The Effect of the Salt Concentration and Counterion Valence on the Aggregation of Latex Particles at the Air/Water Interface

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Received June 22, 2001; accepted January 12, 2002; published online March 26, 2002

An experimental study on colloidal aggregation in two dimensions is presented. This study shows that a high amount of electrolyte concentration is necessary to screen the particle interactions and to induce the aggregation process. Our results indicate that the stability of the colloidal particles, with a diameter of 735 nm, increases when they are trapped at the air–water interface. The reason for this stability is the existence of long-range repulsive interactions between the external parts of the particles that are propagated at the air phase. The subphase electrolyte concentration that separates the slow aggregation rate region from the fast aggregation rate region, the critical coagulation concentration (C.C.C.), has been determined for counterions with a different valence. Two regimes can be distinguished: at low salt concentration the aggregation process becomes slower and the aggregation is reaction limited. At high ionic strength the repulsive interactions between the immersed part of the particles are very weak and the aggregation rate tends to grow. However, because of the aerial repulsive interactions, pure diffusion-limited cluster aggregation is never found.

Key Words: two-dimensional aggregation; interface; fractal dimension; kinetics; critical coagulation concentration.

1 INTRODUCTION

Aggregation processes have been widely studied in three-dimensional systems, where colloidal particles are immersed in a liquid (water, organic solvents, etc.). Unstable conditions may be easily induced by the addition of salt. Since the counterions screen the electrostatic repulsive barrier, the aggregation rate increases progressively with the salt concentration until the so-called critical coagulation concentration (C.C.C.). Above this value the repulsive barrier has already been eliminated and the aggregation is controlled only by the diffusion time of the aggregates (DLCA).

In recent years attention has also been paid to the study of colloidal aggregation in two dimensions due to the interesting phenomena observed in this kind of system, as fractal cluster growth, formation of mesostructures, intercluster spatial ordering, etc. (1–5). Significant efforts have been made to understand the aggregation process and the kinetic, structural, and topological aspects of the two-dimensional coagulation processes have been studied by means of theories (6), simulations (7–9), and experiments (3, 4).

In this paper, a particular case of a two-dimensional system consisting of latex colloidal particles, with a diameter of 735 nm, spread at the air–liquid interface is studied. Once latex particles are dispersed at the interface, they remain trapped because of surface tension effects and electrostatic forces. In two-dimensional aggregation, additional theoretical and experimental complexities appear in comparison with coagulation of bulk colloidal suspensions (1,10–12). On the one hand, since the particles are trapped at the interface, the interaction force between them depends on their degree of wetting (10, 13). Consequently, the interaction between the wet parts of the colloidal particles is quite different from the interactions between the external parts, and the theoretical treatment for determining the energy requires numerical computation (14). Moreover, from an experimental point of view, the deposition procedure of colloidal particles at the interface is a delicate process due to the difficulty of avoiding initial heterogeneities and fluctuations in the particle surface dispersion.

Although similar aggregation behavior for the C.C.C. is expected in the two-dimensional case, actually there is a big difference in relation to three dimensions. In two dimensions, a large amount of salt is necessary for inducing particle coagulation (15, 16). This phenomenon suggests that strong repulsive interactions are involved in the aggregation process, leading to a much higher C.C.C. for aggregation at the interface than for colloidal particles at the solution interface.

In this work, the kinetic and morphological behavior of colloidal aggregation for polystyrene cationic latex particles confined at the air–water interface has been studied as a function of the salt concentration. Then, the C.C.C., i.e., the salt concentration at which transition from slow coagulation to rapid coagulation occurs, has been determined from both kinetic and structural properties and a good accordance between both results has been achieved. Moreover, the influence of ionic nature on...
the aggregation process has also been analyzed, specifically the
effect of the counterion valence.

This paper is organized as follows. In section 2 a theoretical
revision regarding the kinetic aspects of the aggregation, dy-
namic scaling, and fractal structure is presented. In section 3
the system features, experimental procedures, and experimen-
tal devices are described. The kinetic and structural results are
presented and discussed in section 4. Finally, we summarize the
results and conclusions in section 5.

2. THEORETICAL BACKGROUND

The aggregation process can be characterized in different
ways, depending on which physical properties are considered.
The most important and useful aspects are the fractal cluster
structure and the temporal growth of the cluster size distribu-
tion (17, 18). Both descriptions are closely related to the particle
interactions forces.

It is well known that aggregates formed by coagulation of
spherical particles have an inner branching structure that can be
characterized by the fractal dimension, $d_f$ (19, 20). As men-
tioned above, the value of the cluster fractal dimension is af-
fected by the particle interactions. When the interaction poten-
tial between particles shows a strong enough repulsive barrier,
many collisions are necessary for two aggregates to stick to-
gether (RLCA) and the aggregation process becomes slower (21,
22). In this regime the aggregation rate is principally determined
by the reaction time (21, 23, 24). As the aggregates have to col-
lide many times, they interpenetrate deeper and so more com-
 pact structures with a higher fractal dimension are generated.
The corresponding cluster fractal dimension obtained by simu-
lations (25) and experimental measures (15, 26) for pure RLCA
are $2.10 \pm 0.03$ and $1.55 \pm 0.04$ for three and two dimensions,
respectively. When no interactions exist between particles and
aggregates, i.e., for DLCA, every collision leads to coagulation
(27). At this limit, more linear structures are obtained with a
fractal dimension close to 1.75 and 1.45 for each case.

To estimate the cluster fractal dimension, several methods can
be applied. One of the most widely used is the radius of gyration
method. It states that, for a cluster formed by $i$ particles, the
radius of gyration is expressed as $R_g \sim i^{-1/d_f}$ (20), where $d_f$
is the fractal dimension. As an evident consequence, it can be eas-
ily deduced from this relationship that more compact structures
have a higher fractal dimension and a lower radius of gyration.

Besides cluster morphology, the kinetic aspects of coagulation
must also be considered to obtain a more complete description of
the aggregation process. The fundamental variable in this case is
the cluster size distribution, $n_i(t)$, defined as the average number
of clusters formed by $i$ monomers at time $t$. The time evolution
of the cluster size distribution is generally assumed to verify the
Smoluchowski equation (28), given by

$$\frac{dc_i}{dt} = \sum_{j=1}^{i-1} k_{i-j} c_j(t)c_{i-j}(t) - \sum_{j=1}^{\infty} k_{i-j} c_i(t)c_{i-j}(t),$$

where $c_i(t) = n_i(t)/S$ is the average surface concentration and
$S$ the area of the interface. The aggregation kinetics is totally
determined by the kernel, $k_{i-j}$, which represents the aggregation
rate between two $i$ and $j$ size clusters. The exact form of $k_{i-j}$ is, in
most cases, very difficult to obtain. However, important features
of the aggregation process can be deduced from the asymptotic
dependence on the cluster size. One generally parameterizes the
asymptotic behavior of the kernel in terms of two exponents, $\lambda$
and $\mu$ (29).

$$k_{i-j} = a^\lambda k_{i,j} \quad i, j \gg 1$$

$$k_{i,j} \sim i^\mu j^{\lambda-\mu} \quad j \gg i,$$

where $a$ is a large positive constant. Kernels with $\lambda \leq 1$ de-
scribe non-gelling aggregation kinetics whereas for $\lambda > 1$, the
Smoluchowski equation predicts the formation of an infinite
cluster at finite time. The homogeneity exponent, $\lambda$, controls
the cluster reactivity for large cluster sizes. For $\lambda < 0$, small ag-
gregates react faster than large ones. In contrast, for $\lambda > 0$, the
cluster reactivity increases with the cluster size.

The temporal cluster size growth is determined by the time
evolution of the weight-average cluster size, defined as $S_w(t) =
\sum n_i(t)/\sum i n_i(t)$. It has been observed in both simulations
and experimental measures that the cluster size distribution
reaches a scaling behavior at long times (17, 27, 30). The cluster
concentration is then given by

$$c_i(t) \sim S_w(t)^{-2} \phi(t/S_w(t)).$$

Here, $\phi(x)$ is the scaling function, the shape of which depends
on the value of the exponent $\mu$. In the scaling region of systems
with $\lambda < 1$, $S_w(t)$ depends on time as a power law

$$S_w(t) \sim t^z,$$

where $z$ is a scaling exponent that controls the growth of the
weight-average cluster size for long periods of time. It is re-
lated to the homogeneity exponent $\lambda$ through the equation
$z = 1/(1 - \lambda)$. The exponent $z$ depends strongly on the aggrega-
tion regime and on the reactivity among aggregates: for aggrega-
tion conditions where large clusters coagulate more frequently
than smaller ones, a larger value for the exponent $z$ is expected.
In contrast, if the reactivity of big aggregates is smaller than small
ones, $z$ takes a smaller value. Furthermore, it has been observed
by computer simulations (8) that the exponent $z$ also depends on
the particle surface fraction at the interface. Specifically, both $z$
and $\lambda$ grow as the particle surface fraction increases. For very
dilute systems and DLCA conditions, $\lambda = -0.69 \approx -1/d_f$
and $z = 0.59$.

This paper is focused on the determination of the structural
and kinetical description of the aggregation process for our
two-dimensional colloidal system, particularly on the C.C.C. and the dependence of $d_f$ and $z$ as a function on both the salt concentration and the counterion valence.

3. EXPERIMENTAL METHODS

The colloidal particles used in our experiments were cationic polystyrene latex beads, which were prepared from styrene by free-emulsifier emulsion polymerization with azo $N,N'$-dimethyleneisobutyramidine hydrochloride (AMDBA) as an initiator and NaCl as a buffer. The polymerization was carried out in a reactor fitted with a reflux condenser, stainless steel stirrer, and nitrogen inlet tube. The size distribution was obtained by transmission electron microscopy. The average particle diameter was $(735 \pm 36)$ nm and the polydispersity index was 1.006. Latex dispersion was cleaned first by serum replacement and second with mixed-bed ion exchange resin. The surface charge density of $\left( +0.090 \pm 0.008 \right) \text{C/m}^2$ was determined by conductometric titration.

Salt solution was introduced into a Teflon cell. Then, latex particles were placed at the liquid–air interface using a micro syringe. This interface has to be as planar as possible to prevent the particle emigration as a consequence of gravity. The immersion of latex beads into water was avoided by dispersing the particles using methanol as a spreading agent, according to procedures described in Refs. (10, 15). For this purpose, colloidal suspensions were prepared in a methanol solution and were sonicated for 5 min to assure a good initial monodispersity. It should be noted that the use of methanol in the deposition procedure is essential for obtaining a uniform monolayer. After methanol evaporation, the cell is covered by a thin glass plate to prevent the contamination of the monolayer and the convective fluxes produced by the air motion.

The aggregation process has been monitored using a phase contrast microscope and a CCD camera attached to it with $1024 \times 1024$ pixels. Possible vibrations were avoided by placing the system formed by the cell, microscope, and camera on an antivibratory table. The magnification of the objective was fixed so that the pixel diameter was close to the particle size. Thus, the number of pixels of an aggregate corresponds approximately to its size, $i$. The images were acquired by a frame grabber. The video information generated by the camera was digitalized and processed for identifying the clusters at the interface at different aggregation times and both the fractal structure of the aggregates and the time evolution of the cluster size distribution were determined. Figure 1 shows two pictures of a typical colloidal aggregation experiment. As can be seen, the fractal nature of the aggregates is only manifested for long aggregation times.

For the purpose of studying the effect of counterion valence on the kinetics and the cluster fractal structure, three salts have been used to induce the coagulation process: KBr, Na$_2$SO$_4$, and Na$_3$PO$_4$. Consequently, the counterion corresponds to the negative ions Br$^-$, SO$_4^{2-}$, and PO$_4^{3-}$, respectively.

4. RESULT AND DISCUSSION

The influence of the counterion valence on the aggregation process has been studied using three different salts: KBr, Na$_2$SO$_4$, and Na$_3$PO$_4$. For each one of them, the fractal dimension and the exponent $z$ have been obtained for different values of salt concentration. Since the effectiveness of the double-layer screening for the immersed part of colloidal particles increases for more charged counterions, the C.C.C. is expected to be lower.
for experiments with $\text{PO}_4^{3-}$ and higher for $\text{Br}^-$. Additionally, the pH of $\text{Na}_3\text{PO}_4$ solutions increases with the salt concentration and so, in this case, the double-layer screening of the cationic latex particles becomes stronger. Nevertheless, these predictions are not completely obvious because of the existence of interactions between the external parts of the particles and they have to be confirmed experimentally.

Using the gyration radius method (Fig. 2), the fractal dimension of the aggregates was determined at different aggregation times. In all experiments, the fractal dimension is higher at early stages of coagulation. However, during the aggregation, its value decreases continuously and finally reaches a stationary value at moderate times. Figure 3 shows this phenomenon for an experiment with a high electrolyte concentration. Initially, the fractal dimension of the aggregates is close to 1.52, but it decreases to 1.46, close to the expected value for DLCA. The reason for this effect could be searched at first instance in the fact that the fractal nature of the aggregates is manifested for large enough structures and so the correct fractal dimension only could be obtained at long aggregation times. However, computer simulations of RCLA and DLCA processes demonstrate that even small aggregates have the correct fractal dimension. Although fractal dimension is a manifestation of the compactness of the clusters structure, which could be affected by the limited, size effect of this aggregates, we think that in our experiments this initial compactness of the aggregates may be caused by the turbulent initial spreading process and also by different phenomena such as air movement, liquid convection, etc., that occur in the minute spent between the spreading and the covering of the cell.

The behavior of fractal dimension as a function of salt concentration for the three salts is shown in Fig. 4. All curves for different electrolytes have a similar form: for small concentrations, the fractal dimension is close to 1.54, in agreement with the expected value for RLCA. This value seems to decrease slowly for several amounts of salt. However, when salt concentration is large enough, the fractal dimension decreases sharply to 1.45, and this value remains constant for larger concentrations. A rough estimate of the $\text{C.C.C.}$ can be obtained from these curves for the salt concentration at which the fractal dimension goes down. For electrolyte concentrations above the $\text{C.C.C.}$ this fractal dimension remains constant, indicating that the repulsive electrostatic barrier is already screened. According to this argument, we have that the $\text{C.C.C.}$ is 1, 0.5, and 0.3 M for KBr, $\text{Na}_2\text{SO}_4$, and $\text{Na}_3\text{PO}_4$, respectively.

These results, however, do not give enough information about the transition between RCLA (small salt concentration) and DLCA (large salt concentration). That is, it is impossible to conclude if the crossover is continuous or abrupt. Moreover, although the fractal dimension here obtained agrees with computer simulation results, it is not clear if the lower fractal dimension of 1.45 corresponds to an increase of the aggregation rate and if the 1.54 value means a lower rate. To check this correspondence and to observe more clearly the transition, the kinetic aspects of the aggregation have to be taken into account.

For this purpose, the weight-average cluster size has been determined as a function of time for all experiments. Two different temporal regions can be distinguished (see Fig. 5). The first one corresponds to the beginning of the aggregation. Here, the size growth is quite slow and the power law dependence is still not manifested. After some time, i.e., when bigger clusters exist at the interface, $t_{min}$, 50, the coagulation rate increases and a potential growth appears, $S_w(t) \sim t^z$. This qualitative time growth of $S_w(t)$ has also been found in computer simulations (9, 25) and experiments (16), in both three and two dimensions. As can be seen comparing Figs. 3 and 5, this change occurs at the same time that the fractal dimension reaches its limiting value ($t = 50$ min).

The exponent $z$ has been calculated from the fits of the long time behavior of $S_w(t)$ at several salt concentrations for the three salts studied. The results are shown in Fig. 6. As a particular case, we now consider the experiments for KBr electrolyte. $z$ is close
to 0.33 for the lower salt concentration and increase continuously with the ionic strength until 0.6 at $[KBr] = 1$ M (Fig. 6a). From this point, the exponent $z$ takes a constant value, independent of salt concentration. According to these experimental results, a conclusion similar to the one mentioned before using the fractal dimension is deduced: the repulsive electrostatic barrier between the immersed part of the particles decreases with salt concentration due to the screening of the electric double layer. Hence, the aggregation rate and so, also the exponent $z$, increase with salt concentration. At $[KBr] = 1$ M, the electric double layer is totally screened and the C.C.C. is reached. It is interesting to note that the C.C.C. for these particles trapped at the air–water interface is larger, than that in the three-dimensional case ($C.C.C. (3D) = 0.15$ M). It is clear from this comparison that important repulsive interactions are present when particles are trapped at the interface.

It should be pointed out that our results for the $z$ exponent differ from that reported by Robinson and Earnshaw (16) and Hansen and Bergström (31). They reported exponent values for the DLCA regimen that are greater than those we have found, but for the RLCA regime the values obtained by Hansen are similar while those reported by Robinson are greater. As they indicated, the anomalous large $z$ values for the DLCA regime can be explained by convective effects that affected their experiments. However, we have done our experiments in a diffusive regime, without convection, and so we have not obtained so large exponents.

Although it seems from Fig. 6a that the KBr can cause an extra stabilization for the lowest concentration, the comparison with Fig. 4a for the fractal dimension values suggests the contrary, a destabilization. However, both values are included between the experimental uncertainty for the average values of $z$ and $d_f$ at low KBr concentration. Thus, this is not a relevant effect.

Similar results were obtained for the experiments with $Na_2SO_4$ and $Na_3PO_4$ and so the same argument can be applied. We have found that the C.C.C. was close to 0.5 and 0.3 M, respectively (Figs. 6b and 6c), in clear agreement with the values predicted using the fractal dimension. These experiments show that the valence of the counterions, $v$, does not affect the qualitative behavior of the aggregation properties, but it already changes the C.C.C. We have found that

$$C.C.C.(v) \propto \frac{1}{v}.$$  \[5\]

It should be pointed out that although for salt concentrations above the C.C.C. the DLVO potential for the immersed part
of the particles does not exhibit any repulsive barrier, the total interaction potential contains more repulsive terms. The most important one is the repulsive dipolar interaction between the external parts of the particles. This external interaction through the air is very important because it cannot be screened by an electrolyte. Moreover, it is totally independent from the electrolyte concentration of the dissolution and so all experiments are influenced in the same way. Depending on the dipole fraction around the particle surface, the repulsive barrier height may be more important. Furthermore, the dipolar term is not a short-range interaction, and the repulsive effects may be observed at several particle diameters. Hence, we can assure that a repulsive interaction exists that prevents the aggregation from reaching the DLCA regime, even above the C.C.C.

Recently, off-lattice simulations of the aggregation process in two dimensions have been performed in DLCA conditions (8). For this case, no interaction exists and so the aggregation rate is totally controlled by the Brownian diffusion of the clusters. It has been observed that the kinetic exponent \( z \) increases strongly with the particle surface fraction, \( \psi_s \). It starts from 0.60 for very dilute systems and increases with \( \psi_s \) according to the law \( z = 0.595 + 0.807 \psi_s^{0.599} \). In our particular case, all experiments have been done with a particle surface fraction approximately equal to 0.04 and so according to the simulated data for this surface fraction, a value \( z \approx 0.712 \) is expected for salt concentrations above the C.C.C. However, in real experiments \( z \approx 0.60 \) has been obtained. This result clearly indicates that, even at high salt concentrations, the pure DLCA regime is never reached because there are dipolar repulsive interactions between the external part of the particles that are independent from the subphase salt concentration. Hence, also at the C.C.C., which separates the slow and fast coagulation regions, a repulsive energy barrier for the particle interaction still exists.

Both DLCA and RLCA regimes have been widely studied in two and three dimensions by computer simulations. RLCA regime may be modeled using a sticking probability, \( P_0 \), defined as the fraction of total collisions that actually lead to coagulation. The sticking probability is related to the height of the repulsive barrier. For instance, a low \( P_0 \) corresponds to a very high repulsive barrier and then many collisions are necessary to produce aggregation. The most important result deduced from simulations for different \( P_0 \) values is that the exponent \( z \) increases as \( P_0 \) decreases (6, 9, 25). Larger values of \( z \) imply larger values of \( \lambda \). Consequently, reactivity of big aggregates increases for very low sticking probabilities.

At first glance, these simulation results seem to contradict our experimental curves, which show that the exponent \( z \) actually decreases when the repulsive barrier increases. That is, experimentally large aggregates are less reactive than small ones at low salt concentration. However, this phenomenon can be perfectly explained since the sticking probability used in RLCA simulations is only capable of describing short-range repulsive interactions. In our experimental system, the long-range dipolar repulsive interaction has to be considered. According to this, when one particle approaches an aggregate with more than one particle, it feels the long-range repulsion produced by all monomers that constitute the aggregate. Consequently, large aggregates are less reactive at lower salt concentrations; i.e., exponent \( \lambda \) is lower and the same occurs for \( z \). This result shows that the pure DLCA regime cannot be obtained for any salt concentration and emphasizes the importance of the dipolar repulsive interaction to understand the colloidal stability at the air–water interface.

**FIG. 6.** Kinetic exponent, \( z \), as a function of salt concentration for (a) KBr, (b) Na\(_2\)SO\(_4\), and (c) Na\(_3\)PO\(_4\). The C.C.C. is obtained from these plots as the salt concentration at which \( z \) reaches its maximum value, close to 0.6.
5. CONCLUSIONS

Experiments with the three salts, KBr, Na$_2$SO$_4$, and Na$_3$PO$_4$, respectively, show that the colloidal system becomes more unstable at high values of the ionic strength of the subphase. The cluster fractal dimension is close to 1.45 and 1.54 for high and low salt concentrations, respectively. The exponent $z$ increases as the salt concentration increases and reaches a maximum value close to 0.6 for the C.C.C.

The C.C.C. has been found to decrease with the counterion valence according to the law $C.C.C.(v) \propto v^{-1}$. Furthermore, it has been observed that the stability of colloidal particles increases when they are trapped at the air–water interface due to long-range dipolar interactions between the external parts of colloidal particles. Since this dipolar interaction propagates through the air, it does not depend on the subphase electrolyte concentration and remains constant for all experiments. Because of this repulsive interaction, the pure DLCA limit is not found even at the highest ionic strength. Furthermore, the long-range dipolar repulsion makes big aggregates become less reactive than small ones and so the exponent $z$ diminishes for decreasing salt concentration.

ACKNOWLEDGMENT

Financial support from "Ministerio de Ciencia y Tecnología. Plan Nacional de Investigación Científica, Desarrollo e Innovación Tecnológica (I+D+i)". MAT99-0662-C03-02 is gratefully acknowledged.

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