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Observations of orientational ordering in aqueous suspensions of a nano-layered silicate

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Abstract

We have studied colloidal suspensions of clay particles in aqueous salt solutions. These suspensions make excellent model systems for the study of interactions between plate-shaped particles, due to the inherent possibility of tuning their electrostatic repulsion with the concentration of the salt. Various gel and sol structures are possible, including nematic liquid crystalline order, although only qualitative identification of the latter in clay colloids has been available so far. Here, we briefly review our earlier synchrotron X-ray diffraction from gravity dispersed solutions of Na fluorohectorite, a synthetic swelling clay, over a large NaCl concentration range. Our use of liquid X-ray scattering techniques allowed us to identify regions in which particles reorient from horizontal to vertical alignments in strata coexisting at different heights within the sample. We thus identified two distinct gel regions characterized by differences in orientational anisotropy and domain size. In addition, we for the first time, present visual observations of birefringence in these systems; these new observations support the interpretation of our X-ray experiments, and thus our new results provide further evidence for nematic order.

1. Introduction

Understanding the role of salt in stabilizing dense clay phases has practical significance, for example, in the context of clay formations originally sedimented in salt water, which can be progressively destabilized by subsequent fresh-water rinsing. Clay is one of the traditional materials, whose applications have played important roles throughout human history. Common present day uses of 2:1 clays thus include building materials, ceramics, rheology modification, catalysis, paper filling, oil well-drilling and -stability, etc. [1].

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Smectite 2:1 clay particles dispersed in salt solutions have been studied for decades [2]. More recently there has been a growing activity in the studies of complex physical phenomena in clays [3,4]. The individual 2:1 particles are composed of one or more silicate lamellae that stack by sharing exchangeable cations between their faces (Figs. 1a and 1b). Much effort has gone into relating the structural and rheological properties of clay–salt suspensions to optical observations, which find birefringent domains with defect textures characteristic of nematic liquid crystals [5,6]. Small-angle neutron scattering measurements have also suggested the presence of local orientational correlations in smectite clay gels [7]. Direct in situ structural evidence for parallel alignment of platelets, however, has only recently been obtained [8,9].

Although the layered subunit is crystalline, relative registry and orientations between lamellae are usually quite disordered. Substitution of metals within the silicate layer produces a surface charge, which together with exchangeable intercalated cations affects the absorption of water into the interlayer space, and hence controls the layer spacing [10]. These features determine a net negative surface charge for the particle, and in combination with the particle size and the interactions with the screening salt in solution, produce a rich phase behavior in the clay suspensions [2,5,11].

The complexity arises from the several ways in which attractive and repulsive forces act. When van der Waals attraction between the particles is balanced by electrostatic repulsion, particles can remain dispersed, settling only slowly out of solution. Ions from an electrolyte, if present, can screen the repulsive forces between particles and allow them to aggregate together. This aggregation or "flocculation" may cause the particles to quickly settle out of suspension [2].

On the other hand, attracted particles may join to form extended networks, resulting in gels. Because the particles will, in general, have a negative surface charge partly compensated by positive charge at the particle edges, it is often suggested that the particles are connected in edge-to-face configurations (Fig. 1c): the result is a suggested isotropic, so-called "house of cards" structure that has inspired many theoretical investigations [12], although most recent experimental work has failed to verify this model. Alternative and very interesting structural correlations that may be expected in these systems are those of liquid crystal phases [13].

Within the physics community, there has been particular interest in nematic phases in platelet systems in general, i.e. parallel orientation of the platelets without long-range positional order [13–15]. If the system is made dense enough, it becomes favorable for anisotropic particles

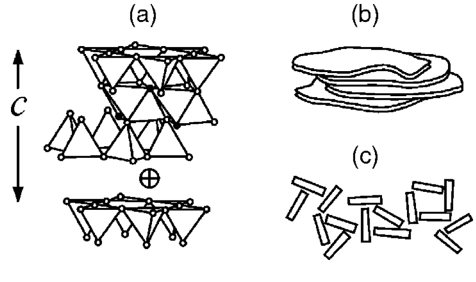

Fig. 1. Taken from DiMasi et al. [8]: (a) Generic structure of fluorohectorite synthetic clay. (b) Micron-scale clay particle formed from stacked lamellae. (c) Face-to-edge and edge-to-edge aggregation of clay particles.