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Report:

In proposal 01-02-905 we used Small-Angle X-ray Scattering (SAXS) at DUBBLE's BM26B beamtime in order to investigate the effects of temperature – in the range from 24 ^{o}C to 88 ^{o}C – on liquid crystalline phases formed in systems of clay nanoplatelets dispersed in saline solution. We determined that heat can induce significant structural changes in such systems.

There is presently a growing scientific activity associated with synthetic clay materials since clay suspensions are examples of complex liquids, showing incredibly rich phase behaviours, and as such the study of these complex fluid systems are of great interest from the point of view of basic science. Indeed, if smectite clays are dispersed in water, they have the ability to form liquid crystalline phases due to the highly anisometric shape (plate-like) of the clay particles. Our interest is in the internal structure of synthetic clay dispersed in saline solutions in order to elucidate the organization of clay building blocks on different length scales, with the aim of understanding the relationship between microscopic structure and macroscopic behaviour.

The system we study consists of a synthetic layered smectite clay, namely sodium fluorohectorite (NaFh), in saline solution. The NaFh particles have diameters ranging up to several micrometres while the particle thickness is around 100 nm [1]. Each clay particle is a lamellar structure that is built up of around 1 nm thick unit layers which carry a net negative charge of $1.2e^{-}$ per unit cell that is compensated for by interlayer cations. In addition, NaFh can adsorb water and other species into these interlayers causing the particles to swell in the direction perpendicular to the stacking of layers [2].

We have previously given the first direct structural evidence of spontaneous parallel alignment (nematic order) in a NaFh system using a specialized spectrometer for liquid surfaces (9ID-C at APS) [1]. The work was done on solutions with adjustable ionic strength in order to control the electrostatic repulsion

between the clay platelets. Also, we have determined the phase diagram for these NaFh systems, as a function of the particle fraction and salt concentration [3]. In order to accomplish this we employed SAXS data (BM26B at ESRF): the anisotropy of the obtained scattering patterns was quantified, and, together with x-ray absorption measurements, this provided a precise determination of the phase boundaries, as well as a measure of the orientational ordering of the clay colloids in the various phases.

To date, the main parameters studied in complex liquids of NaFh have been clay concentration and electrolyte concentration. The former is important owing to the lyotropic nature of these systems, i.e. phase transitions are dependent of the solvent concentration, whereas the latter directly influences the double layer interactions. In the present experiment we are interested in a parameter which is usually disregarded despite its role in the Debye screening length: temperature. Indeed, we performed preliminary SAXS experiments (SAXS1 at LNLS) which displayed structural changes in the particle aggregates when the samples were heated above about 70 ^{o}C. This caused broad peaks to appear in the small-angle scattering, something which is accompanied by an increase in the degree of anisotropy, indicating that the temperature increase causes an increase in the degree of orientational ordering that is accompanied by the emergence of positional correlations. The position of the peaks in q-space correspond with real-space lengths of around 10-20 nm.

The samples in the current study were prepared as dispersions containing 3 wt % sodium fluorohectorite in saline solutions, contained in Hilgenberg capillaries (Mark tubes) of 1 or 2 mm in diameter. The different NaCl concentrations studied were: 0, 1 and 10 mM. The samples were allowed to settle under the influence of gravity for 11 or 34 days before the allocated shifts started.

The sample capillaries were placed in a sample holder made of copper. The lateral sides of the capillaries were in contact with the sample holder which was heated by a bath circulator. Data was collected 20 minutes after the temperature setpoint was achieved. However, instead of using the setpoint temperature of the circulator as the sample temperature, we employed the temperature at the sample holder which was read by a thermocouple.

The experiment was performed at BM26B using a wavelength of 1.24 Å with a sample-to-detector distance of 7.8 m and a beam spot of about 300 x 200 µm at the sample. The x- and y-translation stages of the beamline allowed data collection along the symmetry axis of the capillaries, i.e. vertical scans at the center of the capillary. Data was collected using a 2D multiwire gas-filled SAXS.

Before discussing results, two important specifics must be noted. Firstly, after the experiment, and because of it, we tested our sample holder and noticed that as the temperature increased its vertical position was displaced by as much as 2 mm between room temperature and 88 ^{o}C, hence we cannot compare different temperatures as if they represent the same position of the sample. Secondly, we noticed that for some vertical scans the data collection started from the second point instead of the first and, hence, the data in those cases lacks the first point and shows the last point twice. The former problem was fixed after the experiment. The latter problem, when noticed, was noted down as it happened; in case it was not noticed during the experiment, it is possible to identify it from the vertical scan patterns.

Figure 1 represents the changes observed in the phases at the bottom of the samples. The data collection started with a frame at 24 ^{o}C, then the temperature was increased in steps; at some point between 35 and 50 ^{o}C (depending on the sample) the sample started displaying a correlation ring, see 1b. Further increasing in temperature leads to strengthening of the peak as seen in 1c. In order to test the reversibility the sample stayed at room temperature for 24 hours before a new scattering pattern was collected, this showed that the process is either not reversible or that there is some hysteresis in it, as evidenced by 1d. Further studies are needed before we can fully understand this correlation ring and its irreversibility. Possible explanations include: change in stack size, modification of stacking distances (gel-glass transition) or a new correlation length after delamination of clay stacks. Also, it seems that the correlation peak appears at the cost of the

scattering at smaller angles (see Figure 2), however further studies at smaller angles are needed before we can comment on this. From Figure 2, it is possible to notice that upper parts of the sample also display changes as the sample is heated up (see Figure 2b), however they are not as dramatic as bottom-most phases (represented in Figure 1 and Figure 2a).

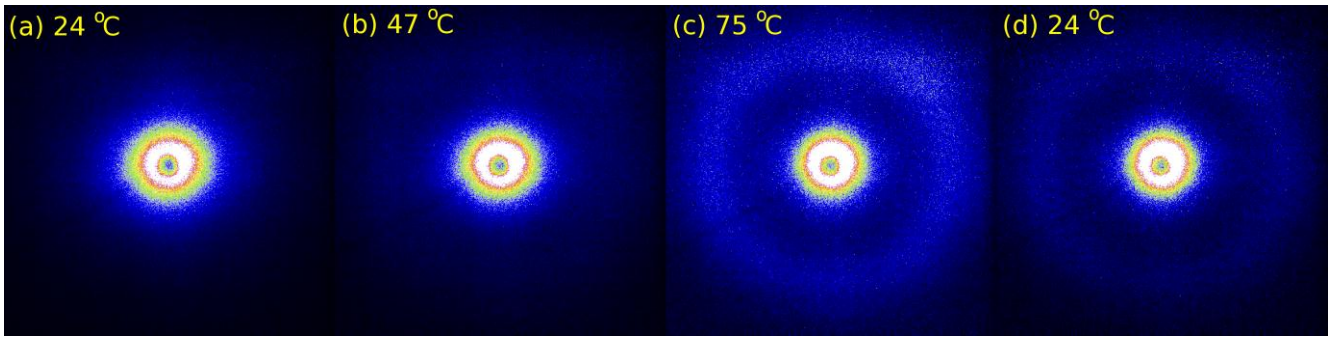

Figure 1. Temperature-induced changes in sample. In (a) to (c) one can note that as the temperature is increased a correlation peak appears, (d) shows that these changes are preserved even after the sample is kept at room temperature for 24 hours. The sample in question is 3 w/w% NaFh and 10 mM NaCl in a 2 mm capillary after 34 days of settling.

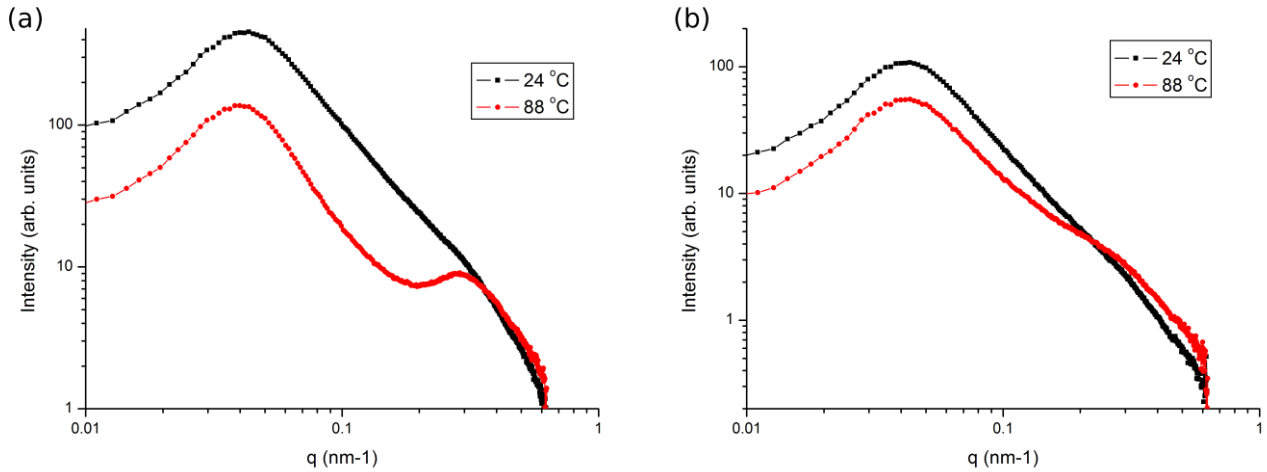

Figure 2. Modifications of the integrated intensity at different sample heights. (a) 7 mm above bottom of sample; (b) 15 mm above bottom of sample. Sample is 3 w/w% NaFh and 1 mM NaCl in a 1 mm capillary after 11 days of settling.

Furthermore, at a previous experiment at LNLS, we noticed that the two bottom-most phases of the sample merged into a single phase for temperatures above 85 °C. We were not able to reproduce that as evidenced by visual observations with and without crossed-polarizers. One possibility is that the samples did not stay long enough at temperatures above 85 °C.

The present experiment brought a substantial amount of information compared to our previous knowledge owing to the number of studied samples and parameters. However, more experiments are needed to corroborate some of the findings and also in order to answer questions raised by the present experiment, such as isolating the effect of each parameter.

References

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