N82 32066 D8
27

Flocculation of Colloidal Sols:
Diffusion-Controlled vs. Agitation-Induced Flocculation

John W. Vanderhoff
Center for Surface and Coatings Research
Lehigh University
Bethlehem, Pennsylvania 18015

Colloidal sols comprise dispersions of submicroscopic particles in water. The particles are stabilized by the combination of electrostatic repulsion arising from the charge on the particle surfaces and the London-van der Waals attraction arising from the difference in dielectric constant between the particles and the medium (1). Colloidal particles are also stabilized sterically by adsorption of uncharged polymer molecules, which with their water of hydration give a mechanical barrier to flocculation (2). The same uncharged polymer molecules may also cause flocculation of the colloidal sol by "bridging" i.e., the adsorption of a single polymer chain on more than one colloidal particle (see "Flocculation of Colloidal Suspensions by Polymeric Flocculants"). The resultant stability of a given colloidal sol depends upon the contributions of all these factors --- electrostatic and steric repulsion as well as London-van der Waals attraction and flocculation by adsorbed polymers.

The flocculation of colloidal sols has long been of scientific and industrial interest. The scientific interest arises, not only because of its practical implications, but also because there are theories of flocculation that can be tested experimentally. The industrial interest arises from the use of this process in reclaiming land from the sea, production of synthetic rubber, ABS resins, and latex foam, dewatering of sludges, water purification, waste water treatment, beater addition in paper production, and recycling of wastepaper. There is a gap between the scientific and industrial application of the principles of flocculation: the scientific theories are best tested in the beginning of the flocculation and are difficult to apply to the complete process from beginning to end; the industrial interest is in the completeness of the flocculation, the clarity of the supernatant phase, the form of the flocs, and the ease in their filtration and washing.

Theories have been developed for two types of flocculation: diffusion-controlled flocculation and agitation-induced flocculation. The diffusion-controlled flocculation theory (3) assumes that, for a stable colloidal sol comprised of uniform-size primary particles which is suddenly subjected to conditions that cause flocculation, each primary particle acts as a center to which other particles diffuse and flocculate and that all particle-particle collisions are effective in giving flocculation.

95+96

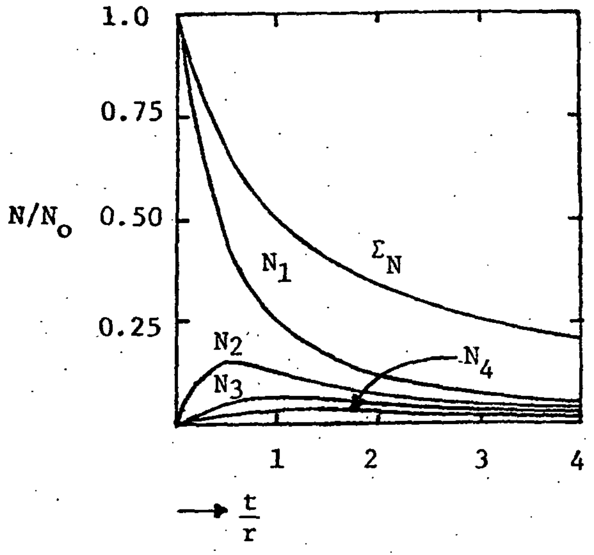
~~66~~

$$-dN/dt = 8\pi DRN^2$$

where N is the number of primary particles, D the diffusion constant, and R the collision radius. Equation 1 shows that the rate of flocculation is proportional to the square of the number of particles. However, this equation is applicable to the early stages of flocculation, since the flocculation produces aggregates of particles which also act as centers for flocculation. For aggregates of various sizes

$$-d\sum_{k-1}^{\infty} N_k/dt = 4D_1R\left\{N_o/(1 + t/T)\right\} \qquad (2)$$

where t is the time of flocculation, and T the time in which the number of particles is halved. Figure 1 shows the variation of the number of particles (expressed as N/N_o with time (expressed as t/T). Typically, for water media at 25°, the value of T is about ca. $2 \times 10^{11}/N_o$.



The total number of particles as well as the number of singlets decreases monotonically throughout the flocculation; however, the number of doublets, triplets, and quartets increases to a maximum as the flocculation proceeds and then decreases as these aggregates flocculate to form larger particles.

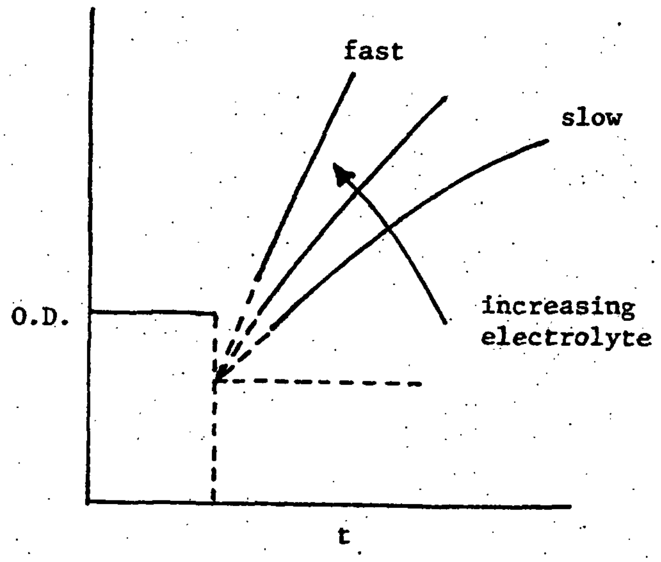
The foregoing treatment assumes that all particle-particle collisions are effective in causing flocculation. For most colloidal sols, there is a potential energy barrier which must be surmounted before flocculation can occur (4). This energy barrier means that only a certain proportion of particle-particle collisions are effective in causing flocculation. Therefore, the types of flocculation can be divided into <u>fast</u> flocculation in which all particle-particle collisions are effective and <u>slow</u> flocculation in which a certain proportion of collisions are effective.

fast flocculation: $T = 1/4\pi D_1 R N_o$ (3)

slow flocculation: $T = 1/4\pi D_1 R_n N_o \alpha$ (4)

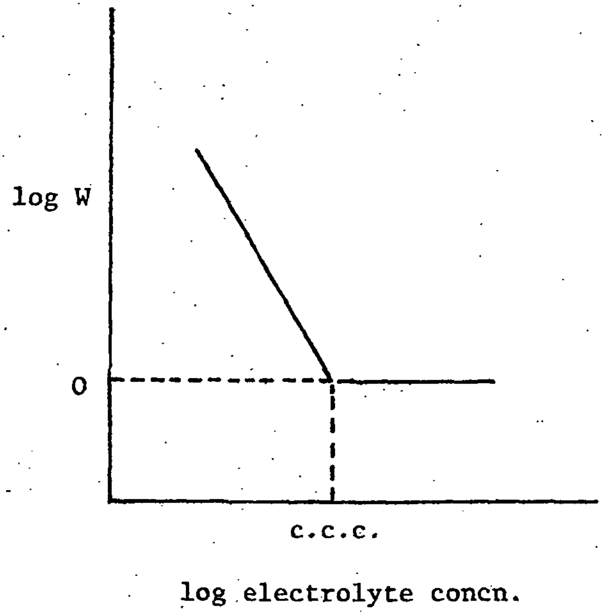
where α is the proportion of collisions that are effective in causing flocculation.

Experimentally, the rates of flocculation are measured in different ways; however, one of the most widely used methods is to measure the optical density of the colloidal sol during the flocculation process. For example, for the flocculation of a colloidal sol by electrolyte, the sol is placed in the spectrophotometer cell and its optical density is read off from a chart recorder; at the desired time, the electrolyte solution is added and mixed with the sol; then, the variation of optical density with time gives a measure of the rate of flocculation, as shown in Figure 2.



The addition of electrolyte dilutes the sol slightly; this reduction in optical density can be calculated from Beer's law. The measured variation can then be extrapolated to zero time and zero degree of flocculation. The rate of flocculation is taken as the initial slope of the optical density-time curve. As can be seen in Figure 2, increasing electrolyte concentration gives an increasing slope of this curve until a limiting slope (fast flocculation) is reached.

The rates of flocculation (initial slopes) are plotted as the log reciprocal slope relative to that for fast flocculation (or stability factor W) (4) versus log electrolyte concentration as shown in Figure 3.



It can be seen that log W decreases linearly to a plateau value of 0, i.e., the fast flocculation region in which further increases in electrolyte concentration give no further increase in flocculation rate. The intersection of the descending straight line with the horizontal line gives the <u>critical coagulation concentration</u> or c.c.c., i.e., the electrolyte concentration that denotes the onset of fast flocculation. The literature contains many examples of measurement of rates of flocculation of colloidal sols of various types.

Agitation-induced flocculation has also been analyzed theoretically (5,6). The probability J of collision of a central particle i with particle j, of which there are N per cc, is

$$J = (4/3)\ N(R_{ij})^3(du/dz) \qquad (5)$$

where R_{ij} is the collision radius and (du/dz) is the velocity gradient. This equation is difficult to test experimentally because the velocity gradient varies from one part of the sample to another. However, the probability of agitation-induced flocculation can be related to that of diffusion-controlled flocculation (6).

$$I = 4\pi D_{ij}R_{ij}N \qquad (6)$$

where I is the probability of diffusion-controlled (Brownian) collisions. The ratio of these two probabilities is given by

$$J/I = \eta(R_{ij})^3(du/dz)2kT \qquad (7)$$

where η is the viscosity of the medium and k the Boltzmann constant.

For a colloidal sol of 0.1μm initial particle size and a velocity of 1 $\sec^{-1}$, the ratio J/I is ca. 10^{-3}, i.e., in the initial flocculation, agitation-induced flocculation is negligible compared with diffusion-controlled flocculation. However, as the flocculation proceeds and the size of the particle aggregates increases, the ration J/I increases. For example, at an average diameter of ca. 1μm, J/I is ca. 1, i.e., the contributions of diffusion-controlled and agitation-induced flocculation are about the same. At an average particle diameter of ca. 10μm, J/I is much greater than unity, i.e., the agitation-induced flocculation is much more important than the diffusion-controlled flocculation.

The foregoing estimated J/I ratios show that, for an agitated industrial flocculation which proceeds from a small primary particle size to a large-size floc, the predominant mechanism of flocculation shifts from diffusion-controlled to agitation-induced as the flocculation proceeds from beginning to end. Furthermore, it shows that the growth of aggregates by agitation-induced flocculation is auto-accelerating.

Thus there are problems in correlating the theories of flocculation with the practical industrial examples. The initial rates of flocculation of a given colloidal sol can be measured spectrophotometrically, but these rates are those of the diffusion-controlled flocculation. Industrial flocculations always proceed past the initial stage of diffusion-controlled flocculation to the final stage of agitation-induced flocculation. Moreover, industrial flocculations almost always involve agitation, e.g., in mixing the electrolyte or other flocculant with the colloidal sol. Thus the industrial flocculation begins in the diffusion-controlled range and ends in the agitation-induced range. Experimentally, it is difficult to separate the diffusion-controlled flocculation from the agitation-induced flocculation. The flocculation may be followed to the end spectrophotometrically, but the large flocs tend to settle and thus are not represented in the overall measurement of optical density. The settling can be obviated by faster agitation rates, but this affects the rate of flocculation and, in extreme cases, can break down aggregates as well as form them. The net result is that there are very few examples in the literature where the rate of industrial flocculations from the beginning to end have been correlated with the theories of flocculation.

Carrying out such flocculation experiments in microgravity would give several advantages that might allow such a correlation between theory and experiment. First, all particles, whether single primary particles or aggregates of primary particles, would not settle or cream at any agitation rate, or even in the absence of agitation. This failure to separate or cream would keep all aggregates "active", i.e, still serving as centers for diffusion-controlled flocculation. Keeping all particles suspended would allow the possibility of determining the total number of particles as a function of time from beginning to end of the flocculation (laser holography may enhance the possibility of such a determination). Finally, experiments in microgravity would allow a definite separation of diffusion-controlled and agitation-induced flocculation by studying diffusion-controlled flocculation with and without agitation.

References

1. E.J.W. Verwey and J.Th.G. Overbeek, "Theory of Stability of Lyophobic Colloids," Elsevier, New York, 1948.

2. W. Heller and T.L. Pugh, J. Chem. Phys. 22, 1778 (1954); R. H. Ottewill, in "Nonionic Surfactants", M. Schick, editor, Marcel Dekker, New York, 1967.

3. M. von Smoluchowski, Physik, Z. 17, 557, 585 (1916); ibid. Z. Physic. Chem. 92, 129 (1917).

4. N. Fuchs, Z. Physik 89, 736 (1934).

5. M. von Smoluchowski, Z. Physik. Chem. 92, 155 (1917); P. Tuorila, Kolloidchem. Beihefte 24, 1 (1927); H. Mueller, Kolloidchem. Beihefte 27, 223 (1928).

6. J. Th. G. Overbeek, in "Colloid Science Vol. 2", H. R. Kruyt, editor, Elseview, New York, 1952, p. 290.