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Size distribution of latex aggregates in flocculating dispersions

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Résumé. — La distribution en taille d'amas de latex en croissance sous l'effet de chocs en diffusion brownienne est analysée par comptage direct des particules. Aux grands temps, la distribution en taille peut être exprimée sous la forme d'une fonction unique de variables réduites. Dans le régime asymptotique, le nombre d'amas varie comme l'inverse du temps et sur la base des équations cinétiques, on déduit que le coefficient de diffusion des amas est inversement proportionnel au rayon de giration.

Abstract. — The size distribution of latex aggregates undergoing Brownian motion is measured *in situ,* using automatic particle counting. The data are analysed from the point of view of dynamic scaling. At large time, an asymptotic distribution in terms of reduced variables is well observed. In that regime, the number of clusters is found to vary as the inverse of the time which on the bases of the theory means that the hydrodynamic radius is proportional to their radius of gyration.

Introduction.

The kinetic aggregation of small particles under Brownian motion is a widespread phenomenon, taking place in different areas in physics, chemistry and biology. The aggregation of colloids is an important example. On the bases of numerical simulations, a wealth of informations on the size of the cluster-cluster aggregates was gained during the last years and it is now well established that large colloidal aggregates formed by the association of many primary particles have a self-similar structure with a fractal dimension D equal to 1.75-1.80. This aspect is well summarized in recent reviews or conference proceedings [1-4]. From the experimental side, light scattering or small angle neutron scattering which yields the values of D from the power law decay of the structure factor was most often applied [5-8]. The growth of the size of the particles with time was also investigated by inelastic light scattering [5]. Only a few informations are however available on the size distribution of the particles and its time evolution. Schulthers *et al.* in using a resistive pulse analyser have studied the kinetic evolution of the cluster size distribution of antigen coated latex crosslinked by complementary antibody [9]. The size distribution was represented by a theoretical formula in which the role of the number of active sites was emphasized in terms of a *sticking* parameter and the application of percolation theory was also examined. More recently, a particle by particle counting method using laser light scattering was developed [10-12]. This technique permits accumulation of results only in a time period were the aggregation number remains very small.

In the present work, we present data on the evolution in a large time interval of the size distribution of particles formed by the aggregation of latex particles flocculating in presence of an electrolyte. The data which were obtained from automatic particle counting are analysed within the theory of dynamic scaling. In that context, it is worth to emphasize that many years ago, Friedlander *et al.* have investigated the size distribution of similar hydrosols [13]. They introduced the idea of a *self-preserved* distribution, but did not use the concept of fractal geometry which was not developed at that time.

Experimental and methods.

1. LATEX PARTICLES. — Latex of spherical shape and narrow size distribution was obtained by polymerization under emulsifier free conditions as reported previously [14]. They had following characteristics :

diameter $\bar{D}_v = 840$ nm (QELS), $\bar{D}_w = 866$ nm (Microscope), $\bar{D}_n = 860$ nm (Microscope), surface charge $\sigma = 1.43$ μC/cm^2, determined by conductometric titration using NaOH as titrant. The latex was in Na^+ form.

2. FLOCCULATION. — The Brownian motion flocculation experiments were carried out by adding aqueous electrolyte solution at pH 3.5 and $T = 18$ °C to a stable suspension at the same pH, so that the final composition was 0.16 g/l latex in 0.15 M NaCl aqueous solution at pH 3.5. In appendix A, it is demonstrated, taking into account the dimensions and surface charge of the colloid, that 0.15 M NaCl corresponds to a situation of *excess* electrolyte which ensures diffusion limited strong aggregation. Small samples of the coagulating suspension of approximatively 1 ml were removed at intervals, diluted 10^2 times with 0.15 M NaCl at pH 3.5 and analysed by the Coulter technique to obtain the particle size distribution as described in the following section. The sampling was made through a 3 mm bore needle at a slow rate to prevent shear effects to cause damage to the aggregates. The latex suspension was prior to use, ultrasonicated. From the calibration curve of the particle size analyser, the dimensions of the latex was found to be 900 nm, which compares quite well with the microscopic observations.

3. SIZE DISTRIBUTION DETERMINATION. — The recording of the number of aggregates comprising a given number of associated colloids was performed with the Coulter-Counter technique, using a 16 channel T Coulter with variable threshold adapter and an aperture of 50 μm [15]. When a particle or a cluster composed of many associated particles is within the orifice, the electrical resistance of the orifice (which is recorded as a potential difference), is assumed proportional to the total volume of colloidal matter which is gv_0 if the aggregate is composed of g primary particles, v_0 being the volume of the primary latex particle. A histogram is given in figure 1a ; the ordinate represents the % of total colloid volume stored in a channel i with energy thresholds corresponding to diameter D_i and $D_i + \Delta D_i$ with $\Delta D_i = (2^{1/3} - 1)\, D_i$. The distribution curve of the volume fraction $V(D)$ was obtained by interpolation, in spliting each channel i into n_i equal intervals, the width of each representing the addition of one primary latex particle, i.e.,

$$n_i = \frac{\pi}{6\, v_0} D_i^3 . \qquad (1)$$

When flocculation had progressed, so that no primary particles were left — cf. figure 1a — in which channels 1 and 2 are empty — $V(D)$ could well be fitted with the following distribution :

$$V(D) = C \exp[-h^2(\bar{D} - D)^2/D] \qquad (2)$$

where h and $\bar{D}$ are ajustable time depending parameters, C is a constant. From this, the particle size distribution $c(g, t)$ was computed :

$$c(g, t) = V(D)/V_D \qquad (3)$$

$$V_D = v_0\, g . \qquad (4)$$

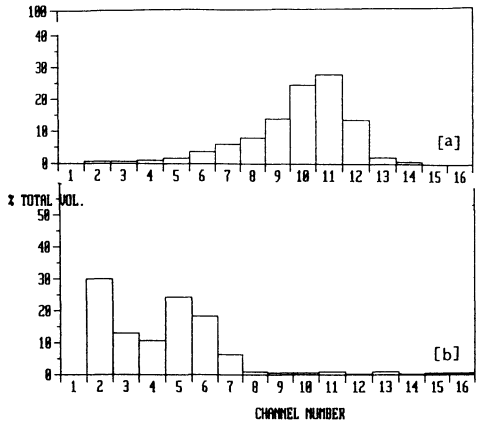

Fig. 1. — Example of histogram with the volume % of colloid in each channel : (a) when no primary (unassociated) particles are left ; (b) with a bimodal distribution when a fraction of 43 % primary particles are left.

When as illustrated by the bimodal distribution of figure 1b, non-associated primary particles are left, the volume distribution for all $g \geqslant 2$, was computed according to following expression :

$$V(D) = C\varphi' \exp[-h^2(\bar{D} - D)^2/D], \qquad D \geqslant \left(\frac{12\, v_0}{\pi}\right)^{1/3} . \qquad (5)$$

The total latex volume, noted C, includes non-associated particles of volume $C\varphi$ and associated particles of volume $C\varphi'$, φ' was computed *via* equations (6), (7) :

$$\varphi' = 1 - \varphi \qquad (6)$$

$$C\varphi = (0.7)^{-1}\, V_2 \qquad (7)$$

V_2 being the volume of non-associated particles stored in channel 2. The factor 0.7 originates from the fact that the setting of the apparatus was such that the dispersed latex, which is slightly polydisperse in size, was stored in channels 2 and 3 in a volume ratio of 7/3. Furthermore, channel 2 did not *contain* any 2 fold particles by virtue of the calibration scale of the technique. Clusters of g fold particles with $g \geqslant 2$ were stored in channels 3 to 16. The principles and practice of the Coulter method have been described elsewhere [15, 16]. Sources of errors are

essentially of two kinds : (i) the Coulter treats the aggregates as if they were solid systems ; this supposes that the electrolyte included into the enveloppe of the floc, has the same conductivity as in the absence of the latex. However the electrolyte conductivity is altered in the Debye-Hückel layer around the charged surface ; since in the present case, this layer in presence of 0.15 M NaCl has a thickness of 10^{-7} cm, which is indeed very small compared to the 8.6×10^{-5} cm particle diameter, the effect is less than 1 %. (ii) Shear of large aggregates is likely to occur at the entry of the orifice, however, if a floc is sheared at the entry, it is counted as the sum of its broken parts as they would pass simultaneously through the orifice and shearing does therefore not matter. The probability of coincidence (simultaneous passage of two or more aggregates) was also negligibly small in account of the experimental conditions.

4. SEDIMENTATION EFFECTS. — The Coulter technique is adapted for particles of diameter > 600 nm. In that range, sedimentation effects might not be negligible. However, because of the almost equal densities of latex and solvent, the effect is not important in the aggregation domain we considered. More indications on this point are given in appendix B.

Results and discussion.

1. THEORETICAL PART. — Friedlander [13, 17] has supposed a self-preserved distribution at large time of the form :

$$c(g, t) = N^2(t)\, \psi(gN(t)) \tag{8}$$

$$N(t) = \int_0^\infty c(g, t)\, \mathrm{d}g \tag{9}$$

$N(t)$ is the total number of aggregates at time t and the function ψ does not depend explicitly on time. The analytical form of $N(t)$ was determined by Lushnikov using a scaling argument and Smoluchowski's equations as starting point [18] :

$$\frac{\partial c(g, t)}{\partial t} = \int_0^g K(g-n, n)\, c(g-n, t)\, c(n, t)\, \mathrm{d}n - 2\, c(g, t) \int_0^\infty c(n, t)\, K(g, n)\, \mathrm{d}n . \tag{10}$$

The right hand side term is the increase in g fold particles caused by collisions between $g - n$ and n fold particles, while the second represents the decrease due to collisions between g fold and any sized particle. The collision frequency $K(g, n)$ is expressed as :

$$K(g, n) = a(R_g + R_n)(D_g + D_n) \tag{11}$$

R_g, R_n and D_g, D_n being the radius of gyration and the diffusion coefficients of g and n clusters respectively. a is a constant depending on the solvent viscosity. It was shown that equation (10) is invariant under following scaling transformations :

$$c(g/g_0, t) = g_0^2\, c(g, g_0^{(1-\lambda)} t) \tag{12}$$

$$K[g_0(g-n), g_0 n] = g_0^\lambda\, K[g-n, n] . \tag{13}$$

If the radius R_g and the diffusion coefficient D_g scale with the number g of associated particles like

$$R_g \sim g^\nu \tag{14}$$

$$D_g \sim g^\gamma \tag{15}$$

then the degree of homogeneity λ is related to the scaling exponents ν and γ by equations (11) and (13)-(15) :

$$\lambda = \nu + \gamma . \tag{16}$$

If equation (13) holds, $c(g, t)$ and $N(t)$ can be expressed as following :

$$c(g, t) \sim t^{-\frac{2}{1-\lambda}}\, \psi\left[g t^{-\frac{1}{1-\lambda}}\right] \tag{17}$$

$$N(t) \sim t^{-\frac{1}{1-\lambda}} . \tag{18}$$

In modeling the aggregation of Brownian particles by computer simulations, Kolb *et al.* [19] and Meakin [20] verified simultaneously equation (14) with $\nu = 0.554 \pm 0.038$ and more recently, Meakin *et al.* [21], in calculating the diffusion coefficient according to the Kirkwood-Risemann theory, have verified equation (15) with $\gamma = -0.544 \pm 0.014$. In both cases, the scaling behaviour was found to hold for cluster sizes as small as 4.

Equation (17) was also verified by Monte Carlo simulations and for the long time behaviour, the dynamic scaling function was found to be [22-24] :

$$c(g, t) \sim t^{-z(2-\tau)} g^{-\tau}\, f\left(\frac{g}{t^z}\right) \tag{19}$$

where τ and z are scaling exponents. However for $\gamma < 0$, which corresponds to the realistic physical situation, τ was found to be zero and equation (19) with $z = (1-\lambda)^{-1}$ is then similar to equation (17) derived from the conventional Smoluchowski equation (10).

2. EXPERIMENTAL RESULTS. — In figure 2, we have reported the size distribution $c(g, t)$ at different times in a time interval of 2 to 367 min. One observes that the distribution broadens with time and the apparition of a maxima at large time. After 6 h the largest cluster has a size of about 1.5×10^3 elementary particles and the average cluster size $\langle g \rangle$ is of the order of 28.

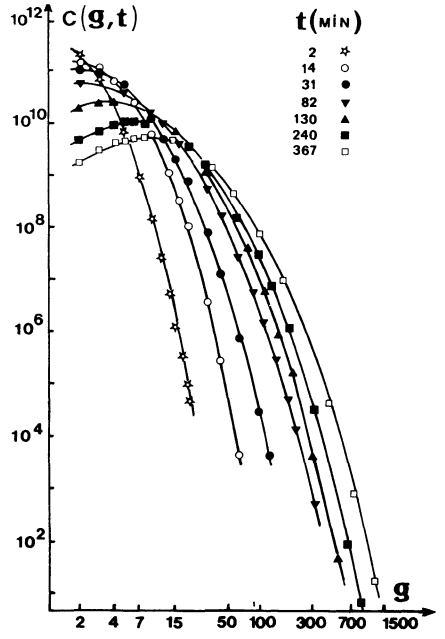

Fig. 2. — Particles size distribution at different times.

In figure 3 is reported Ln $[c(g, t)/N^2(t)]$ as a function of Ln $[gN(t)]$ for $t \geqslant 85$ min. All the data fall well on a single curve as predicted by equations (17, 18). In figure 4, data are reported for $t < 85$ min ; one notes that the size distribution departs from the asymptotic behaviour for $t < 30$ min. Indeed, at small time, the size distribution cannot be represented by a continuous function, nor can Smoluchowski's equation be expressed by the integro-differential form (10) ; therefore the scaling argument (12) is not valid at small time.

In plotting Ln $[N(t)]$ as a function of t, we obtain the representation of figure 5. For approximatively $t > 30$ min, $N(t)$ follows well a power law $N(t) \sim t^{-1}$ with the exponent defined to an accuracy of $\pm 5\,\%$. The small discrepancy of the points corresponding to the time period of 30 to 130 min is also reflected on the master curve in figure 3, where points (O) and (*) do not exactly follow the representation at large $gN(t)$ values. This slight divergence finds its origin in the fact that the set of points for $80 < t < 130$ min are results of a separate floccu-

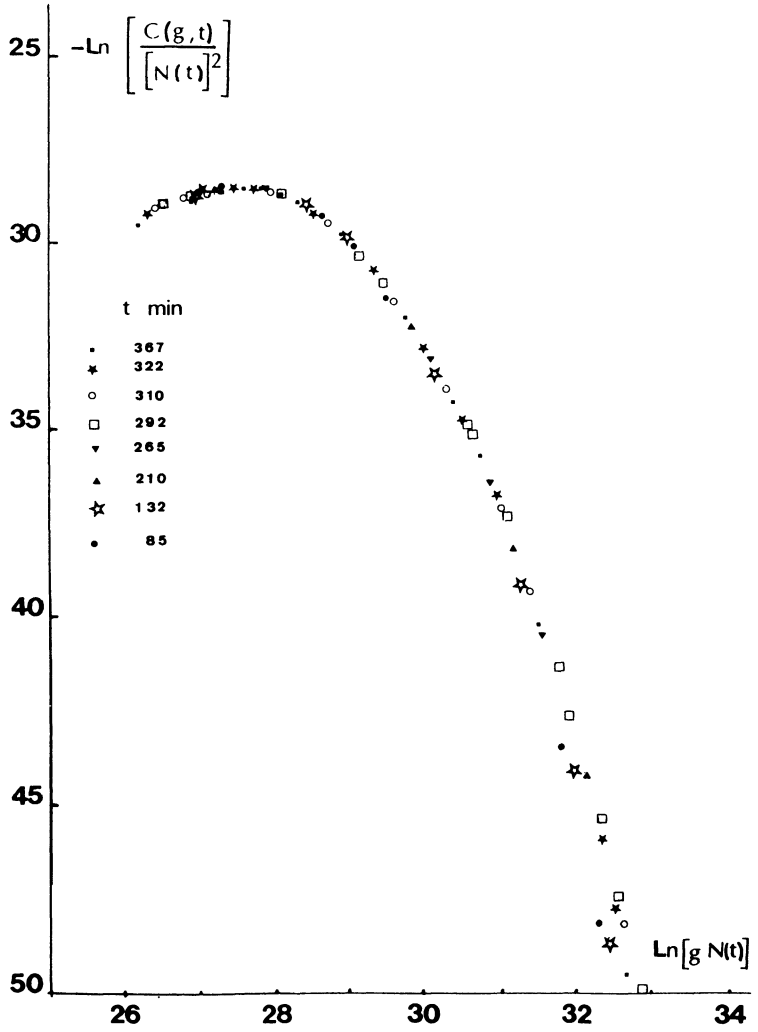

Fig. 3. — Size distribution represented according to equation (17) for $t \geqslant 85$ min.

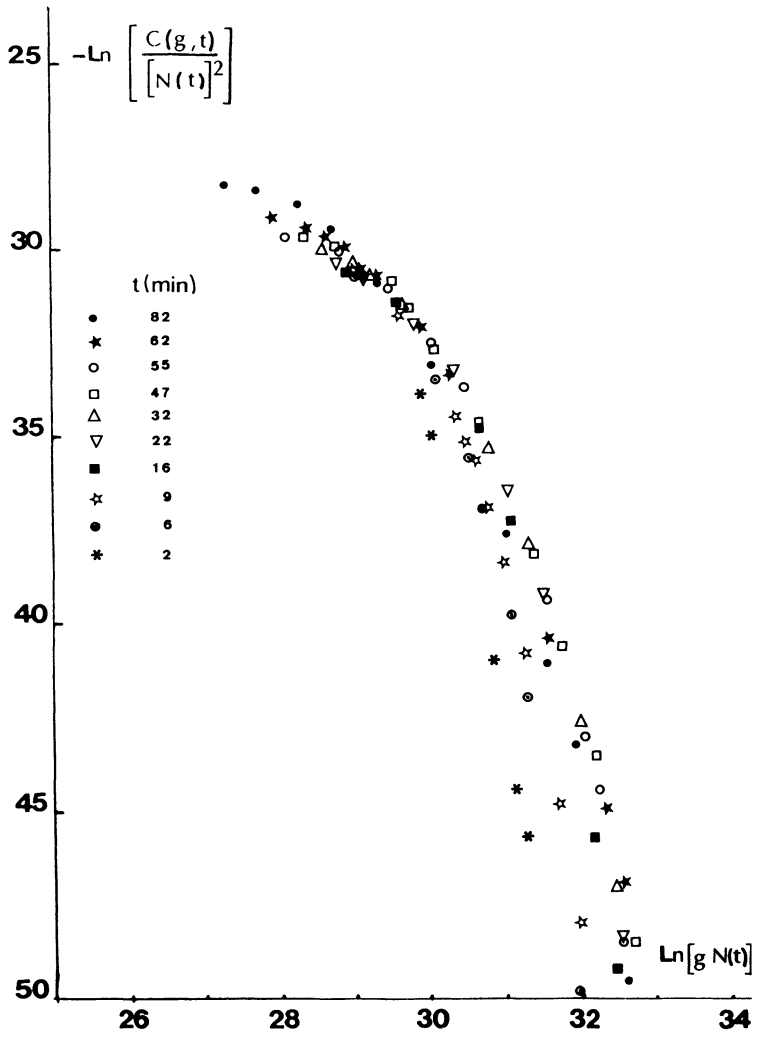

Fig. 4. — Size distribution represented according to equation (17) for $t \leqslant 85$ min.

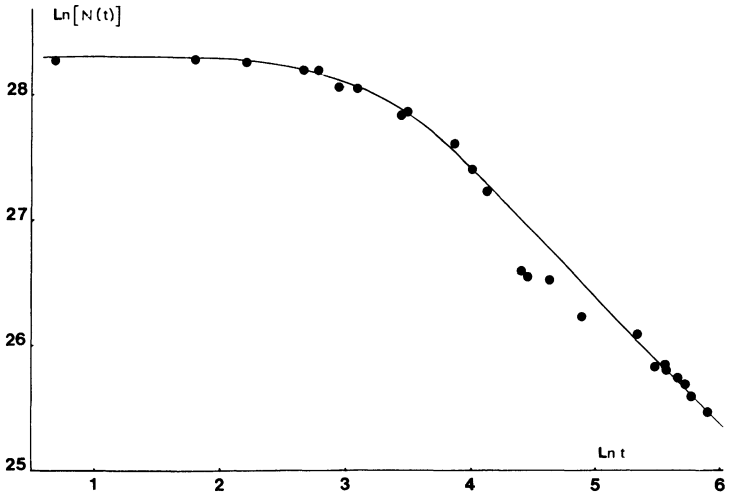

Fig. 5. — Total number of clusters as a function of time t (min), (cf. Eq. (18)).

lation run, reflecting therefore the more or less reproducibility of separate experiments performed under identical conditions.

According to equations (16) and (18), $N(t) \sim t^{-1}$ signifies $\lambda = 0$ or $\nu = -\gamma$. This observation is in good agreement with the recent results of computer

simulation experiments for aggregation of Meakin *et al.* [21]. From Meakin's values, $\nu = 0.554$ and $\gamma = -0.544$, the value of λ is 0.08. Though the γ values in Meakins computations are defined to ± 0.014, the author suggests that the slight difference in the exponents for R_g and the hydrodynamic radius $R_{h,g}$ could as well be attributed to a slow approach of $R_{h,g}$ to the asymptotic regime $g \to \infty$, as for polymers [25].

From figure 2, we note that a non negligible amount of small aggregates are present in the suspension even at large time ; in order to find $\lambda = 0$, we need for the scaling argument to be valid, that ν and γ do not vary with the cluster size over the whole size spectrum. Though we do not have any direct evidence, it is not unreasonable to assume this to be correct in considering the data for ν and γ obtained from the computer simulations as a function of the size g [1, 21]. The values of ν and γ obtained from simulation reflect typical constant fractal dimension for aggregation numbers as small as 3 or 4. For more details, the reader is referred to figure 2 in reference [21] and figure 14 in reference [1] which gives the representation of γ and ν as a function of the size g.

Cahill *et al.* in using a particle by particle light scattering analysis have recently discussed the time behaviour of 0.1 μm polymer latex undergoing aggregation in *excess* electrolyte [26, 27]. They investigated the time dependence of the concentration of singlets to tetramers. In analysing their data by Smoluchowski's equations, the best fit for the ν and γ values was 0.35 and 0.12 respectively. The low value of γ was questioned (the minimum value of γ which corresponds to the situation were particles do coalesce being 0.33). Agreement with the variation of the total number of aggregates $N(t)$ with time was achieved by allowing γ to vary linearly between 0.1 and 0.55 in a range of $g = 1$-50.

Clearly we analyse our data in a different way. The behaviour of the size distribution at large-time is investigated, and emphasis is lead on the description of the aggregation process in terms of an asymptotic distribution function of the reduced variable $g/\langle g \rangle$, $\langle g \rangle$ being the average cluster size.

It was shown that the function $\psi(x)$, $(x = g/\langle g \rangle)$, represented in figure 3, is the solution of an ordinary integro-differential equation (Eq. (37) in Ref. [18] and Eq. (21) in Ref. [28]).

Approximate solutions were derived in closed form for the upper and lower end of the distribution by Friedlander *et al.* [28]. Unfortunately in the latter work, the volume was taken as independent variable which supposes that particles of any sizes coalesce after collision to form a resulting particle of spherical shape with no included water (f.i., an oil-water emulsion). This is not the case here. An analytical curve for the reduced cluster size distribution was also given in reference [29], (cf. Eq. (7)). According to the authors, the distribution was derived for $\lambda < 0$, a comparison with our results with $\lambda = 0$, is therefore not relevant.

From simulations carried out on a three dimensional square lattice, it was shown that the mean-field Smoluchowski's equation (10) is appropriate as well as the form of $K(g, n)$ given by equation (11), to describe the aggregation of particles [30]. (In Smoluchowski's theory, fluctuation in concentration are neglected and only binary collisions are taken into account).

Conclusion.

We have examined the evolution of the particle size distribution of latex particles flocculating in *excess* electrolyte under the effect of Brownian collisions. At large times, an asymptotic time invariant size distribution function with a reduced size variable is well observed. This kind of approach does however not provide any information neither on the geometry of the aggregates nor on their kinetic properties, only the quantity $\nu + \gamma$ can be extracted from the results, with $R_g \sim g^\nu$ being the radius of gyration and $R_{h,g} \sim g^\gamma$ being the hydrodynamic radius ; we found $\gamma = -\nu$ which signifies that the Stokes radius is inversely proportional to the radius of gyration over the whole size distribution.

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Appendix.

1) In applying the DLVO theory, we need to calculate the Van der Waals potential V_A and the repulsive double layer potentials V_R :

$$V_A = -\frac{A}{12}\frac{R}{H} \tag{1}$$

$$V_R = 2\,\pi\,\varepsilon_0\,\varepsilon_r\,\varphi_0^2\,\mathrm{Ln}\,(1 + e^{-\kappa H}) \tag{2}$$

A is the Hamaker constant for polystyrene ($A \sim 10^{-20}$ J in Ref. [31]), R is the radius of the sphere, H the distance of separation, φ_0 the electrical surface potential and κ^{-1} the Debye-Hückel length :

$$\varphi_0 = \frac{\sigma}{\varepsilon_0\,\varepsilon_r\,\kappa}, \quad e\varphi_0/kT \ll 1 \tag{3}$$

$$\kappa^2 = \frac{2\, C_s\, N_{AV}\, e^2}{\varepsilon_0\, \varepsilon_r\, kT} \times 10^3 \qquad (4)$$

with $\sigma = 1.43\ \mu c/cm^2$, $c_s = 0.15$ M, $\varepsilon_0\, \varepsilon_r = 6.37$ (c.g.s.), it is easy to show that the electrical potential never exceeds the absolute value of the V.W. potential V_A :

$$\frac{A}{24\, \pi\, \varepsilon_0\, \varepsilon_r\, \varphi_0^2} = 7.14 \times 10^{-18}\ \text{cm} \qquad (5)$$

$$H\ \text{Ln}\ (1 + e^{-\kappa H})\big|_{max} = 2.5 \times 10^{-8}\ \text{cm}\ . \qquad (6)$$

2) For primary particles of diameter 860 nm, the drift ($cm\ s^{-1}$) due to gravitation is given by :

$$d_1 = \left(1 - \frac{\rho_0}{\rho}\right) \frac{mgD}{kT} \qquad (7)$$

the density ρ of the particle is 1.045, ρ_0 the density of the solvent is 1.005, g is the gravitational acceleration, m the mass of the particles, D their diffusion coefficient. Taking

$$D = 6\, \pi \eta R_0 \qquad (8)$$

we find for the largest experimental time :

$$d_1\ (6\ \text{h}) = 3.4 \times 10^{-2}\ \text{cm}\ .$$

For a typical experimental geometry (20 cm hight of suspension), the precipitation time at the beginning of the flocculation is large compared to the time of the experiment. As flocculation goes on, we have for a cluster size g :

$$\frac{d_g}{d_1} = \frac{gR_0}{R_{h,g}}\ . \qquad (9)$$

As $R_{h,g} \sim R_g$, R_g being the radius of gyration of a g-cluster. Taking $g \sim R_g^{1.8}$ we obtain :

$$\frac{d_g}{d_1} \sim g^{0.44} \qquad (10)$$

which gives a factor of 4.2 for the average cluster size $\langle g \rangle = 28$ for $t = 6$ h and a factor of 28 for the largest cluster size g of the order of 1500. For the very large clusters, diffusion might therefore not be the dominant mechanism causing the clusters to collide.

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