

COMPUTER SIMULATION OF FLOC FORMATION IN A COLLOIDAL SUSPENSION

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ABSTRACT

Aggregates which form by successive random addition of individual spherical particles without internal rearrangement as the floc grows are shown to have a roughly isometric "core" in which the density diminishes slowly from 54 volume per cent at the center to $54 m^{-0.29}$ volume per cent at the edge of the core, where m is the number of primary particles encompassed. The particles not included in the core form projecting "tentacles" which give the total aggregate a rough surface and a mean extent about five particle diameters larger than the core diameter. The fraction of total particles within the core increases with increasing floc size and is nearly unity for visible flocs. The model is capable of accounting for the hitherto anomalously large sediment volume of silica sols in organic solvents.

Previous work (1-3) has calculated sediment volume using a Monte Carlo procedure on the assumption of particle by particle addition to an unchanging sediment. This model fails when applied to real systems with fine particles capable of flocculation. In these cases the kinetic unit during the settling is the floc. The present paper attempts to calculate the volume density of particles in an average floc and applies previous results to calculate the volume density in a sediment composed of flocs. Volume per cent solids in either floc or sediment is preferred as a unit to the more traditional c.c./gram of sediment volume because it is independent of the density of the primary particles, which may not be known, even though some assumption about it will have to be made when the calculations are compared with experiment. Others (4-6) have found the kinetic units in some suspensions to be flocs rather than primary particles.

EXPERIMENTAL PART

Materials

Dispersions were made from "Cab-O-Sil M5" kindly supplied by Godfrey L. Cabot, Inc. Its surface area was determined by nitrogen adsorption at -195°C . using the BET method (thanks are due to Dr. Hakam Singh of this laboratory for the determination) as 136 sq. meters/gram. Combined with the reported specific gravity of 2.1 this figure yields a particle diameter

(equivalent sphere) of 21 millimicrons, this is in good agreement with the manufacturer's report of 15–20 from electron microscopy and suggests that the primary particles are indeed isometric and nonporous. Zettlemoyer, Hollabaugh, and Chessick (7) characterized the surface of a similar material, by measurement of the heat of immersion, as intermediate in polarity between a strongly polar surface such as that of calcium fluoride and a low-energy surface such as that of Teflon. The polarity is probably due to chemisorbed water which is retained when the material is dried to constant weight at 105° in laboratory air (average humidity 30%). Our sample may, of course, be more or less hydroxylated than that of Zettlemoyer and co-workers.

Initially the various dispersion media were used directly from fresh, still sealed bottles of reagent quality materials. Later they were distilled from appropriate dehydrating agents (8), but these precautions were ineffective in overcoming the irreproducibility observed in the sediment volumes. In view of the report of Wightman and Chessick (9) that minute traces of water changed the sediment volume of a fully hydroxylated silica in decane by 60%, it was thought that this factor might be controlling. Direct comparisons are not possible since the latter authors report only relative values (cubic centimeters observed for an unspecified amount of dispersion), and also the initial concentration of their manually dispersed material was larger than that observed in the final stable gelled sediment, unchanged for weeks, in most of our experiments. In one set of experiments manual dispersion was made in benzene saturated with water. The sediment volume decreased by 15%–20%. Hence any major influence of water as a contaminant has already occurred in the traces still present in our "dried" suspensions.

The observed sediment volume depended also upon the initial concentration of the suspension in some cases. However, it was found that by far the most significant factor affecting the reproducibility was the type and extent of agitation used in preparing the dispersions; in general, means which might be expected to yield more complete dispersion led to larger sediment volumes. Once a dispersion had been prepared (in a 50 ml. graduated cylinder with a ground-glass stopper further protected from ingress of moisture by a plastic film) redispersion with only the agitation consequent on a few inversions of the cylinder resulted in exact (1%) reproducibility of the volume of sediment in the given cylinder. As the vigor of the agitation is increased, the viscosity of the resulting dispersion increases for a given concentration and also the dependence of the sediment volume on initial concentration tends to disappear. Eventually a point was reached where further increase in time or vigor of agitation did not further increase the sediment volume. This situation may correspond to dispersion into primary particles.

The dispersions are unstable and agglomerate as soon as the agitation ceases into huge flocs which form a weak gel and settle quite rapidly with always a sharp boundary between gel and supernatant liquid. The difference between the volume occupied by the settled gel after 24 hours and after several weeks is negligible. Generally 1 to 5 minutes elapses before settling begins and the sharp boundary becomes clearly visible. Settling rates were measured and appeared to follow the equation proposed by LaMer and Smellie (6), with $t = 0$ chosen after any induction period, although in several cases the fit to this equation was not very good at long times. Analysis of the settled column (withdrawal by pipette and evaporation of liquid) indicated that the concentration was very nearly uniform throughout although the analysis was not very reproducible (5% of the value).

Experimental Results

Figure 1 shows the results obtained by manual dispersion of "dry" Cab-O-Sil in "dry" and water-saturated benzene keeping the conditions of agitation as nearly constant as possible (90 shakes in 1 minute through a 90° 18-inch arc in a glass stoppered 50 ml. graduated cylinder). The cylinders were nearly identical and were about $\frac{3}{4}$ filled with liquid. The 50 ml. mark generally corresponded to a height of 15 cm. They are plotted as

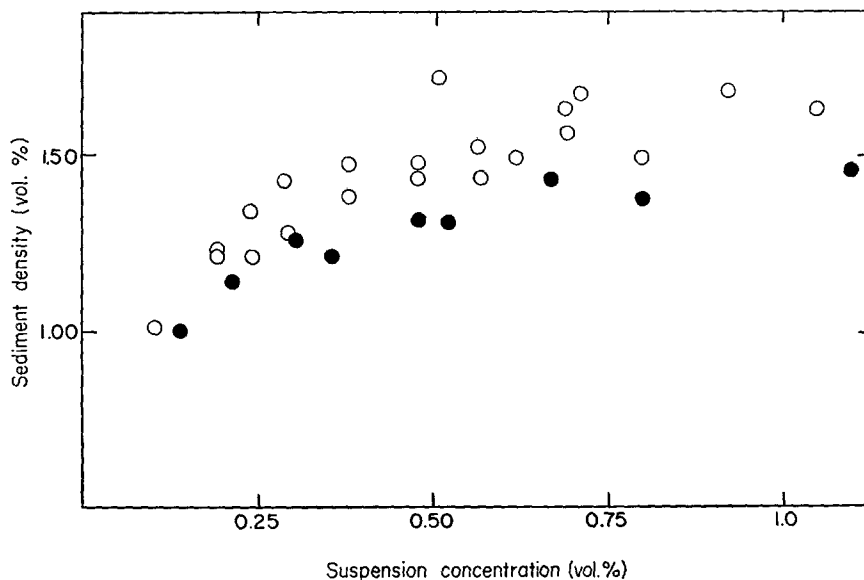


FIG. 1. Sediment density for manually dispersed Cab-O-Sil M5 in benzene as a function of suspension concentration. ○, Well-dried solvent; ●, Solvent saturated with water.

sediment density in volume per cent (assuming a specific gravity of 2.1 for the silica) for more ready comparison with the calculational model. A sediment density of 1% corresponds to a sediment volume of 47.6 ml./g. silica. Sediment densities in the "dry" systems averaged about 10% higher than those in benzene initially saturated with water. The range is about 1.0 to 1.7 in volume per cent sediment density with a distinct trend to higher values with more concentrated initial suspensions.

A representative group of data obtained under varying conditions is assembled in Table I. With only hand shaking as a means of final dispersion the settled sediments contained between one and two volume per cent solids, and it proved difficult to determine whether or not there was any significant difference dependent on the liquid used. When mechanical means were employed the sediment density decreased as the vigor of the agitation increased. It proved necessary to use very dilute suspensions to find the limiting value beyond which the sediment density was independent of further agitation; otherwise continued agitation produced nonsettling gels. Again the value seemed not to depend critically on the liquid used, benzene, carbon tetrachloride, and iso-octane all giving essentially the same results as shown in the table for chlorobenzene. The limiting sediment density appears to be about 0.3 volume per cent solids (sediment volume 160 ml./g. Cab-O-Sil M5).

COMPUTER SIMULATION OF FLOC FORMATION

Model flocs have been generated by the successive addition of primary particles, taken as spheres of unit radius, to the growing aggregate in a completely random manner. The first sphere (primary particle) was located at the origin. Pseudo-random numbers¹ between 0 and 2π and 0 and π served as the spherical coordinates θ and ϕ for the initial position of the center of the next primary particle whose radius vector (R) was taken 2 units larger than the maximum distance between the origin and the center of any particle already in the floc. Next three additional pseudo-random numbers were generated to serve as the Cartesian coordinates of a point lying anywhere within the sphere of radius R surrounding the growing floc. The primary particle being added to the floc was then moved along the straight line joining its initial position and this arbitrary point until it had either contacted a previous particle in the floc or passed entirely through the sphere. If it contacted the aggregate it was assumed to become rigidly anchored in the contact position.

The output from each calculation comprised the coordinates of the center

¹ A procedure for generating pseudo-random numbers according to the method of Rotenberg (10) was developed for our Honeywell 800 computer by Mr. L. Engelman. The resulting numbers (lying between 0 and 1) were converted to the desired spread in magnitude by appropriate multiplication.

TABLE I
Sediment Densities of Dispersions of Silica in Various Liquids^a

A. Manual dispersions (0.475 vol. %) in dried liquids

Liquid	Sed. dens. (%)	Liquid	Sed. dens. %
Acetonitrile	1.75	Cyclohexane	1.78
Carbon tetrachloride	1.52	Benzene	1.45
Chlorobenzene	1.38	<i>n</i> -Heptane	1.30
Chloroform	1.19	Iso-octane	1.56
Bromobenzene	1.25	Ethylene dichloride	1.35

B. Manual dispersions in benzene of a grease (7 g./100 ml. benzene) prepared in a Waring Blendor operated at 10,000 r.p.m. for 10 minutes

Initial conc. (%)	Sed. dens. (%)	Initial conc. (%)	Sed. dens. (%)
0.30	1.26	0.475	1.31
0.30	1.25	0.67	1.43
0.475	1.32	0.67	1.40

C. Dispersion by shaking 2 min. in "Red Devil" paint mixer of 55 ml. 0.124% suspension in chlorobenzene with varying numbers of $\frac{1}{4}$ " balls

No. balls	Sed. dens. (%)	No. balls	Sed. dens. (%)	No. balls	Sed. dens. (%)
25	0.63	100	0.42	250	0.32
50	0.45	150	0.39	370	0.31

D. Dispersions prepared directly in chlorobenzene in a Waring Blendor (10,000 r.p.m. for the indicated times)

Initial conc.	Time (min.)	Sed. dens. (%)	Initial conc. (%)	Time (min.)	Sed. dens. (%)
0.124 ^b	2	0.30	0.124	8	0.28
0.124	4	0.29	0.166	10	0.29
0.124	6	0.28			

^a All sediment densities and initial concentrations are given in volume per cent calculated from the measured weight per unit volume assuming a density of 2.1 g./ml. for the silica.

^b This initial concentration seems to be the lowest at which initial gel formation will occur in chlorobenzene. At lower concentrations huge partly gelled clumps formed which settled rapidly with much turbulence and such an irregular top surface that observation of the sediment volume was difficult.

of gravity of the completed floc, its radius of gyration, the distances of individual particles from the center of gravity, their coordinates, their order number in the growth process, and the order number of the particle against which they rested. This output was obtained at four equally spaced intervals during the growth of each floc.

As the floc grows the probability decreases for a newly added particle to penetrate deeply into the interior of the floc before coming in contact with any of its members. Accordingly it is to be expected that the number of primary particles distant by less than a given amount from the center of gravity will approach a limit as the size of the floc increases. It is also to be expected that when the growth process is terminated by exhaustion of the supply of primary particles the external part of the aggregates will be quite sparsely populated. Since real flocs will contain many more primary particles than it is feasible to incorporate in model calculations, it is necessary to determine how large a floc must be generated for its calculated properties to be significant.

To answer this question pragmatically two flocs of sizes varying from 101 to 401 in four equal steps were generated and the significant structural features examined for each size. It was found that if the number of particles within a given distance from the center of gravity were plotted against that distance, the same curve was obtained up to about the first 80 or so particles for all sizes equal to or exceeding 201. Despite this result, examination of the output showed that several (as many as 15 in one case) of the second 200 particles lay among the first 80 in distance from the center of mass of the floc. Accordingly 40 additional flocs of 201 members were generated. Since the variation in properties from floc to floc is not great this number is sufficient to yield significant average values.

Results

Figure 2 is a plot of the number of particles with distances from the center of gravity less than a given value against the value for a 400-particle floc at four stages of its growth. The four curves each have an S-shape, the same for all at the beginning but breaking away into a rapid upturn when the number of particles is about 40%–60% of the total at that stage. Figure 3 is similar plot for a different floc but on a logarithmic scale. From this figure it is seen that the radius of the central core of the floc which is not readily penetrated by newly added particles depends on a fractional power of the number of particles as given by the slope of the linear part of the graph, but only roughly 40%–60% of the particles are contained within the core.

It is assumed that the flocs will approximate spherical symmetry since there is nothing in the detailed mechanism of their construction to yield a preferred direction of growth. That spherical symmetry is maintained is

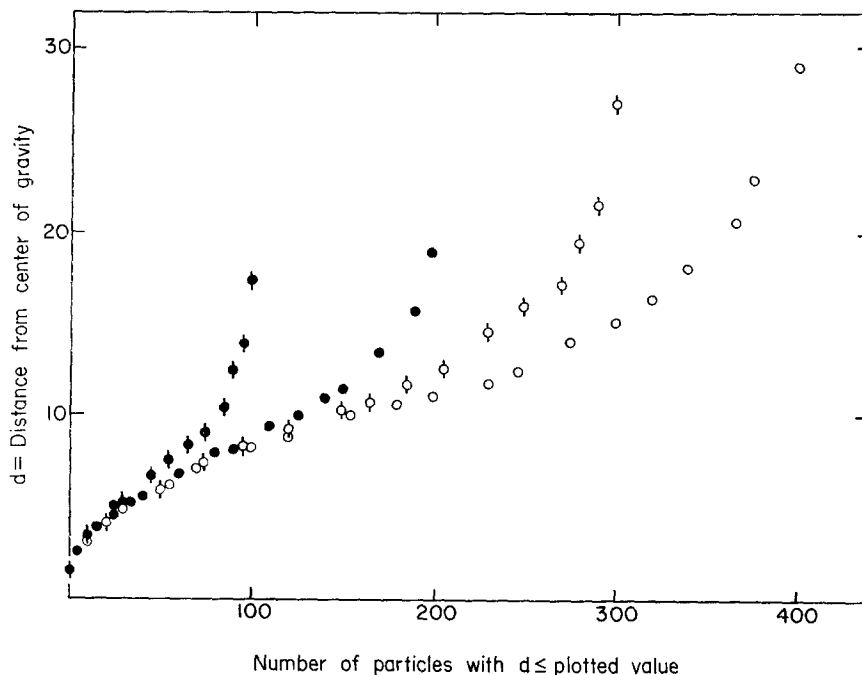


FIG. 2. Linear plot of the growth pattern of a random floc. Primary particles are of unit radius. The same floc is recorded at four intervals: size 100, 200, 300, and 400 primary particles. The significant feature is the superposition of the curves near the center of the floc.

indicated by the fact that center of gravity of the 201 particle flocs is never more than 1 to 1.5 particle radii from the origin. Figure 4 shows the XY projection of a typical floc at size 76 primary particles. It is seen that the structure is indeed describable as consisting of a central core and an outer region and further that the outer region is well described as a group of projecting "tentacles" somewhat resembling the "random coils" of linear polymers except that there is no fixed bond angle and no inherent restriction to a single fixed number of the number of contacts between one sphere and others.

The structural characteristics of the flocs are summarized in Table II. The most significant one is that the mean slope of the lines similar to Fig. 3, drawn for each floc, is greater than 0.33 and shows relatively small fluctuations. Fifty per cent of the flocs show slopes within 6% of the mean value, and even the extreme values differ from it by less than 20%. The value of d for a given n is taken as the radius of the central core of the floc when the core contains n primary particles. It follows that the mean density of the core decreases as its size increases and also that the density decreases

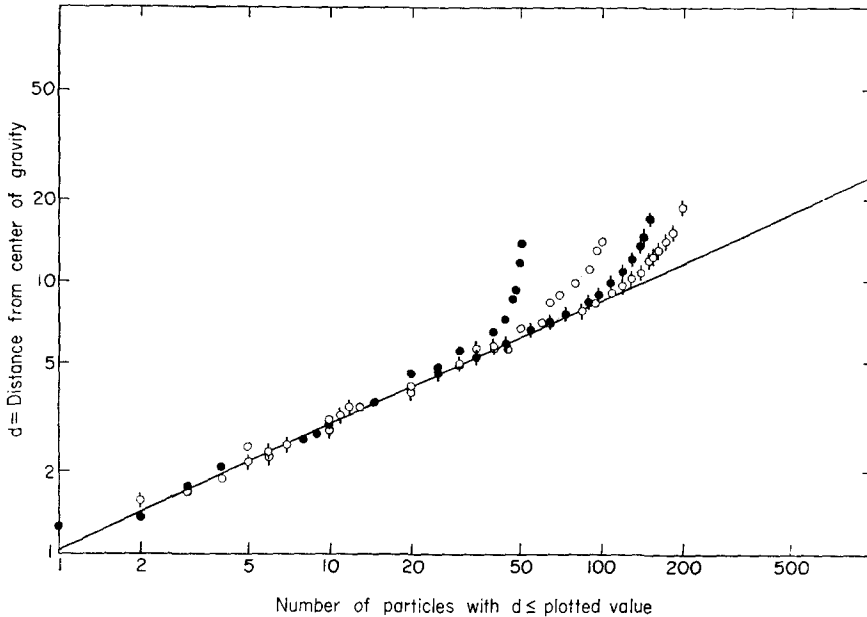


FIG. 3. Logarithmic plot of the growth pattern of a random floc. Primary particles are of unit radius. The same floc is recorded at four intervals: size 51, 101, 151, and 201 primary particles. The significant features are that a common straight line is approached in the central region of the floc, and that the slope of the line is unambiguously larger than $1/3$.

from the center towards the edge of the core. The empirical equations for these two densities (in volume per cent) are:

$$\bar{\rho}_c = 69 n^{-0.29}; \quad [1]$$

$$\rho_s = 54 m^{-0.29}. \quad [2]$$

Here $\bar{\rho}_c$ is the mean density of the core containing n particles and ρ_s is the density in a thin spherical shell of the core just outside the first m particles. Naturally these empirical equations do not apply to small m or n , since the

$$d = 1.13 n^{0.429} \quad [3]$$

mean equation based on graphs such as Fig. 3 fails for $n = 1$, where the correct value of d is zero.

The radius of gyration appears to be increasing with increasing floc size at a somewhat slower rate than is the core diameter. This would not be possible without the contribution of the tentacles. Since each particle contributes to the mean square radius of gyration according to the square of its distance from the center of mass, the contribution of the tentacles is

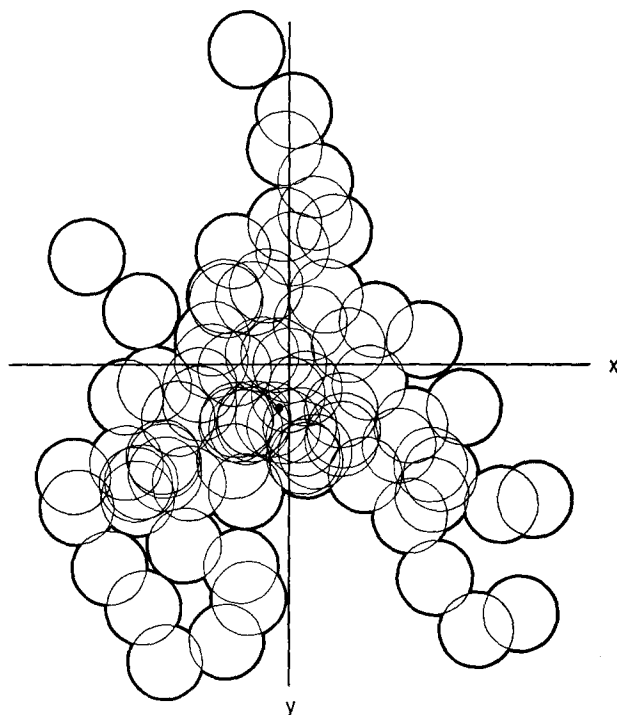


FIG. 4. XY Projection of the structure of a typical random floc (76 primary particles). Each circle represents one primary. The solid point is the center of gravity. The shape justifies considering such flocs as consisting of a central core with projecting tentacles of the order of five particle diameters in extent.

large at first, when the whole floc is small, and then diminishes. If very large flocs were generated one would expect the gyration radius to be proportional exactly to the core radius.

The structure of the floc regarded as a central core plus an outer peripheral region composed of "tentacles" seems validated by both Figs. 3 and 4. It is a reasonable assumption that the number of tentacles would be proportional to the number of primary particles in the core surface. But the subdivision of any given floc into distinct parts is difficult. It can be seen, for example in Fig. 3, that the rapidly rising terminal region of the curve joins with the linear part virtually asymptotically. If one writes pragmatically,

$$N - n = k \frac{\Delta n}{\Delta d_c}, \quad [4]$$

where N is the number of particles in the floc, n the number in the core, and d_c the core diameter, and reads from Fig. 3 and its equivalents for all

TABLE II
Structural Characteristics of Model Flocs

Characteristic	Median	Extreme values		25th and 75th percentile	
Slope ^a of plot $\log d$ vs. $\log m$	0.429	0.365	0.502	0.406	0.452
Core radius for 200 particles in core (primary $r = 1$)	11.0	9.2	13.0	10.2	11.3
Largest d value 201 particle floc ^c	21.5	15.7	28.0	19.9	23.9
Gyration radius 201 particle floc ^b	10.2	8.6	12.2	9.6	10.8
Slope of plot \log gyr. rad. vs. \log no. particles in floc	0.38	0.25	0.58	0.35	0.42
Per cent of part. inside gyr. rad. size					
51	60.7	53	78	59	63
101	60.4	55	70	58	62
151	61.6	56	76	60	65
201	62.7	57	75	61	67
Fraction of ineffective collisions ^c size					
51	0.59	0.42	0.77	0.54	0.75
101	0.61	0.45	0.88	0.57	0.65
151	0.62	0.44	0.81	0.59	0.68
201	0.68	0.55	0.88	0.61	0.73

^a d is the distance from the center of gravity of the floc and m is the number of primary particles within that distance.

^b Largest distance of any particle from the center of gravity of the floc.

^c Fraction of the initially randomly placed primary particles which by-passed or penetrated the floc during its growth.

flocs generated the mean result $n = 80$ for $N = 200$, then k has the value 9.75. If each particle in the core surface acts as a nucleus for further growth this number is the mean extent of the tentacles in multiples of the radius of the primary particle. Equation [4] leads to a ratio of n/N which approaches unity as the size of the floc increases.

The above result means that in applying the model to experimental data Eq. [1] can be used for the overall density of large spherical flocs which, in caducous (11) systems such as the present one, will have a sediment density of 13 volume per cent aggregates (1). It is unfortunate that the result for sediment volume will still contain an undetermined parameter, namely, the number of primary particles per floc.

APPLICATION OF THE RESULTS TO SUSPENSIONS OF CAB-O-SIL M5

The experimental sediment density of suspensions of Cab-O-Sil M5 in chlorobenzene dispersed initially as nearly as possible to primary particles

is 0.3 volume per cent. Individual aggregates are large enough to give the whole a granular appearance and to form a weak gel, presumably by interpenetration and probable contact of tentacles even at a concentration of 0.12 volume per cent. Accordingly the mean density of the individual flocs is of the order of $0.3/0.13 = 2.3$ volume per cent. Here 0.13 is the volume fraction of solids in a sediment of spherical particles; note that according to reference 1 it is independent of both particle size and particle size distribution. If it is assumed that the flocs are large enough for virtually all primary particles to be contained in the core, or alternatively, that in forming a sediment the tentacles are interlaced so that the given density within the floc is described by Eq. [1], the aggregation number comes out 1.2×10^5 .

Use of Eq. [3] together with the known diameter of the primary particles, $21 \text{ m}\mu$, leads to a floc diameter of only 3.6μ . It is apparent that these flocs are not those which give visible grain to the suspensions. They are too small. Not only that but their settling rate of the order of 0.15 cm./min. is several thousand times *faster* than could be expected of particles of this diameter on any basis involving separate settling of individuals.

The results lead to the hypothesis that highly caducous suspensions have a particle structure which is organized on *three* levels. There are *primary particles*, *flocs* composed of primary particles and held together by strong forces (in the case of Cab-O-Sil M5 in chlorobenzene hydrogen bonds involving chemisorbed water is the likeliest source of these forces), and loose *aggregates of flocs* held together by little, if anything, more than mechanical entanglement of the occasional tentacles which will be formed in the course of random floc formation. The aggregates or clusters of flocs are capable of forming weak gels.

This hypothesis of a three-level structure has also been advanced by Michaels and Bolger (5) for aqueous suspensions of kaolin flocculated by electrolytes. These investigators used settling rate as a primary tool for investigating the structure. Gaudin and Furstenau (12) reached a similar conclusion by studying the sediment density, also of aqueous systems, during settling. They considered back flow of liquid as rate-determining during settling and found evidence for two different orders of magnitude of holes. One was interpreted as spaces between primary particles in flocs and one as larger spaces between flocs in the sediment.

The contribution of the present work is that it shows how the second level of structure is capable of accounting for the voluminous settled volume. This part is quantitative, even though there is not yet an independent means of checking the calculated floc size. The qualitative observation of visible graininess and the high settling rate are in accord with the existence of a third level of structure.

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REFERENCES

1. VOLD, M. J., *J. Colloid Sci.* **14**, 168 (1959).
2. VOLD, M. J., *J. Phys. Chem.* **64**, 1616 (1960).
3. VOLD, M. J., *J. Phys. Chem.* **63**, 1608 (1959).
4. REICH, I., AND VOLD, R. D., *J. Phys. Chem.* **63**, 1497 (1959).
5. MICHAELS, A. S., AND BOLGER, J. C., I., *E. C. Fundamentals* **1**, 153 (1962).
6. LAMER, V. K., AND SMELLIE, R. H., *J. Colloid Sci.* **11**, 704, 710, 720 (1956).
7. ZETTLEMOYER, A. C., HOLLABAUGH, C. M., AND CHESSICK, J. J., *J. Phys. Chem.* **63**, 1241 (1959).
8. WEISSBERGER, A., "Techniques of Organic Chemistry," Vol. 7, "Organic Solvents." Interscience, New York, 1955.
9. WIGHTMAN, J. P., AND CHESSICK, J. J., *J. Phys. Chem.* **66**, 1217 (1962).
10. ROTENBERG, A., *J. Assoc. Comp. Mach.* **7**, 75 (1960).
11. MYSELS, K. J., "Introduction to Colloid Chemistry," p. 77. Interscience, New York, 1959.
12. GAUDIN, A. M., AND FURSTENAU, M. C., *Eng. Mining J.* **159**, 110 (1958); *ibid.* Preprint of Paper for Intern. Mining Proc. Congress, London, April, 1960.