Highly Ordered Microstructure of Flocculated Aggregates

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ABSTRACT

By contrast to recent descriptions of fractal aggregates, we report the structure of non-fractal aggregates of silica spheres made by polymeric flocculation. Using small angle neutron scattering, we measure a highly uniform distance on the order of 1–2 particle diameters between particles in a floc. Thus there is a distinct short range order in the floc structure which is not apparent from macroscopic measurements of the system. Conversely, the structure of aggregates resulting from coagulation by the addition of an inorganic electrolyte ($CaCl_2$) shows no preferred distance between particles. The application of SANS to the study of aggregation by flocculation and coagulation is discussed.

INTRODUCTION

Considerable interest exists in the structure of aggegates, both in industrial and engineering practice, such as beneficiation of mineral fines (Somasundaran, 1980), water purification (Axelos et al., 1985), paper making (Pelton, 1986), as well as in a multitude of other fields ranging from biology (blood clotting and aggregation of fibrin monomers, cf. Wiltzius et al., 1982; flocculation of bacteria, cf. Tarasova et al., 1984) to astronomy (clusters of galaxies, cf. Burns, 1986). The study of solid particle aggregates is problematic: colloids of practical interest generally fall outside the applicability of X-ray studies; often the aggregates are dense masses which are opaque to light, and are unsuitable to be studied macroscopically by sedimentation or viscometry.

Recently, fractal theory has been very successfully used to study aggregation. This type of analysis is used to give a statistical description to certain types of aggregates (diffusion limited aggregation, cluster–cluster aggregation) and thus to distinguish different structures and to elucidate the mechanism of formation (Witten and Cates, 1986). Indeed, the field has been practically dominated by the application of fractals, and one might conclude that aggegation processes which are controlled by kinetic factors rather than

equilibrium conditions, will generally lead to scale invariant structures (Witten and Sander, 1981). By contrast, we report in this paper non-fractal aggregates made by addition of polymer to a suspension of particles.

METHODS

We applied small angle neutron scattering to study the structure of aggregates of silica particles which have been flocculated by cationic polyacrylamide. Scattered intensities for $0.004 < Q < 0.18$ ($Å^{-1}$) were measured on the camera PACE of the Laboratoire Leon Brillouin, SACLAY, France. Here Q is the scattering vector for a scattering angle of 20° with neutron wavelength λ.

$$Q = 2\pi\sin\theta/\lambda$$

Spectra were corrected for sample transmissions, background scattering and detector efficiencies.

The particles used were of silica made by precipitation (a variation of the method of Stober et al., 1968); they were spheres of 400 Å in diameter which, from light scattering and electron micrography, showed little polydispersity. The narrow size distribution was also evident from a spectrum of a dilute suspension of this silica. As seen in Fig. 1, the scattering curve shows the expected primary oscillation for spheres: the peak at log $Q = -1.52$ ($Q = 0.03$ $Å^{-1}$ or $R \approx 205Å^*$) is the result of the particle form factor, $P(Q)$, i.e. interferences arising from scattering centers from within the sphere. It compares favorably
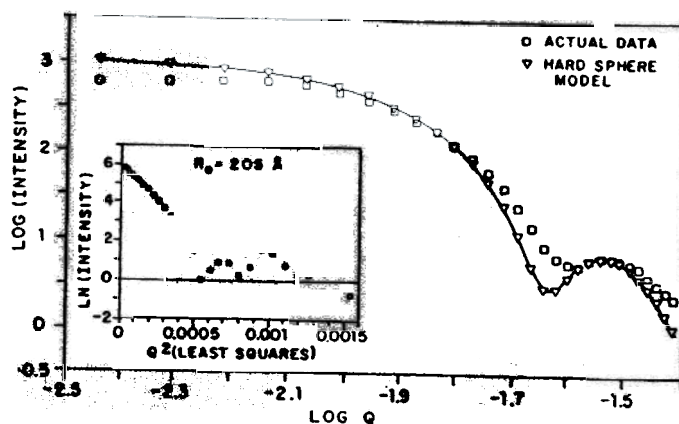

Fig. 1. Isolated silica spheres — oscillation at large Q (log $Q = -1.55$) indicates spheres diameter is ca 400 Å and that the sample is very monodispersed. Hard-sphere model (400 ± 40 Å) shows good agreement with the experimental results. Insert: Guinier plot of isolated spheres; from the slope, the outer radius computed is $R_0 = 205$ Å.

*For ordered structures, the distance, D, in real space is inversely proportional to Q as given by the Bragg relation, $D = 2\pi/Q$.

with a simulation* of scattering for non-interacting (isolated) spheres of 200 ± 20 Å radius. Also from the Guinier plot (insert), the calculated outer radius is 205 Å.

The flocculant we used, kindly provided by the Laboratoire de Physico Chimie (Ecole Superieure de Physico-Chimie Industrielle, Paris) is a co-polymer of acrylamide and trimethylaminoethyl acrylate (5 mol.%), with a molecular weight of ca 1.7×10^6 daltons, henceforth "PAM5%+". Thus the co-polymer is slightly cationic and can adsorb to the negatively charged silica surface.

Preparation of the floc samples made with polymer consists of shaking vigorously (10 s) ca 1 mg PAM5%+ per m^2 silica; the floc which sediments immediately is then transferred to the irradiation cell. Preliminary results suggest that neither polymer concentration (ca 150–1500 ppm) nor handling of the floc alter the structure at the scale of distances accessible with this camera. These samples are prepared immediately before the measurement. The coagulated sample is made by adding $CaCl_2$ (44 mM) to a suspension of spheres; this is left overnight, then measured.

RESULTS

Figure 2 shows a typical log–log scattering spectrum of a floc. Two peaks in intensity are observed. Beginning at large Q, a "subsidiary" peak (log
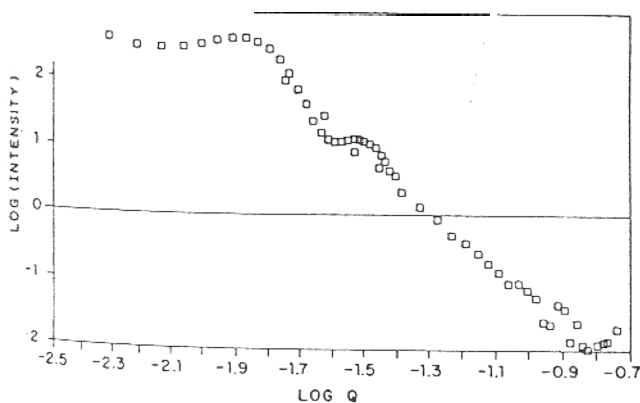

Fig. 2. Floc of silica made with cationic polyacrylamide (5%) ca 1 mg m^{-2}, natural pH (7.4). Oscillation at low Q (log $Q = -1.9$) indicates highly ordered structure in floc with preferred nearest neighbor distance on the order of 1-1.5 diameters.

*The scattering $I_1(Q)$ for a sphere of radius R and volume V, and differences of scattering length density p is given by Rayleigh (1911) as

$$I_1(Q) = p^2 V^2 \left[3 \frac{\sin QR - QR \cos QR}{(QR)^3} \right]^2$$

$Q = -1.52$) emerges from typical Q^{-4} behavior in the Porod region; it corresponds to the same intra-particle peak as seen in the spectrum for free spheres. Indeed this is anticipated since aggregation of this type should not change the particles shape nor size. The peak at low Q (log $Q = -1.92$) results from interferences between objects which are ca 520 Å apart: the distance corresponds to the center to center distance between spheres*.

Continuing from large to small Q, the subsequent decrease in intensity and intensity minimum (ca log $Q = -2.2$) indicates that there are certain positions in space with respect to a reference sphere which are "forbidden" to other spheres, i.e. there are uniformly void region between the spheres. Finally, the increase at small Q suggests that the overall dimension for the scattering objects are very large, beyond the longest distance seen in this experiment.

Negatively charged silica particles can be coagulated using inorganic electrolytes. The spectrum for an aggregate formed by coagulation with $CaCl_2$ is given in Fig. 3. It can be seen that the intra-particle peak is still clearly observable at the high Q end, however the absence of an oscillation in the low Q region indicates that there is no preferred distance between particles. Clearly
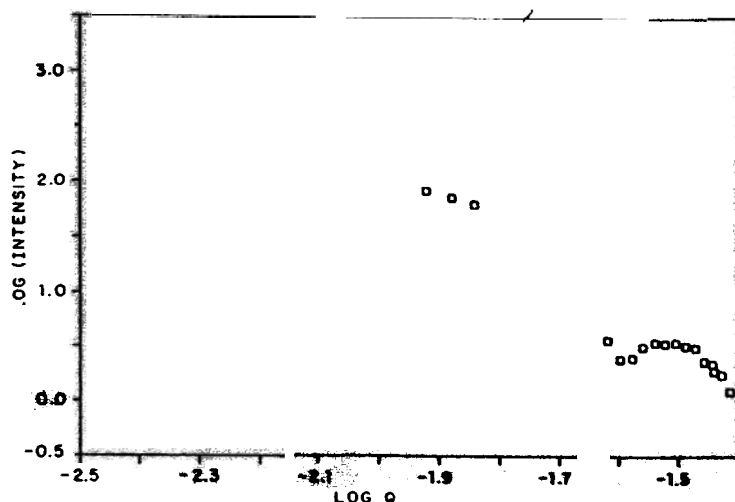

Fig. 3. Silica coagulated with $CaCl_2$ (44 mM). Absence of an oscillation at intermediate Q shows reduction in short range structural order for aggregates made with inorganic electrolyte. Apparent fractal behavior at large scale (low Q).

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*The complete structural description is given by the pair-pair correlation function, $g(r)$, which is the fourier transform of the structure factor $S(Q)$,

$$g(r) = \int\limits_{0}^{\infty} S(Q) \exp(-iQr) \, d^3Q$$

the microstructure of these aggregates is different from those resulting by flocculation with polymer. The log I versus log Q plot is nearly linear at small angles: thus it is tempting to speculate that at a larger scale of distances the system can be described by a fractal exponent. However, such considerations may only be addressed when measurements have been extended to lower Q.

DISCUSSION

Strikingly different spectra result from aggregates made by flocculation with this polymer and by coagulation with salt. Dissimilar structures may, therefore, be attributed to the aggregates, and subsequently different mechanisms may be hypothesized. According to current models, coagulation and flocculation are the two main categories of aggregation. Thus it is of interest to reconcile the data with these models.

Coagulation is mediated by salt (or concentration changes in the potential determining ions); it results from compression of the double layer, subsequent dominance of van der Waals attractive forces and ultimately destabilization of the suspension. Recent spectroscopic work has exclusively studied coagulation. Scale invariant symmetry with fractal exponents (for an euclidean dimension of 2) varying from 1.5 (ghost model of Ball, 1984), 1.75 (Weitz, 1984), 2.08 (Cannell and Aubert, 1986), to 2.12 (Schaeffer et al., 1984) have been found, and in general the work has supported diffusion limited and cluster–cluster aggregation models.

On the other hand, flocculation of particles in suspension by adsorption of organic polymers is widely accepted to be either "physical" (bridging) or electrical (charge neutralization as above in the case of salts). The former model, and variations on it (patchwork bridging: Gregory, 1973; Sato and Ruch, 1980; Mabire et al., 1984), envisions long polymer arms attaching to the surface of particles and gathering them into a volume which is a fraction of the original. Aggregation by flocculation is generally very rapid and largely irreversible by simple dilution.

The spectra in Figs 2 and 3 indicate dissimilar structures in the samples. With two such different mechanisms operational in flocculation and coagulation, this is perhaps expected. However, it is quite surprising that flocs show such regular short order structure as evidenced in the inter-particle peak for the scattering curve. Whether structural order of this type proves to be a feature unique to flocs, the consequences it has on possible subsequent fractal behavior and finally its effect on macroscopic properties of the material, are areas which remain to be understood.

The ability to observe flocculation at the microscopic level enables us to ask several questions about the process, which has, thus far, only been possible indirectly, if at all. Among these are, what is the role of polymer (chain length, type of interaction with particle), of particle (charge, size) and solution prop-

erties on the structure of a floc. Furthermore, the ease with which the current models of aggregation can accomodate these new informations will be a test of their validity and limits.

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REFERENCES

Axelos, M., Tchoubar, D., Bottero, J.Y. and Fiessinger, F., 1985. J. Phys. (Paris), 46: 1587-1593.
Ball, R.C., 1984. Physica B, 127: 87.
Burns, J., 1986. Sci. Am., 255: 30-39.
Cannell, D.S. and Aubert, C., 1986. In H.E. Stanley and N. Ostrowski (Eds), Proc. NATO Adv. Study Ins. on Growth and Form, Vol. 100, pp. 187-197.
Gregory, J., 1973. J. Colloid Interface Sci., 42: 448.
Mabire, F., Audebert, R. and Quivoron, C., 1984. J. Colloid Interface Sci., 97: 120-136.
Pelton, R.H., 1986. J. Colloid Interface Sci., 111: 475-485.
Rayleigh, L., 1911. Proc. R. Soc. London Ser. A, 84: 25.
Schaeffer, D.W., Martin, J.E., Wiltzius, P. and Cannell, D.S., 1984. Phys. Rev. Lett., 52: 2371.
Sato, T. and Ruch, R., 1980. Surface Science Series, Vol. 9, Marcel Dekker, New York.
Somasundaran, P. (Ed.), 1980. Fine Particles Processing, Am. Inst. Min. Metall. Pet. Eng., New York.
Stober, W., Fink, A. and Bohn, E., 1968. J. Colloid Interface Sci., 16: 341.
Tarasova, G.V., Teslenko, A.Ya., Lazarenko, E.N. and Alekseeva, V.V., 1984. Kolloidn. Zh., 47: 737-744.
Weitz, D.A. and Oliveria, M., 1984. Phys. Rev. Lett., 52: 1433.
Wiltzius, P., Dietler, G., Kanzig, W., Haberli, A. and Straub, P.W., 1982. Biopolymers, 21: 2205.
Witten, T.A. and Sander, L.M., 1981. Phys. Rev. Lett., 47: 1400.
Witten, T.A. and Cates, M.E., 1985. Science, 232: 1607.