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Kinetics of salt-induced aggregation in polystyrene lattices studied by quasielastic light scattering

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We investigate the kinetics of aggregation of polystyrene particles of 481 nm in a solution of a univalent-univalent salt in the concentration range from 0.05 to 2.6 mol/l. Using quasielastic light scattering to measure the linewidth and hence the hydrodynamic radius of the clusters, we find the value 1.75 ± 0.03 for the fractal dimension of the aggregates in the fast coagulation regime, when the salt content is high, while we get a slow exponential kinetics with low salt content. Using scaling arguments and the mean-field Smoluchowski equation we describe our results in terms of collisions of clusters during purely Brownian diffusion.

I. INTRODUCTION

The mechanism of coagulation and flocculation of lyophobic colloids has long been studied,[1] but the interest in this form of irreversible aggregation phenomenon has considerably recently increased. One of the reasons is related to the various attempts to understand this type of nonequilibrium phenomena in terms of properties of scale invariance of the resulting clusters. The clusters are usually characterized, from a geometrical point of view, by their fractal dimension d_f, i.e., the exponent that relates the total mass M of the aggregate to its typical size R, $M \sim R^{d_f}$.

Aggregation processes induced by a chemical agent have been investigated by means of different experimental techniques, and among these light scattering has provided a powerful tool for characterizing the kinetics of aggregation. Measurements of the scattered intensity and of the linewidth in a quasielastic experiment give information on the fractal dimension and the hydrodynamic radius of the cluster. The latter is proportional to the inverse of the diffusion coefficient measured by the linewidth. A series of very interesting measurements have been recently performed on different colloids, under various experimental conditions. The most widely used systems are gold colloids (particles of 7.5 nm) where the aggregation was induced by adding appropriate amounts of pyrydine[2] and silica colloids[3] (particles in the range 2.7—7 nm) in NaCl solution at various concentrations (0.5 to 1.25 mol/l) and various pH values. Polystyrene spheres[4] (22 nm) and more complex biological colloids[5] have also been used. The general picture that emerges can be summarized as follows.

(i) Two regimes of irreversible aggregation exist, a slow reaction-limited regime[2] characterized by an exponential growth of the hydrodynamic radius of the clusters and a fractal dimension ranging from 2 to 2.12. A fast regime, which is diffusion limited, characterized by $d_f = 1.75$.

(ii) In the fast aggregation regime there is a power-law increase with time of the cluster size $R \sim t^{1/d_f}$.

(iii) The above quoted values of the fractal dimensionality are independent of the system studied and suggest the existence of universality classes of the aggregation kinetics.

(iv) The fast aggregating clusters restructure after a sufficiently long time[6] to give more compact objects with $d_f = 2.08$.

(v) The value of d_f depends on the physicochemical properties of the aqueous phase,[6] in particular on the pH of the solution.

(vi) The values of the fractal dimension obtained experimentally seem to be in agreement with the predictions of numerical simulations.

Lyophobic colloids, whose stability is based on the existence of an electric charge on the particle surface due to the ionization of surface end groups, provide an excellent model system for the study of the kinetics of aggregation. Among these, polystyrene lattices, owing to the effective surface charge resulting from the partial dissociation of the proton in the surface carboxyl groups, make a quantitative comparison with stability theories possible.

In this paper we report an investigation by means of quasielastic light scattering of the kinetics of aggregation of relatively large, but still Brownian, polystyrene particles induced by a univalent-univalent salt. We want to stress the fact that in our measurements we used polystyrene monomers (481 nm in diameter) of a size much larger than used previously by other authors. With this kind of particle a measurement of the scattered intensity would require a very small angle since the condition $kR \ll 1$ must be fulfilled, with k the scattering wave vector. This condition is not necessary when the quasielastic scattering is used to evaluate the hydrodynamic radius of the aggregate. Moreover, the large interval of concentration of the aggregating agent we use (from 0.05 to 2.6 mol/l), allows us to extend the validity of the aggregation growth laws to a much larger range. Our measurements indicate that there are two regimes of aggregation with different behaviors. We find the value 1.75 ± 0.03 for the fractal dimension of the aggregates in the fast coagulation regime, while we get a different regime of the kinetic growth mechanism when the salt content is low.

Finally we mention the fact that the kinetic behavior governed by the power law $R \sim t^{1/d_f}$ can be obtained directly from the Smoluchowski equation for cluster-cluster aggregation. This is the consequence of the application of simple scaling arguments to the cluster distribution and indicates the purely Brownian character of the kinetics.

II. EXPERIMENTAL

A. Latex preparation

The lattices studied in this investigation were monodisperse polystyrene lattices purchased from the Dow Chemical Company, containing particles of diameter 481 nm with a standard deviation of 5 nm. The lattices were received as suspensions of 10% by volume and were diluted to the desired concentration with water of very low conductivity $[(0.7\text{—}0.8)\times 10^{-6}\ \text{mho}\,\text{cm}^{-1}$ at 20 C]. All lattices were filtered through a 0.22-μm Millipore filter to remove unwanted oligomeric and polymeric contaminants from the dispersion as prepared. Solid volume fractions were estimated to be of the order of 0.01 mg/ml. The original emulsifier was removed as much as possible by extensive dialysis against deionized water, using an ultrafiltration cell Amicon mod. 12 with ultrafiltration membrane XM100, until a conductivity of about 5×10^{-6} $\text{mho}\,\text{cm}^{-1}$ was reached.

A univalent-univalent electrolyte (NaCl) was used as flocculating agent. The stability of the colloidal suspensions before the addition of the salt was checked over a period of 2—3 days by measurements of the mutual diffusion coefficient to ensure that irreversible aggregation of polystyrene spheres does not take place. The apparent hydrodynamic radius obtained from the Stokes-Einstein equation was 248 nm slightly larger than the manufacturer's nominal value of 241 nm. Differences of this order of magnitude are to be expected and are reported by some authors.[7]

B. Dynamic light scattering measurements

We have measured the photocurrent autocorrelation function

$$C(\tau)=A+B\,|g(\tau)|^2\,, \tag{1}$$

where

$$g^2(\tau)=\frac{\langle I(0)I(\tau)\rangle}{\langle I\rangle^2}$$

is the normalized intensity autocorrelation function. For noninteracting, monodisperse particles, it can be shown that

$$g(\tau)=\exp(-Dk^2\tau)\,, \tag{2}$$

where D is the translational diffusional coefficient and k the scattering vector. For polydispersed systems, containing noninteracting particles with different size distribution, the nonexponential behavior of the autocorrelation function must be analyzed by the method of cumulants.[8] It consists in expanding $g(\tau)$ in a power series in τ

$$\ln[g(\tau)]=K_0+K_1\tau+K_2\tau^2+\cdots \tag{3}$$

and the first cumulant K_1 is used to obtain the effective translational diffusion coefficient D and consequently, from the Stokes-Einstein relation, the apparent hydrodynamic radius of the aggregates. Photon correlation measurements were made at a scattering angle of 90° with a 128-channel photon correlator using a 5-mW He-Na laser operating at a wavelength of 6328 Å and a standard photomultiplier. All measurements were performed at room temperature and the diffusion coefficients were corrected to the standard conditions taking into account the temperature dependence of the viscosity of the aqueous phase.

The background contribution to the correlation function has been measured in each run using the method of delaying the last few channels of the correlator by a suitable amount of time. In this way a reliable estimate of the uncorrelated contribution is obtained. As a further advantage one is then able to use a polynomial fit to the correlated part of the measured function. In order to test the accuracy of our fitting procedure for the evaluation of the cumulants, we performed a series of fits progressively reducing the range of channels used until a constant value of the first cumulant was reached. In this way we were able to obtain the asymptotic value of it with a small fitting error, weighing appropriately the contribution of the channels which contain the relevant information. The effect of higher-order cumulants was seldom needed to reproduce the experimental spectra.

III. RESULTS AND DISCUSSION

We have measured the effective hydrodynamic radius R of the growing aggregates upon the addition of different amounts of NaCl electrolyte at nine values of the concentration in the range from 0.05 to 2.6 mol/l. The rate of the aggregate formation depends on the electrolyte concentration and results in different dynamic processes. As pointed out by Weitz *et al.*,[2] this behavior is quite common to a wide class of systems, including biological colloids, and, to a first approximation, any growth process can be reduced to one of these class of aggregation. We shall discuss separately these effects. Adding a small amount of electrolyte results in a slow aggregation process reflected in a moderate increase of the apparent hydrodynamic radius of the aggregates. Similar results were found by Cornell *et al.*[9] by the direct observation of the particle motion in polystyrene lattices. Lattices at the NaCl concentration in the range from 0.05 to 0.5 mol/l show this behavior. The growth of the aggregates is well characterized by

$$R(t)=R_0\exp(Ct) \tag{4}$$

and the constant $1/C$, dependent on the experimental conditions, assumes values of the order of 1 h. Preliminary measurements on a polystyrene latex with particles 91 nm, reported in Fig. 1(a), show clear evidence of this exponential-like growth in the slow aggregation regime. As the amount of the added salt is increased, a different aggregation regime with irreversible coagulation occurs.

Every collision results in the formation of a permanent aggregate. The rapid cluster-cluster aggregation (CCA) displays a power-law kinetics with

$$\frac{R-R_0}{R_0}=G(t-t_0)^{1/d_f}=\left[\frac{t-t_0}{t_1}\right]^{1/d_f}, \tag{5}$$

where R is the hydrodynamic radius of the cluster at time t, t_0 is the time when the aggregation process starts, and $G=t_1^{-1/d_f}$ a constant prefactor. Figure 1(b) shows the percentage increase $[R(t)-R_0]/R_0$ of the cluster size as a function of time for a latex of 481 nm in 0.85 mol/l NaCl electrolyte solution. This behavior, characterized by a faster aggregation, is common to all the samples investigated in the NaCl concentration range from 0.75 to 2.6 mol/l. Moreover, Aubert and Cannell[6] have pointed out that this kinetic should be characterized by two different dimensions of the resulting clusters. They find that in silica colloids, when prepared under rapid aggregation conditions, the CCA aggregation is followed by a stage in which the cluster restructure showing a scaling behavior with the mass depending on the radius according to

$$M \sim R^{d_f}. \tag{6}$$

In this case the commonly accepted value for d_f falls in the range 2.02 to 2.12 depending on the system. For the system we investigated even the longest observation in time did not show this type of transition. Actually, the largest clusters tend to precipitate before restructuring, due to the large size of our monomers.

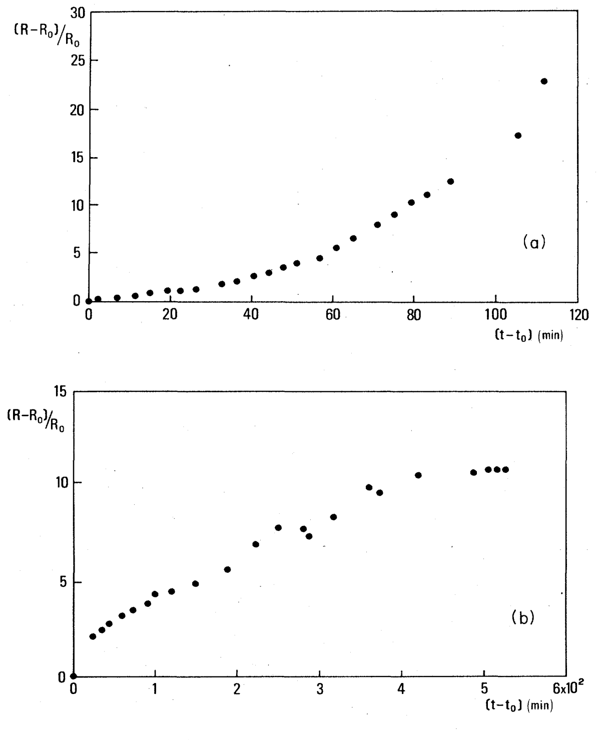

FIG. 1. (a) Percentage cluster radius increase $[R(t)-R_0]/R_0$ as a function of time in the slow growth regime. (b) Percentage cluster radius increase $[R(t)-R_0]/R_0$ as a function of time in the rapid growth regime.

An interpretation of the two different aggregation regimes is based on the existence of two minima in the potential energy curves. A first minimum leads to an irreversible coagulation of the colloid while a secondary minimum is responsible for reversible flocculation. According to the theory developed by Derjaguin and Landau, and Verwey and Overbeck,[10] the total interparticle interaction energy of two colloidal particles will display a mutual repulsion, modified by the interactions of the diffuse ion atmosphere surrounding the particles, over a mutual attraction term due to the London—van der Waals dispersion forces. Lyophobic colloids, being intrinsically unstable, will flocculate at a rate which depends on the total interaction energy. Combination of electrostatic and attractive potentials, depending on the dielectric constant, the radius of the particle, the surface potential (Stern potential), the Debye screening length, the effective Hamaker—van der Waals constant of the system, give rise to different physical situations that can describe the different macroscopic behavior of the colloidal system. Particularly, this theory is able to take into account the kinetics of flocculation in the secondary minimum, i.e., the transition involving equilibrium between a dispersed phase consisting essentially of singlet particles and a flocculated phase consisting of a randomly packed aggregates having interparticle surface-to-surface separations considerably greater than atomic dimensions. For the system under test, the London—van der Waals potential between two spheres of radius a is given by[11]

$$V_A=-\frac{A}{12}\left[\frac{1}{x^2-1}+\frac{1}{x^2}+2\ln\left[1-\frac{1}{x^2}\right]\right], \tag{7}$$

where A is the composite Hamaker constant, $x=r/2a$ and r the distance between the centers of the spheres. The repulsive potential, due to the electrostatic interaction of the double layer can be written, to a first approximation, as[12]

$$V_R=\epsilon_m a\phi_d^2\ln\{1+\exp[-2k_D a(x-1)]\}, \tag{8}$$

with ϵ_m the dielectric constant of the aqueous phase, $1/k_D$ the Debye-Hückel screening length, and ϕ_d the diffuse layer potential. Exact experimental determination of the surface potential is not usually possible. However, when the surface charge density is not too high, ϕ_d can be approximated by the ζ potential determined from the electrophoretic mobility. We assume $\phi_d=21.5$ mV and for the Hamaker constant of polystyrene in water the value[13] of 0.95×10^{-13} erg. Figure 2 presents the interaction potential for the systems investigated. As it can be seen the profiles of the interaction pair potential can be classified in two general classes of shapes that determine the different aggregation regimes. At lower ionic conductivity, up to 0.75 M NaCl, all the curves clearly show the presence of a secondary minimum responsible of the reversible association (flocculation) corresponding to stable systems with average aggregates of several particles. The reversibility of these flocculated states at electrolyte concentration of the order of 0.01—0.5 mol/l NaCl has been also

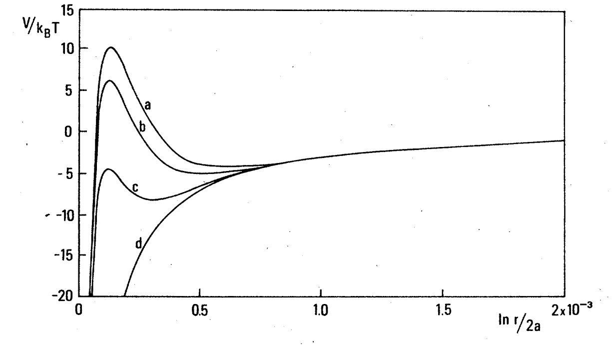

FIG. 2. Potential energy curves for some of the measured samples (*a*, 0.05; *b*, 0.1; *c*, 0.5; *d*, 2.6 mol/l NaCl). The parameters used are quoted in the text.

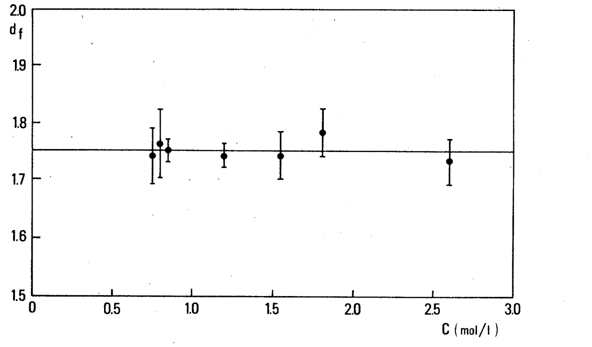

FIG. 4. Fractal exponent d_f for various NaCl concentrations.

experimentally evidentiated by Cornell *et al.*[9] As the ionic conductivity is increased, the potential energy barrier, which directly influences the amount of particles that stick together, is reduced. At the critical coagulation concentration the situation is represented by a curve of the type *d* in Fig. 2 were a deep potential is present well indicating that the particles are strongly seized together.

From a macroscopic point of view the aggregation kinetics can be described in terms of cluster-cluster interactions, by means of the Smoluchowski equation.[14] This is a mean-field approach which makes a balance between the increase and the decrease of the number of the aggregates of various sizes due to the collisions during diffusion. The relevant quantity is the concentration c_n of clusters containing n particles, which obeys the rate equation

$$\frac{d}{dt}c_n(t)=\frac{1}{2}\sum_{i+j=n}^{\infty}K_{ij}c_i(t)c_j(t)-c_n(t)\sum_{j=1}^{\infty}K_{nj}c_j(t)\ . \tag{9}$$

The first term takes into account collisions of smaller clusters to form a larger aggregate of n monomers and the second term collisions that diminish the concentration of n clusters. The reaction kernel K_{ij} gives the rate of the various processes, and can be modeled in various ways. The original Smoluchowski's suggestion was to consider collisions during purely Brownian diffusion, leading to

$$K_{ij}=C(R_i+R_j)(D_i+D_j)\ , \tag{10}$$

where R_i and D_i are the radius and the diffusion constant of a cluster of i particles, and C is a constant that takes into account the initial monomer radius and diffusion coefficient and the probability of sticking of the cluster upon collision. The fractal nature of the aggregate can be accounted for by the dependence $R_i \sim i^{1/d_f}$. For purely Brownian motion one would expect a diffusion constant $D_i \sim R_i^{-1} \sim i^{-1/d_f}$ but a more general dependence on the mass of the aggregate can also be investigated, $D_i \sim i^{-\gamma}$. We will therefore assume

$$K_{ij} \sim (i^{\beta}+j^{\beta})(i^{-\gamma}+j^{-\gamma})\ , \tag{11}$$

with $\beta=1/d_f$.

The scaling properties of the aggregation kinetics can be evidentiated[15] both at the level of the kernel and at the level of the cluster distribution. In the former case scaling implies the homogeneity relation

$$K_{ai,aj}=a^{\lambda}K_{ij}\ , \tag{12}$$

which introduces the homogeneity index λ. Scaling in the cluster distribution[15] gives, on the other hand,

$$c_n(t) \sim n^{-2}\Phi[n/s(t)]\ , \tag{13}$$

where Φ is a scaling function and $s(t)$ the typical cluster size

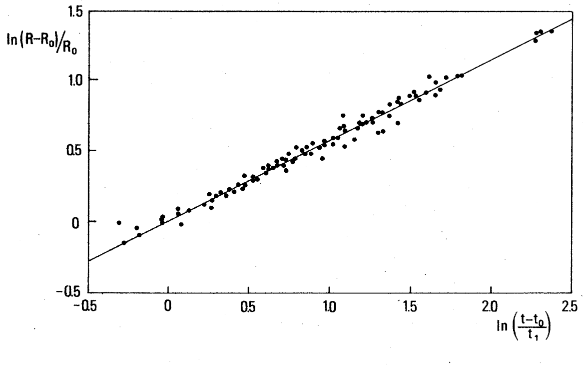

FIG. 3. Cumulative log-log plot of the measured hydrodynamic radii $[R(t)-R_0]/R_0$ as a function of $(t-t_0)/t_1$.

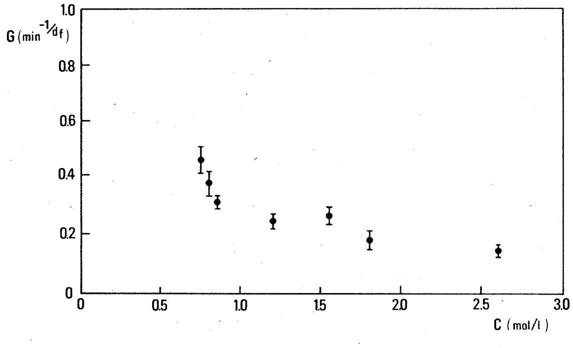

FIG. 5. Amplitude factor G for various NaCl concentrations.

$$s(t)=\sum_n n^2 c_n(t) \Big/ \sum_n n C_n(t) \ . \tag{14}$$

Asymptotically for t going to infinity $s(t) \sim t^z$ and it can be shown[15] that the well-known result $z = 1/(1-\lambda)$ holds. In the case we are considering $\lambda = \beta - \gamma$. The important consequence of the scaling of c_n is the fact that all the moments of the distribution can be written as powers of the typical size $s(t)$.

We are now in the position to evaluate the hydrodynamic radius $R(t)$ we measure in a scattering experiment. In fact, taking into account the polydispersity of the clusters, the average diffusion coefficient is given by the sum of the diffusion coefficient of each cluster weighted with the square of its mass

$$D=\frac{\sum_n c_n n^2 D_n}{\sum_n c_n n^2} \sim \frac{\sum_n c_n n^{2-\gamma}}{\sum_n c_n n^2} \sim [s(t)]^{-\gamma} \tag{15}$$

and the hydrodynamic radius

$$R \sim D^{-\beta/\gamma} \sim s^{\beta} \sim t^{\beta/[1-(\beta-\gamma)]} \ . \tag{16}$$

When the diffusion is purely Brownian $\gamma = \beta$ and we recover the result of Eq. (5), which shows that the Brownian kernel of Eq. (11) with $\beta = 1/d_f$ gives a good mean-field description of the kinetics.

Our experiments clearly confirm and extend the validity of Eq. (5) over a wide concentraion range of the flocculating agent. Figure 3 shows the dependence of the percentage growth of the cluster radius R over the radius R_0 of the monomers on time. The latter has been scaled with a fixed time t_1 starting from the instant t_0 when the mixing with the aggregating agent takes place.

The solid line corresponds to Eq. (5) with $d_f = 1.75$ which is the weighted average of our seven determinations. The corresponding uncertainty is 0.03. The exponent d_f in the various experiment runs is shown in Fig. 4. As it can be seen, in the concentration range from 0.75 to 2.6 mol/l, the growth of the colloidal aggregates proceeds with an equal fractal dimension d_f according to the CCA model. This evidentiates the wide independence of the aggregation kinetics on the experimental conditions, once the interparticle potential has assumed the characteristic shape without the potential barrier. In Fig. 5 we report the amplitude factor G that appears in Eq. (5) as a function of NaCl concentration. This quantity does not affect the determination of the fractal dimension from the data. In fact for each salt concentration we get a value of G which gives the intercept in a log-log plot of $(R-R_0)/R_0$ versus $t-t_0$. In Fig. 3 we use the variable t_1 in order to be able to scale all the curves on a single straight line. The behavior of this amplitude could be justified as follows. The number of sites in the solution where the aggregation process starts increases with the salt concentration thus leading eventually to clusters of smaller average size, due to the constancy of the total number of monomers.

In this note we have analyzed the main features of the aggregation process induced by a simple salt in a well-defined colloid of relatively large particles. The important result is the universality of the aggregation kinetics, in the fast growth regime, over a wide ionic concentration range. Further questions remain open, in particular the influence of the particle radius, the density of the surface charge and the chemical properties of the flocculating agent on the kinetics of aggregation. Investigations along these lines are under way and will be reported shortly.

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