Experiment nº 16 02 18 – 'SAXS study of aggregation on Imogolite fibers'

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Introduction and objectives

This experiment dealt with the aggregation properties of synthetic Imogolite, a nanotubular clay of interesting colloidal properties and a promising material with different functional applications as, for instance, catalysis or hydrogen storage technologies.

Imogolites are a common mineral in the clay fraction of volcanic soils. They develop a large specific surface, between 700-1000 m^2/g. The inner and outer surfaces of Imogolite have different nature: the inner surface is formed by Si-OH groups, with the point of zero charge (PZC) at pH 2-3. The outer surface is gibbsite-like, that is, it is composed of Al_2-OH groups with PZC at pH 10. This makes Imogolite an unusual mineral, able to sorb cations and anions. The aggregation properties of Imogolite are strongly affected by its pH dependent charge.

Tthere remain some open questions about the structure of Imogolite. Some authors claim that the synthesis procedures known do not allow the formation of completely closed structures, with openings on the walls that may allow contacts between different fibers through their inner surfaces. This may lead to aggregation at low pH (near the point of zero charge of the inner surface).

Another point of interest is the formation of different lyotropic colloidal phases. While a complete phase diagram of Imogolite has not yet been completed, some information about nematic phases has been published in the last decade.

The main objectives of our experiment were:

1) To study the role of the pH on the aggregation. This gives us a direct insight of the surface chemistry of Imogolite and of the structure of the nanotubes.
2) To study the aggregation of the Imogolites as a function of the concentration.

The SAXS technique is perfectly suited for our study. The nanotubes have external diameters ranging from 20-23 Å (0.31 - 0.37 $Å^{-1}$) which may be the minimum unit of length for any aggregate formed upon increase of concentration or variation of pH. We have studied samples at three different pH values and at 4 different concentrations.

Results

1.- The diffraction patterns of the samples at different pH values present a clearly tendency towards aggregation with the pH value. This is consistent with the hypothesis of completely closed tubular structures, allowing only contacts between the external parts of the tubes, being more favorable at pH 10. Moreover, the slope has dependence with q^{-1}, accounting for a form factor of a tubular structure (Figure 1).

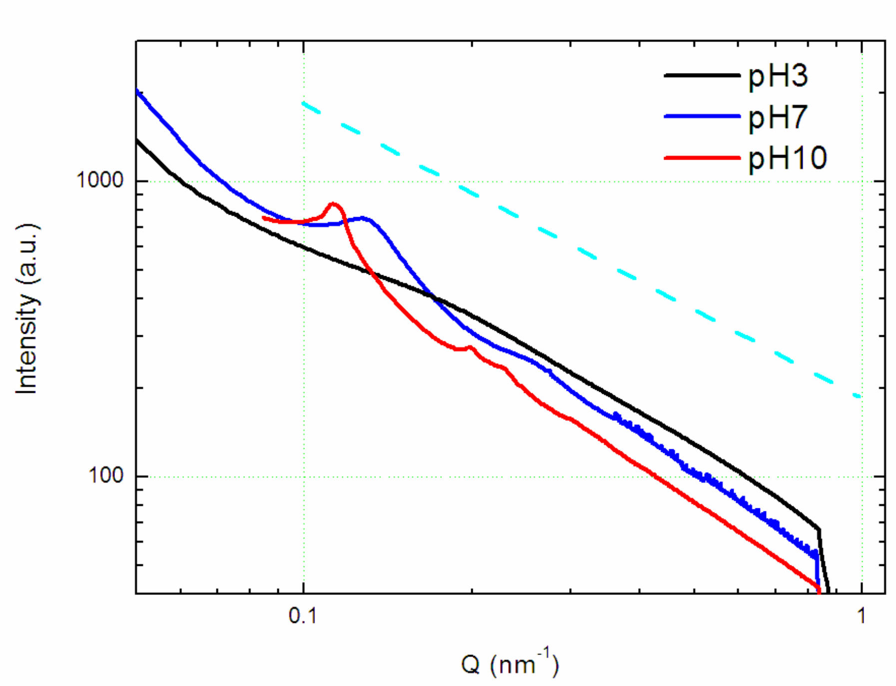

Figure 1. The tendency towards aggregation is shown: three peaks can be distinguished on the red line (pH 10) corresponding to an hexagonal phase. On the opposite, the black line (pH 3) shows only a bump that may correspond to an effect of the polydispersity effect, but no signs of an ordered structure factor are seen. The dotted cyan line is shown for comparison: it has a q-1 dependency according with the form factor of tubular objects.

2.- Data of samples at high concentrations shows the appearance of a highly 'liquid-crystalline' phase, which has been identified as hexagonal from the analysis of the structure factor. This structure seems to be quite stable in the range of concentrations that we have analyzed, with slight changes in the distances. The occurrence of this phase is a very interesting result. Existence of a hexagonal-like phase had been reported by others, but any synthesis procedure was known until the moment.

3.- Another interesting result is the anisotropy developed by using different sample holders. Linear and in-plane anisotropies are found respectively in the case of capillaries and planar sample-holders, while a perfect isotropic phase has been found when measuring a single drop of Imogolite solution without any sample-holder. Evaporation of the solvent by the beam has been observed in all cases, being this point a drawback of the measurements, as it can vary the concentration of the colloids. Use of attenuators may be recommendable for future measurements.

Conclusion

The two objectives planned for these measurements have been completed partially. New experiments may help us to complete the phase diagram of Imogolite. The high quality of the data obtained and the easy and perfectly optimized instrumentation available at BM16 makes it very suitable for our study. Future proposals will be sent in the near future for the completion of this work.