Crossover from flocculation to gelation in two-dimensional aggregation induced by an alternating electrical field

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The crossover from flocculation to gelation in the two-dimensional colloidal aggregation induced by an external alternating electrical field is experimentally studied. It is shown that the crossover is accompanied by a sharp percolation transition of the aggregated particles at threshold $p_c \approx 0.42$. The scaling properties of clusters are analyzed in terms of percolation theory. The fractal dimension is found to increase from 1.50 to 1.75 with the particle concentration p increasing, and then to saturate for $p > p_c$. The results show a similarity to the standard percolation in the scaling behavior, but some exponents are different.

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The aggregation of diffusing particles or atoms to form large clusters is a common phenomenon in diverse natural and synthetic processes, and has been extensively studied both theoretically and experimentally since the introduction of the concept of fractal and critical scaling [1–4]. Studies to date have focused mainly on aggregation in the limit of extreme low concentration, i.e., the flocculation regime. It has been demonstrated that structures produced by irreversible aggregation are fractals, with the fractal dimension being 1.45 in the diffusion-limited case (DLCA) and 1.50 in the reaction limited case (RLCA) in two dimensions [4].

If the initial particle concentration is increased, the aggregation process will mix with the percolation process, and this should result in a crossover of the system from flocculation to gelation regimes, where a sol-gel transition takes place at a finite time t_g; that is, an infinite cluster spanning the system occurs. Computer simulations in two dimensions show that the fractal dimension of clusters at high density is 1.75 ± 0.07, which is different not only from that in flocculation but also from that of the infinite cluster in percolation. So far, the coeffect of particle concentration and aggregation has been scarcely studied [5,6], and is less than well understood; e.g., little is known about the crossover, the scaling characteristics of the spanning cluster, etc.

In this paper, we present experimental results about the effect of the particle concentration on the two-dimensional aggregation induced by an alternating electrical field, which may lead to insight into the aggregation process at different concentrations, and into percolation of attractive aggregated particles. Geometrical features of the aggregated particles at different concentrations p are analyzed in terms of the scaling theory of percolation. It is shown that the aggregated patterns undergo a percolation transition at a threshold $p_c \approx 0.42$, i.e., the crossover of the system from flocculation to gelation is a sharp transition. We also calculate the probability $P_N(p)$ of particles in the largest cluster, and show that near p_c $P_N(p) \sim (p - p_c)^\beta$ for $p > p_c$ with the exponent $\beta \simeq 0.15$, which is close to that value in the two-dimensional percolation process. Below p_c, by studying the clusters with the radius-of-gyration method, we find that the fractal dimension changes approximately continuously from 1.50 to 1.75, with p increasing from 0.20 to p_c. Above p_c, the finite cluster and its backbone (the infinite cluster without all dangling bonds) are shown to be self-similar on length scales up to a correlation length ξ with fractal dimensions ~ 1.75 and 1.63, but homogeneous on larger length scales than ξ. These results indicate that the scaling behavior of the percolation transition observed during the crossover is analogous to the standard percolation; only some scaling exponents are different.

The experimental setup is the same as previous [6–8]. Briefly, the monodisperse polystyrene colloidal suspension, which was synthesized by us through two-step swollen emulsion polymerization according to Ref. [9], is confined between two glass slides with conductive coatings, forming a two-dimensional system. By applying an external alternating electrical field perpendicular to the cell, one can modify interparticle forces by changing the frequency and strength of the field, and cause particles to aggregate if the frequency is in the range from several hundred Hz to several ten kHz. The aggregation process is observed *in situ* and recorded in tapes or photos for latter image processing through an optical microscope matched with a video system or a camera. The experimental conditions are summarized as follows: the cell is 50 μm in thickness and of about 1×1 cm^2 in area, the particle diameter is 1.4 μm, the field frequency 1.5 kHz, the field strength 0.55 V/per 50 μm, and the particle concentration p (defined as the area fraction of particles in pictures) varies from 0.2 to 0.8 [10].

The interparticle interaction induced by the external field has been addressed by us [11]. It was demonstrated that the electrical-field-induced interparticle forces are dependent mainly on the field frequency and the field strength. Accordingly, it is an advantage of the system that only the effect of particle concentration is included and can be investigated by varying only the particle concentration while keeping the same interparticle forces. Moreover, due to the electrical image interaction between particles and the cell surface, the particles are restricted near the cell wall surface, and the particle movability perpendicular to the cell surface is highly suppressed while the lateral movability is nearly unchanged. Therefore the system is two dimensional, although the cell thickness 50 μm is rather larger than the particle diameter.

Typical photographs of aggregated particles are shown in Fig. 1. It can be seen that on small scales particles close pack, forming a triangular lattice; on larger scales, however, the external structures of clusters are irregular. Figure 1(a) with $p=0.24$ is far below the threshold, and clusters are all finite and droplike. Figure 1(b) with $p=0.39$ is near the threshold, and clusters are stringy or ramified and still finite. Figure 1(c) with $p=0.43$ is just above the percolation threshold, and the largest cluster connects two sides. Figure 1(d) with $p=0.48$ is far above threshold, and almost all particles are in the networklike spanning cluster. Evidently the increase of particle concentration has resulted in a percolation transition in the aggregated particles, or that the system crosses over from nongelling to gelling regimes.

The standard percolation (SP) transition, signaling the sudden occurrence of an infinite cluster spanning the system, is a kind of geometrical transition, and mathematically equivalent to a second order phase transition [12,13], and it is static and has only one parameter, the

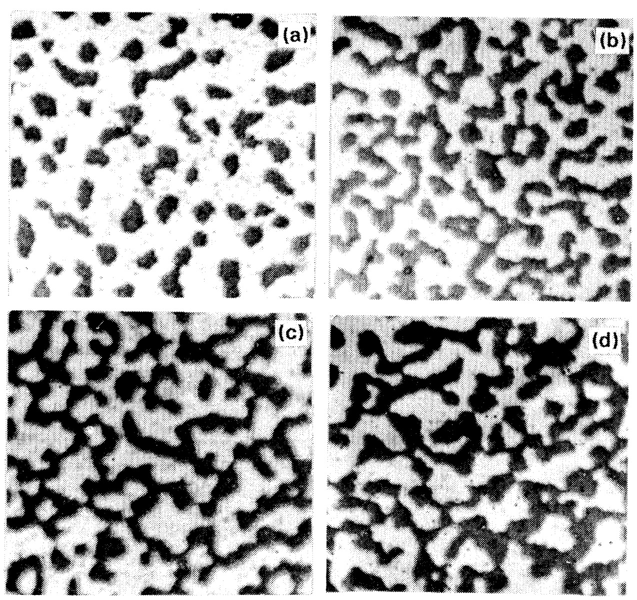

FIG. 1. Typical photos of aggregates at different initial concentrations under the field $V=0.55$ V. (a) $p=0.24$, (b) $p=0.38$, (c) $p=0.43$, and (d) $p=0.48$.

particle concentration p. The order parameter in percolation is the percolation probability $P_\infty(p)$, defined as the probability that a randomly chosen site belongs to an infinite cluster that will percolate the system. Note that the probability for a site being occupied is p. Just as the magnetization in magnetic phase transitions, $P_\infty(p)$ vanishes as a power law near $p_c P_\infty(p) \sim (p-p_c)^\beta$ for $p>p_c$, where the critical exponent β is shown $\beta=5/36\approx0.14$ and universal in two dimensions. Another essential problem in percolation is the cluster geometry, since many physical properties are associated with it. Below p_c, the scaling theory argues that finite clusters generally obey $N\sim R_g^{D'}$ with the exponent $D'=1.5$. Computer simulations have confirmed this, but the exponent is concentration dependent and increases from 1.5 to 1.75 as p changes from 0 to p_c [12]. Above p_c, any clusters of order ξ or larger are proved self-similar for length scales L below the correlation length ξ, and homogeneous for $L>\xi$ just as in other phase transitions. The correlation length ξ divergences at p_c with a power law $\xi\sim|p-p_c|^\nu$. Certainly the infinite cluster and the backbone obey this scaling behavior, or the density of the infinite cluster and of the backbone contained in a square of size $L\gg\xi$ should be a constant and should scale as $\rho(L)\sim L^{D-2}$ at a length scale $L<\xi$, where D is fractal dimension. Percolation theory predicts the fractal dimension of the infinite cluster and the backbone to be $D=1.89$ and $D^{\rm BB}=1.60$, respectively.

However, the percolation in our system is the coeffect of two parameters: particle density and time (i.e., the aggregation process). For only one sample with a particle concentration larger than percolation threshold p_c, the aggregation of particles is a kinetic process, and an infinite cluster spanning the system will emerge at some time t_c in the aggregation process which indicates a gelation transition. The time t_c is the gel time (or gel point), which is dependent on the magnitude of the interparticle attraction force. At the experimental condition here t_c is around 5 min, and the time for whole aggregation process is around 10 min. A small decrease in t_c is observed as p increases. For a series of samples with different concentrations, the increase in concentration will result in a percolation transition of the final pattern of aggregated particles. A concentration larger than the percolation threshold not only implies that an infinite cluster will occur in the aggregated patterns of particles, but also means that the aggregation process in this regime will undergo a gelation. Our interest in this paper is focused mainly on the percolation behavior of the aggregated particles.

In order to study whether the percolation transition occurring in our system can be described by the percolation theory, we analyzed all these features of the aggregated patterns. At first the pictures are digitized by using a scanner with a resolution of 240×240, with three pixels corresponding to about two particle diameters. Then the probabilities in the largest cluster P_N, i.e., the area fraction in the largest clusters, are calculated as a function of particle concentration p, and the results are shown in Fig. 2. Another series of data at the field strength 0.80 V per

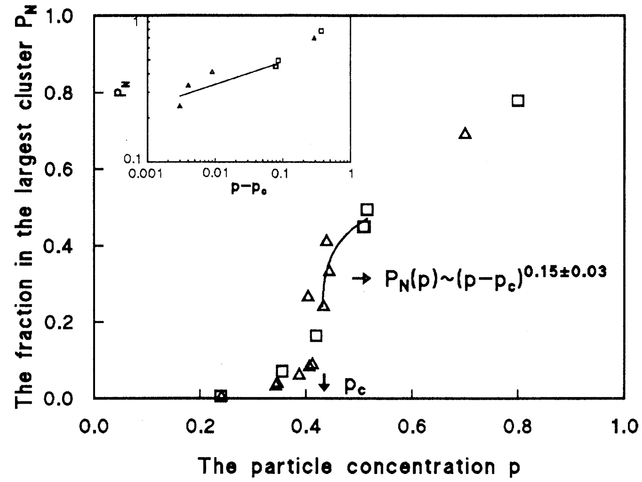

FIG. 2. The probability $P_N(p)$ of the area fraction in the largest cluster as a function of the particle concentration. The arrow shows the threshold $p_c = 0.42$. △, $V = 0.55$ V; □ $V = 0.80$. The solid line is a power fit $P_N \sim (p - p_c)^\beta$ to Δ and □ data points near p_c, and the inset is a log-log plot of P_N vs $p - p_c$.

50 μm are also presented. It can be seen that the date trend is very similar to that in SP[13]; little deviation can be seen between data of different field strength. For low p, P_N is negligible. As p is increased, P_N increases drastically near $p_c = 0.42$, and then increases almost linearly. From its definition, $P_\infty = \lim(P_N)$ for N becomes infinite. As will be shown below, the density of the infinite cluster is approximately a constant for length scale above ξ, and also ξ is less than the view size, therefore P_N for $p > p_c$ here can be approximately considered as the percolation probability P_∞. A best fit of the data near p_c ($p > p_c$) with $P_N(p) \sim (p - p_c)^\beta$ yields $\beta \simeq 0.15$, which is very close to the value $\frac{5}{36}$ in percolation theory. The error in Fig. 2 is only mean root deviation of the fit. We need to point out that since the exponent derived is sensitive to the value p_c used for data fit, and that the value of p_c cannot be accurately determined; thus a large uncertainty may exist in the β obtained.

The external geometries of the clusters in Fig. 1 are studied by using two methods, respectively for p below and above p_c. For $p < p_c$, we investigate the relation between the mass N and the radius of gyration R_g of clusters. One would expect $N \sim R_g^D$, where D gives the fractal dimension. For $p > p_c$, we study only the scaling of the mass density of infinite clusters. A square of linear size L is chosen centered on the infinite cluster, and the mass $M(L)$ within it is counted to obtain the mass density $\rho(L) = M(L)/L^2$. For fractal objects, one expects $\rho(L) \sim L^{D-d}$, where D is the fractal dimension.

Typical results for the clusters in Fig. 1 are shown in Fig. 2. For $p < p_c$, it can be seen in Fig. 3(a) that the clusters obey $N \sim R_g^D$ and the average dimension varies with the concentration. Interestingly, although the clusters in Fig. 1(a) are droplike and not fractals, the power law still exists between N and R_g.

For $p > p_c$, it can be seen in Fig. 3(b) that the densities of the infinite clusters are scale dependent. A lower cutoff (about six pixels) is obvious, which is due to the finite width of the cluster branches. Within the length scale $\xi \sim 66$ pixels, the density follows a power law. The best linear fit yields the fractal dimensions $D \simeq 1.66$ and 1.78, respectively, for the cluster in Figs. 1(c) and 1(d), where the errors are mean root deviations of the fits. Beyond ξ, the density becomes nearly flat. This fact is similar to the SP[12,13]; however, the fractal dimension is different from that in percolation, but close to the computer simulation result of DLCA at high concentration [5]. In percolation, the correlation length ξ, which should be proportional to the average cluster size, does grow very large as p goes to p_c. However, the correlation length for $p > p_c$ in the figure, obtained from the cross-

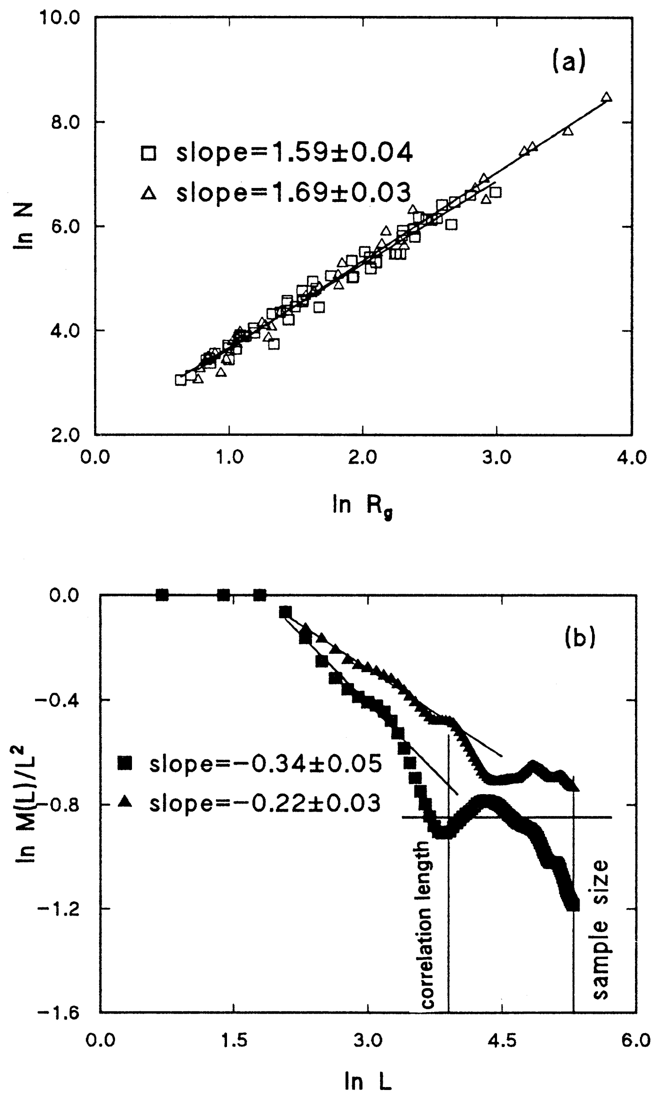

FIG. 3. Scaling analysis of the clusters in Fig. 1. (a) log-log plot of N vs R_g. □, $p = 0.24$; △, $p = 0.39$. (b) log-log plot of the density $\rho(L)$ of the infinite clusters within a box of size L around an occupied point. ■, $p = 0.43$; ▲, $p = 0.48$. The errors are the mean root deviation of the fit of data.

over of the density, is insensitive to the concentration p and does not diverge near p_c. Maybe this is related to the fluctuation in the density data, or to other reasons.

The fractal dimensions at different particle concentrations are summarized in Fig. 4. In the low-p limit, the dimension approaches 1.50, which is close to the value of RLCA or DLCA in the flocculation limit, and also to the value 1.50 in SP. As p increases, the fractal dimension increases nearly continuously, and at p_c approaches the value 1.75 of the computer simulation of Kolb and Herrman [5], and then saturates for $p > p_c$. The saturation fractal dimension is estimated about 1.75. The results of computer simulations of percolation are quite similar: for $p < p_c$, the average dimension obtained from the mass radius of gyration relation increases as p increases; for $p > p_c$, the fractal dimension equals a constant [12].

The geometry of the backbone is also an important problem in percolation because of its association with conductivity. If the cluster is considered to be composed of conductors, the current flows only through the backbone. In our experiment, we first cut off the dangling bonds of the infinite clusters in the pictures by a knife, and then digitize the pictures obtained. The mass densities are calculated in the same way as for the infinite cluster, and the results of the backbones of the infinite clusters in Figs. 1(c) and 1(d) are shown in Fig. 5. The behavior of the data is quite similar to that of the infinite clusters. Best linear fits of the data in the intermediate scaling regime yield the fractal dimensions of backbones $D^{BB} \simeq 1.60$ and 1.65. Taking their average as the fractal dimension of the backbone, i.e., $D^{BB} \simeq 1.63 \pm 0.05$, it is interesting that the fractal dimension of the backbone here is close to that value in SP, although the fractal dimension of the infinite cluster is different from that in SP.

Cluster-cluster aggregation (CCA) has generally been considered a good model for studying the sol-gel transition (polycondensation type) [5]. However, it cannot be applied here since there is no threshold in it, or its threshold $p_c = 0$. This has been shown by Saxton through

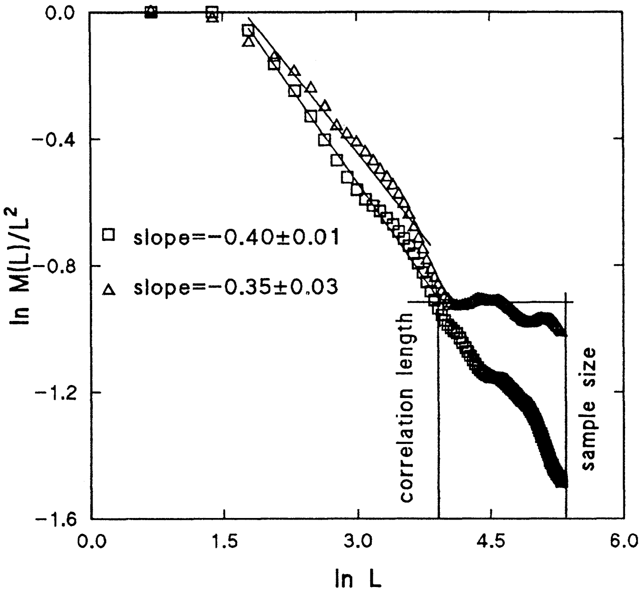

FIG. 5. Log-log plot of $\rho(L)$ vs L for the backbone of the infinite clusters in Figs. 1 (c) (□) and 1(d).

computer simulations [14], and also can be derived from simple scaling arguments. The cluster movability in CCA, $v \sim m^{\alpha}$ ($\alpha < 0$), is not zero, although it becomes indefinitely small as m grows larger, so there exists only one cluster at the end of CCA. Considering the scaling relation between the mass m and size L of cluster $m \sim L^D$ ($D < d$, d is the space dimension), and that the percolation threshold corresponds to an L equal to the system size L_0, one obtains the percolation threshold $p_c = m / L_0^d \sim L_0^{D-d}$, which is dependent on system size and tends to zero as L_0 goes to infinity.

The aggregation kinetics should be concerned with understanding the geometrical results. The two main kinetic effects are the growth and mobility of the clusters that determine the gelation mechanism. Here we describe the result for aggregation kinetics through direct observation. The mobility v of the clusters is observed to be inversely proportional to their mass, $v \sim m^{\alpha}$ ($\alpha < 0$), i.e., larger clusters move more slowly. Specifically, clusters of a mass larger than a maximum of about several ten particles cannot move. Due to these characteristics of movability, the aggregation process goes through two stages. In the first stage, some clusters larger than the maximum, which are static and unmovable and may be considered as the nuclei in crystal growth, are formed through clustering of clusters of different sizes. In the later stage, static large clusters grow by consuming the small clusters (mainly monomers) between them. When two neighbor clusters grow large and intersect, a larger cluster forms. In fact, the infinite cluster is composed of many finite clusters, therefore the fractal dimension and the scaling behavior should be different from those in SP. The fractal dimension should equal to that of finite clusters just below p_c.

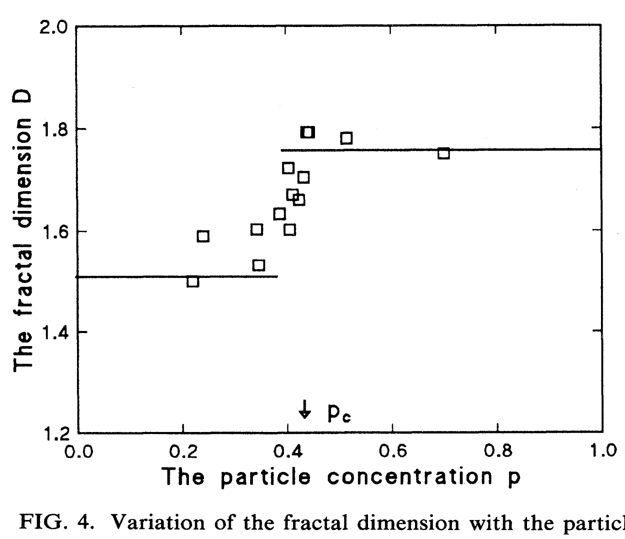

FIG. 4. Variation of the fractal dimension with the particle concentration.

Based on this, we consider that the CCA model should be modified by taking into account the movability characteristic to explain the percolation observed in this system. Defining a maximum mass above which the cluster movability equals zero, we have performed computer simulations in the algorithm of CCA. The preliminary results indicate that a percolation of aggregates indeed occurs as the initial concentration increases, and that the observed crossover may be explained with the modified CCA model.

Although these results may be only a specific phenomenon of this system and not universal to other aggregation processes such as aggregation induced by salts (Refs. [3,4]), where the CCA model applies, they are still significant at least in two aspects: (1) Percolation is affected not only by particle concentration, but also by the aggregation process. The threshold and scaling exponents of percolation would be different in the presence of aggregation. (2) These results should be universal for the modified CCA model where the movability of clusters of mass larger than one maximum equals zero. Further, we think this model is relevant to some actual cases. Recent experiments with lateral diffusion of fluorescent lipid probes have shown a percolation transition during lateral phase separation in binary lipid mixtures with percolation thresholds smaller than that of SP[15]. Saxton [14] used MDLA (multicenter diffusion-limited aggregation) to interpret the percolation. In fact, the centers in MDLA are equivalent to the nuclei observed in our experiments, thus the MDLA is just a simulation of the latter step aggregation in our system. However, the gel process is a kinetic process, and it is physically more reasonable that clusters of the gel phase are exactly unmovable as their masses grow larger or above some maximum; hence modified CCA may be more relevant.

In conclusion, a detailed structural analysis of the aggregated particles shows that, accompanying the crossover from flocculation to gelation, a percolation transition takes place which cannot be described by the theory of standard percolation, but the scaling behaviors of clusters are similar to the standard percolation, except that some scaling exponents are different. These results may provide a description of the crossover. Clearly more works are needed with other systems and computer simulations to determine how general these conclusions may be.

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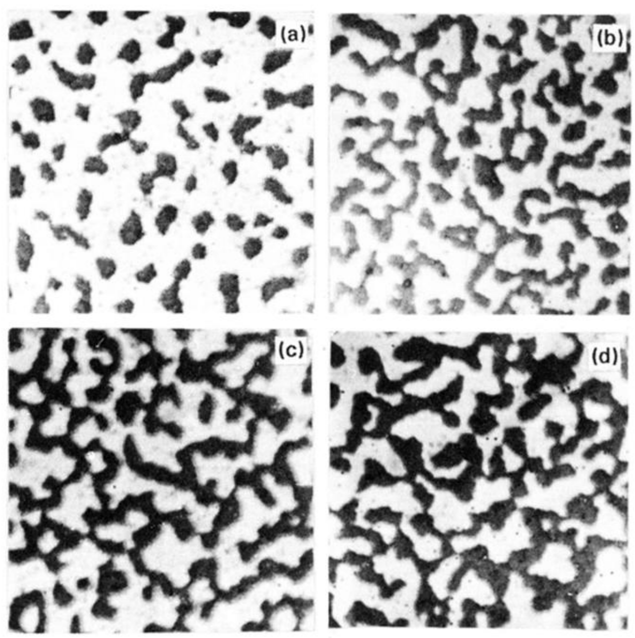

FIG. 1. Typical photos of aggregates at different initial concentrations under the field $V=0.55$ V. (a) $p=0.24$, (b) $p=0.38$, (c) $p=0.43$, and (d) $p=0.48$.