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Fractal colloidal aggregates with finite interparticle interactions: Energy dependence of the fractal dimension

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We have studied the aggregation of colloidal gold particles with finite interparticle attraction energies with static light scattering and the combination of conventional transmission electron microscopy (TEM) and high-resolution TEM. The finite interparticle attraction energies are achieved by adding a surfactant in the suspension via adsorption. The interparticle interaction can be changed by changing the amount of the surfactant. Using a modified Derjaguin-Landau-Verwey-Overbeek theory to describe the interparticle interaction, we show that (i) the aggregates of colloidal particles can still be fractal objects with a finite interparticle attraction and (ii) the fractal dimension changes with the interparticle attraction energy, in agreement with the computer simulations of Shih, Aksay, and Kikuchi [Phys. Rev. A **36**, 5015 (1987)].

I. INTRODUCTION

Colloidal aggregates have attracted much research interest since it was shown that the concept of a fractal dimension D can be used to characterize the structure of a disordered system, such as a random aggregate that is formed under nonequilibrium conditions.[1] However, under most circumstances, only certain values of the fractal dimension have been found with small gold, silica, and polystyrene particles (size ≤ 0.1 μm): $D = 1.75$ for fast aggregation,[2-4] and $D = 2.02-2.12$ for slow aggregation.[5-7] Occasionally, the $D = 1.75$ aggregates may at a later time restructure to a higher fractal dimension $D = 2.08-2.1$ (Ref. 3) and 2.4 (Ref. 4). Computer simulations of the diffusion-limited cluster-aggregation model[8,9] (DLCA) yield $D = 1.78$ in three dimensions (3D) and seem to represent the fast aggregation in the colloidal systems. Although computer simulations of the reaction-limited cluster-aggregation model[10] (RLCA), which is a modification of the DLCA model with a sticking probability p with p approaching zero and yielding $D = 2.0$ in 3D, seem to be coincident with the result of slow aggregation, the RLCA model cannot account for the restructuring of the aggregates. Both the DLCA and RLCA are irreversible aggregation models.

For the reversible aggregation process of colloidal particles, modifications of the DLCA model have been considered since the DLCA model seems to represent colloidal aggregation under irreversible conditions. Kolb[11] has modified the DLCA model with random bond breaking, which yields $D = 2.03$ in 3D at dynamic equilibrium. Although the Kolb (Ref. 11) model seems to be able to explain the restructuring of silica aggregates,[3] it cannot explain the fractal dimension $D = 2.4$ for gold aggregates[4] at a later time. Shih, Aksay, and Kikuchi[12] (SAK) have modified the DLCA model with a finite interparticle bonding energy, which yields aggregates with various fractal dimensions ranging from 1.4 to 2.0 in 2D, depending on the interparticle bonding energy and time. The fractal dimension $D = 1.4$ is the result of the DLCA model in 2D, which corresponds to the case of an infinite interparticle bonding energy in the SAK model. Furthermore, in the SAK model,[12] bond breaking is not random, but instead is controlled by a Boltzmann factor because a finite interparticle bonding energy is considered. A brief description of the SAK model is contained in the Appendix.

The experimental observation of aggregates with various fractal dimensions first occurred with the use of larger polystyrene particles in 2D (size > 1 μm).[13] Skjeltorp has observed aggregates with $D = 1.7-2.0$ in fairly concentrated suspensions by changing the particle concentration and/or the salt concentration, where the minimum fractal dimension $D = 1.7$ in 2D is more consistent with the computer simulations of the diffusion-limited aggregation model (DLA).[1] While Skjeltorp has been able to obtain a band of values of D and to correlate the fractal dimension with the growth rate of the aggregates, he did not address the correlation of the change in the fractal dimension with either the particle concentration or the salt concentration, both of which can change the interparticle interaction in colloidal systems.[14] So far, it is not clear experimentally how interparticle interactions lead to different structures of colloidal aggregates and why in some cases, one sees restructuring and in other cases, one does not. A detailed quantitative investigation of how the interparticle bonding energy affects the structure of the aggregates is therefore needed.

The purpose of this paper is to provide a detailed experimental investigation of how the interparticle interaction affects the aggregation of colloidal particles. In particular, we would like to know whether one can still grow fractal aggregates with a *finite* interparticle interaction energy. If so, we would like to establish the correlation between the change in the fractal dimension and the interparticle attraction energies. With the use of static light scattering, as well as the combination of the conventional transmission electron microscopy (TEM) and the high-resolution transmission electron microscopy (HRTEM), we are able to examine colloidal aggregates of small gold particles of about 15 nm in diameter in great detail. The use of HRTEM allows us to look at the interparticle structure down to the atomic resolution, which enables us to have a direct knowledge about the interparticle bonding. The finite interparticle attractions are achieved with an appropriate additive, i.e., a surfactant, via adsorption. With the surfactant, we are able to keep particles within an aggregate well separated at a distance of about 1–2 nm, about twice the width of the adsorbed surfactant layer, to avoid the infinite interparticle attraction at contact. With the modified Derjaguin-Landau-Verwey-Overbeek[15] (DLVO) theory to describe the interparticle interaction, we find that one can still grow fractal aggregates even when the interparticle attraction is finite. Moreover, the fractal dimension of the aggregates depends on the interparticle attraction energy: the minimum fractal dimension D we have obtained is about 1.74 for large interparticle attraction energies. D increases when the interparticle attraction energy is decreased. Our D-versus-attraction-energy curve resembles qualitatively that of the computer simulations of the SAK (Ref. 12) model, although the simulations were done in 2D, indicating that the reversible aggregation process in a colloidal system is represented by the SAK model rather than the Kolb (Ref. 11) model.

II. EXPERIMENTS

Colloidal gold particles are produced by reacting gold chloride with sodium citrate in an aqueous environment at 100 °C.[16] The weight concentration of gold is about 0.0025% and that of sodium citrate is about 0.05%. The particles produced are roughly spherical, with a diameter of about 15 nm. Aggregation of particles is induced by adding pyridine as in Refs. 2, 4, and 5, or by adding different amounts of a surfactant at room temperature. In this paper, we will focus on the use of surfactant additives. The advantage of using a surfactant will become clear later.

Static light-scattering experiments are performed to obtain quantitative structural information, such as the fractal dimension D of the aggregates. The instrument has a 50-mW helium-neon laser with wavelength $\lambda = 632.8$ nm and was manufactured by the Brookhaven Instrument Corporation. For fractal aggregates, the scattering intensity of a given wave number q is related to the fractal dimension D in the form

$$I(q) \sim q^{-D} \tag{1}$$

over the range $R_G^{-1} < q < a^{-1}$, where a is the radius of the particles and R_G is the average radius of gyration of the aggregates.[17] Thus, the fractal dimension D of aggregates can be obtained by plotting $I(q)$ versus q on a double-logarithmic paper, where q is related to the scattering angle θ by $q = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the fluid. The negative of the slope of the double-logarithmic plot of $I(q)$ versus q in the power-law region gives the fractal dimension D of the aggregates.

The TEM studies are carried out with a Philips EM300 operated at 100 keV. The TEM studies are mainly used for direct visualization of the aggregates. In some cases when the aggregates are more ramified (for example, when the fractal dimension D is smaller than 2.0), and particles do not overlap severely, we can also obtain quantitative information, such as the fractal dimension D of the aggregates, by box counting.[17] The fractal dimension obtained for the TEM micrographs can be compared with that obtained from static light-scattering experiments. TEM samples are made by transferring a small amount of suspension onto a carbon film suspended on a TEM copper grid.

In addition to static light-scattering experiments and conventional TEM studies, we also performed HRTEM studies to examine the interparticle regions down to the atomic length scale. The HRTEM studies allow us to gain a *direct* knowledge about the interparticle bonding which is difficult to obtain otherwise. The HRTEM studies are carried out with a Philips 430T operated at 300 keV.

III. RESULTS AND DISCUSSION

Various amounts of a cationic surfactant (Adgon 462, quaternary ammonium salt) are added to the initially dispersed suspension of gold particles of 15-nm diameter at room temperature to induce aggregation. This surfactant is chosen because (i) it is soluble in water in a wide range of pH and (ii) it is positively charged so that when it is adsorbed on the gold particle surface, it will neutralize the charges on the gold particles to induce aggregation. The initial negative charges on the particle surface are the result of the adsorption of negatively charged citrate during the growth process of gold particles.[18,19]

Figures 1(a)–1(f) are the TEM micrographs of gold particles with various surfactant concentration c: (a) $c = 0$, (b) 1.87×10^{-5}, (c) 4.67×10^{-5}, (d) 9.33×10^{-5}, (e) 3.73×10^{-4}, and (f) 5.61×10^{-4} wt. %. One can see that with an increasing amount of surfactant additives, gold particles change from well dispersed, as in Fig. 1(a), to aggregated, and the structure of the gold aggregates changes from dense to ramified as shown in Figs. 1(b)–1(d), and back to dense again, as in Figs. 1(e) and 1(f). The static light-scattering intensity of the aggregated samples corresponding to Figs. 1(b)–1(e) is shown in Fig. 2, where the double-logarithmic plots of $I(q)$ versus q clearly show a power-law behavior. The deduced values of the fractal dimension D, which are the negative of the slopes in Fig. 2 are as follows. $D = 2.68$ for (b), $D = 1.91$ for (c), $D = 1.74$ for (d), and $D = 2.03$ for (e). Both static light-scattering experiments and TEM micrographs indicate that the aggregates at $c \geq 5.61 \times 10^{-4}$ wt. % become compact objects. It is worth mentioning that for $D \leq 2.0$, the values of the fractal dimension obtained from static light scattering are identical to those obtained from box counting on TEM micrographs. For $D > 2.0$, particle overlapping prohibits accurate evaluation of D from TEM micrographs. The resultant fractal dimension D as a function of the added surfactant concentration c is shown in Fig. 3. The value of D first decreases as the surfactant concentration c is increased and it reaches the minimum value 1.74 at $c = 9.33 \times 10^{-5}$ wt. %, above which the value of D increases again.

The role of the surfactant is to change the interparticle interaction via adsorption. The adsorption of the surfactant on the gold particle surface is evident by the onset of aggregation of gold particles in our experiment. This point will become clear later when we show the interparticle interaction quantitatively. More detailed adsorption studies of similar surfactants have been done on colloidal silver surfaces.[20,21] The adsorption behavior of the surfactant we use in the present experiment on gold particle surfaces should be similar to that described in Refs. 20 and 21 because of colloidal similarity. Initially, the adsorbed surfactant ions on the gold particle surface help reduce the surface charge of the particles and hence increase the net interparticle attraction. The reason is that the surfactant ions and the gold surface initially have opposite charges. As the surface charge on the gold particles is completely neutralized, the net interparticle attraction reaches a maximum; further adsorption of the surfactant only increases the surface charge of the gold particles, which now have an opposite sign, and thus reduces the net interparticle attraction. The observed minimum fractal dimension at $c = 9.33 \times 10^{-5}$ wt. % corresponds to the maximum in the interparticle attraction. The minimum D value of 1.74 we have obtained at $c = 9.33 \times 10^{-5}$ wt. % is quite reasonable, for it agrees with both the computer simulations of the irreversible diffusion-limited cluster-aggregation model corresponding to the case of an infinite interparticle attraction and the previous aggregation studies of gold particles with pyridine addition in the fast aggregation regime.[2,4]

The difference in using a surfactant instead of pyridine to modify the interparticle interactions is revealed in the HRTEM micrographs in Figs. 4(a) and 4(b), where gold aggregates with the surfactant and with pyridine are shown. With the surfactant, the gold particles remain

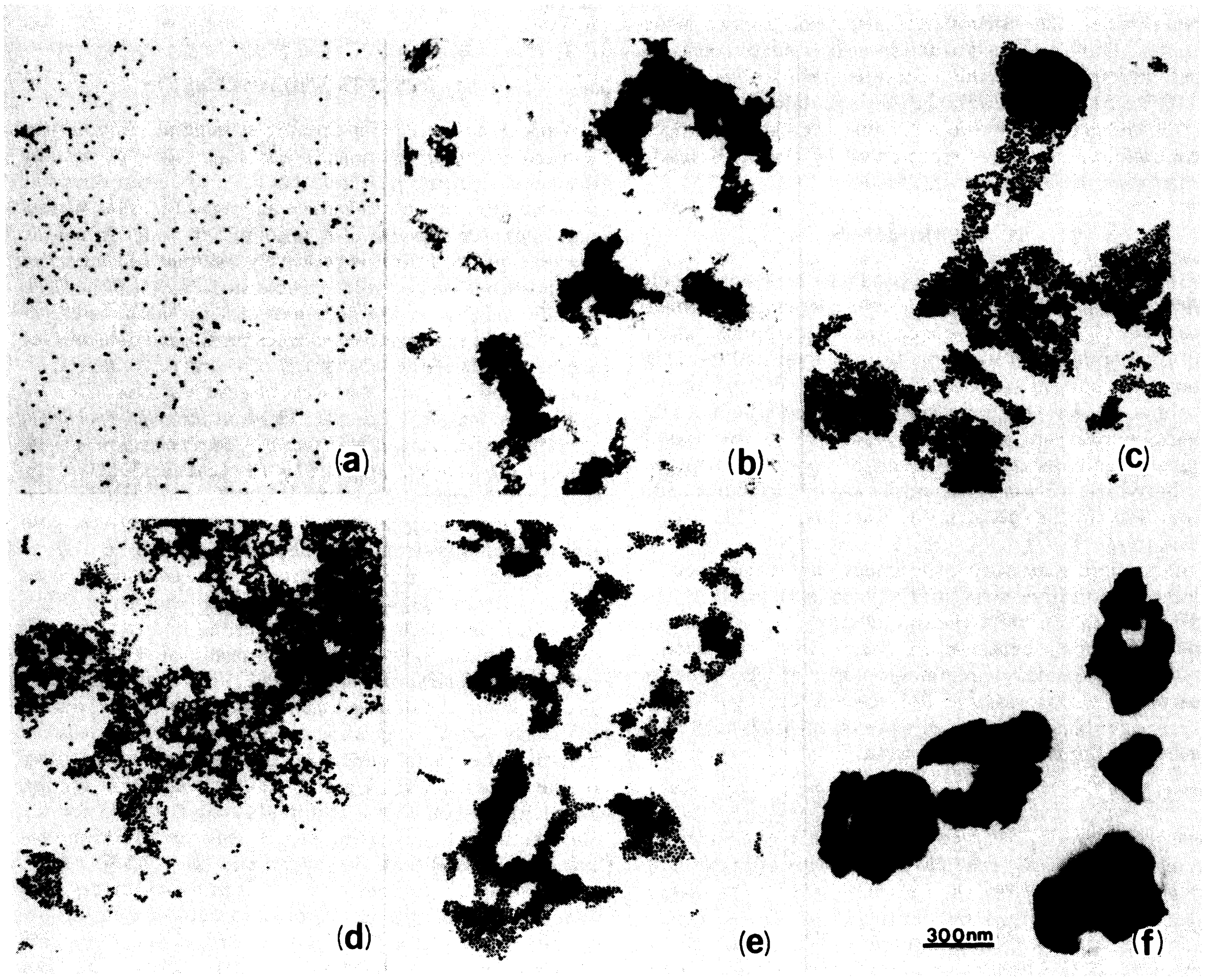

FIG. 1. TEM micrographs of gold particles at various surfactant concentrations c: (a) $c = 0$, (b) 1.87×10^{-5}, (c) 4.67×10^{-5}, (d) 9.33×10^{-5}, (e) 3.73×10^{-4}, and (f) 5.61×10^{-4} wt. %.

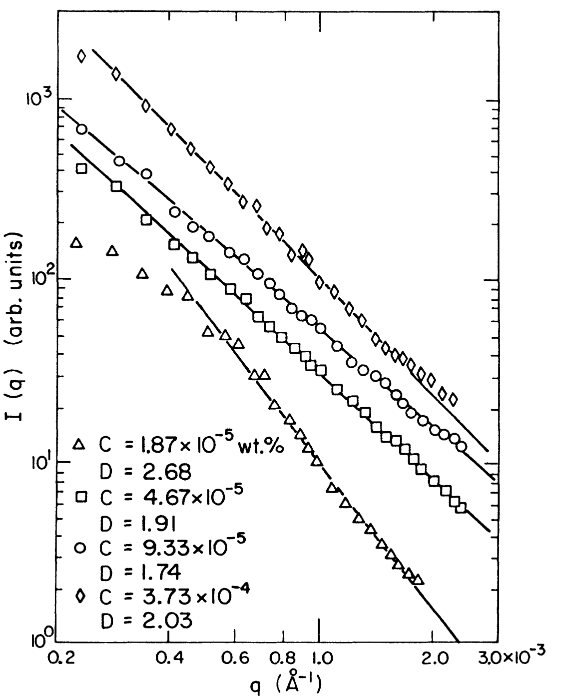

FIG. 2. Static light-scattering intensity of the aggregated samples corresponding to Fig. 1(b) $D=2.68$ (△), Fig. 1(c) $D=1.91$ (□), Fig. 1(d) $D=1.74$ (○), and Fig. 1(e) $D=2.03$ (◇), where D is the fractal dimension of the aggregates.

well separated at a distance of about 1–2 nm, which is about twice the width of the adsorbed surfactant layer,[22,23] as evidenced by the clear gaps between the gold particles in Fig. 4(a). In contrast, with the addition of pyridine, necks form between adjacent gold particles as shown in Fig. 4(b). This may explain why in the previous aggregation studies of gold particles with pyridine, change in the structure of aggregates has seldom been observed and only certain values of fractal dimension have been obtained, i.e., 1.75 for fast aggregation and 2.0 for slow aggregation. From Fig. 4(b), one can see that it is very difficult to break the necks once the necks are formed. Consequently, with pyridine, rearrangement of particles within a cluster is almost impossible.

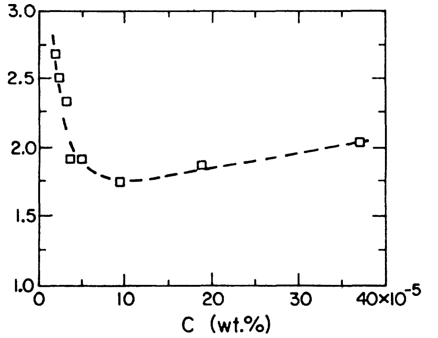

FIG. 3. D vs c where D is the fractal dimension and c is the surfactant concentration.

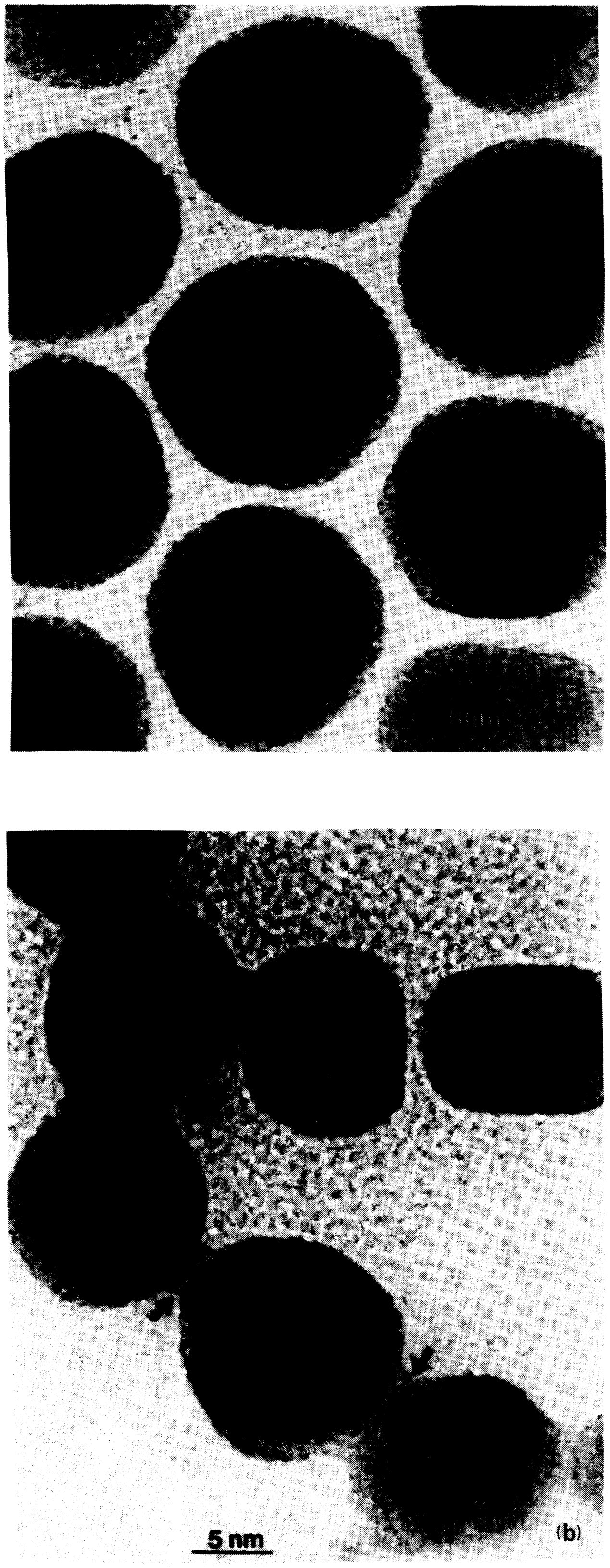

FIG. 4. HRTEM micrographs of gold aggregates (a) with the surfactant and (b) with pyridine. Gold particles are well separated at a distance of 1–2 nm with the surfactant, while necks form between particles with pyridine.

It is not known why the use of the surfactant has such a drastically different effect on the interparticle bonding from that of pyridine. The interparticle diffusion of gold atoms is almost impossible with surfactant adsorption. It may be because the adsorbed surfactant layer extends farther out from the surface (about 0.5–1 nm)[22,23] and/or because the charge distribution in a surfactant molecule is not uniform. However, for our purpose, the use of the surfactant enables us to have gold particles that remain well separated even at the closest distance, i.e., twice the length of the adsorbed surfactant layer. It is therefore possible to talk about the interaction between gold particles in the case of surfactant addition. Since our experiments are done in very dilute suspensions and we now know that the particles remain as separated particles even at the closest approach of about 1–2 nm, it is adequate to describe the interparticle interaction with a modified DLVO theory. Under the electrostatic condition, the interaction between gold particles $V(s)$ has two terms

$$V(s)=V_C(s)+V_a(s)\ , \tag{2}$$

where $V_C(s)$ is the screened Coulomb interaction, with the Debye-Hückel approximation, which is justified under our experimental conditions where both the particle and electrolyte concentrations are low, $V_a(s)$ is the van der Waals attraction, and s is the surface-to-surface interparticle distance. In cgs units, $V_C(s)$ takes the form[14]

$$V_C(s)=\frac{Z^2e^2}{\epsilon r}\left[\frac{e^{qa}}{1+qa}\right]^2 e^{-qr}\ . \tag{3}$$

Here a is the radius of a particle, $r=s+2a$ is the separation between the centers of particles, Z is the surface charge of a particle, ϵ is the static dielectric constant of water, e is the electronic charge, and q is the inverse screening length which satisfies

$$q^2=\frac{4\pi e^2}{\epsilon k_B T}\sum_i n_i z_i^2\ , \tag{4}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and z_i and n_i are the charge and the number density of the ith species of ions, respectively. The term in large parentheses in Eq. (3) is the size correction, which takes into account the fact that part of the volume of the suspension is not available for screening due to the finite size of the colloidal particles.

The van der Waals attraction takes the following form in cgs units:[15]

$$V_a(s)=\frac{A}{6}\left[\frac{2a^2}{s^2+4as}+\frac{2a^2}{s^2+4as+4a^2}+\ln\left[\frac{s^2+4as}{s^2+4as+4a^2}\right]\right]\ , \tag{5}$$

where A is the Hamaker constant. To calculate the interparticle interaction, we use a Hamaker constant of 2.2×10^{-12} erg which is typical of metals.[24] For the screening length q^{-1}, we include the contributions from all ions in the solution: the pH is about 5. The number concentrations of Cl^-, Na^+, and citrate are about 1.56×10^{16}, 1.74×10^{18}, and 0.58×10^{18} cm^{-3}, respectively. The surfactant concentration is on the order of 10^{-5} wt. %. The dominant contribution is from Na^+ ions. Using Eq. (4), we obtain a value of about 7 nm for the screening length $l=q^{-1}$. For the effective surface charge Z of a particle, we have measured the electrical mobility of the particles μ to be 4.83×10^{-4} cm^2/(V s) in the absence of the surfactant. From the electrical mobility measurement, we deduce the ζ potential of the particles to be about 100 mV. By approximating the ζ potential V_ζ in the cgs units to be

$$V_\zeta=\frac{Ze^2}{\epsilon a}\ , \tag{6}$$

we estimate the charge Z of each particle to be about 42 in the absence of surfactant ions. It should be noted that this effective charge Z may differ from the real surface charge. However, it is the effective charge Z that determines the electrostatic repulsion between particles. The surface charge Z is taken to be 0 at the surfactant concentration $c=9.33\times10^{-5}$ wt. % where the fractal dimension $D=1.74$ is the minimum. When complete adsorption of surfactant molecules is assumed, the surface charge of particles at a given surfactant concentration c can then be linearly interpolated in the range $0<c<9.33\times10^{-5}$ wt. %. By complete adsorption we mean that all the added surfactant ions are on the gold particle surface. For example, the interpolated values of the effective surface charge Z are 34 for $c=1.87\times10^{-5}$ wt. % [Fig. 1(b)], and $Z=21$ for $c=4.67\times10^{-5}$ wt. % [Fig. 1(c)], respectively. We do not extrapolate the value of Z for $c>9.33\times10^{-5}$ wt. %. The asymmetry of D versus c near the minimum in Fig. 3 indicates that the assumption of complete adsorption of the surfactant is no longer valid for $c>9.33\times10^{-5}$ wt. %.

Using the estimated values of Z, q, A, etc., we then calculate the interparticle interaction $V(s)$ for the surfactant concentration range $0<c<9.33\times10^{-5}$ wt. %. The result is shown in Fig. 5. The closest separation between two particles, which is about twice the length of an adsorbed surfactant molecule (1.5 nm), is indicated by the dashed line at $s=1.5$ nm, which is a reasonable value when the structure and the configuration of the adsorbed surfactant are considered.[22,23] We approximate the contribution of the steric repulsion between two adsorbed surfactant layers to the interparticle interaction as a hard-wall repulsion at the average separation $s=1.5$ nm. As the surfactant concentration c is increased, one can see that the interaction at $s=1.5$ nm changes from repulsive to attractive at about $c=1.87\times10^{-5}$ wt. %, which agrees very well with the onset of aggregation in the experiment. As the surfactant concentration c is further increased, the net attraction at $s=1.5$ nm becomes larger, which is consistent with the decrease in the fractal dimension shown in Fig. 3.

As we have mentioned above, the onset of aggregation of the gold particles serves as evidence of the adsorption of the surfactant on the particle surface. The reason is as follows. If the surfactant ions do not adsorb on the gold particle surface, but remain in the suspension, given the

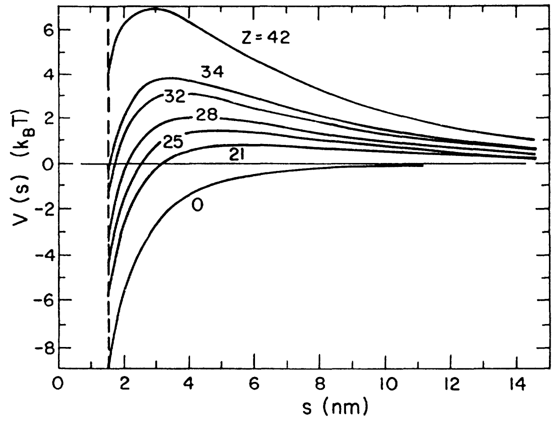

FIG. 5. $V(s)$ vs s for various values of the effective surface charge Z of gold particles where $V(s)$ is the interparticle energy in units of $k_B T$ and s is the surface-to-surface interparticle distance. The dashed line at $s=1.5$ nm indicates the closest interparticle separation due to surfactant adsorption. The different values of Z are the result of different adsorption amounts of surfactant ions on the gold particle surface.

low surfactant concentrations as we have used, just the screening of the free surfactant ions in the suspension would not reduce the Coulomb repulsion between gold particles enough to induce aggregation.

The value of $|V(s)|$ at $s=1.5$ nm is the maximum attraction energy that two particles can experience since they cannot get any closer. In Fig. 6, we plot the fractal dimension D as a function of the absolute value of the net attraction at $s=1.5$ nm, $|V_{1.5\,\mathrm{nm}}|$ for the aggregated cases in the range $0<c<9.33\times10^{-5}$ wt. %. First, one sees that with the addition of the surfactant the interparticle attraction energy now remains finite. Second, with finite interparticle attraction energies, the gold particles still form fractal aggregates. The fractal dimension remains around 1.74 at large values of $|V_{1.5\,\mathrm{nm}}|$ and increases as $|V_{1.5\,\mathrm{nm}}|$ decreases. Also plotted in Fig. 6 is the curve of D versus the nearest-neighbor attraction energy $|E|$ of the computer simulations of the SAK model in 2D (Ref. 12) for comparison. Note the similarity of the two curves, although the simulations were done in 2D: the values of the fractal dimension D in both curves remain constant for large values of the attraction energy and increase when the attraction energy is about $4k_B T$. The close resemblance between the two curves suggests that the reversible aggregation process in a colloidal system is represented by the SAK model. While effects of the structural change have been studied by other investigators, none of these studies can explain our observed *continuous* change of the fractal dimension with interparticle interactions. For example, random bond breaking only increases the fractal dimension from 1.75 to 2.03 in 3D.[11] The RLCA model gives a fractal dimension $D=2.0$ in 3D.[10] The rotational adjustment of one cluster around the center of another cluster at collision to allow a second bond to form only increases the fractal dimension slightly in 2D (Ref. 25) and by about 0.3 in 3D.[26]

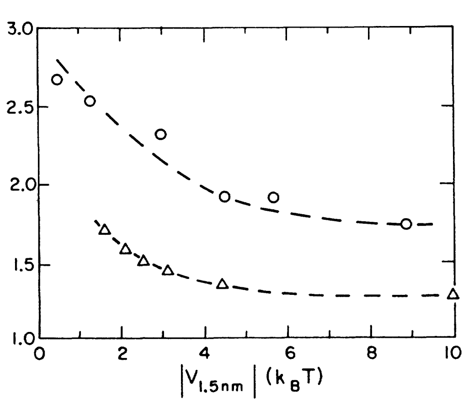

FIG. 6. D vs $|V_{1.5\,\mathrm{nm}}|$ for the aggregated samples (○), where D is the fractal dimension and $|V_{1.5\,\mathrm{nm}}|$ is the net interparticle attraction energy at $s=1.5$ nm. Also plotted is D vs $|E|$ from the computer simulations of Ref. 12 (△), where $|E|$ is the nearest-neighbor attraction energy in Ref. 12. Both $|V_{1.5\,\mathrm{nm}}|$ and $|E|$ are in units of $k_B T$.

The choice of the attraction energy at $s=1.5$ nm may appear somewhat arbitrary since the interparticle separation in the HRTEM micrographs ranges from 1 to 2 nm. However, the conclusion one can draw from Fig. 6 would not be altered if the interaction energy at a different value of s is chosen. For instance, we could have used the interaction at $s=1$ or 2 nm instead, which would only change the specific values of the interaction energy but not the qualitative behavior of the fractal dimension versus the interaction energy.

In the computer simulations of the SAK model, the fractal dimension can also change with time: D may change with time continuously or be saturated at some value for a long period of time, depending on the interparticle attraction energy and the ratio of two time constants, i.e., the diffusional time constant, τ_D and the relaxational time constant for bond breaking, τ_R. In our present study, we have not observed the change of D with time. It could be that our present system represents the case where the fractal dimension D is saturated at some value for a long time. However, in a separate study of the growth of colloidal gold particles, we did observe the change of D with time.[27]

IV. SUMMARY

We have extensively studied the aggregation of colloidal gold particles with a finite interparticle attraction energy, using TEM, HRTEM, and static light scattering. We have been able to achieve finite interparticle attraction energies by using a surfactant additive instead of pyridine. The surfactant modifies the interparticle interaction energies via adsorption. The adsorbed surfactant layer keeps two particles separated to prevent the infinite interparticle attraction that would take place at contact. Furthermore, the interaction energy at finite distances changes with the amount of the adsorbed surfactant. We have used a modified DLVO theory to describe the interparticle energy. We have shown that it is possible to grow *fractal* colloidal aggregates with a finite interparticle attraction energy. Moreover, the fractal dimension D changes with the interparticle attraction energy: $D = 1.74$ for large interparticle attraction energies, and D increases from 1.74 as the interparticle attraction energy decreases. Our observations agree qualitatively with the results of the computer simulations of the SAK model,[12] although the simulations of the SAK model were done in 2D, which suggests that the reversible aggregation process in a colloidal system may be represented by the SAK model.

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APPENDIX

The Shih-Aksay-Kikuchi model is a modification of the diffusion-limited cluster-aggregation model. The computer simulations were done in a 2D square lattice with periodic boundary conditions. The diffusion and the aggregation part of the SAK model is the same as in the DLCA model. Namely, the simulation starts with a given number of particles uniformly distributed on the lattice. Particles are performing Brownian motion (random walk). When two particles collide, they form a cluster. A cluster, just like a particle, then random walks as a unit and may collide with particles or clusters to form a larger cluster later. In the SAK model, the diffusion time constant for all clusters is assumed to be the same, since the cluster-size dependence of the diffusion time constant does not change the fractal dimension of the cluster.[8,28]

The major difference of the SAK model is that it considers a *finite* nearest-neighbor interparticle interaction $-E$ so that at finite temperatures, a particle within a cluster may break its bonds with its neighboring particles. At temperature T, the rate for a particle to unbind from its neighbors is $(1/\tau_R)e^{-nE/T}$ where τ_R is the time constant for unbinding and n is the number of neighbors of the particle. Here the units are chosen such that the Boltzmann constant is unity.

The unbinding time constant of a particle τ_R may be different from the diffusion time constant τ_D. τ_R would depend more on the surface properties of the particles and τ_D would depend more on the particle size.

The bond-breaking process is simulated with the Monte Carlo method. That is, in every τ_R, each particle is checked with a random number ranging from zero to unity. If the random number is larger than the Boltzmann factor $e^{-nE/T}$, the particle breaks all the bonds with its neighbors or stays unchanged otherwise. After the particle breaks the bonds with its neighbors, it then goes to one of the unoccupied neighboring sites at random. This way, a cluster may break into as many as three segments as illustrated in Fig. 7. Each individual segment then becomes an independent cluster and may collide with one another at a later time.

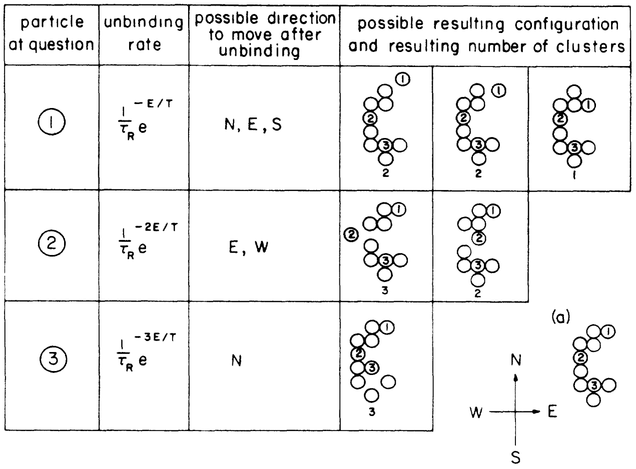

FIG. 7. Illustration of the unbinding processes of particles 1–3 in cluster (a). Unbinding takes place according to the rate $(1/\tau_R)e^{-nE/T}$, where n is the number of neighboring particles, and is simulated with the Monte Carlo method. Possible resulting configuration and possible number of resulting clusters, which is below the configuration, are shown for each case.

The bond-breaking processes allow clusters to restructure and densify. One may regard the restructuring and densification in the SAK model as thermal annealing of the aggregates since the bond-breaking processes are controlled by the Boltzmann factor. The DLCA model corresponds to the case when E is infinite and may be regarded as the quenched state.

In the simulations, only the translational motion of particles and clusters is considered explicitly. However, when there is sufficient sampling from the simulations to allow many configurations of two colliding clusters, the rotational motion should not affect the fractal dimension of the clusters.[29] The main results of the SAK model are summarized as follows. (i) The cluster size may become saturated and finite, and the saturated cluster size increases exponentially with the value of E at a given particle concentration. (ii) With restructuring and densification, the clusters can still remain fractal objects with the fractal dimension increasing with time. For large values of τ_R/τ_D and E, the fractal dimension can first increase from around 1.35 and then saturate at some larger value for a very long time. (iii) For a given time, the fractal dimension of clusters increases with a decreasing value of E, as shown in Fig. 6.

The major emphasis of the SAK model is the thermal annealing of the clusters and the dependence of the structures of the aggregates on the interparticle bonding energy, as well as time. Other effects such as the rotation of one cluster around another at collision to allow a second bond to form between the two colliding clusters are not considered since these effects may change the value of the fractal dimension slightly but qualitatively would not change the dependence of the fractal dimension on the bonding energy and time.

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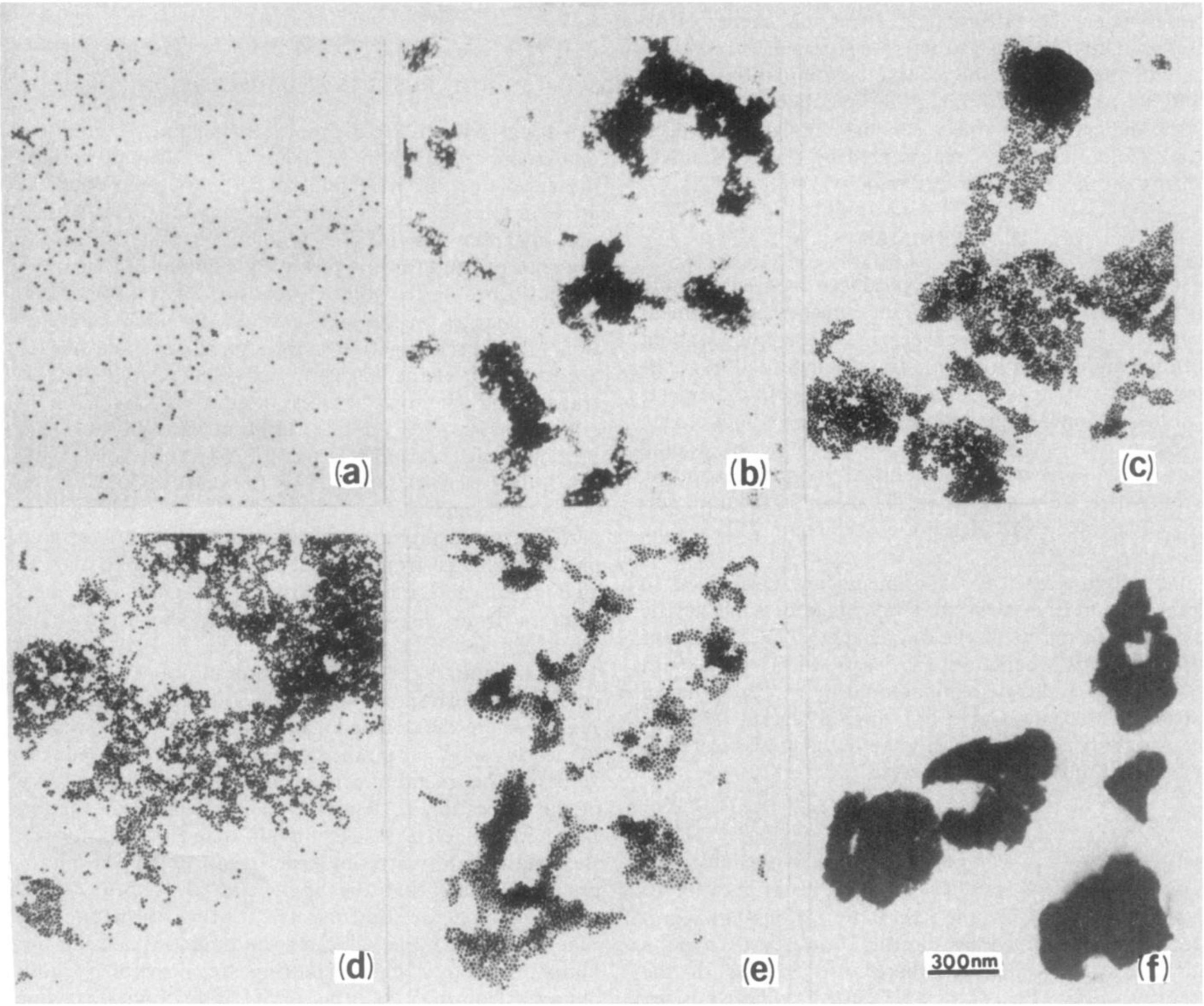

FIG. 1. TEM micrographs of gold particles at various surfactant concentrations c: (a) $c=0$, (b) 1.87×10^{-5}, (c) 4.67×10^{-5}, (d) 9.33×10^{-5}, (e) 3.73×10^{-4}, and (f) 5.61×10^{-4} wt. %.

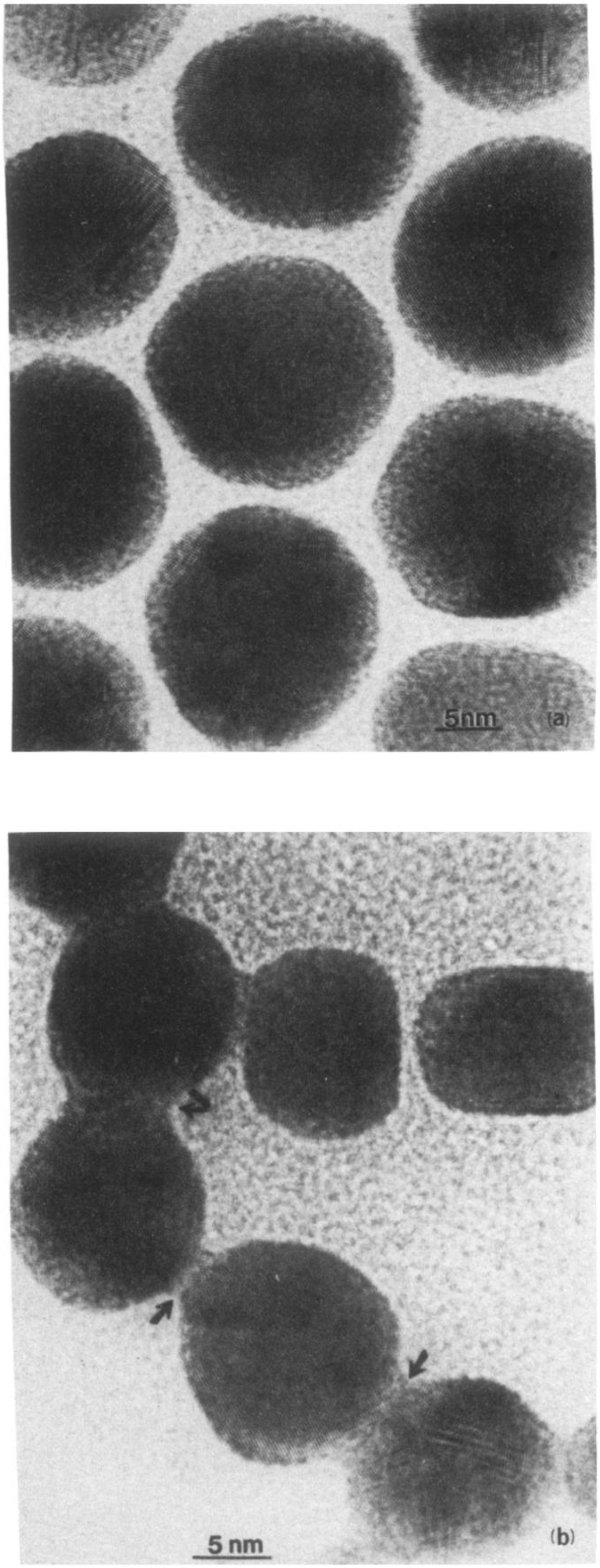

FIG. 4. HRTEM micrographs of gold aggregates (a) with the surfactant and (b) with pyridine. Gold particles are well separated at a distance of 1–2 nm with the surfactant, while necks form between particles with pyridine.