



	Experiment title: Flocculation of anisotropic colloids induced by polyelectrolytes: a SAXS study	Experiment number: SC-4313
Beamline: BM26	Date of experiment: from: 24 Oct 2016 to: 27 Oct 2016	Date of report: 07 Jul 2017
Shifts: 6	Local contact(s): Daniel HERMIDA	<i>Received at ESRF:</i>

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Report: Flocculation is a key process in numerous environmental and industrial technologies. In order to tune and optimize the process, it is crucial to understand the formation and structure of the aggregates formed throughout flocculation. The experiment dealt with flocculation of clay (plate-like) colloids in water induced by ionenes. These are a class of water-soluble model cationic polyelectrolytes, which possess a simple chemical structure, as well as regular and tuneable linear charge density. During the allocated 6 shifts, we were able to measure the scattering signal from clay-ionene aggregates as a function of (a) ionene chain charge density (b) ratio of clay platelets and ionene chains, (c) initial clay concentration, (d) clay platelet size, (e) polyelectrolyte chain length, by comparing aggregates formed by ionenes and PDADMAC and (f) make tests concerning the kinetics of flocculation.

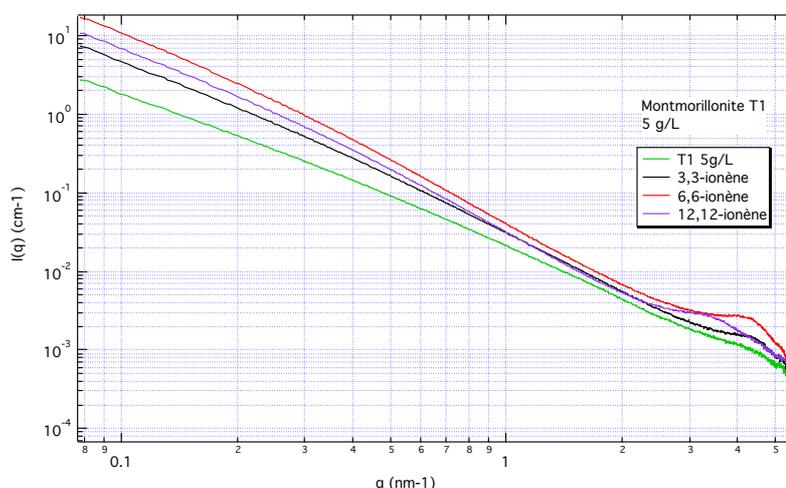


Figure 1: Scattered signal from a suspension of montmorillonite clay particles (lateral dimension of 490nm) at 5g/L (green), the same suspension flocculated by three types of ionenes, as indicated in the legend.

Figure 1 features the scattered signal from aggregates of montmorillonite clay particles flocculated with three types of ionene chains, differing in their charge density (3,3-ionenes are the most densely charged chains; 12,12-ionenes the most weakly charged chains), together with the signal of the non-flocculated clay suspension, at a concentration of 5g/L. The two main observations are: (a) the appearance of a broad

correlation peak beyond 2nm^{-1} in the flocculated samples and (b) the change in scattering intensity and slope in the region below 1nm^{-1} .

The correlation peak beyond 2nm^{-1} is made more visible in the $q^2I(q)$ representation featured in Figure 2. This representation allows us to highlight the deviations from the q^{-2} behaviour, characteristic of the form factor of the individual clay platelets, i.e. a planar surface. In this representation, the signal from the non-flocculated clay suspension is constant (possibly with a hint at a correlation peak centered on 4.3nm^{-1}). The three flocculated systems present clear correlations peaks, which give evidence for a face-to-face stacking of the clay platelets within the aggregates formed. The position and the FWHM of the peaks give access to the stacking periodicity and the number of platelets in the stack, respectively. We note that both of these quantities evolve with the ionene chain charge density, especially between 6,6-ionenes and 12,12-ionenes. The stacking periodicity is approximately 1.5nm for the aggregates containing 3,3- and 6,6-ionenes, and increases to 1.8nm for aggregates with 12,12-ionenes.

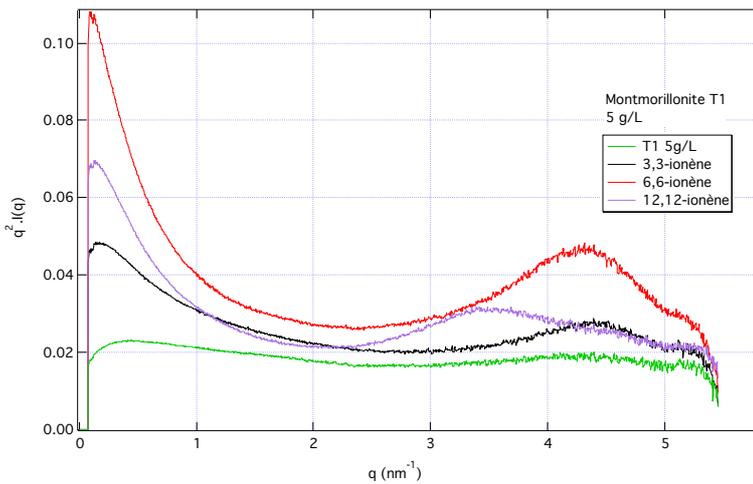


Figure 2: Scattered signal, in a $q^2I(q)$ representation, from a suspension of montmorillonite clay particles at 5g/L (green), the same suspension flocculated by three types of ionenes, as indicated in the legend.

For a given ionene, we observed a gradual appearance of the above-mentioned stacking peak, as we increased the ionene content in the aggregates. While growing in intensity, the peak featured no shift in position. It is therefore the ionene chain density that decides the stacking periodicity and not the ionene concentration. Also the stacking periodicity is not affected by the initial clay concentration. Interestingly, clay aggregates flocculated by PDADMAC (which possesses the same chain charge density as 3,3-ionene, but has longer chains and a bulkier backbone structure), featured no stacking peak.

We have equally made measurements using the stop flow apparatus on BM26 to follow the kinetics of aggregate formation between clay particles. We conclude that the interesting changes in aggregate structure must be taking place for times below 2ms from the moment of ionene and clay mixing (2ms is the dead time of the flow apparatus on BM26). Beyond 2ms after mixing, we observe no changes in the aggregate structure, as is shown in Figure 3.

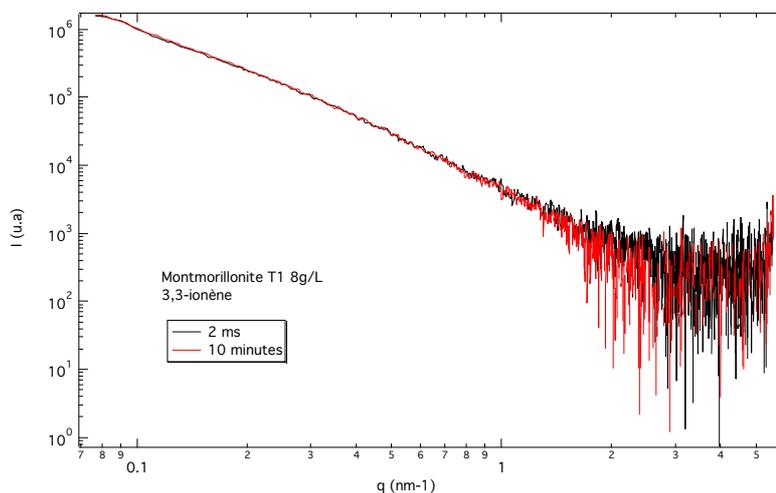


Figure 3: Scattered signal from a suspension of montmorillonite clay particles at 8g/L after 2ms and 10minutes following the addition of 3,3-ionene to induce flocculation.