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ORIGINAL CONTRIBUTION

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Aggregation of laponite in the presence of magnesium ions and polyacrylic acid

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Abstract The average mass and size characteristics of ageing laponite/$MgCl_2$ and laponite/$MgCl_2$/polyacrylic acid were determined in aqueous dispersions at pH 10 using a Coulter counter and laser diffractometry methods. Comparison between mass and size characteristics showed the two systems to temporarily acquire a structure where particles are more densely packed. The relatively higher packing observed for laponite/polymer was attributed to conformational changes of the polymer adsorbed on neighbouring surfaces. Analysis of the reduced mass and size distribution functions confirmed the self-similarity of the distributions. The reduced mass frequency continuously decreased, while the reduced size frequency showed a linear decrease combined with bell-shaped populations. The volume packing observed for the laponite/polymer was attributed to a typical class of aggregates of large size, which was present at the maximal concentration in the bell-shaped distribution.

Key words Laponite · Polyacrylic acid · Aggregation · Mass distribution · Size distribution

Introduction

Laponite is an inorganic material synthesised using inorganic reactants. Solutions of salts of sodium, magnesium and lithium are combined with sodium silicate at controlled rates and temperatures. The resulting amorphous precipitate is partially crystallised by thermal treatment. The product is filtered, washed, dried and then milled to a fine white powder. The final product consists of platelike particles of very irregular shape, which have been idealised as discs of about 30 nm in diameter and 2 nm in thickness on the basis of light scattering experiments [1]. Aqueous suspensions of laponite are characterised by high viscosity and may develop gel-like structures even at small solid concentration [2]. Although details of the structure of the suspension and the origin of some special behaviour of the system remain unknown, many studies have attempted to correlate structural and surface characteristics. At low pH values, since the edge of the crystal bears positively charged groups and the upper and lower faces are negatively charged, card-house networks were expected to occur, whereas above pH 6, the platelets are negatively charged [3–5]. Nevertheless, as observed for montmorillonite, different types of association between basal and/or lateral faces may occur [6]. Piles of individual platelets separated by a few layers of water were determined to be present in suspension. Small- and large-scale organisations were observed by employing small-angle neutron and light scattering methods. Pignon et al. [7] gave a schematic representation of the structure of laponite suspensions at rest. The network is made of two types of characteristic aggregates. Subunits of oriented clay particles define the first length scale of about a few nanometres. Aggregates of tight isotropic distribution of subunits define the second length scale of about 1 μm. Loose connections of these micrometre-sized aggregates ensure an isotropic equilibrium structure. A scattering technique was usually applied to suspensions of solid content ranging from 0.2 to 4%.

Divergent observations on the suspension characteristics were attributed to slow dissolution of laponite, which releases magnesium ions in the aqueous phase, the rate and extent of the dissolution being pH-dependent [8, 9]. The presence of divalent cations is expected to exert a major influence on the colloidal stability of very dilute laponite suspensions and to fully modify the stability characteristics of the clay in the presence of polymer [10–13]. We found that, at very short times and in the absence of Mg^{2+}, laponite dispersions do not aggregate in the presence of various polymers, like polyacrylamide, hydrolysed polyacrylamide and polyacrylic acid, even in dilute NaCl aqueous solution. The different mode of actions of polymer in the colloid destabilisation were determined and characterised on the bases of numerical models of aggregation [14]. Usually, fractal aggregates result from such processes.

The situation may be not usual when very small colloids interact with polymer of high-molecular weight, a situation which has been thoroughly investigated by Stoll and Buffle [15–17] using numerical simulation and experiments. Elaissari and Pefferkorn showed that changes in the kinetics of aggregation of a small latex particle in the presence of polyelectrolyte of very high molecular weight was attributed to the progressively denser packing of aggregated particles during aggregate growth on the bases of a numerical model of aggregation processes [18–20]. According to the kinetic model of Smoluchowski and the corresponding kernel [21], compacting or extending of aggregate structures must have a strong impact on the cross-sectional area and the mobility of the aggregates. Thus, it is interesting to confirm this assumption by determining both mass and size characteristics of the growing systems.

Further interest in the laponite/polyacrylic acid system arises from the fact that polyacrylic acid induced oxide and clay destabilisation or dispersion, in a way similar to humic acid [22]; therefore, laponite/polyacrylic acid may serve as a model system to study the behaviour of the more complex system. It was recognised that aggregation of clay particles plays an important role in the transport of pollutants in estuaries. Since pollutants adsorb to the surfaces of bare inorganic particles or particles coated with natural organic matter, the fate of these particles determines the transport of the pollutants. When fresh water mixes with salt water, the suspended clay particles are destabilised and aggregate. The situation may be more complex when hydration layers oppose van der Waals forces and/or preclude polymer adsorption. Therefore, the present investigation may serve to determine the destabilisation characteristics of small colloids in the presence of polymer, in a situation where divalent cations induce clay instability.

Experimental

Materials

Laponite XLG, manufactured by Laporte, was kindly provided by the Laboratoire de Rhéologie, Université Joseph Fourrier, Grenoble. The chemical composition (w/w) is 66.2% SiO_2, 30.2% MgO, 2.9% Na_2O and 0.7% Li_2O, [23]. The laponite at a concentration of 0.1% was suspended in distilled water and the pH of the suspension was set to 10 by addition of NaOH. The suspension was degassed under vacuum for 2 h and then stirred for 12 h at 25 °C. A transparent colloidal solution was obtained, which served as the standard dispersion. At pH 10, dissolution of laponite was retarded at least for short periods [9].

Polyacrylic acid was synthesised by radical polymerisation, and was purified and characterised at our institute. Light scattering experiments yielded molecular weights of 83,200 and 367,000.

Methods

Particle counting

The mass distribution of the colloidal particles was measured with a Coulter Multisizer II (Coultronics) [24, 25] (aperture of 50 μm). Counting was performed on samples taken from the suspension after dilution by an electrolyte solution of ionic strength of 0.15 and at pH 10. The technique and methodology used for determining the aggregate mass distribution, $c(n)$ versus n, was described elsewhere [26]. Precautions were taken in order to perform nondestructive sampling. Transferring the sample from the initial medium of ionic strength of 5×10^{-3} to the medium of ionic strength of 0.15 is expected to shrink the structure of individual aggregates but to have no effect on the mass characteristics insofar as the suspension is highly dilute. The dilute suspension and the sample were then homogenised under very mild conditions for several minutes. No influence of the low-shear rate on systematic analyses was detected while maintaining low agitation for longer periods of times. To define the mass characteristics of the laponite clay in the presence of $MgCl_2$ and at pH 10, the dispersion was analysed immediately after mixing. Although a priori single crystals of laponite cannot be detected by the Coulter counter owing to their very small solid volumes, the dispersion contained aggregates characterised by a bell-shaped distribution with a peak at 1.24 μm. From the observation that the concentration of aggregates of diameter smaller than 0.7 μm dropped to zero, we concluded that single laponite particles were absent. The mass 1 was attributed to these aggregates of 1 μm^3. Larger aggregate of mass n are thus constituted by n of these units. This choice does not affect the value of the exponent of the kinetic power law used to characterise the aggregate growth nor the exponent characterising the aggregate mass distribution.

Particle sizing

The aggregate size distribution, $c(d)$ versuss d, was measured with a Coulter LS100 (Coultronics). The scattered light was focused with a Fourier optic. The intensity in the focal plane at certain distances from the optical axis corresponds to certain scattering angles. The instrument applies a software routine assuming a size distribution to calculate a radial intensity distribution. Owing to the large size of the basic units, Fraunhofer theory was applied so that the complex refractive index was not required. All parameters measured by the instruments are related to the volume of the aggregates.

Flocculation experiments in the presence of $MgCl_2$

The laponite dispersion at a concentration of 0.1% and at pH 10 was mixed with an aqueous solution of 0.004 M $MgCl_2$ and at pH 10 so that the final concentration was 0.05% laponite in 0.002 M $MgCl_2$. The pH was controlled and adjusted to 10 if necessary. The vessel was closed and freed of air. The system was rotated slowly to prevent deposition of the laponite aggregates. The time of mixing was set as the time zero of flocculation.

Flocculation experiments in the presence of $MgCl_2$ and polyacrylic acid

The aqueous solution of polyacrylic acid at pH 10 was added to the previous system aged for 1 h so that the final concentration of polyacrylic acid in the suspension was 0.008 or 0.006%. This procedure has been validated since the characteristics of the system laponite/$MgCl_2$ were determined to show no great variation during the first hour. This allows us to set the particle of mass 1 as the constitutive unit once more. The time of mixing laponite/$MgCl_2$ and polyacrylic acid was set as the time zero of flocculation.

Characterisation of the flocculating systems

To characterise the flocculating systems, the number-average mass, N, and weight-average mass, S, (Eq. 1) as well as the harmonic mean diameter, d_h, of the volume distribution (Eq. 2) were calculated using the distribution functions of the mass, $c(n)$ versus n, and size, $c(d)$ versus d. The relative volume, V/V_0, occupied by the dispersed aggregates is given by Eq. (3), where V_0 is the volume occupied by the aggregates determined just after mixing, when the mean harmonic diameter is $d_{h,0}$:

$$N = \frac{\sum_n nc(n)}{\sum_n c(n)}; \quad S = \frac{\sum_n n^2 c(n)}{\sum_n n(n)} \quad , \tag{1}$$

with $\sum_n nc(n) = N_0$, N_0 being the number of basic units contained in 1 ml solid matter.

$$d_h = \left(\sum \frac{c(d)}{d}\right)^{-1} \quad , \tag{2}$$

$$\frac{V}{V_0} = \frac{d_h^3}{N} \times \frac{N_0}{d_{h,0}^3} \quad . \tag{3}$$

In order to check the self-similarity of the aggregate mass distribution throughout the process, the reduced concentration of aggregates of mass n determined at time t, $c(n,t)S^2(t)/N_0$ is represented as a function of the reduced mass, $n/S(t)$. Similarly, the same representation is chosen for the reduced size distribution, $c(d,t)S^2(t)/N_0$ versus $d/S(t)$. From the concentration, $c_{app}(d,t)$, of aggregates of size d determined by laser diffractometry at time t, the true concentration, $c(d,t)$, has to be derived taking into account that the value of $c_{app}(d,t)$ is given for a constant volume constituted of solid matter and intraaggregate voids. Correlation between $c(n,t)$ and $c(d,t)$ requires that the single reference volume is the constant volume V_{sm} of solid matter composed of units of diameter d of 1.24 μm, which serve as reference in particle counting (V_{sm} is chosen to be 1 ml). The total volume, $V(t)$, developed by the $N^{-1}(t)$ aggregates of average diameter, $d_h(t)$, present at time t is given by [27]

$$V(t) = V_{sm} \frac{d_h^3(t)}{N(t)d^3} \quad . \tag{4}$$

Obviously, $c_{app}(d,t)$ must be corrected by the term $V(t)$ since $V(t)$ changes with time, whereas the total solid mass is constant. This correction makes the mass and size distributions strictly comparable.

Results and discussion

Laponite in the presence of $MgCl_2$

The weight-average mass, $S(t)$, and the number-average mass, $N(t)$, of the laponite aggregates are shown as a function of time in Fig. 1. Mixing immediately gives rise to aggregates of mass $N(t)$ and $S(t)$ close to 1.6 and 2.6 (Eq. 1), respectively, and an increase in the masses is inhibited for around 2 h. Then, the masses increase slowly with time as given by the scaling law (Eq. 5):

$$N(t) \propto S(t)\alpha t^{0.25} \quad . \tag{5}$$

The mean harmonic diameter, d_h, of the laponite aggregates is represented as a function of time in Fig. 2. The value of d_h does not vary with time for 1,000 min and then increases as $t^{0.7}$. The relative volume, $V(t)/V_0$, which is attributed to the suspended laponite aggregates is shown as a function of time in Fig. 3. The curve indicates the existence of a constant value of $V(t)/V_0$, then a decrease and finally a rapid increase after a period of around 2,000 min.

Laponite in the presence of $MgCl_2$ and polyacrylic acid

Average mass and size characteristics

Figure 1 represents $S(t)$ and $N(t)$ of the aggregates as a function of time for laponite/$MgCl_2$/polyacrylic acid

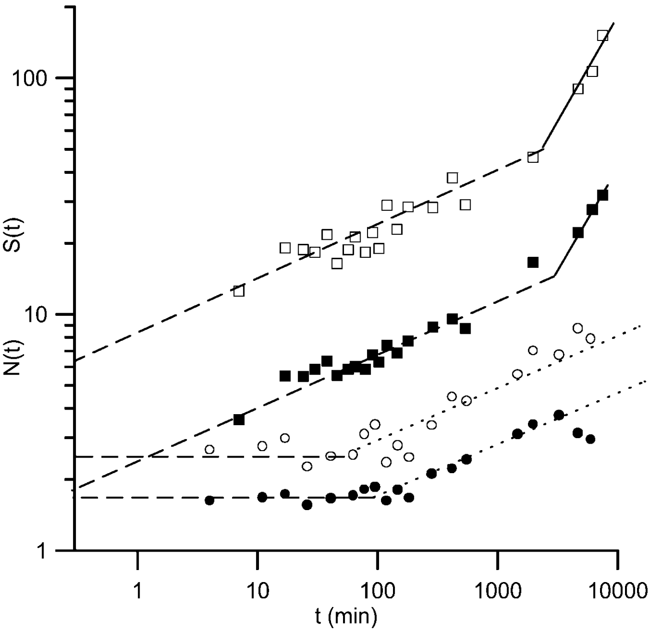

Fig. 1 Number-average and weight-average mass of aggregates as a function of time for laponite [$N(t)$, ●; $S(t)$, ○] and laponite/polyacrylic acid [molecular weight 83,200, $N(t)$, ■; $S(t)$, □]

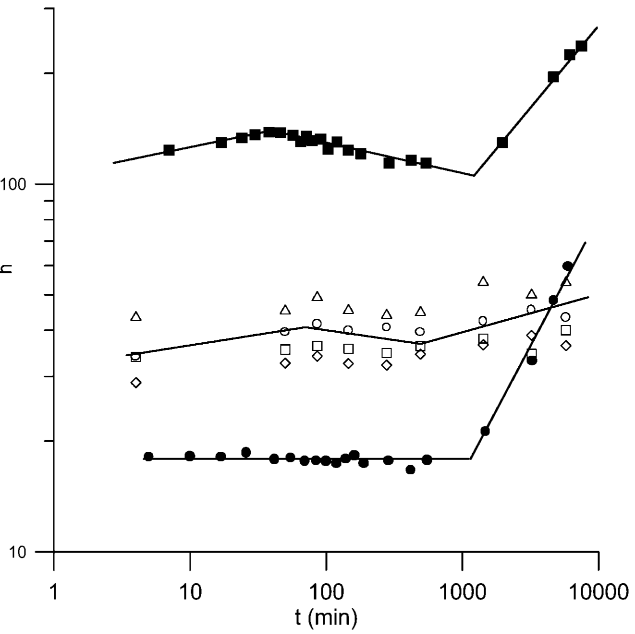

Fig. 2 Weight-average harmonic diameter, d_h, of aggregates as a function of time for laponite (●) and laponite/polyacrylic acid [molecular weight 83,200 (■) and 367,000 (*open symbols* correspond to four identical experiments)]

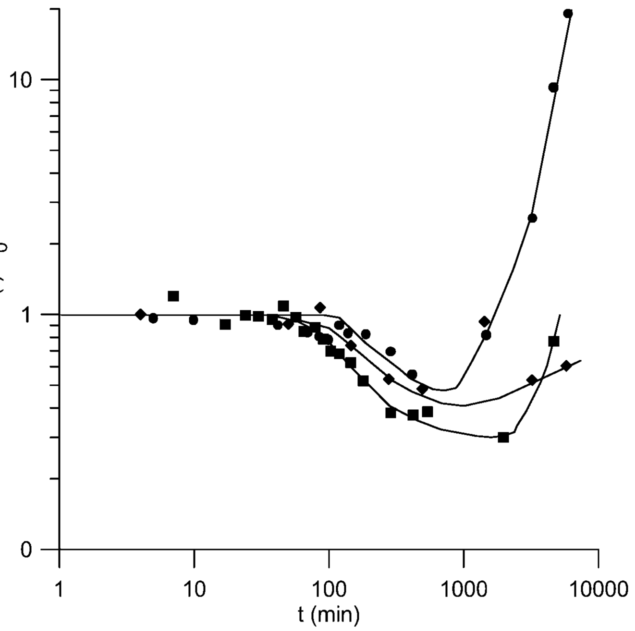

Fig. 3 Relative volume, $V(t)/V_0$, of aggregated laponite as a function of time for laponite (●) and laponite/polyacrylic acid [molecular weight 83,200 (■) and 367,000 (◆)]

(molecular weight of 83,200) at pH 10. Immediately after mixing and for a period of about 2,000 min $N(t)$ and $S(t)$ increase slowly (Eq. 6). After 2,000 min, the aggregate mass increases linearly with time (Eq. 7):

$$N(t) \propto S(t) \alpha t^{0.25} \ , \tag{6}$$

$$N(t) \propto S(t) \alpha t \ . \tag{7}$$

Since the $N(t)$ of the laponite and the laponite/polymer aggregates are quite comparable immediately after mixing, mixing of the constituents similarly reduces the number of particles which were present in the initial dispersion of laponite.

The growth of the aggregate masses in the presence of polyacrylic acid and $MgCl_2$ seems to be influenced by the molecular weight of the polymer. Experiments carried out using 0.006% polyacrylic acid of molecular weight 367,000 show the mass varying as $S(t) \propto N(t) \propto t^{0.13}$ (Fig. 4). The scattering of the values of $S(t)$ and $N(t)$ indicates the degree of reproducibility of the mass determination when various experiments were successively carried out under constant experimental conditions. We noted that larger aggregates immediately formed after mixing than shown in Fig. 1 when the growth was slower. Obviously, the experiments presented here do not correspond to optimal flocculation conditions in the presence of polymer, for which the formation of large flocs was instantaneous.

Figure 2 shows d_h of the laponite/polymer aggregates as a function of time for molecular weights of 83,200 (square) and 367,000. It was interesting to test the reproducibility of the size determination by these experiments with polyacrylic acid of molecular weight 367,000. Although the variation of d_h with time

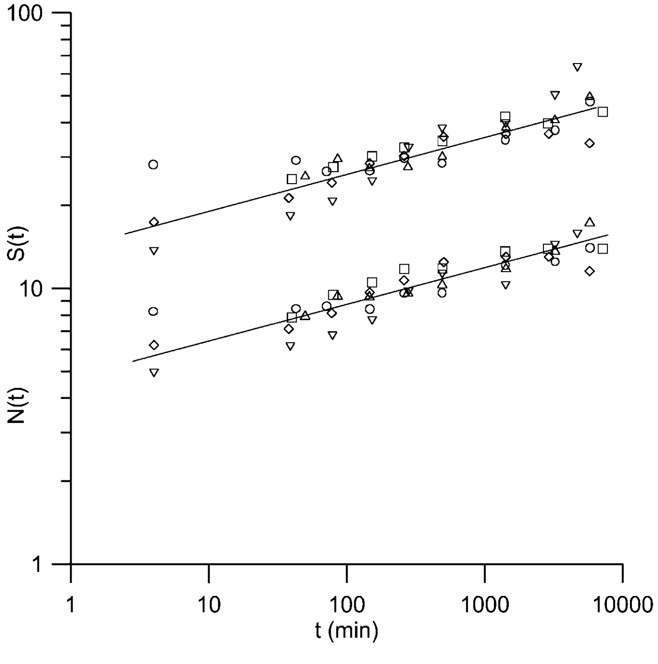

Fig. 4 $N(t)$ (*bottom*) and $S(t)$ (*top*) of aggregates as a function of time for laponite/polyacrylic acid (molecular weight 367,000). The five *symbols* correspond to five identical experiments

displayed the same shape, the scattering of the absolute values seems to indicate that the mixing procedure does not provide aggregates of well-fixed size and masses. This result confirms our usual observation that mixing gives only poorly reproducible absolute masses and size, whereas the exponents of the scaling laws are strictly identical.

Obviously, the variation of d_h with time displays different regimes and the normally expected increase seems to be strongly limited by a permanent process of slow compacting of the aggregate structure.

Figure 3 shows the relative volume, $V(t)/V_0$, which is attributed to the suspended laponite/polymer aggregates as a function of time. Although the three types of aggregates are compacted then expanded, compacting of laponite/polymer aggregates is more effective and retards expansion after 1,000 min.

Ageing of laponite suspensions in the presence of $MgCl_2$ or $MgCl_2$ and polyacrylic acid induced differences in the aggregate mass and size. For laponite/$MgCl_2$, the period of size stability exceeds that of the mass stability, and the volume compacting observed after 100 min in Fig. 3 seems to result from a high interpenetration of colliding aggregates rather than from a simple sticking which would increase the volume of the resulting agglomerate. Therefore, the volume reduction does not result from a decrease in size of individual aggregates but from the reduction in the number of aggregated particles. The final increase in size which develops from 1,000 min will not be discussed in the present context. For laponite/$MgCl_2$/polyacrylic acid, the volume reduction between 100 and 1,000 min shown in Fig. 3 results from the concomitant effects of the thickening of individual aggregates measured by d_h (Fig. 2) and the reduction in the number of aggregated particles measured by $N_0/N(t)$ (Fig. 1).

Mass and size frequencies

The reduced mass distribution for the laponite (curve a) and laponite/polymer (curve b) are shown in Fig. 5. The various points correspond to the aggregation period between 10 and 2000 min. It should be noted that the representation of curves a and b implies that the concentration, $c(n)$, of aggregates of mass n is the same for the two systems containing aggregates of the same average mass, $S(t)$, at least in the range of common $n/S(t)$ values. For laponite/polymer, the slope of the reduced distribution at small $n/S(t)$ values is –1, whereas values of –1.5 to –1.65 were derived from the slopes of the mass distribution for polymer-induced reaction-limited aggregation processes [28, 29]. During the period for which $S(t)$ and $N(t)$ grow as $t^{0.25}$ the system is further characterised by the correlation between time, average mass and mass distribution (8):

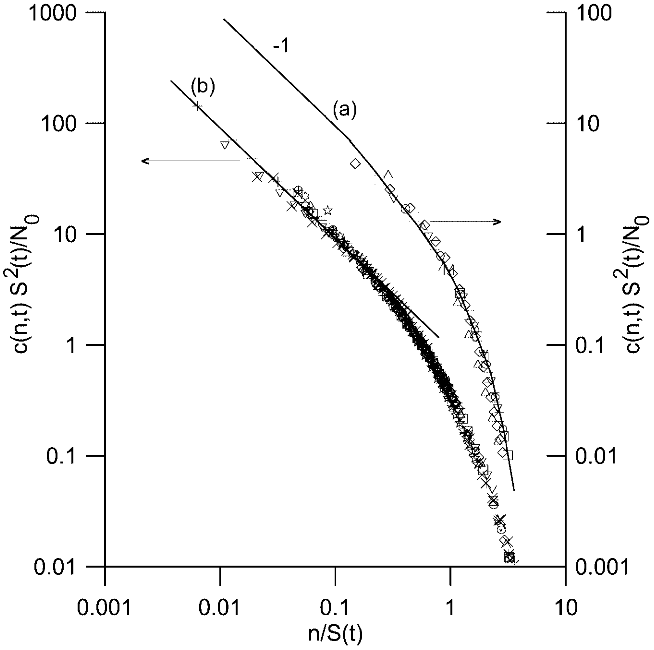

Fig. 5 Reduced mass distribution, $c(n,t)S^2(t)/N_0$, as a function of the reduced mass, $n/S(t)$, for aggregation periods up to 2,000 min for laponite (*a*, *right ordinate*) and laponite/polyacrylic acid (molecular weight 83,200) (*b*, *left ordinate*). The *symbols* refer to various times corresponding to some values of $S(t)$ reported in Fig. 1 in the domain of $S(t) \propto t^{0.25}$. The *black line* projects the reduced mass frequency of laponite/polyacrylic acid on that of laponite to show the self-similarity of the mass frequencies

$$nc(n,t) \propto t^{-0.25} \quad . \tag{8}$$

The reduced size distribution for laponite (curve a) and laponite/polymer (curve b) for aggregation periods between 5 and 2000 min and between 5 and 100 min, respectively, is shown in Fig. 6. For laponite/polymer, this corresponds to $S(t)$ values ranging from 12 to 20, which characterise the aggregate growth under constant $V(t)/V_0$ values close to 1 (Fig. 3). The size distributions represented by curves a and b show the presence of at least two aggregate populations of well-differentiated size. The first population is characterised by a monotonous decrease of $c(d,t)$ as $d^{-2.4}$ and the second one is bell-shaped, the maximal concentration $c(d,t)$ is obtained for aggregates of size d close to $3S(t)$. For laponite/polymer, the population varies as $c(d,t) \propto d^{-0.75}$. However, the aggregation modes of laponite and laponite/polymer become different for aggregates of the polymer system with decreasing $V(t)/V_0$: the $S(t)$ increase from 20 to 50 (Fig. 7).

The size-frequency curves in Fig. 7 also indicate the presence of at least two populations. The slope of $c(d,t)$ at small values of the reduced size, $d/S(t)$, is –1.3, while $d/S(t)$ of the aggregates present at the maximal concentration of the bell-shaped population decreases when the

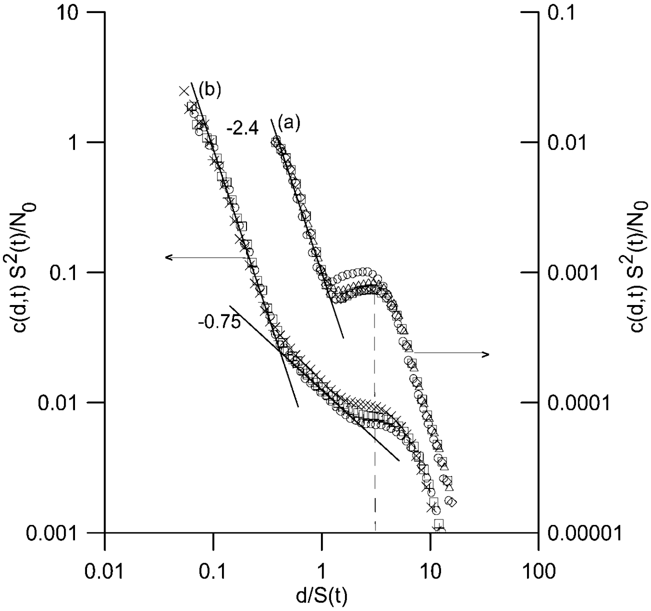

Fig. 6 Reduced size distribution, $c(d,t)S^2(t)/N_0$, as a function of the reduced size, $d/S(t)$, for laponite (*a*, *right ordinate*) up to 2,000 min and laponite/polyacrylic acid (molecular weight 83,200) (*b*, *left ordinate*) for $12 < S(t) < 20$, where $V(t)/V_0$ values are very close to 1

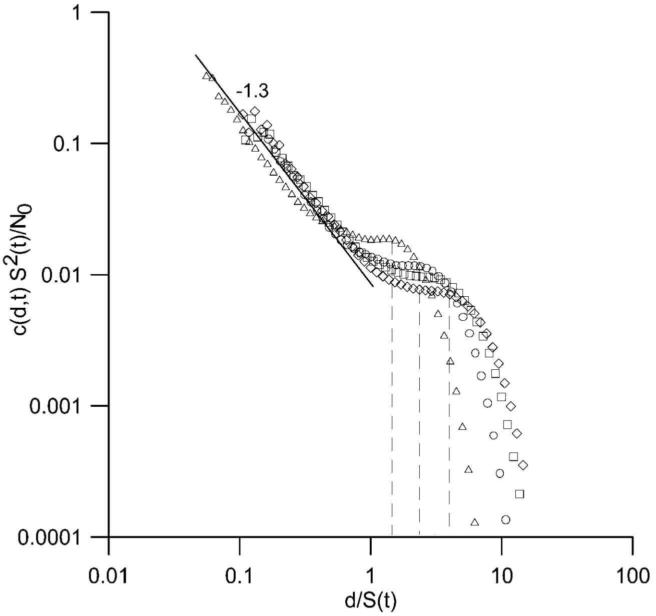

Fig. 7 $c(d,t)S^2(t)/N_0$ as a function of $d/S(t)$ for laponite/polyacrylic acid (molecular weight 83,200) for $20 < S(t) < 50$, where the $V(t)/V_0$ values are decreasing. The *vertical dashed lines* locate the peaks at $d/S(t)$ of 4, 3, 2.3 and 1.3, corresponding to increasing times of 91, 120, 180 and 540 min, respectively

aggregation period increases. As shown in Fig. 7, the size of the aggregates formed at the maximal concentration is $4S(t)$, $3S(t)$, $2.3S(t)$ and $1.3S(t)$ for increasing aggregation periods of 91, 120, 180 and 540 min. This result indicates that the thickening process seems to mainly affect aggregates of the second population, while the size distribution of aggregates belonging to the first population remains globally self-similar.

Destabilisation and aggregate growth

Since correlation between $S(t)$ and d_h was not found during the development of the aggregation process, information on the fractal dimension of the aggregates cannot be derived from the comparison of the mass and size frequencies, as previously observed for simpler systems [27]. Nevertheless, the self-similarity in the aggregate mass and size distributions (Figs. 5, 6) allows us to interpret the aggregation of laponite and laponite/polymer on the basis of the similar increase in the average masses as $t^{0.25}$. Although the initial mixing of laponite units, with polydispersity index $S(t)/N(t)$ close to 1.6, and the fact that polymer does not produce a larger reduction in the number of aggregates compared to laponite and $MgCl_2$, the sticking process immediately starts after mixing by generating aggregates with an $S(t)/N(t)$ close to 3.3. In the absence of polyacrylic acid, the growth process is apparently delayed in time. Moreover, the adsorbed polymer slightly changes the aggregate size-frequency curve a observed for laponite and generates curve b (Fig. 6), showing the presence of typical aggregates characterised by the monotonous size decrease of slope −0.75 around $d = S(t)$.

Taking into account both the similarity and the difference observed in the mass and size growth processes of laponite and laponite/polymer, we conclude that the usual mechanism involved in the fractal growth processes cannot serve to interpret all the experimental results. Mixing of laponite and Mg^{2+} may immediately give rise to aggregates of typical mass and size. These aggregates may resemble loose networks sustaining aggregation and fragmentation phenomena with no changes in the observed mass and size. After 2 h the small increase in mass is not accompanied by a concomitant increase in size, so we assume that aggregation merely occurs by interpenetration of loose networks of aggregates. Divalent cations exert the major effect [30, 31, 32, 33]: Mg^{2+} cations at a concentration of 2×10^{-3} mol/l serve as ligands between laponite and polymer as well as between the polymer molecules present at a concentration of 1.1×10^{-3} Eq/l. It should be noted that d_h of the laponite/polymer aggregates immediately attains values close to 30 and 120 μm, which largely exceed that of laponite. The large values of d_h may result from the very large "swelling" of the basic units induced by the Mg^{2+}-mediated polymer adsorption on the laponite subunits. This basic unit of average diameter of

18.11 μm (Fig. 2) contains such an amount of solid material which occupies in the coalesced form a sphere with a diameter of 1.5 μm [derived from the value of 1.8 for $N(t)$ at t near zero, Fig. 1]. "Swelling" of this structure occurs by penetration of the polymer molecules into the voids within the basic units and, further, by bridging of neighbouring subunits by macromolecules. Since the accessibility of the voids should be greater for polymers of small size with a higher mobility than for large ones, the swelling is expected to be larger for polymers of molecular weight of 83,200 than for polymers of molecular weight of 367,000. The size reduction between 60 min and a few hundred minutes (Fig. 2) is expected to be due to conformational changes of the polymers bridging the subunits [34–38]. As previously shown, adsorbed polymer undergoes conformational changes on starved surfaces, which induce flattening of the adsorbed macromolecules. The same phenomenon brings the particles closer when the polymer chains form links between opposed surfaces. This process seems to be slow since the final swelling of laponite/polymer aggregates finally has a slower rate than laponite/$MgCl_2$. Reconformation simultaneously affecting a great number of macromolecules connected to a great number of subunits may produce the observed reduction in d_h of laponite/polymer aggregates. Such aggregates merely resemble loose networks with the laponite subunits tightly connected by polymer bridges.

Definite interpretation on the aggregation mechanism for the last aggregation period where $S(t)$ and $N(t)$ increase linearly with t cannot be presented owing to the reduced number of experimental results and the unusually high increase in the aggregate size observed in that domain. Further complementary investigations are absolutely necessary to interpret such phenomena.

Conclusion

The limited growth of laponite/$MgCl_2$ or laponite/$MgCl_2$/polyacrylic acid systems cannot be viewed as resulting from the progressive sticking of colliding assemblies, which usually leads to fractal aggregates. Since the average size of the laponite aggregates does not increase, while the average masses slowly increase with time, the decrease in the concentration of aggregates of constant average size should be attributed to the interpenetration of colliding aggregates. Mixing of aggregates with polymer principally induces "swelling" as the average diameter increases from 18 to 30 or 120 μm. Ageing of these aggregates first preserves the initial structure as mass and size simultaneously increase. When reconformation of the polymer bridges induces dense packing, this process essentially affects aggregates of great sizes. Since the aggregate mass distribution is the same for laponite and laponite/polymer, the growth mechanism in the presence of polymer should mainly correspond to network interpenetration. As long as no packing affects the aggregates [for $V(t)/V_0 = 1$], for the two systems the reduced size frequencies of the smallest aggregates have an initial slope of −2.4. The observed small difference mainly concerns aggregates of diameter around $d = S(t)$. When packing occurs the initial slope of the size distribution of laponite/polymer decreases from −2.4 to −1.3 and the self-similarity is lost. The "swelling" and "packing" processes of the laponite/polymer aggregates are attributed to adsorption of polymer on the aggregate subunits and interparticle bridging and to the reconformation of the polymer chains constituting the bridges.

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