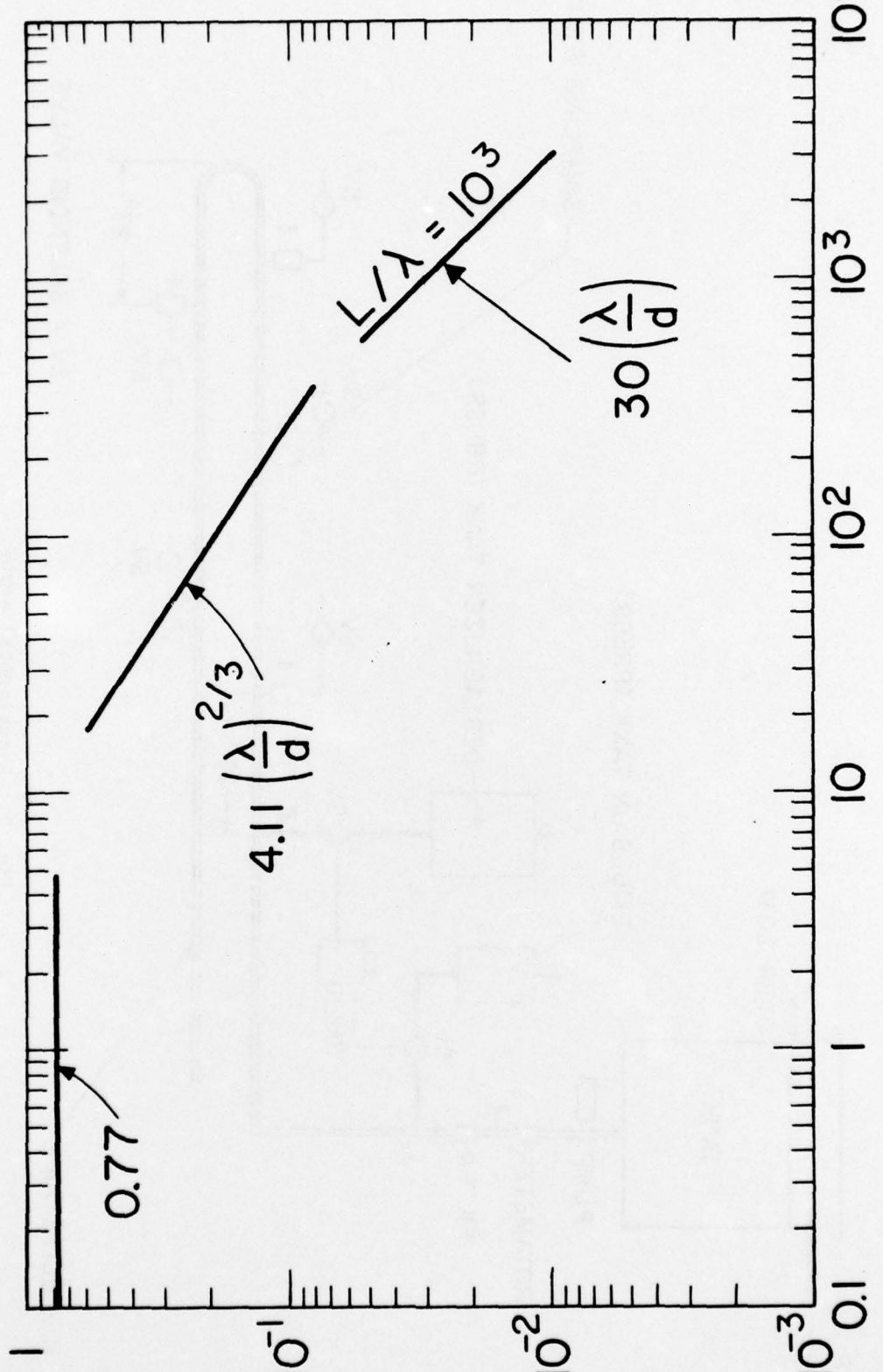

Fig. 1. Theoretical reduced coagulation rate between particles in isotropic turbulent flows as a function of the ratio of the particle size (d) to the Kolmogorov microscale (λ).

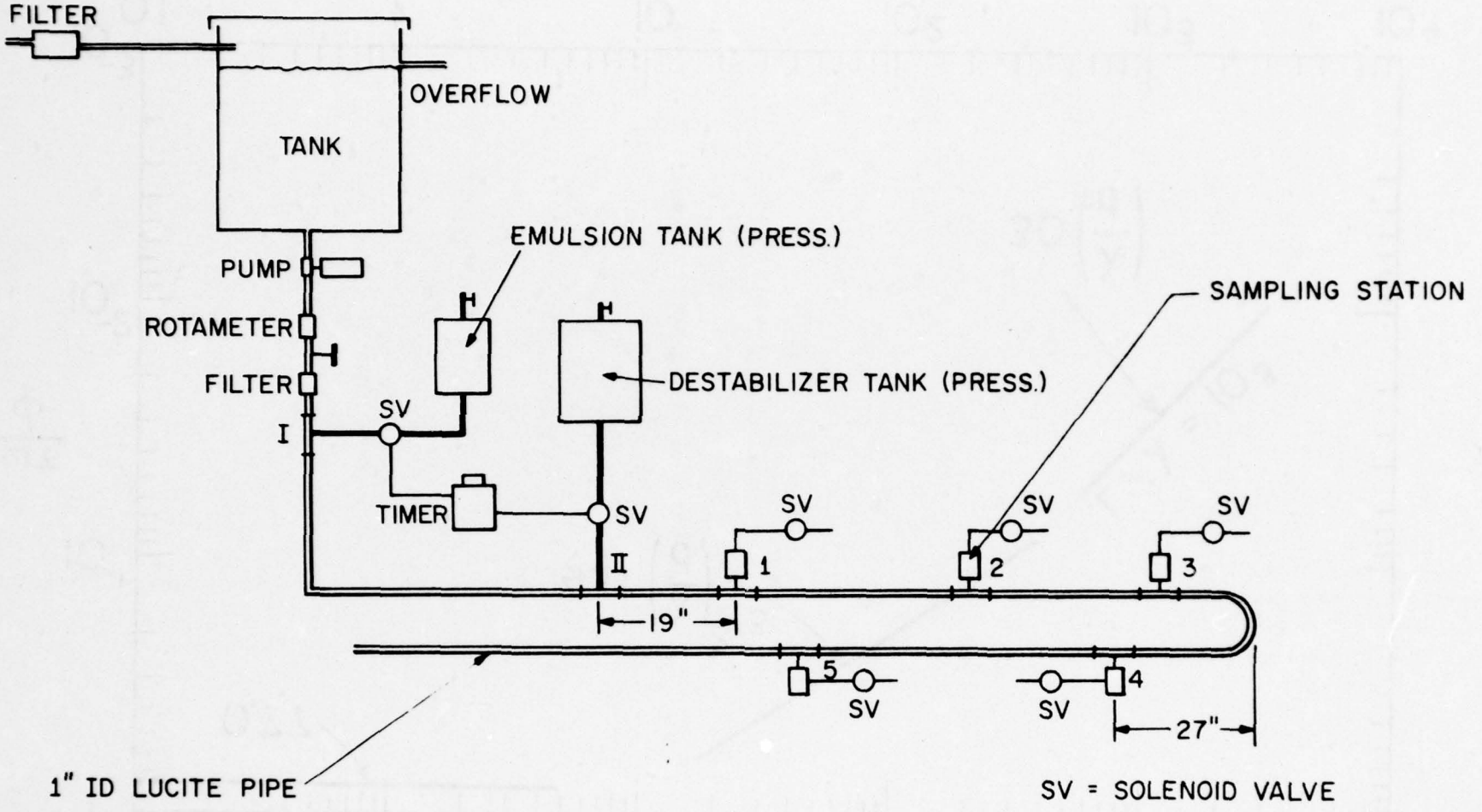

Fig. 2. Experimental setup.

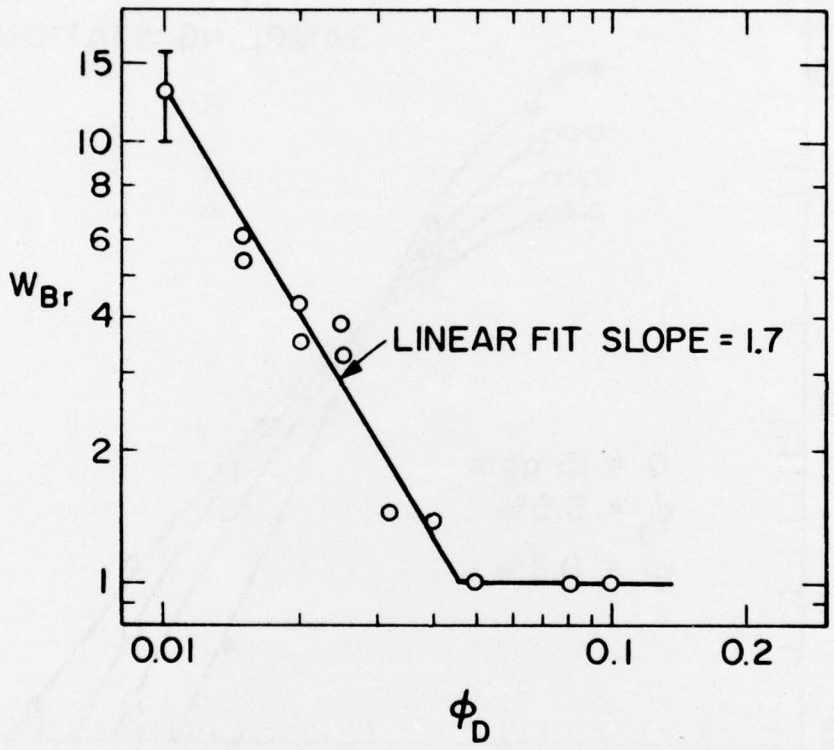

Fig. 3. Stability factor as a function of destabilizer concentration for Brownian coagulation.

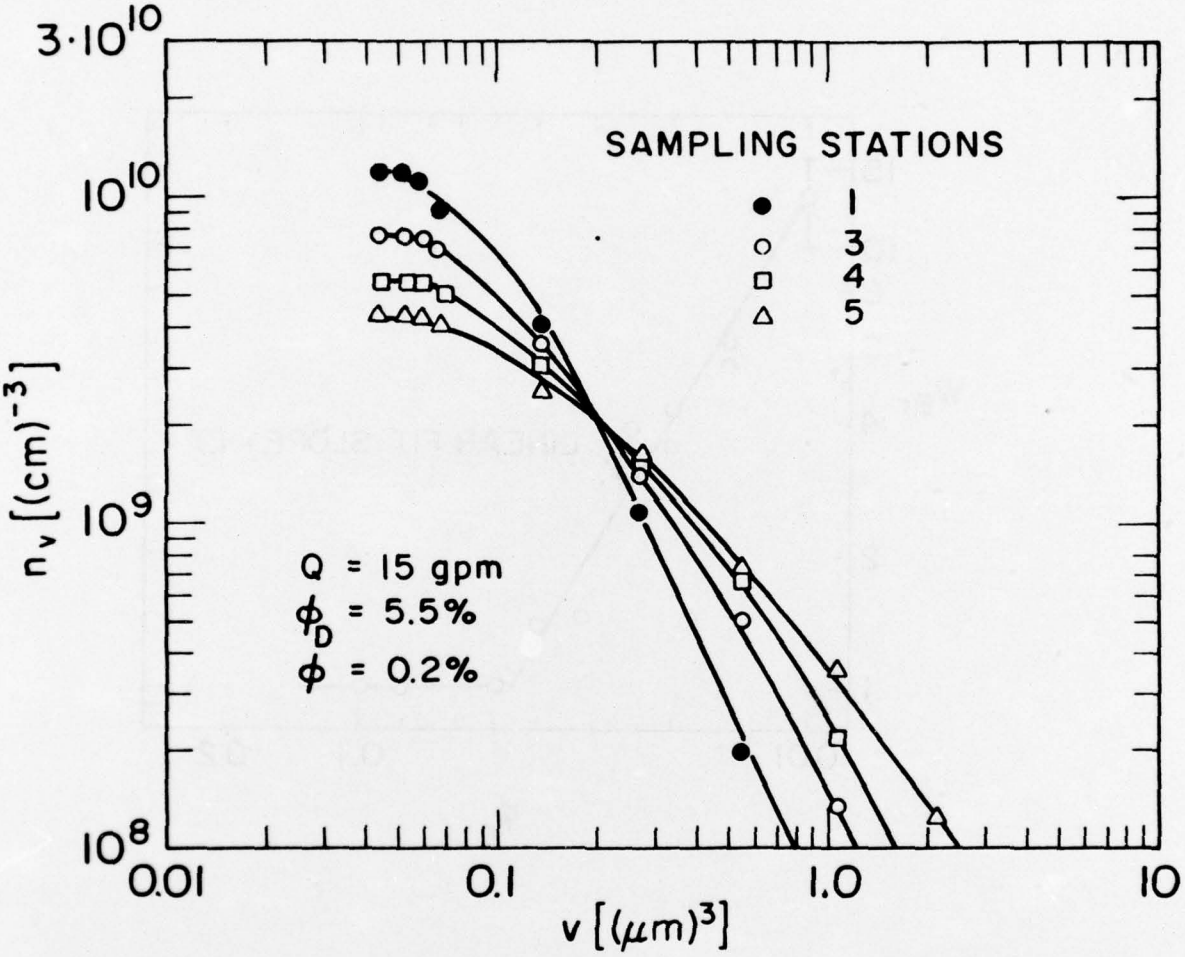

Fig. 4. Cumulative particle size distribution at different sampling stations along pipe.

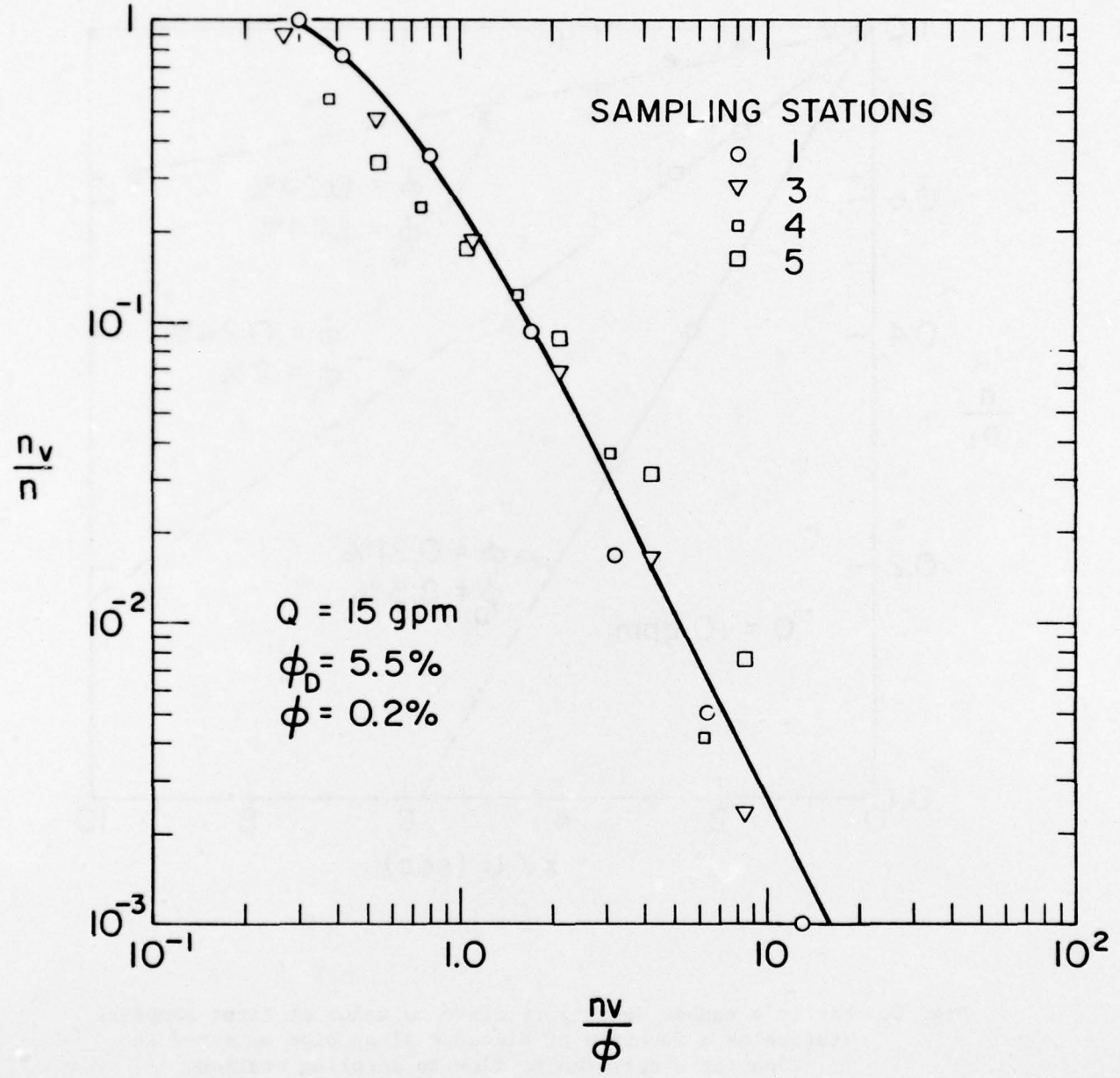

Fig. 5. Cumulative particle size distribution at different sampling stations along pipe plotted in reduced similarity variables.

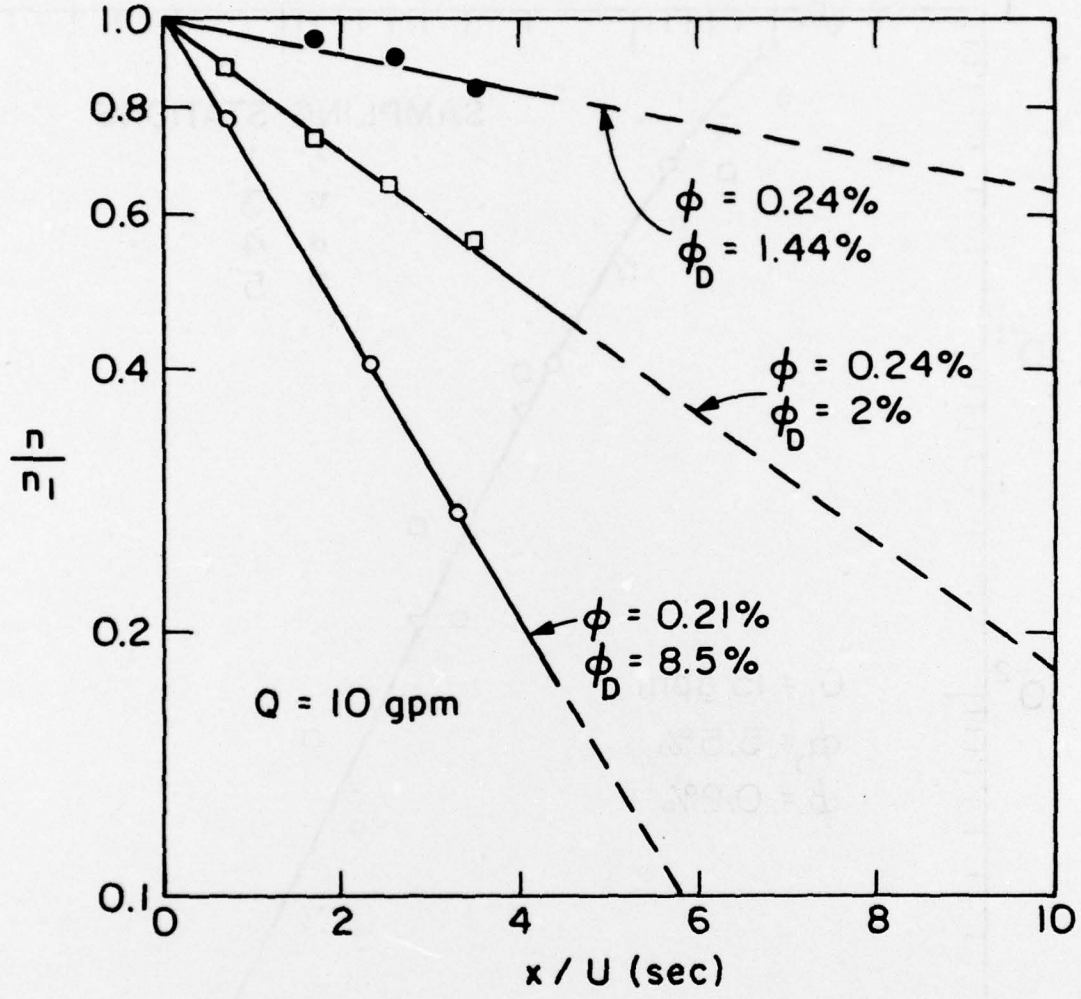

Fig. 6. Particle number density relative to value at first sampling station as a function of distance along pipe measured in time for dispersion to flow to sampling station.

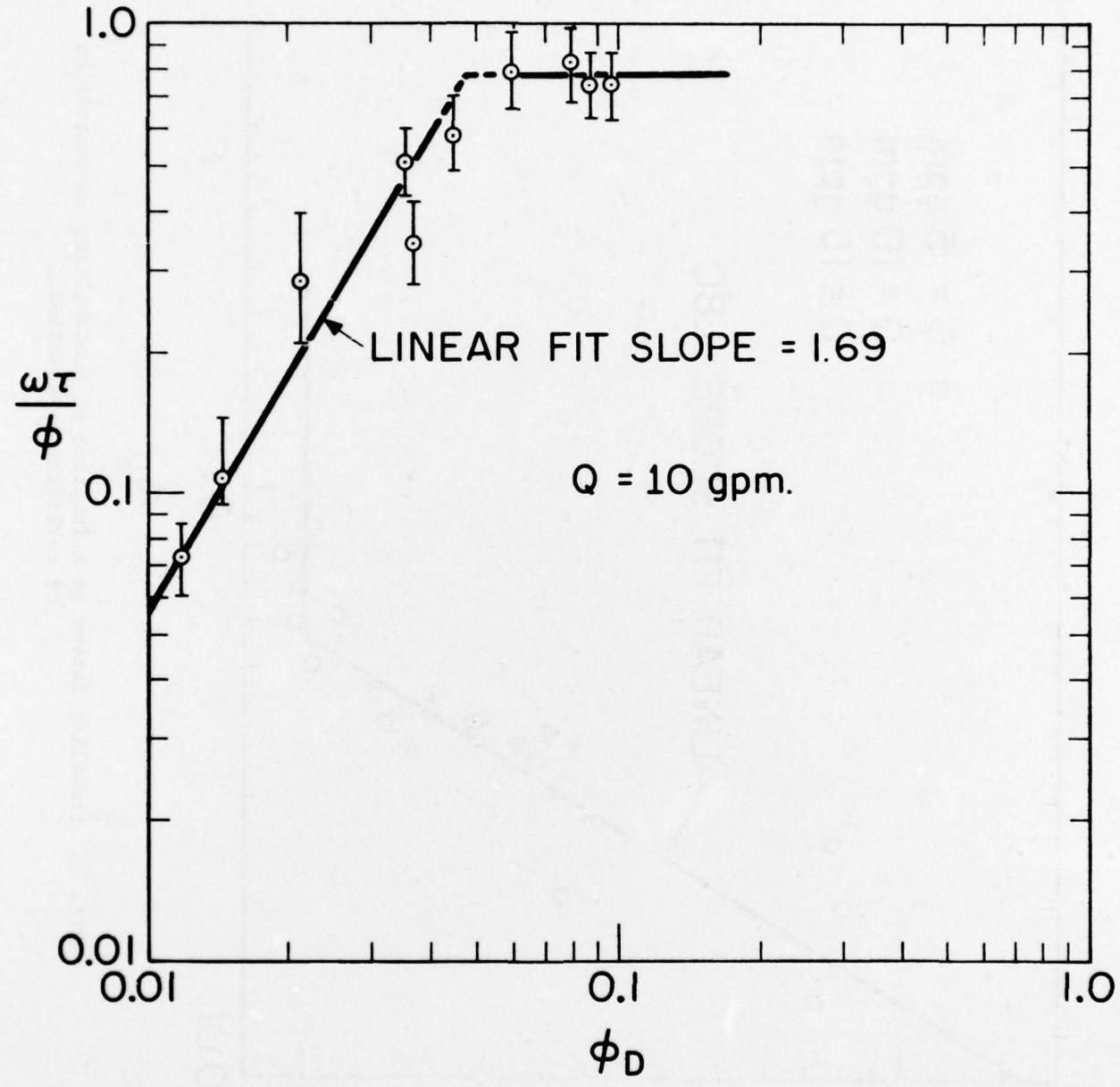

Fig. 7. Reduced coagulation rate as a function of destabilizer concentration.

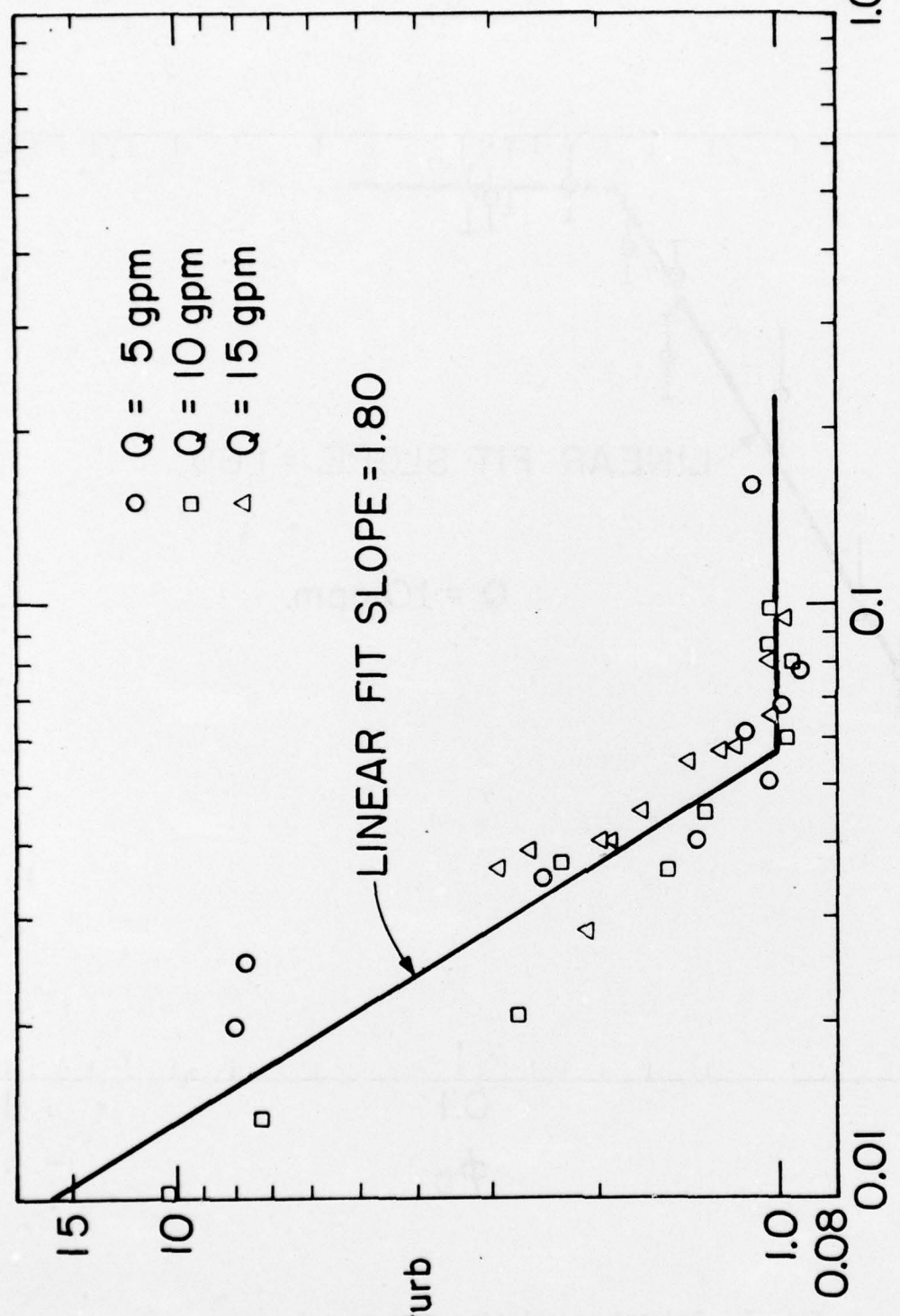

Fig. 8. Stability factor as a function of destabilizer concentration for turbulent coagulation.