Long-term gelation of laponite aqueous dispersions

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(Received 24 December 1997)

The origin of the long-term gelation of clay suspensions was recently questioned. We have investigated this problem by looking at the chemical stability of the laponite solid particles as a function of the preparation, the long-term storage, and the age of the suspensions. Under ambient atmosphere, Mg^{2+} is released from the laponite, suggesting that carbon dioxide from the atmosphere promotes acidification of the dispersions, resulting in a progressive laponite dissolution and a slow increase of the ionic strength. These factors induce a sol-gel transition, leading to the observation of fractal aggregates above the micrometric length scale. Such an evolution is not observed if the samples are carefully handled under N_2 atmosphere for a long period of time. In these circumstances, the suspensions stay free of Mg^{2+} and undergo a fluid-solid transition along a defined transition line in the plane (volume-fraction–ionic-strength). In this situation, one interesting question concerns the unusual coincidence between a mechanical transition and an incomplete nematic transition. [S1063-651X(98)51005-7]

PACS number(s): 82.70.−y

INTRODUCTION

In recent years, the suspensions of colloid platelike clay particles of laponite have been the subject of intense investigations. Of prime importance was the study of the morphology effect of the colloidal particles, and their anisotropy, on the occurrence of phase transitions [1–5]. Many methods were used in order to clarify the mechanisms of gelation of these suspensions, the structure of the gel phase, and the rheological properties. Recently, Gabriel *et al.* have observed typical nematic liquid-crystal textures for laponite suspensions in the gel or solid phase [6]. At low particle concentration, in the sol or liquid phase, the suspensions observed between cross-polarizers appear isotropic. In the gel phase two successive domains are observed: an optically isotropic gel at low particle concentration and a permanent nematic one at a higher concentration. This study focused on the nematic liquid-crystal texture of laponite but it did not shed light on the structure of the nonbirefringent gel phase and on the nature of the sol-gel transition.

The sol-gel transition of laponite suspensions was also investigated using Monte Carlo simulations [7,8]. Each charged particle of laponite and its double layer was considered to be a rigid point quadrupole. The numerical calculations showed a sol-gel transition when the particle concentration was increased. The structure of the model gel suspension was found to be compatible with the ''house of cards'' structure, proposed some years ago by Van Olphen [9], in which the particles are edge to face with each other and without any direct contact. However, no experimental evidence exists of such structure in the case of laponite suspensions and the computed phase diagram does not reproduce the salt effect.

The large scale of the structure of the gel phase (above 1 μm, wave vector $Q < 10^{-4}$ Å) was also investigated by means of static light scattering (SLS) measurements by Pignon *et al.* [10,11]. These authors confirmed the general feature of the previously published data at large Q ($>10^{-4}$ Å) [1,3]. Their insight concerned the evolution of the scattering intensity at very large length scale, over a large period, after sample preparation. It was shown that the suspensions of laponite, prepared beyond a critical volume fraction and aged more than ten days, exhibit a fractal behavior of dimension D, at micrometric scales [11]. Above the sol/gel transition point, the data show two distinct gel structures with two different fractal dimensions. Just after the transition point and below a critical concentration value, the structure of the gel becomes fractal with D increasing regularly from 0 for fresh samples and reaching 1 for suspensions aged more than 100 days. It was noted that as the fractal structure grows, the mechanical properties of the sample evolve to those of a gel. For suspensions having concentration above the critical value, the fractal dimension increases with the age of the suspensions but seems to stabilize around 1.8 for suspensions having aged 300 days or more. The 1.8 fractal dimension is close to the classical value for the three-dimensional (3D) cluster-cluster aggregation [12,13].

The results of Pignon *et al.* have similarities to those of Kroon *et al.* [14,15]. These authors observed long-term changes in the mechanical comportment of laponite suspensions by performing a dynamic light scattering (DLS) on suspensions of different ages. By recording the time evolution of the second moment of the scattering intensity, Kroon *et al.* observed that at a particular time after preparation, the measured function changes from a smooth value characteristic of a fluidlike structure to widely scattered values. This delay coincides with the gelation time at which the transition from a liquid to a gel phase occurs. It was shown that the gelation time increases exponentially as the clay concentration decreases, becoming longer than 2000 hours for clay concentrations below 2 wt. %. Thus, their study was limited to suspensions with higher clay concentrations. It was also reported that a stock sample of 1 wt. % concentration showed a gel structure after a period of one year, indicating

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a very low threshold for the sol-gel transition. Interestingly enough, these authors proposed to consider the laponite gelation as a glass transition.

All of these recent investigations raise some questions concerning the phase diagram of laponite suspensions that we have previously reported [1]. They suggest that our measurements were taken too rapidly and before reaching the gel phase, leading to an overestimation of the critical concentration of the transition [10,11,14,15]. At the same time the structure of the gel phase became disputable, depending on some kinetic history, which can be different from group to group. From our experiments, we generally observed that aged suspensions prepared at low particle concentrations, ~ 1 wt. %, do not gel at low ionic strength. However, we have found that some suspensions exhibit a rapid gelation time, less than two months, when other samples of the same concentration remain in a liquidlike phase even one year later. All of these observations raise interesting questions on the long-term evolution of the laponite suspensions and the mechanism behind it. For this purpose, we started a study on the long-term gelation of laponite suspensions by checking the evolution of the chemical composition of the samples aged between 0 and 300 days. This chemical analysis was correlated with the mechanical behavior of each sample and with the structural evolution as probed by static light scattering.

EXPERIMENTAL PROCEDURE

The suspensions investigated are those of laponite RD, a hectorite synthetic clay, dispersed in doubly distilled water at pH 10 by addition of NaOH. This choice of the pH is chosen since the dissolution of the clay particles is avoided due to the very low concentration of hydrogen ions, prohibiting the release of silicate, Na^+, Li^+, and Mg^{2+}. At lower pH values, laponite dissolves according to the following equation [16]:

$$Si_8Mg_{5.45}Li_{0.4}H_4O_{2\,4}Na_{0.7}+12H^++8H_2O\rightarrow0.7Na^++8Si(OH)_4+5.45Mg^{2+}+0.4Li^+. \tag{1}$$
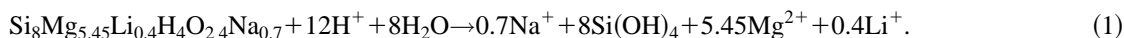
The chemical analysis of the laponite powder reveals the existence of a small amount of calcium corresponding to a maximal concentration of $10^{-4}M$ (assuming a complete dissolution of Ca^{2+}) in suspensions prepared at 1 wt. %. Some suspensions were purged with N_2, sealed and stored in a glove box in a N_2 atmosphere. Other suspensions were sealed and stored at room atmosphere.

The analysis of dissolved Mg^{2+} was carried out using complexometric titrations [17]. The method is based on the formation of Mg^{2+}-eriochrome black T complex. The suspension color change, associated with the formation of this complex, is from blue to red. The color remains blue for suspensions free of Mg^{2+}. The concentration of Mg^{2+} is determined by titrating with ethylenediamine tetra-acetic acid (EDTA). At the end point the color changes from red to pure blue.

In order to measure the scattering intensity in the very-low-Q range, we have used a setup comparable to the one built by Rouw *et al.* [18]. A laser beam at 6328 Å was directed onto the sample contained in an optical cuvette of a 1-mm-length path. The scattered light was collected by a rotatable mirror, located very close to the cuvette, and directed towards a photomultiplier. The linearity of the photomultiplier was checked using several neutral optical-density filters. Scattering of diluted suspensions of monodisperse latex particles, having a diameter ranging from 2000 to 20 000 Å, was used to validate the accuracy of our experimental setup. Successive light-scattering spectra were recorded, for each suspension studied, by changing the illuminated point on the sample. The final curve was averaged over all of the recorded spectra.

RESULTS AND DISCUSSION

As already mentioned, two sets of laponite suspensions were prepared with the same pH (pH$=10$), but having dif-

ferent solid fractions. The first set of samples (set 1) was purged with N_2 after preparation, sealed, and stored in a glove box under N_2 atmosphere. The second set (set 2) was sealed and stored in an ambient atmosphere. The amount of Mg^{2+}, due to the dissolution of the laponite particles, and the mechanical behavior of each sample are reported in Fig. 1 for the suspensions at $C=1$ wt. % solid concentration. Initially, all these samples were in a liquidlike state. All suspensions that contain Mg^{2+} were part of set 2. The suspensions with a zero magnesium concentration have never been exposed to the atmosphere. All the samples containing more than $5\times10^{-4}M$ Mg^{2+} formed a viscoelastic gel. Interesting enough is the evolution observed for the sample $s1$: it remained a liquid for a period of 170 days and the determina-
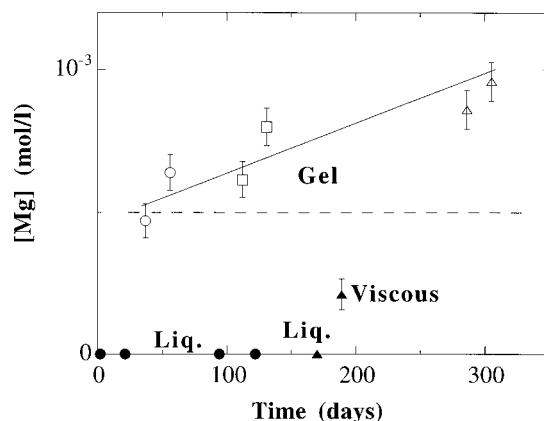

FIG. 1. Determination of the concentration of magnesium ions as a function of the age of the suspensions at $C=1$ wt. % and $10^{-4}M$ initial ionic strength (NaOH). ($\bullet$) sample $s0$, part of set 1, is liquid; ($\blacktriangle$) sample $s1$ was part of set 1 until first analysis. ($\bigcirc$, $\square$, and $\triangle$), part of set 2, are gels. The horizontal line is the limit of gelation. The continuous line is drawn as a guide.

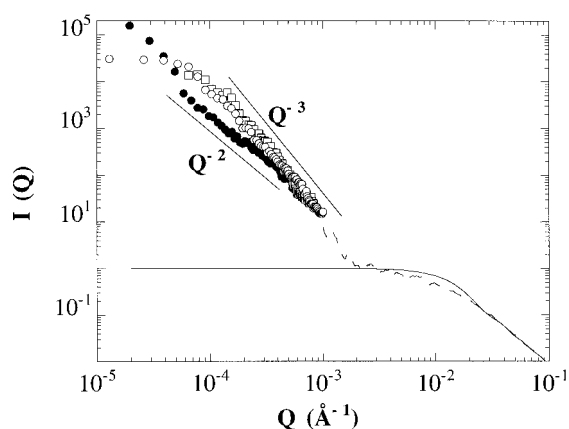FIG. 2. Static light-scattering measurements on laponite suspensions. ($\bigcirc$, $\square$) viscoelastic gels free of magnesium at pH$=10$; age$=50$ days, $C=2.35$, and 3.5 wt. %; [NaCl]$=2\times10^{-3}$ and $6\times10^{-3}M$, respectively. ($\bullet$) viscoelastic gel at 1.5 wt. %; [Mg^{2+}] $=10^{-3}M$; pH$=10$, and age$=280$ days. (- - -): small-angle x-ray scattering data for a viscoelastic gel at 3.85 wt. %; [NaCl] $=10^{-2}M$, pH$=10$. The continuous line is the form factor of laponite.

tion of Mg^{2+} did not show any chemical dissolution of the particles (absence of Mg^{2+}). After this first analysis, the sample was stored in an ambient atmosphere for 19 days. On second analysis, it showed a non-negligible concentration of Mg^{2+} associated with the formation of a very viscous suspension.

The presence of calcium can interfere during the colorimetric titrations. However, the amount of Ca is well below the measured ionic concentration and cannot explain the total increase of the ionic strength.

Two conclusions can be drawn. (i) Magnesium ion concentration in laponite suspensions increases for all suspensions having been exposed to the ambient atmosphere. (ii) A viscoelastic gel phase is observed above some Mg^{2+} concentration.

The structure of the viscoelastic gels was examined by SLS. Figure 2 shows the light-scattering intensity of two different samples with $C=2.3$ and 3.5 wt. % at an ionic strength (NaCl) of $2\times10^{-3}M$ and $6\times10^{-3}M$, respectively. Also shown in this figure is the SLS intensity of a third sample with $C=1.5$ wt. % and $10^{-4}M$ initial ionic strength (NaOH). The chemical analyses established that the first and the second gels, prepared by the osmotic stress method and stored in a N$_2$ atmosphere, were free of magnesium ions, while the third one at $C=1.5$ wt. %, which was part of set 2, contained $10^{-3}M$ Mg^{2+}. This last sample was initially liquid, and the SLS intensity was very weak. To recall, we show in Fig. 2 the small-angle x-ray scattering curve, previously recorded for a suspension of 3.85 wt. % solid concentration at $10^{-2}M$ ionic strength (NaCl) [1]. The effect of the presence of magnesium in the suspensions is observable in the SLS data in the Q range from 5×10^{-5} to 5×10^{-4} Å^{-1}. The viscoelastic gels, free of magnesium ions, show a divergence in the scattering intensity going as Q^{-3}, in agreement with the previously reported data obtained in the Q range from 5×10^{-4} to 2×10^{-3} Å^{-1} [1,3], and followed by a plateau at very small Q. The sample containing Mg^{2+} exhibits a nearly Q^{-2} divergence up to $Q\rightarrow0$, and this

result is in good agreement with the data reported by Pignon *et al.* for aged suspensions of the same particle concentration [11].

These experiments show a direct relationship between the presence of magnesium ions and the mechanical and structural behavior of the aged suspensions. The presence of magnesium is due to the dissolution of laponite particles. As the congruent dissolution requires the presence of hydrogen ions [16], it seems that contamination of the suspensions by atmospheric carbon dioxide is sufficient to promote the acidification of the samples. Thompson and Butterworth showed that a very low H$^+$ concentration, with a pH of the suspensions ranging between 8 and 9, promotes the dissolution of the laponite particles [16]. These results support our measurements concerning the role of exposure to ambient atmosphere and the resulting effect in structural and mechanical properties.

Our investigation questions the temporal evolution of the gelation. Let us consider the phase diagram of laponite suspensions. We have shown previously that at a solid concentration of 1 wt. % the transition occurs for an ionic strength of $3\times10^{-3}M$ with monovalent ions [1]. A simple view of Fig. 1 leads to an estimation of the Mg^{2+} concentration at which the gelation occurs: roughly $5\times10^{-4}M$. This value allows for the determination of the corresponding ionic strength given by $I=\Sigma c_i z_i^2$. The sum considers all the counterions of concentration c_i and valency z_i. If we consider the contribution of the ions resulting from the dissolution of the particles (Na$^+$, Li$^+$, and Mg^{2+}), and the contribution of the initial ionic strength, we find a final ionic strength of 2.2 $\times10^{-3}M$. This value is very close to the one estimated from the phase diagram [1]. This resulting ionic strength of the suspensions can explain the long-term gelation of laponite, using the phase diagram. However, the structure of the gels is different, depending on the presence of magnesium ions. One should remember the effect of divalent ions in colloidal suspensions. It is known that the presence of these kinds of ions induces ionic correlations that promote attractive interactions between the colloidal particles [19]. This phenomenon can explain the fractal structure of aged samples observed in laponite suspensions in the very-low-Q domain. It is worth noting that clay suspensions having divalent counterions are unstable and flocculate rapidly.

CONCLUSION

The long-term gelation of laponite suspensions was explained by involving a long-term mechanism leading to the formation of glassy systems having a fractal structure. Our results confirm the reported long-term gelation mechanism. However, we show that chemical modification of the colloidal particles can play a central role in the evolution of the colloidal system. In an ambient atmosphere, dissolution of the particles increases the ionic strength and promotes the liquid-solid transition. At the same time, the release of divalent cations can promote aggregative processes leading to the observation of mass fractal structures above some micrometers.

In a N$_2$ atmosphere, when the suspensions remain free of Mg^{2+}, we have previously shown that suspensions of laponite undergo a fluid-solid transition without any chemical

modification of the solid particles. The phase diagram raises several interesting questions that are not completely settled. It appears that the fluid-solid transition, without phase separation, is observed in the same regime in which permanent birefringence properties appear and in which a pseudoplateau is observed for the osmotic pressure. This coincidence is a key point to explain. The first-order phase transition that seems to be missed is probably an isotropic-nematic transition. What is the origin of this frustration? Why does an ill-defined nematic transition occur at the same time as a mechanical transition? Such a situation is unusual for anisotropic colloids (V_2O_5, for example [20]).

To summarize, laponite suspensions are certainly interesting materials, and a model, to study anisotropic colloidal dispersions of charged particles. However, they are very sensitive to pH. This effect was already pointed out by Thompson and Butterworth by studying the consequence of low pH (below 9) on the chemical stability of the particles. Our study shows that one must take extreme care in their preparation and their storage.

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