Restructuring of Colloidal Silica Aggregates

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(Received 28 October 1985)

We present experimental results showing that colloidal silica spheres can be induced to aggregate either slowly or very rapidly. The slow process always yields clusters with a fractal dimensionality $d_f = 2.08 \pm 0.05$, but the rapid process can produce clusters with either $d_f = 1.75 \pm 0.05$ or $d_f = 2.08 \pm 0.05$. However, clusters with $d_f = 1.75$ are always observed to restructure so as to yield $d_f = 2.08 \pm 0.05$.

In a recent Letter, Weitz et al.[1] presented results showing that rapid aggregation as originally observed in gold colloids,[2] and slow aggregation closely resembling that previously observed for silica colloids,[3] could both be observed with the gold system. They characterized these two classes of aggregation, both assumed to be irreversible, in terms of the apparent rate-limiting step in the process, as being either diffusion limited or reaction limited. In the former case clusters or individual particles stick with high probability upon contact and yield clusters with a fractal dimension $d_f = 1.75 \pm 0.05$. This rapid diffusion-limited aggregation process was found to exhibit power-law kinetics with $R \propto t^{1/d_f}$, where R is the hydrodynamic radius of the clusters and t is the time. On the other hand, the slow reaction-limited aggregation process, observed when the sticking probability was very low, resulted in clusters with $d_f = 2.05 \pm 0.05$. In this case, exponential kinetics were found, with $R \propto e^{\Gamma t}$, with Γ depending on the experimental conditions. This reaction-limited behavior is apparently identical to that previously observed for the aggregation of colloidal silica particles,[3] which resulted in clusters with a fractal dimension of 2.12 ± 0.05 and which also exhibits exponential kinetics.[4] Furthermore, numerical simulation[5] of the cluster aggregation model[6,7] in the limit of vanishing sticking probability has been found to yield clusters with $d_f = 2.00 \pm 0.08$. It thus appears possible that the *irreversible* aggregation of aqueous colloids in general falls into only two classes, differing fundamentally in both aggregation kinetics and the fractal dimension of the resulting clusters.

It is the purpose of the present work to report the results of a detailed study of the aggregation process for colloidal silica spheres. We find that extremely rapid aggregation can be induced in certain ranges of pH and silica concentration, but when measured a few minutes after aggregation the resulting clusters may have *either* $d_f = 1.75 \pm 0.05$ or $d_f = 2.08 \pm 0.05$. Furthermore, aggregates which are formed rapidly, and have $d_f = 1.75$, invariably restructure within a period of minutes to hours, and their fractal dimensionality changes from 1.75 to 2.08, after which they are com-

pletely stable. Measurements of the time required for the completion of the restructuring process indicate that under the conditions where we observe rapid aggregation with $d_f = 2.08$, restructuring should occur in less than 5 min, which is about the time required for us to measure d_f. The rapid process yielding $d_f = 2.08$ could thus be viewed as rapid aggregation, presumably with $d_f = 1.75$, followed by restructuring to $d_f = 2.08$ before the measurement of d_f can be made. In any event it is clear that the bonds formed during the process of rapid aggregation are not fully irreversible, and, in principle at least, this may also be true of those formed during the slow process as well.

The system studied was Ludox, which consists of amorphous silica spheres ~ 220 Å in diameter, and aggregation was induced by suspending the spheres in $1M$ NaCl solution, with the pH adjusted by the addition of NaOH or HCl. Under conditions described below, aggregates having radii $\gtrsim 1$ μm were formed within less than 30 sec. The fractal dimension of the resulting aggregates was determined from the static structure factor $S(q)$ by means of classical light scattering, over the range of scattering wave vectors 1.2 μm$^{-1} \lesssim q \lesssim 26$ μm^{-1}, by use of instrumentation which has been described previously.[8] Once the aggregates had grown to more than a few microns in size $S(q)$ exhibited simple power-law dependence on q $[S(q) \propto q^{-d_f}]$ enabling d_f to be determined quite easily, as reported previously[3] for the slow aggregation process.

Data for $\log S(q)$ vs $\log q$ for slow aggregation as well as for the two fast processes are presented in Fig. 1. All three data sets were obtained at 0.01 wt.% silica, and the pH was changed so as to vary the type of aggregation and d_f. Curve c, obtained at pH of 6.7, is the result of the slow aggregation process and gave a fractal dimension of 2.11 ± 0.05. Under these conditions, ~ 2 d were required for $S(q)$ to develop power-law behavior over the q range studied, and during this time sedimentation of the clusters reduced the intensity considerably. Curve a, with essentially the same slope, was obtained at pH of 9.6, but required less than 30 sec to produce large aggregates. Curve b,
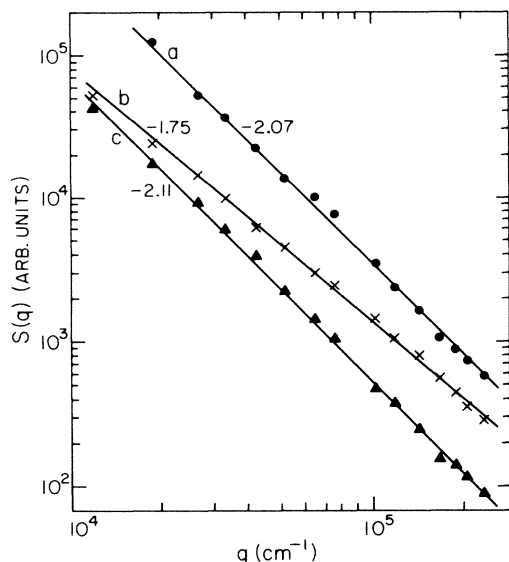

FIG. 1. The logarithm of the static structure factor $S(q)$ vs the logarithm of the scattering wave vector q for aggregates of colloidal silica spheres formed at different pH values of 0.01 wt.% silica in $1M$ NaCl. The triangles (pH = 6.7) show data for a slow process requiring $\sim$ 2 d and yielding a fractal dimension $d_f = 2.11$. The circles (pH = 9.6) yield the same d_f, but the aggregation process occurred in $\leq$ 30 sec. The crosses (pH = 8.6) are also for rapid aggregation but yield $d_f = 1.75$.

which was obtained at an intermediate pH of 8.6, apparently corresponds to a diffusion-limited aggregation process like that observed in gold colloids, since aggregation was very rapid ($\leq$ 30 sec) and the aggregates had $d_f = 1.75 \pm 0.05$. However, the fact that these aggregates can restructure indicates that the bonds are
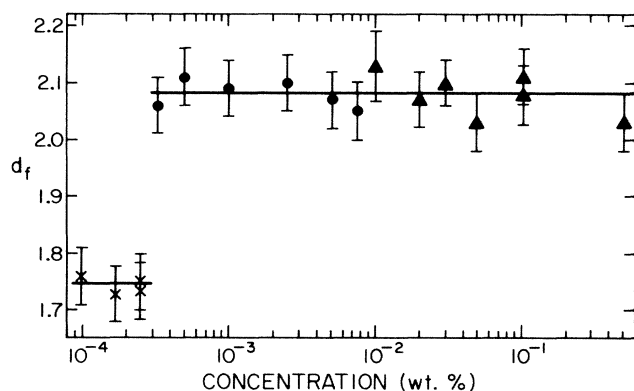

FIG. 2. The fractal dimension of silica clusters as a function of silica concentration at nearly constant pH ($7 \leq p$H ≤ 8). The crosses and circles are for rapid aggregation (≤ 30 sec to reach micron sizes), and the triangles are for slow aggregation (typically days to reach micron sizes). The circles are probably the result of rapid restructuring of aggregates with $d_f \simeq 1.75$ to $d_f \simeq 2.08$ (see text).

not fully irreversible.

Somewhat surprisingly the same three types of aggregation can also be encountered by varying silica concentration with the pH fixed at ~ 7.5. This is shown by the data of Fig. 2, which is a plot of the fractal dimension of the aggregates as a function of silica concentration, $c (7 \leq p$H $\leq 8)$. The triangles are the result of slow, possibly reaction-limited, aggregation, while the circles correspond to very rapid aggregation, but with $d_f = 2.08 \pm 0.05$. The crosses show the results of rapid aggregation with $d_f = 1.75 \pm 0.05$. As mentioned above, the latter type of aggregates restructure so as to yield $d_f = 2.08 \pm 0.05$. The abrupt change in behavior near $c = 0.01$ wt.% is quite striking; at $c = 0.01$ wt.%, aggregation occurred over about 2 d, while at $c = 0.0075$ wt.% less than 30 sec was required to reach a similar degree of aggregation. The change in d_f observed at $c \simeq 3 \times 10^{-4}$ wt.% is also quite sharp, but is only indicative that for $c \gtrsim 3 \times 10^{-4}$ wt.% the time for restructuring has decreased to below the time needed to make the measurement.

In order to delineate the conditions under which each of the three aggregation processes occur, we have studied the concentration range 10^{-4} wt.% $\leq c \leq 0.1$ wt.%, and the pH range from 4 to 12. These results are summarized in Fig. 3, with triangles corresponding
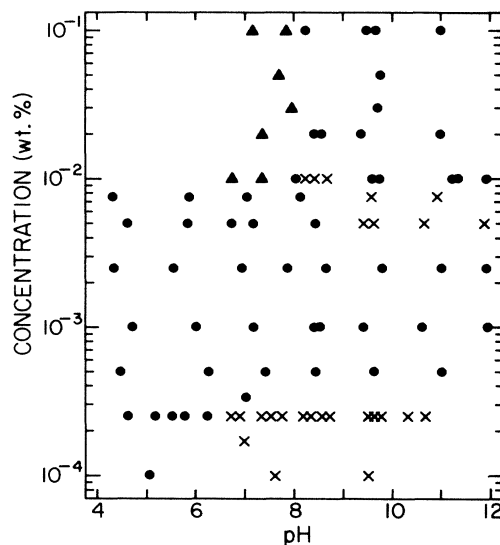

FIG. 3. Dependence of the aggregation rate and fractal dimension of clusters formed from 220-Å colloidal silica spheres on silica concentration and pH. Triangles indicate an aggregation time of several days and $d_f = 2.08 \pm 0.05$, while circles and crosses are the result of aggregation requiring ≤ 30 sec. They correspond to $d_f = 2.08 \pm 0.05$ (circles) or $d_f = 1.75 \pm 0.05$ (crosses) as measured ~ 5 min after the initiation of aggregation. Eventually all aggregates with $d_f \simeq 1.75$ restructure to $d_f \simeq 2.08$, and we believe that the circles are actually the result of such restructuring occurring before we can measure d_f.

to slow aggregation with $d_f \simeq 2.08$, circles to rapid aggregation with $d_f \simeq 2.08$, and crosses to rapid aggregation with $d_f \simeq 1.75$. The picture presented for the rapid aggregation processes should be viewed as a snapshot taken ~ 5 min after preparation of the samples. It is possible, as mentioned above, that an instantaneous measurement would show only triangles and crosses. The data for d_f presented previously in Fig. 2 correspond to points in the range $7 \leq pH \leq 8$, and are typical of the accuracy obtained in the measurement of d_f. The absence of data in the upper left-hand region of the figure is the result of the immense time scales involved. Even after 90 d, samples in this region showed only partial, or very nearly no, aggregation. The general features of the "phase diagram" presented in Fig. 3 seem to reflect the complicated chemistry[9] of silica in aqueous solution. Obviously they would be difficult to explain by simple van der Waals forces and Debye-Hückel screening concepts.

We have made similar studies using ~ 70-Å-diam Ludox spheres and found essentially the same overall behavior.[4] We have also verified that treating the Ludox with clean ion-exchange resin before dispersing it in the NaCl solution does not have any effect. This indicates that if impurities do play a role, they must be of a nonionic variety. We have also verified that the time required for the silica spheres to dissolve appreciably is always much longer than the time for the aggregation process to occur, and thus all the aggregates are composed of spheres.

As mentioned previously, aggregates formed rapidly with $d_f \simeq 1.75$ are not stable and apparently restructure over periods of hours or less, while aggregates with $d_f \simeq 2.08$, whether formed slowly or rapidly, are quite stable and in fact are not affected even by ultrasonic agitation. This restructuring process is shown in more detail in Fig. 4, for a sample with $c = 2.5 \times 10^{-4}$ wt.% at pH 8.3. The initial results for $S(q)$ measured within 10 min of the initiation of aggregation are shown as curve a, while curves b and c show the results for $S(q)$ after 60 and 30 min, respectively. For curves a and b the solid lines are fits of the form $S(q) \propto q^{-d_f}$, while for curve c the dashed line is simply intended to guide the eye. In order to show them clearly the data for curve c have been displaced downward. They actually coincide closely with those of curve b for $q > 10^5$ cm^{-1}. We have repeated these measurements numerous times and have always observed the same general behavior shown in the figure. During an intermediate time period, the data become very noisy, and the measured $S(q)$ first achieves a slope of ~ 2.1 at larger q, while retaining a lower slope at smaller q, and then eventually a slope of ~ 2.1 is observed at all q values accessible by light scattering. The reader should be aware that we do not have de-
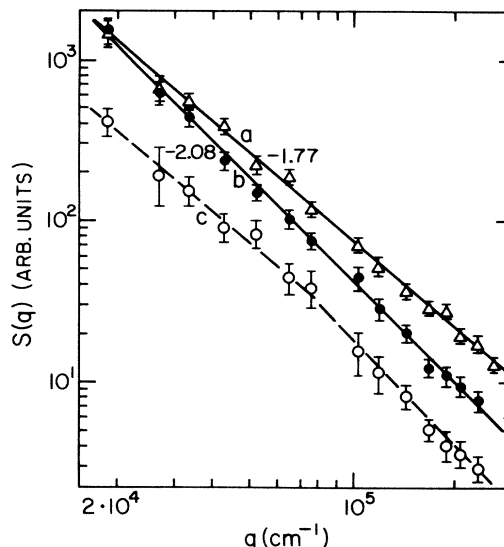

FIG. 4. The evolution of the static structure factor $S(q)$ with time during the restructuring process, for aggregates formed at 2.5×10^{-4} wt.% silica at $pH = 8.3$. Curves a, b, and c were measured ~ 10, 60, and 30 min after aggregation, respectively. Curve c has been displaced downward for clarity; in reality the data very nearly equal those for curve b in the range $q > 10^5$ cm^{-1}.

tailed knowledge of the actual cluster-size distribution, and the measured $S(q)$ is an average over that distribution and weights the largest clusters heavily. Previous work on both silica[3,4,10] and gold[1,11] colloid aggregates indicates that the q dependence of $S(q)$ accurately reflects d_f for individual large clusters; however, if the process we interpret as restructuring is accompanied by a sufficiently radical change in the cluster-size distribution the interpretation would necessarily be more complicated.

Figure 5 shows the dependence of the restructuring time on pH at a fixed silica concentration of 2.5×10^{-4} wt.%. The linear behavior is quite striking, and indicates a power-law dependence on the hydrogen ion concentration, $[H^+]$. The best fit, shown by the solid line, is $t = 0.37[H^+]^{-0.48}$ sec. It is not clear to us, however, why the dependence should be power law, or why the exponent is $\frac{1}{2}$. As can be seen from the figure, the restructuring time has decreased to below 5 min for $pH \leq 6$, which is precisely the region in which we find rapid aggregation with $d_f = 2.08$ at $c = 2.5 \times 10^{-4}$ wt.% (see Fig. 3). We have also verified that the same reduction in restructuring time occurs upon entering the other portions of the "phase diagram" where rapid aggregation with $d_f = 2.08$ is observed. We can thus be reasonably confident that rapid aggregation with $d_f = 2.08$ actually consists of diffusion-limited, but not fully irreversible, aggregation of clusters to yield $d_f = 1.75$, followed or accom-
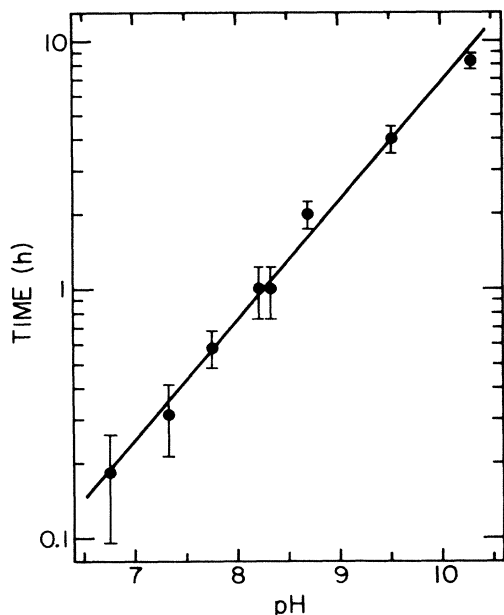
FIG. 5. Dependence of the time for the completion of the restructuring process on pH for aggregates formed at 2.5×10^{-4} wt.% silica. The straight line is a fit which is equivalent to a restructuring time of $0.37[H^+]^{-0.48}$ sec.

panied by rapid restructuring to yield $d_f = 2.08$. Such a process would ultimately yield an equilibrium distribution of objects like lattice animals,[12] provided that the bonds remained reversible. However, another possibility must be considered in the case of silica, namely that, once formed, a bond which persists long enough becomes fully irreversible.[9] If this occurs, depending on the relationship of the various time scales involved, one might "freeze in" structures and cluster-size distributions ranging from those characteristic of irreversible kinetic processes to equilibrium ensembles. In the case of the slow aggregation process, our data cannot distinguish whether the clusters are formed irreversibly with very low sticking probability or represent something much closer to an equilibrium

distribution such as would result from reversible cluster aggregation.[12] We find it quite interesting, however, that the obviously rather complicated process of rapid aggregation and restructuring ultimately yields aggregates having the same fractal dimension as the slow aggregation process.[3]

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