Liquid-Crystalline Phases of Colloidal Dispersions of Layered Double Hydroxides

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Liquid-crystalline phases were discovered more than a century ago.[1] Up to now, tens of thousands of organic liquid crystals were discovered. In contrast, only a few mineral liquid crystals were characterized. In comparison to organic liquid crystals, inorganic ones may possess enhanced electrical, optical, magnetic properties and thermal stability.[1] The currently known lyotropic mineral liquid crystals, which formed in dispersions of anisometric inorganic particles at some critical concentration, were summarized in two review articles.[2,3] The liquid-crystalline phase of V_2O_5 suspensions shows an electro-optic effect and is used for measurement of residual dipolar couplings of unlabeled biomolecules.[4,5] Mineral liquid-crystal moieties can differ largely in size from one system to another, but they are in a colloidal range.

Layered double hydroxides (LDHs) are a class of inorganic compounds that can be easily synthesized in laboratories. They are structurally related to the mineral brucite $Mg(OH)_2$ with certain Mg^{2+} ions replaced by trivalent cation of similar size. This replacement results in a net positive charge on the layers, which is compensated by exchangeable anions placed between interlayers. LDHs receive extensive attention as they are considered to be used as catalysts, catalyst precursors, catalyst supports, adsorbents, anion exchangers, and promising materials for nanocomposites.[6−9] LDH particles are often too large, and it is difficult to exfoliate the layers because of the strong electrostatic attraction between the layers and interlayer anions due to the surface charge density.[6a,9] Only a few reports are related to the colloidal domain of LDHs.[10−12] LDH particles are platelike; such a colloidal system should exhibit liquid-crystalline properties. In this communication, we report the preparation and liquid-crystal phase formation of colloidal Mg/Al LDH.

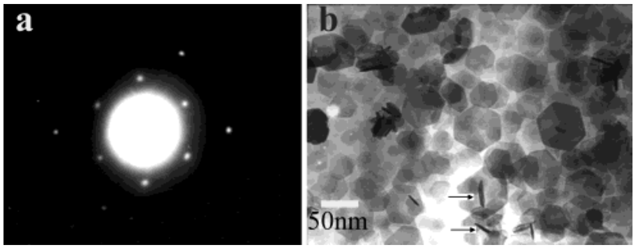

Figure 1. Electron diffraction pattern (a) and TEM image (b) of Mg/Al LDH particles. Only rarely (see arrow) can edges of the particles be seen.

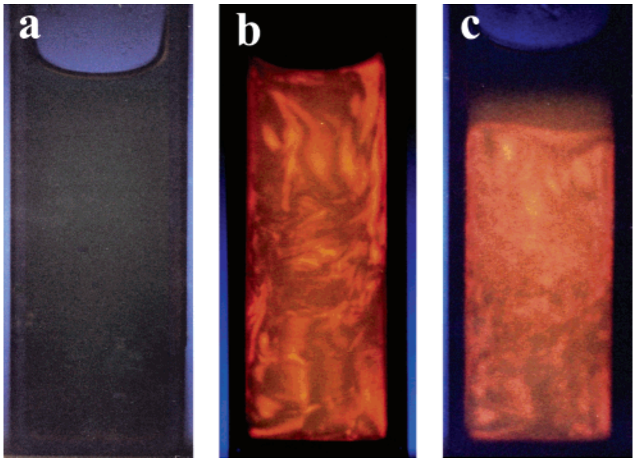

Figure 2. Macroscopic phase behavior of colloidal Mg/Al LDH dispersions as observed between crossed polarizers. (a) Isotropic phase of the 16% (w/w) dispersion. (b) Birefringent nematic phase of the 27% (w/w) dispersion immediately after dilution of the concentrated dispersion. (c) Isotropic−nematic phase separation of the 27% (w/w) dispersion, as observed 7 days after dilution.

The synthesis of colloidal Mg/Al LDH was carried out using a non-steady coprecipitation method.[10] The pH of an aqueous solution of mixed magnesium and aluminum chlorides (total metal concentration 0.5 M, Mg/Al molar ratio 2:1) was raised to 9.5 by adding 3.5 M $NH_3 \cdot H_2O$ under vigorous stirring. The resulting precipitate was aged at room temperature for 1 h. After filtration, the filter cake was washed thoroughly with deionized water. It was then collected and closed in a glass bottle for peptization in a thermostat at 80 °C for 24 h. Well-dispersed colloidal LDH particles were obtained. A part of the sample was air-dried for subsequent analysis whereas the rest was concentrated in a vacuum until the particle concentration was about 39.5% (w/w). The sample was kept in closed flasks under a nitrogen atmosphere to prevent acidification by dissolved CO_2.

Transmission electron microscopy (TEM) investigations were performed with an Hitachi H-800 electron

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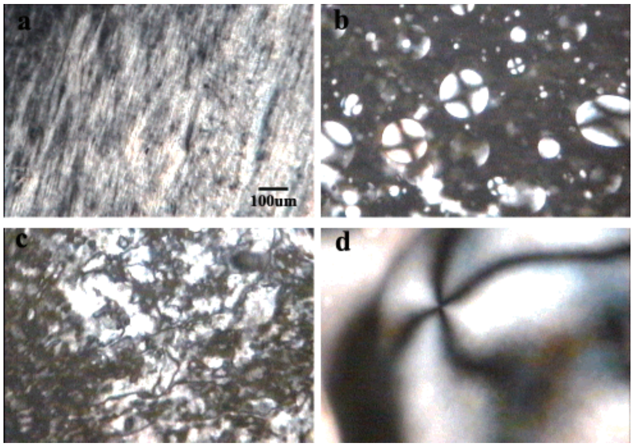

Figure 3. Texture of the nematic phase of colloidal Mg/Al LDH dispersions. (a) 18% (w/w) dispersion between a hollow glass slide and a cover slip. (b) The same sample observed after 7 days and (c) 17 days. (d) Schlieren texture with a point defect surrounded by four dark brushes, observed in the 22% (w/w) dispersion.

microscope at 200 kV. The TEM image showed that most particles were roughly monodisperse platelets hexagonal in shape with diameters between 50 and 80 nm (average diameter ~60 nm), and the electron diffraction pattern showed Mg/Al LDH particles were well-crystallined with hexagonal symmetry (Figure 1). The particles thickness of about 5 nm was also revealed. The ζ-potential of the particles measured with Malvern Zetasizer 3000 was +39 mV.

The birefringence of the dispersions of the Mg/Al LDH platelets was studied between crossed polarizers in cuvettes with a width of 2 mm filled with about 0.6 cm^3 of dispersions. The dispersions of concentrations <16% (w/w) appeared isotropic between crossed polarizers (Figure 2a). At larger concentrations a permanently birefringent nematic phase was initially formed, filling the entire dispersion volume. Some time later it separated into an isotropic upper phase and a permanently birefringent nematic bottom phase, divided by a sharp boundary (Figure 2b,c). The dispersions of concentrations >34% (w/w) formed stable nematic phase and no phase separation could be observed.

Textures of the liquid-crystalline phases were observed by a polarization microscope with samples sealed between a hollow glass slide and cover slip to prevent solvent evaporation (sample thickness of about 100 μm). The dispersion with particle concentration 18%(w/w) initially showed a band-type texture caused by shear or flow during sample preparation (Figure 3a). Then nematic droplets appeared (Figure 3b) and finally developed into a threaded texture (Figure 3c), which is typical of a nematic phase as often is observed in traditional organic liquid crystals. This indicates that the phase separation process of colloidal Mg/Al LDH dispersions involves the nucleation and growth of nematic droplets. Figure 3d shows the liquid-crystal phase at 22% (w/w) containing a disclination core with strength $s = \pm 1$.

Onsager[13] discussed the isotropic–nematic phase transition in suspensions of colloidal plates and rods, where the stability of the nematic phase is caused by the effect that the loss of orientational entropy associated with particle alignment is overcome by the simultaneous gain in excluded volume (configurational) entropy, which was later confirmed by computer simulations.[14] Aqueous montmorillonite dispersions were the first platelike colloidal systems that showed nematic ordering,[15] but more detailed studies revealed that gelation took place before nematic ordering.[16] The I–N phase coexistence could not be observed because gelation prevented phase separation. The ordered structure formed in montmorillonite gels was characterized with synchrotron-based X-ray fluorescence microscopy.[17] Lekkerkerker and co-workers described a nonaqueous platelike colloidal system of sterically stablized gibbsite particles,[18] with coexistence of isotropic–nematic and nematic–columnar phases. Aqueous dispersions of charged gibbsite platelets modified by aluminum polycations also showed I–N phase separation.[19] Brown et al. observed that concentrated dispersions of Ni(OH)$_2$ platelets separated into a columnar phase and a less ordered phase.[20] Concerning LDHs samples, the permanent positive surface charge of the particles arises from ion substitutions in the sheets and can be tuned by varing the ratio of di- and trivalent metal ions, whereas the varible surface charge of the particles can be controlled by electrolytes and pH value. Under this consideration colloidal dispersions of LDHs can serve as better model systems to investigate phase transitions in electrostatically stablized platelike colloids. Furthermore, one can prepare LDHs with particular properties and intercalate functional anions between the layers. This would make LDH platelets-based lyotropic liquid crystals of promising scientific and technological applications.

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