

Observation of Nematic Liquid-Crystal Textures in Aqueous Gels of Smectite Clays

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Aqueous suspensions of two smectite clays, natural bentonite and synthetic laponite B, were prepared at concentrations ranging from 0.01 to 0.1 g/cm³. Viewed at rest between crossed polarizers, concentrated gel suspensions (> 0.024 g/cm³ for bentonite and > 0.020 g/cm³ for laponite B) show optical birefringence which demonstrates the existence of a liquid-crystalline order of the platelike particles extending over macroscopic distances. The textures of these birefringent gels observed with polarized light microscopy are typical of a nematic phase. At concentrations slightly below that of the phase transition, the suspensions show strong pretransitional effects such as shock or flow birefringence. For both systems, large (≈ 1 cm³) macroscopically oriented domains of the nematic phase were grown by slowly drying isotropic suspensions. The phase diagrams of these two systems versus clay and NaCl concentrations have been established. Unexpectedly, the nematic phase of bentonite is stabilized with increasing NaCl concentration; that of laponite B is not sensitive to it. Finally, the origin of the liquid-crystalline character of these suspensions and its consequences upon their physical properties are briefly discussed in the light of previous experimental studies published in the literature.

Introduction

Aside from their natural relevance in geology, swollen smectite clays¹ find numerous applications in many diverse industrial processes such as drilling muds, thickeners, fillers, or ointments.² In the field of materials science, pillared smectite clays are widely investigated for catalysis³ and, combined with organic polymers, for devising composite materials of increased strength.⁴ From a more fundamental point of view, the aqueous suspensions of disklike clay particles have been widely studied as model colloids^{5–10} and because they have a gel phase, the origin of which is still under debate.^{11–14} As early as 1938, Langmuir¹⁵ observed the occurrence of tactoids (i.e., small birefringent domains floating in isotropic suspensions¹⁶), and eventually the coacervation of bentonite sols in two phases, one of which was a birefringent gel. He discussed these phenomena in relation with the liquid-crystalline phases newly discovered at that time, but he concluded that the birefringent phase had a three-dimensional cubic lattice rather than a nematic liquid-crystalline organization. In 1956, using optical microscopy, Emerson¹⁷ observed in swollen clay flakes a banded texture somewhat similar to that displayed by the tobacco mosaic virus. On the theoretical side, an Onsager transition to a nematic phase was indeed predicted in swollen clay suspensions.¹⁸ Subsequently, various scientists investigated aqueous clay suspensions by scattering^{19–30} or NMR^{31–33} experimental techniques but they did not try to assess their possible liquid crystallinity. Our current interest in inorganic nematic phases and tactoids^{34–37} prompted us to examine these swollen clay gels. Through simple optical observations, we will provide clear-cut evidence of the nematic liquid-crystalline character of these suspensions.

Experimental Section

Gels of laponite B (a synthetic microcrystalline clay of hectorite type, manufactured by Laporte, Ltd.) and bentonite

(Wyoming; Ward's Catalog No. 46-0435) were prepared using the following procedure. The clay was dispersed into 18 M Ω water (pH = 6), 1% (respectively 10%) w/v for laponite (respectively bentonite) and stirred vigorously for at least 24 h. The suspensions of laponite (respectively bentonite) obtained were centrifuged at 2000 rpm for 6 h and filtered leading to *ca.* 1% (respectively 0.1%) w/w colorless transparent (respectively yellow, slightly milky) homogeneous fluids which were carefully concentrated at 50 °C under vacuum. The concentrations of the remaining gels were calculated from weight loss observed when samples were dried at 160 °C. The pH of the suspensions was kept between 8 and 9 so as to prevent dissolution and flocculation of the suspensions. The phase diagrams were determined by slowly diluting these gels with calibrated solutions of NaCl in 18 M Ω water.

The birefringence of the samples was studied between crossed polarizers both at a macroscale, using test tubes of 13 mm diameter filled with typically 1–2 cm³ of suspensions, and by optical microscopy using samples sealed in optical flat glass capillaries of thicknesses ranging from 0.05 to 0.2 mm.

Results

When examined at rest between crossed polarizers, the test tubes filled with suspensions in pure water look different according to their concentrations. The suspensions of concentrations lower than a threshold c_{NI} ($c_{NI} = 0.020 \pm 0.002$ g/cm³ for laponite and $c_{NI} = 0.024 \pm 0.002$ g/cm³ for bentonite) appear isotropic between crossed polarizers (Figure 1a,d). In contrast, the suspensions of larger concentrations appear birefringent (Figure 1b,c,e,f) and therefore must be liquid crystalline. This birefringence remained stable over 1 year. For both clays, the concentration c_{NI} at which birefringence occurs is larger than the gelation concentration c_G ($c_G \approx 0.009$ g/cm³ for laponite, $c_G \approx 0.018$ g/cm³ for bentonite³⁸) so that all birefringent suspensions are gels whereas, in the range $c_{NI} - c_G$, the suspensions are in an isotropic gel state. The gel samples are sometimes more difficult to observe because they take a longer time to reach equilibrium. The relation between the nematic

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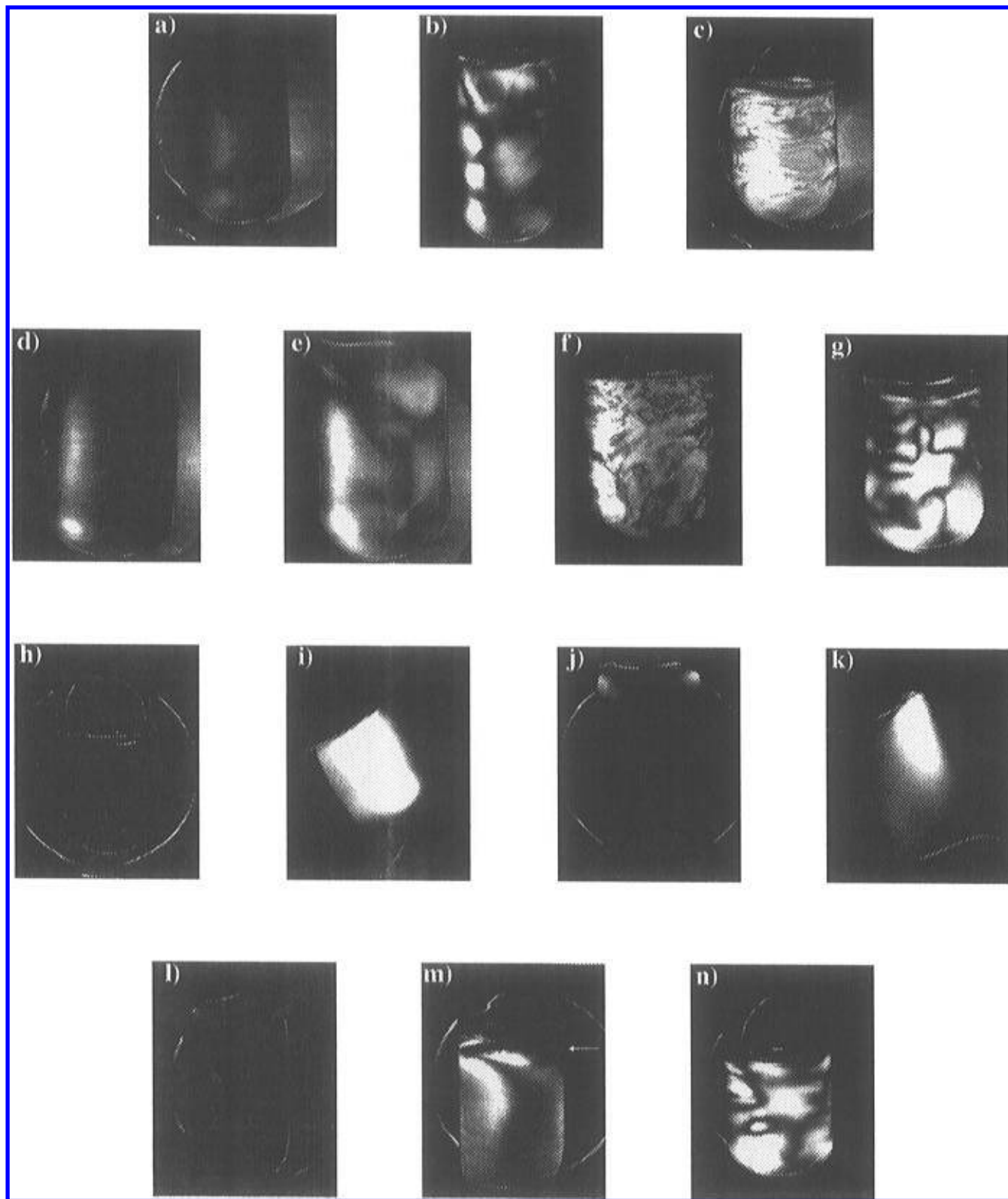


Figure 1. Tubes of aqueous clay suspensions observed between crossed polarizers. (a) Bentonite suspension of concentration 0.019 g/cm^3 in the isotropic state. (b) Bentonite suspension of concentration 0.028 g/cm^3 in the birefringent state. (c) Bentonite suspension of concentration 0.043 g/cm^3 in the birefringent state. (d) Laponite suspension of concentration 0.010 g/cm^3 in the isotropic state. (The bright spot is only the reflection on the test tube wall.) (e) Laponite suspension of concentration 0.034 g/cm^3 in the birefringent state. (f) Laponite suspension of concentration 0.065 g/cm^3 in the birefringent state. (g) Flow birefringence in a bentonite suspension of concentration 0.019 g/cm^3 . The test tube was previously vigorously shaken and was photographed during relaxation. (h) Oriented sample of laponite suspension. The sample looks dark because its principal axes are parallel to those of the polarizers. (i) Oriented sample of laponite suspension. The sample looks bright because its principal axes make an angle close to 45° with those of the polarizers. (j) Oriented sample of bentonite suspension. The sample looks dark because its principal axes are parallel to those of the polarizers. (k) Oriented sample of bentonite suspension. The sample looks bright because its principal axes make an angle close to 45° with those of the polarizers. (l) An isotropic bentonite gel sample ($c = 0.020 \text{ g/cm}^3$, bottom) in contact with pure water (top) remains isotropic. (m) The same sample in contact with brine (5 M) turns birefringent. The arrow points to the interface between the gel and the brine. (n) Bentonite suspension of concentration $c = 0.019 \text{ g/cm}^3$ and 0.25 M NaCl .

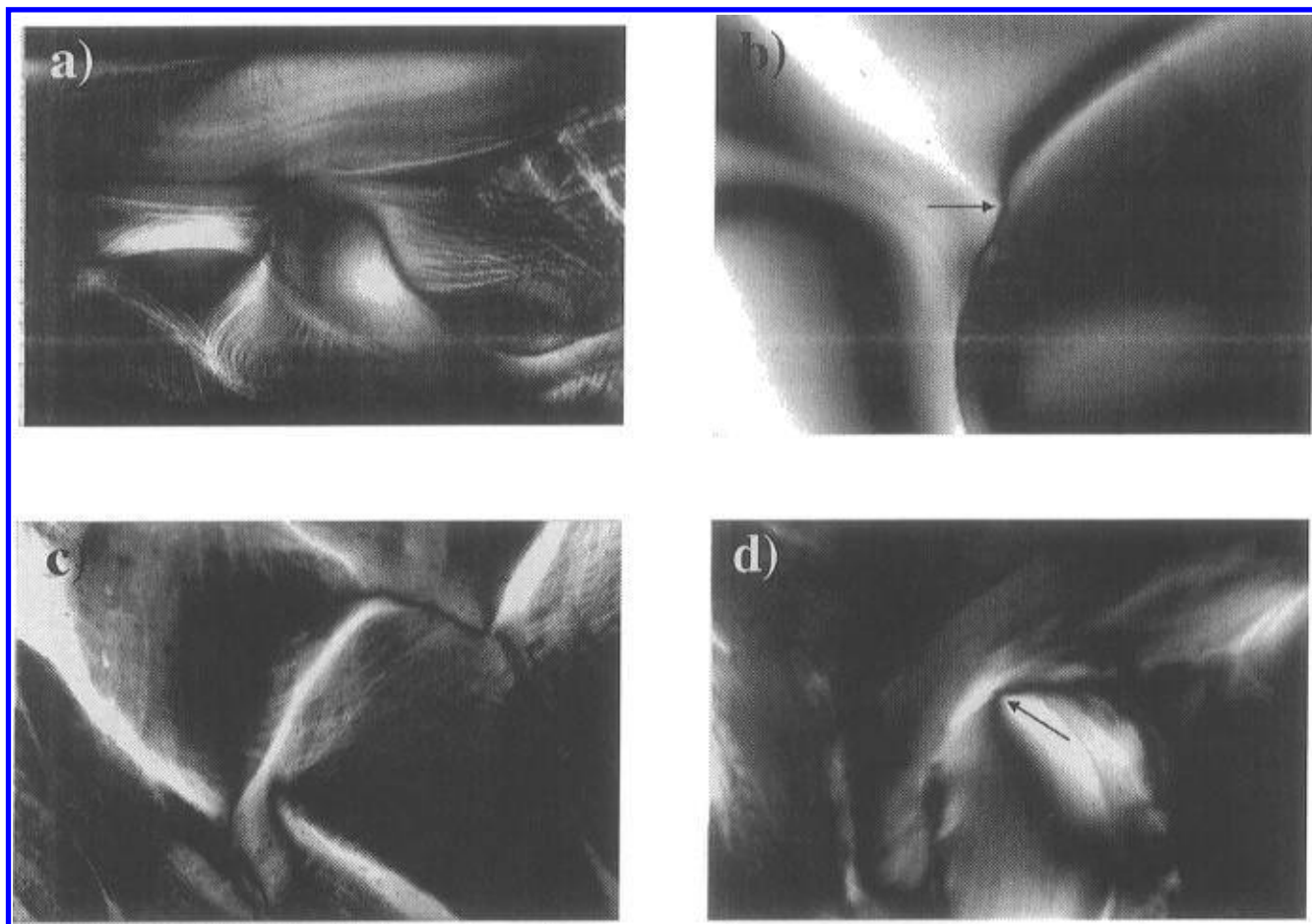


Figure 2. Microscopic observations in polarized light of the textures of the aqueous clay suspensions. (a) Nematic threaded texture of a bentonite suspension (concentration 0.044 g/cm^3 , magnification 50X; reproduction is at 50% of the original size). (b) Detail of a $1/2$ disclination line (arrow) in a bentonite suspension (concentration 0.053 g/cm^3 , magnification 50X; reproduction is at 50% of the original size). (c) Nematic threaded texture of a laponite suspension (concentration 0.065 g/cm^3 , magnification 50X; reproduction is at 50% of the original size). (d) Detail of a $1/2$ disclination line (arrow) in a laponite suspension (concentration 0.034 g/cm^3 , magnification 100X; reproduction is at 50% of the original size).

and gel transitions is considered in the Discussion section below. In a very few cases, biphasic samples could be observed at concentrations around c_{NI} , but this was not generally the case probably because the phase separation is very slow in the gel state. We did not observe any tactoids probably for the same reason. The birefringent test tubes usually display numerous threadlike defects highly reminiscent of nematic textures. The density of these defects increases with the suspension concentration, which may indicate a viscosity increase. More interference colors are also observed with increasing concentration due to a larger birefringence. Though the suspensions of concentrations smaller than c_{NI} are not birefringent at rest, they still have strong pretransitional properties. Gel suspensions of laponite of concentrations around 0.015 g/cm^3 show shock birefringence with a relaxation time around 0.1 s . A sol suspension of bentonite of concentration $c = 0.019 \text{ g/cm}^3$ (Figure 1g) shows a remarkable flow birefringence with a relaxation time around a second. When a laponite (respectively bentonite) isotropic suspension of concentration $c = 0.016 \text{ g/cm}^3$ (respectively 0.019 g/cm^3) $< c_{\text{NI}}$ is left to dry over a few months to reach a concentration $c' = 0.030 \text{ g/cm}^3$ (respectively 0.026 g/cm^3) $> c_{\text{NI}}$, a highly oriented liquid-crystalline domain is obtained (Figure 1h–k) which has no threadlike defect. This experiment demonstrates the possibility of growing very large single domains in the absence of flow. We did not observe any influence of temperature on the transition concentrations up to 90°C . Note that permanent birefringence has also been

observed for concentrated gels of hectorite (California, Ward's Catalog No. 49-5103) obtained using a procedure similar to the one described for bentonite.

The observation of the suspensions in flat optical capillaries reveals typical nematic textures (Figure 2a,c). Despite the small birefringence of the gels, threaded textures are readily seen and also sometimes Schlieren textures are seen.³⁹ These textures arise from the existence of topological defects called disclination lines usually encountered in nematic phases. The optical analysis of these defects (Figure 2b,d) proves that they are disclination lines of strength $1/2$.³⁹ We also sometimes observed a crossed-hatched texture which is typically due to a frozen-in shear structure.⁴⁰ It should be noted that we never observed any topological defects typical of smectic phases. Applying an electric field or a strong magnetic field failed to align the nematic gel phase.

We established the phase diagrams of both systems versus clay and NaCl concentrations (Figure 3). As already reported,¹³ flocculation appears at large values of NaCl concentration, $\approx 0.3 \text{ mol.L}^{-1}$ for bentonite and $\approx 7.10^{-3} \text{ mol.L}^{-1}$ for laponite. In the case of bentonite (Figure 3a), increasing NaCl concentration (compare Figure 1a,n) clearly stabilizes the nematic phase, which is a quite unexpected effect. Indeed, adding some brine to an isotropic sample can make it birefringent though its clay particle concentration actually slightly decreases (Figure 1l,m). In contrast, the nematic phase of laponite is not sensitive to NaCl concentration (Figure 3b).

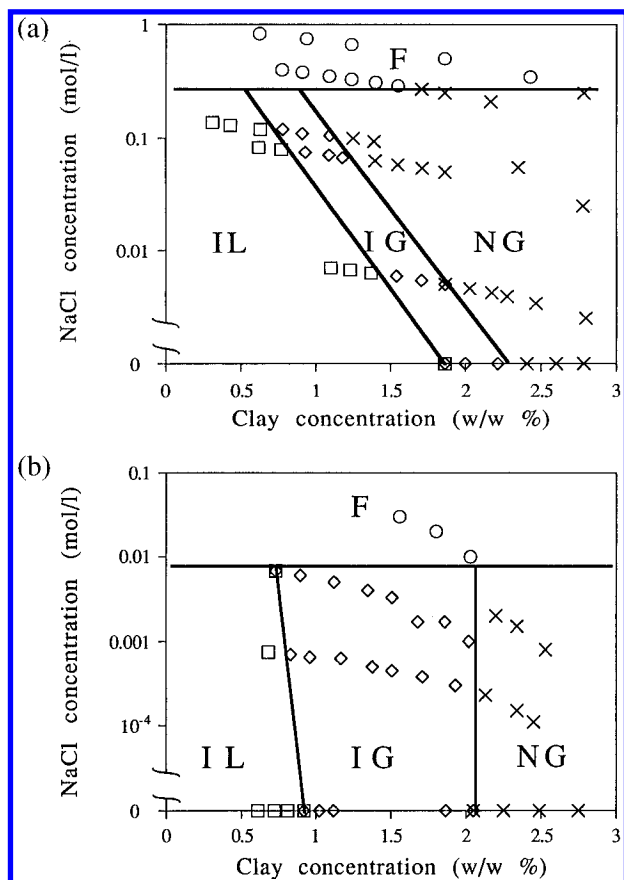


Figure 3. (a) Phase diagram of the bentonite suspensions versus clay and NaCl concentrations. (O, F) Flocculated samples; (□, IL) isotropic liquid samples (◇, IG) isotropic gel samples; (×, NG) nematic gel. (b) Phase diagram of the laponite suspensions versus clay and NaCl concentrations. (O, F) Flocculated samples; (□, IL) isotropic liquid samples; (◇, IG) isotropic gel samples; (×, NG) nematic gel.

Discussion

This section will successively focus on three points: Is there a relation between the gelation and the birefringence of the concentrated suspensions? What is the origin of the nematic ordering? What are the consequences of the liquid crystallinity on the physical properties of these gels?

The proximity of the gel and the nematic transition concentrations, c_G and c_{NI} , in these systems is a problematic feature. Indeed, one may wonder whether the birefringence observed in gel samples is not simply due to some flow which could have occurred during sample preparation and which would not relax. A number of experimental observations go against this assumption. First, the initially isotropic samples left to dry slowly over a few months finally showed birefringence though they hardly experienced any appreciable flow. Second, samples were occasionally observed that showed both the isotropic and nematic phases separated by a sharp border which is just what is expected for a first order phase transition such as the nematic/isotropic one. Third, freshly prepared concentrated birefringent gels show a large density of defects which decreases over a few weeks though the birefringence does not. This implies that local reorientation movements of the platelike particles are not still completely frozen on this time scale. Therefore, if the nematic ordering was not intrinsic, it should also relax. The quick relaxation of the pretransitional effects at concentrations $c_G < c < c_{NI}$ suggests the same conclusion. We are then led to believe that the nematic ordering is intrinsic. Let us note that these aqueous suspensions of clays are very different from those of V_2O_5 ^{36,37} since the clays gel at lower concentration than that

of the nematic/isotropic transition whereas the opposite situation prevails for V_2O_5 .

Let us now try to understand the origin of the nematic ordering. This phase transition may simply come from excluded-volume effects similar to the nematic transition of long rods described by L. Onsager.⁴¹ The theory of the nematic ordering of thin disks is much less documented in literature.^{18,41–43} Nevertheless, considering commonly accepted values^{6,13,25,27,30} for the density, $D \approx 2.5$, the particle thickness, $t \approx 10 \text{ \AA}$, and the particle diameter, $d \approx 3000 \text{ \AA}$ for bentonite and $d \approx 300 \text{ \AA}$ for laponite, we used the crude model of infinitely thin uncharged disks⁴² to predict the particle concentration at the nematic transition. The value obtained for bentonite, $\rho_{NI} \approx 2.4 \times 10^{20} \text{ m}^{-3}$, agrees with the experimental one ($1.4 \times 10^{20} \text{ m}^{-3}$), but for laponite the predicted value $\rho_{NI} \approx 2.4 \times 10^{23} \text{ m}^{-3}$ misses the experimental one ($1.2 \times 10^{22} \text{ m}^{-3}$) by an order of magnitude (a similar situation prevails in a system of boehmite rods⁴⁰). Taking into account the finite particle thickness⁴³ does not markedly improve this situation, but with ρ_{NI} being proportional to d^{-3} , an error of a factor 2 on the particle diameter would explain this disagreement. Nevertheless, the electrostatic interactions between clay particles should also be considered theoretically as was shown by Forsyth et al.,¹⁸ who actually predicted the stabilization of the nematic phase with increasing solvent ionic strength. Accurate measurements of the particle dimensions and of the surface electrical charge are clearly needed to understand better the origin of the nematic ordering.

There are two competing models for the organization of the platelike particles in the gel. One assumes a house of cards organization due to direct attractive electrostatic interactions between the oppositely charged edges and faces of the particles whereas the other considers the electrostatic repulsions between double layers. The optical observations of the nematic ordering clearly conflicts with a house of cards organization and therefore indirectly supports the other. From another point of view, since liquid crystals are anisotropic materials, some physical quantities are also anisotropic, such as the viscosity. This means that, as for any liquid crystal, detailed experiments have to be performed on aligned single domains. Scattering experiments should also be reexamined. Ramsay et al.^{26,27} concluded their series of scattering experiments on sheared gels by stating that, even at rest, some orientational order of the particles should extend over distances larger than 1000 \AA . The experiments shown here (Figure 1i,k) shows that this orientational order can indeed extend over 1 cm and is the distinctive feature of the nematic phase.

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