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Aggregation of Silica Using Cationic Surfactant: A Neutron-Scattering Study

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Neutron scattering is used to look at the structure of aggregates made of silica spheres flocculated with cationic surfactants. With single-chain surfactants, the structures show no local order, but on a certain length scale self-similar behavior is observed and is characterized by an apparent fractal dimension. It is not affected by changes in the surfactant's chain length, but it increases as a function of the surfactant concentration. With a double-chain surfactant, reordering to a liquidlike structure and redispersion are observed. We consider the main features of this system, namely, charge neutralization and the heterogeneity of the adsorbed surfactant layer, and discuss the implications for the formation and structure of these aggregates.

Introduction

Aggregation is a phenomenon of interest to scientists in a multitude of areas ranging from molecular biologists studying subunit association of proteins to mineral engineers selectively separating ore (Villar, 1975; Colombo, 1968). It is also of principal importance in a number of industrial processes, among which are clarification of various liquids ranging from waste waters (Peters, 1986) to champagne, enhanced oil recovery (Somasundaran, 1985), and the synthesis of monodisperse particles (Vanderhoff, 1973). Despite such a multitude of applications, basic experimental information is lacking on the structure of aggregates and how the structure is determined by different chemicals which induce aggregation.

We make use of small-angle neutron scattering (SANS) to record the interference patterns produced by the floc samples. These patterns result from the particular spatial arrangement of silica spheres in the sample; in principle, different arrangements produce different patterns. Neutrons are especially appropriate in these studies primarily due to the large dimensions which can be observed (currently to about 5000 Å—much larger than the spheres used) but also because they easily penetrate dense matter such as aggregates of silica.

Recently, we have found two general classes of structures of silica aggregates (Figure 1); the first class consists of objects which have a liquidlike structure. These show a short-range organization with a full coordination shell at distances on the order of the particle diameter; they are formed when the surface charges are not neutralized by the flocculant, such as in the case of flocculation with polymers of low cationicity. The resultant structure represents an equilibrium between the attractive forces engendered by the bridging polymer and the repulsive ones arising from the residual charges on the spheres. The second class of silica aggregates consists of fractal structures. These, by contrast, show voids at all scales down to the first coordination shell, which is incomplete, and exist at all other distance scales up to textural dimensions. This is the case for aggregates flocculated by highly charged organic and inorganic polymers and multivalent salts: the surface charge of the particles is effectively neutralized by the adsorbing species, the particles stick on contact, and the final structure of the aggregate is determined by the kinetics of growth (Witten, 1981; Jullien, 1987). In particular, the positions of neighboring particles are fixed at contact, and the number of nearest neighbors is much lower than in the case of structures with short-range order.

Thus we have studied the structure of aggregates made by (1) flocculation with organic and inorganic polymers and (2) coagulation by multivalent salts (Wong, 1988). We now report on the structure of silica aggregates induced by cationic surfactants.

Experimental Section

Alkyltrimethylammonium bromide surfactants (SIGMA) with single-chain lengths from 10 to 16 carbons, C_{10}TAB–C_{16}TAB, and a 16-carbon double-chain acetate, $(C_{16})_2$TOAc, were prepared in H_2O at concentrations of 0.02–0.05 mol dm^{-3}. The monodisperse silica spheres (ca. 380- and 200-Å diammeter) were prepared by precipitation of sodium silicate with sulfuric acid; in basic solutions, this silica is highly charged. To make aggregates, surfactant was added to a dilute suspension of silica in a D_2O/H_2O solution, and the mixture was shaken

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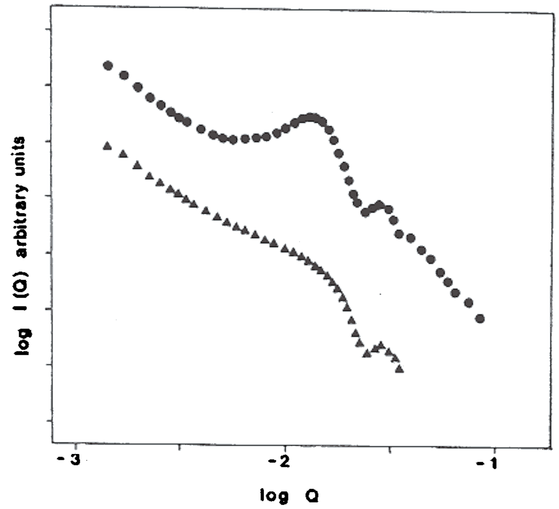

Figure 1. Scattering from two classes of structures found in aggregates of silica 380-Å diameter) flocculated with organic polymers. Circles: polyacrylamide (PAM) 1.7 × 10^6 5% cationic monomer; uniform short-range order produces interferences resulting in a peak at log Q = −1.55. Triangles: PAM 1 × 10^6 30% cationic monomer; heterogeneous structure at distance scales larger than the sphere diameter. Vertically scaled.

Table I. Composition of Samples: Concentration and Maximal Surface Coverage

tail carbons	length, Å^a	cmc, dm^{-3}	concentration, fraction of cmc	no. of monomers per nm^2
10	14.2	6.5 × 10^{-2}	0.031	2.4
12	16.7	1.5 × 10^{-2}	0.13	2.4
14	19.2	3.6 × 10^{-3}	0.56	2.4
16	21.7	9.0 × 10^{-4}	2.3	2.4
			11.3	11.9

^{a} Computed by using (Tanford, 1980) length 1.5 + 1.265 Å (tail carbon).

by hand. A cloudy white precipitate formed immediately upon contact of the two solutions; more formed as surfactant was added. Several hours were in some cases necessary for the precipitate to sediment completely. The final solution contained 30% D_2O to reduce multiple scattering; it was 0.75% (wt/wt) in silica and contained 0.002 mol cm^{-3} surfactant. The pH of the samples was not adjusted, and it remained at pH 9.5. Table I provides further information.

Spectra were taken on the small-angle scattering instruments PACE at the Laboratoire Léon Brillouin (Saclay) and D11 at the Institut Laue Langevin (Grenoble); up to three sample-to-detector distances were used to measure the accessible range of Q values. Standard programs averaged the isotropic scattering data and corrected them for background signal, sample transmission, and detector efficiency (Ghosh, 1981).

Results

Effects of correlations at large distances show up in intensity at small Q whereas those for short distances produce effects at large Q. In Figures 1 and 2, oscillations above log Q = −1.5 provide information on the unit particles (shape, size, discrete interface, and dispersity), while the part of the spectrum below this relates to the correlation of positions between particles and the structure of the aggregates they make. Scattering spectra from aggregates made by the addition of different chain length surfactants and spheres of ca. 380-Å diameter are shown in Figure 2. In Figure 3, spectra from aggregates of smaller silica, 200-Å diameter, are shown for several different $C_{10}TAB$ concentrations. In Figure 4, scattering from aggregates made with the double-chain surfactant $(C_{16})_2TOAc$ is shown. A comparison to the spectra shown in Figure 1 suggests several points:

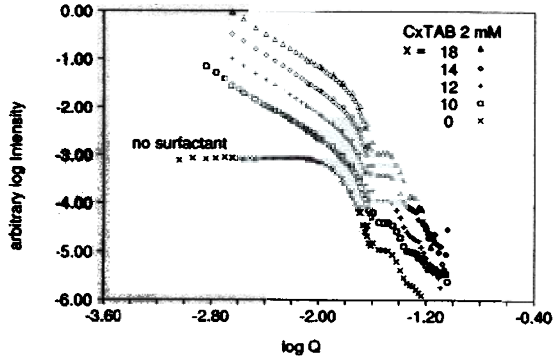

Figure 2. Scattering spectra of silica (diameter 380 Å) aggregates made with trimethylammonium bromide alkanes, 2 × 10^{-3} mol dm^{-3}, with number of tail carbons x as follows: triangles, x = 16; diamonds, x = 14; pluses, x = 12; squares, x = 10; crosses, scattering of silica alone (no surfactant) for comparison. Vertically scaled.

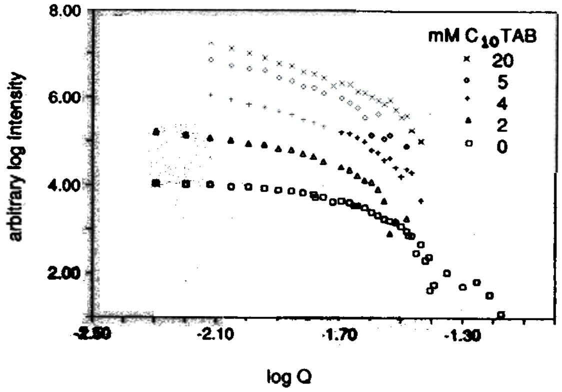

Figure 3. Spectra of aggregates of silica (diameter 200 Å) made with different concentrations of $C_{10}TAB$: crosses, 20 mM; diamonds, 5 mM; pluses, 4 mM; triangles, 2 mM; squares, scattering of silica alone (no surfactant) for comparison. Vertically scaled.

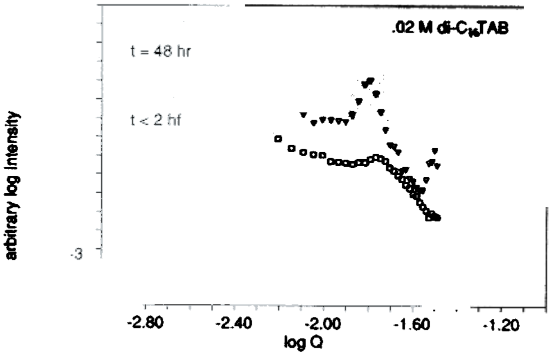

Figure 4. Short-range order in silica aggregates made with dihexadecyldimethylammonium acetate: boxes, restabilized (i.e., supernatant) with 0.02 mol dm^{-3} surfactant; triangles, 48 h later. Vertically scaled.

(1) The scattering curves do not change as a function of surfactant chain length. This indicates that the property which governs structure is not of hydrophobic origin. Instead, it is sufficient to neutralize the charges and diminish the repulsive forces enough for the particles to collide and stick. The structures therefore are not equilibrium structures, but they are determined by rules of collision and sticking; i.e., they are formed according to the laws of aggregation kinetics. Thus they show fractal, self-similar behavior (Jullien, 1987).

Table II. Apparent Fractal Dimension for Aggregates (S200 and C_{16}TAB) Made with Different Concentrations of Surfactant

mmol dm^{-3}	$-\delta \log I/\delta \log Q$
2	1.05
4	1.72
5	1.81
20	2.11
40	2.36

(2) Aggregation induced by single-chain surfactants results in structures with no liquid-like order: a region of self-similarity exists at small and intermediate Q, which merges directly into the oscillations arising from intraparticle scattering.

(3) A closer scrutiny of the crossover between the fractal region and the region of single-particle scattering reveals no hint of a shoulder, which would be expected for particles having average intermediate coordination numbers of 3–4 (cf. Figure 1, where the unordered structure does have a shoulder). Therefore, on the average there are 2–3 nearest neighbors for each particle, such as found with gold colloids (Dimon, 1986).

(4) The apparent fractal dimension D_F of the self-similar region, as computed by the slope of the log $S(Q)$ vs log Q plot, is 1.4 for aggregates of silica (the diameter $2R$ is 380 Å) made with surfactants with chain length 10–16. Here $S(Q)$ is the structure factor where $P(Q)$ is the particle form factor and $I(Q) = S(Q)\,P(Q)$ (Teixeira, 1987). This is quite low and suggests that there is considerable polydispersity of cluster sizes (Martin, 1987). Others have interpreted similar values to mean that a special type of cluster–cluster aggregation occurs (Axelos, 1986).

(5) The qualitative form of the scattering from aggregates is the same over a range of the C_{16}TAB surfactant concentration obtained by using a smaller silica ($2R$ is ca. 100 Å); specifically, no abrupt change is seen in the region of the cmc. However, a significant and systematic increase in the apparent fractal dimension is noted as the surfactant concentration increases (see Table II).

(6) The structure is the same for silica spheres of 200- or 380-Å diameter.

(7) Restabilization together with an evolving liquid-like structure is observed for a double-chain surfactant but not for single chains, even at the highest concentration used (ca. 11 × cmc for C_{16}TAB). The kinetic aspect is probably due to anomalous adsorption behavior of $(C_{16})_2$OAc, is reported by Pashley (1987).

(8) Aggregation is not observed when the nonionic surfactant Triton-X is used as a flocculant, even though it apparently does adsorb (Aston, 1982).

Discussion

The first question to be asked is why is there aggregation when these surfactants are added to the dispersions of silica? Since aggregation is immediate upon addition of surfactants but can take days with equivalent concentrations of simple salts, clearly the hydrophobic nature of surfactants plays an important role. The traditional picture of aggregation induced by surfactants is envisaged as follows: (1) Surfactant monomers adsorb on the particle surfaces by electrostatic interaction. (2) At a specific surfactant concentration, below the critical micelle concentration (cmc), adsorbed monomers undergo chain–chain interaction, and hemimicelles (Somasundaran, 1964) form at the particle surface. (3) Hydrophobic interaction between hemimicelles of different particles reduces the free energy, and this results in aggregation of the particles. These scattering studies add some detail to this picture.

We observe fractal aggregates with structures which are self-similar from the first coordination shell (low number of first neighbors) up to distances on the order of 10 sphere diameters (the structure has voids at all scales). The growth of fractal aggregates depends on three successive mechanisms: a kinetic mechanism for the approach of particles or aggregates, a mechanism for keeping them together after a collision, and a mechanism which allows or prevents reordering at long times within the aggregate. We examine each of these in turn.

Approach. For the silica particles to approach each other and come into contact, their repulsive forces must be nearly cancelled. This is accomplished by the surfactant molecules whose head groups neutralize the charges on the silica surface. (If the particle charge is not neutralized, as in the case of nonionic surfactant, then no aggregation is produced.) In this respect, the first question is whether enough surfactant can adsorb on the surface to neutralize it. At the silica surface, there are ca. 3.5–4.6 silanol (Si–OH) groups/nm^2, of which only 0.5–1.5 are ionized at pH 9. This is to be compared with the packing density of C_{16}TAB surfactant molecules in a dense liquidlike layer, which is 2.2 molecules/nm^2 (Weise, 1974). Thus the cancellation of all charges on the silica surface is easily achieved, but it does not require a dense monolayer of C_{16}TAB, unless the pH is extremely high.

Another question is whether the surfactant molecules will bind strongly enough to the surface to remain on it and cancel its charge. The adsorption free energy of an isolated CTAB molecule would be too low to ensure this; hence the CTAB molecules must be adsorbed in groups whose free energy is lowered by the hydrophobic interaction between neighboring surfactant chains ($\approx 0.6kT/CH_2$ group, hence $\approx 10kT/C_{16}$TAB chain). This is the hemimicelle formation which has been mentioned above. However, such dense surfactant assemblies exceed the *average* charge density borne by the silica surface at pH 9: hence the conclusion that *near the charge cancellation* point the surface carries a number of surfactant-covered patches (hemimicelles) with gaps of surfactant-free surface between them.

Sticking. Once aggregated, the silica particles do not redisperse, even when excess surfactant is added to recharge their surfaces. van der Waals attractions alone would not be enough to prevent redispersion; indeed, many other types of particles, such as clay (Kay, 1972) and alumina (Somasundaran, 1966), in this range of sizes can be redispersed through the adsorption of charged species. Hence there must be a mechanism through which the surfaces stick to each other. Surfactant-covered patches on opposite surfaces will bind through hydrophobic interaction of the surfactant tails which are exposed to water. However, the adsorption of a second surfactant layer, with the heads pointing outwards, should release this mechanism. Alternatively, bare patches, not covered with surfactant, may bind chemically through olation or oxolation of their silanol groups. In the pH conditions of the silica dispersions, this binding is irreversible.

Reordering. With the C_xTAB series of surfactants, we see no evidence of reordering, even at long times. In particular, we do not see the growth of a shoulder or peak at the nearest-neighbor distance, indicating that the aggregated particles cannot reorder to increase their coordination number. However, for silica flocculated with double-chain surfactants we have produced aggregates which do reorder in a few hours to a very nice liquidlike structure. Hence the relative motions of particles within the aggregate depend on some properties of the surfactant layer.

In this respect, the main feature of the surfactant layer is its heterogeneity. Near the charge neutralization point, there are not enough C_xTAB molecules to cover fully the silica surfaces; instead, the monomers adsorb as hemimicelles and cover the surface in patches. This prevents the particles from rolling along each other, because of hydrophobic attractions between hemimicelles which have come into contact and also because of chemical bonds between silanol groups located in patches which are free of surfactant. Conversely, the reordering observed for silica particles aggregated with double-chain surfactants suggests that such surfactants can form full layers before the particles aggregate. This is indeed likely, since this surfactant packs at ca. 1.7 molecule/nm^2 (Pashley, 1986), which is comparable to the surface charge density of silica. We conclude that reordering requires the formation of full surfactant layers prior to aggregation. For this reason, it will depend critically on the surface charge densities of the particles, because they determine the overall coverage near the charge neutralization point; it will also depend on the collision rate of these particles, which determines whether this coverage can be reached before the particles aggregate.

Problems and Future Work

The structures which we observe are broadly characteristic of kinetic aggregation mechanisms. We have presented above a model for such a mechanism, where the main steps are (i) approach, (ii) sticking, and (iii) reordering. This model is consistent with the data on silica particles flocculated with C_xTAB or $(C_{16})_2OAc$ surfactants. Still, it must be tested more thoroughly and refined to yield more quantitative predictions; then its implications for the physical chemistry of oxide surfaces can be considered.

Flocculation Mechanisms. There is no doubt that kinetic aggregation mechanisms, such as those generated by computer simulation (Jullien, 1987; Witten, 1981; Meakin, 1986), will produce structures whose interference patterns are quite close to the ones which we observe. Since such structures show scale invariance, the focus is usually on the fractal dimension D_F, which describes the way in which the structures fill space. Low D_F values correspond to objects which are so tenuous as to be almost one dimensional (the limit $D_F = 1$ is obtained with rods), while high D_F values are associated with ramified, fuzzy structures (at $D_F = 2$ the objects become opaque; at $D_F = 3$ they are compact).

Here the problem is that the measured slopes for the flocs made with surfactant are too shallow to be reproduced by simulations, especially so at low surfactant concentration (cluster–cluster aggregation mechanisms predict $D_F = 1.78$ for the Brownian model to 2.04 for the chemical model, depending on the sticking probability). This implies that the pair correlation function decreases too fast at large distances; i.e., not enough particles are found at large distances from a reference particle. There can be two causes to this: either there are many aggregates which are too small or the aggregates are more tenuous than expected.

The presence of many small aggregates is indeed a common cause of the discrepancy between measured slopes and predicted fractal dimension. This problem has been solved for the case where the distribution of aggregate sizes is also self-similar (Martin, 1987), i.e., $P(M) \propto M^{-\tau}$. Then if $\tau < 2$ the observed law is modified to

$$I(Q) \propto Q^{-D_F(3-\tau)}$$

Hence a slope of −1.4 could be consistent with a fractal dimension of 1.8 if the polydispersity exponent is 2.2. Why should there be so many small aggregates at low surfactant concentrations? Presumably because the surfaces are only sparsely covered, which leaves many aggregates unable to bind to each other if most of the exposed surfaces are either charged or unreactive.

Alternatively, sparse coverage of the surfaces could force the particles to build tenuous aggregates such as necklaces. In fact, both explanations are similar in that they call for a certain fraction of the surfaces to be unreactive toward each other, especially so at low surfactant concentrations. They could be distinguished through further experiments, where the surfactant would be added in two steps, or through measurements of the size distributions of the aggregates.

Reordering Mechanisms. Here as well, the heterogeneity of the surface layers may be the main feature which controls the evolution of the structures. We have examined two types of bonds which may prevent the particles from rolling along each other: hydrophobic attractions between hemimicelles attached to opposing surfaces and the formation of siloxane bridges between. To distinguish between the two, it would be useful to modify either the silica surface or its surfactant layer. Modifications of the silica surface can be obtained through pH variation: these modifications would change the density of SiO^- groups and therefore the extent of coverage with surfactant; they may also affect the reactivity of surfactant-free patches. Further modifications of the surfactant layer can be achieved with a mixture of surfactants, allowing a systematic variation of its charge per unit area. For example, a mixture of a single-chain with a double-chain surfactant, or else a mixture of an ionic surfactant with a nonionic one, could be used to match the spatial variations of the surface charge density of silica. Of course, ESCA should also be used to measure directly the extent of surface coverage with surfactants.

Conclusion

The flocculation of silica particles with cationic surfactants produces a range of aggregates whose structures are controlled by the nature of the silica surfaces. In this study, we have found that the surfaces of precipitated silica are heterogeneous and reactive toward each other. This is hardly a surprising conclusion. Indeed, there have been many previous indications that such surfaces bear a distribution of surface sites and that they may even be covered with a gellike or porous layer. Still, surfactant adsorption and surfactant-induced flocculation are interesting because they reveal and enhance the effects of such heterogeneities. In effect, this is a decoration method which could help in the study of the reactivity of real surfaces in a liquid environment.

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Registry No. $C_{10}TAB$, 2082-84-0; $C_{12}TAB$, 1119-94-4; $C_{14}TAB$, 1119-97-7; $C_{16}TAB$, 57-09-0; $(C_{16})_8TOAc$, 71326-37-9; SiO_2, 7631-86-9.

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