**Names and affiliations of applicants** (* indicates experimentalists):

E. Paineau*, P. Davidson*, I. Dozov*, LPS, UMR 8502, Bât. 510, Univ. Paris Sud, 91405 Orsay Cedex

L. Michot*, I. Bihannic*, LEM, UMR 7569, 15 av du Charmois, 54501 Vandoeuvre

A.M. Philippe*, C. Baravian, LEMTA, UMR 7563, 2 av Forêt de Haye, 50504 Vandoeuvre

J. Landman*, A.V. Petukhov*, H.N.W Lekkerkerker, Van't Hoff Laboratory, Padualaan 8, 3584 CH Utrecht

## 1. Introduction

Concentrated suspensions of anisotropic particles are ubiquitous in natural systems (clays, cellulose fibers, living cells, etc) and extremely frequent in numerous industrial applications (e.g., concrete, coatings, thickeners, reinforcement fibers, drilling fluids). As far as natural clays are concerned, these very anisometric particles display a rich phase behaviour. [1-2] For both fundamental and applied reasons, the addition of colloidal spheres to such suspensions is of prime interest. It was recently demonstrated that the mixtures of synthetic gibbsite platelets with colloidal spheres show various phase transitions. [3] Our current goal is then to move on to clay-spheres mixtures. For this experiment, we explored the phase diagrams of two dioctahedral swelling clays, montmorillonite and beidellite, the latter exhibiting a Isotropic/Nematic transition in addition to the sol-gel transition. [4] The aim of this work is to understand how the addition of small spherical colloids can affect the structural behaviour of such mixtures.

## 2. Experimental results

Small Angle X-ray Scattering (SAXS) experiments were carried out on the DUBBLE BM-26b beamline at a wavelength of $\lambda = 1.001$ Å and a sample to detector distance of 7m. We initially planned to use the microradian setup exploiting a set of Be refractive lenses. However, some problems with their installation before the beginning of this run prevent us to use such setup. The beam was focused at the detector position by bending the second crystal of the monochromator (focusing in the horizontal direction) and by bending the mirror after the monochromator (vertical focusing). The beam size at the detector was of the order of several 100 microns. We also used the Pilatus 1M detector instead of the 9 or 22 µm² Photonic Science detectors due to the weak scattering of clay particles compared to gibbsite suspensions.

Even so, we measured the SAXS patterns of more than 200 samples of beidellite, montmorillonite and some gibbsite references. The scattering is due to the two contributions of the clay platelets and the silica spheres. The clay volume fraction being larger than that of the silica in our samples, we make the assumption that the scattering from the silica spheres can be neglected in the following. Figure 1A presents the variation of the scattered intensity as a function of $q$ for different beidellite-silica mixtures at constant $\phi_{clay}$ and different $\phi_{silica}$.
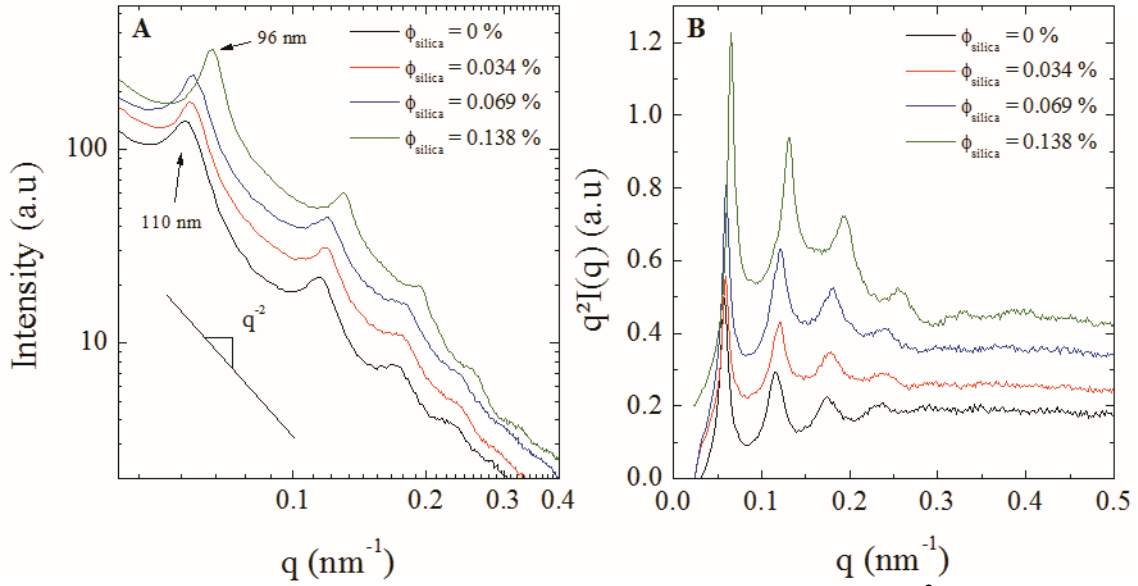
**Figure 1.** Variation of (A) the scattered intensity and (B) the structure factor $q^2I(q)$ as a function of $q$ of beidellite-silica mixtures for $\phi_{clay} = 0.61$ % and various volume fraction of silica $\phi_{silica}$.

In all samples, we observed monotonous decay of the scattered intensity with scattering vector modulus, that scales as $I(q) \sim q^{-2}$. Actually, this feature is the particle form factor that describes the scattering by an isotropic distribution of noninteracting 2D objects, in the so-called "intermediate regime" where $2\pi/D < q < 2\pi/t$ (with $D$ and $t$ the average diameter and thickness of the clay particles, respectively). By neglecting the interplay of positional and orientational correlations of the platelets, their scattered intensity is simply the product of their form factor, $P_{clay}(q)$, by their structure factor, $S_{clay}(q)$. Therefore, we plot $q^2I(q)$ *vs* $q$ to represent $S_{clay}(q)$, which dominates the signal (Figure 1B). At sufficient $\phi_{clay}$, the SAXS curves display strong periodic modulation of the scattered intensity that have been already reported for pure beidellite suspensions and are due to short-range positional correlations of the platelets. [4] For each of the patterns, a typical average interparticle distance $d_{ave}$ can then be deduced from the position of maximum in these oscillations ($d_{ave} = 2\pi/q_{max}$). These interparticle distances have been reported in figure 2 as function of $\phi_{silica}$ and $\phi_{clay}$ the latter representing the so-caled swelling laws.
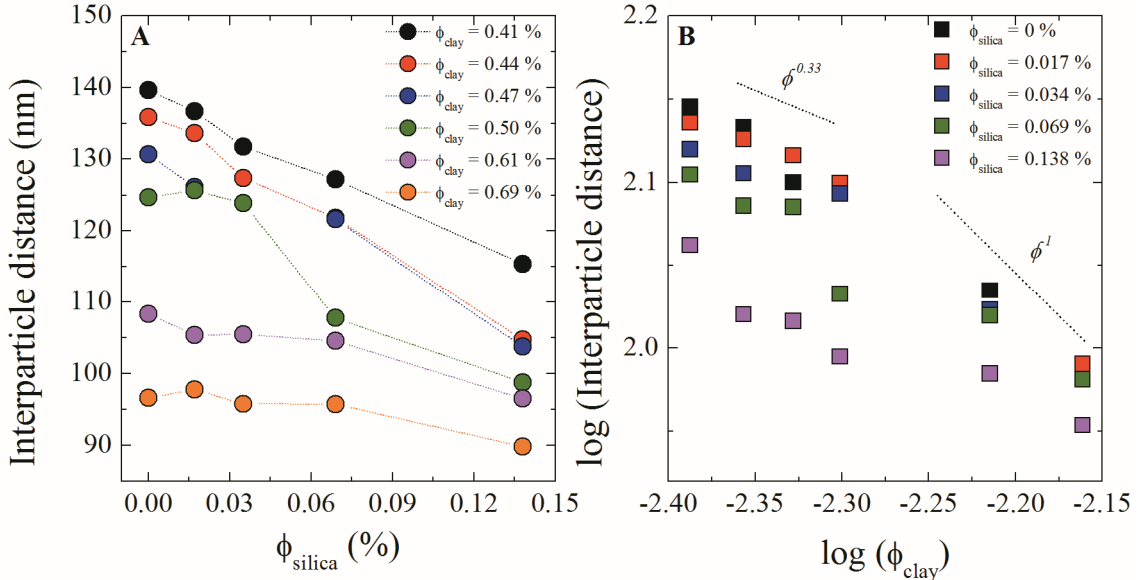


**Figure 2.** Variation (A) of the interparticle distances $d_{ave}$ as a function of $\phi_{silica}$ and (B) in the swelling laws as a function of $\phi_{clay}$.

We noticed from optical observations that an increase of $\phi_{silica}$ induced a shift of the isotropic/nematic transition to higher $\phi_{clay}$. Here, we see that silica sphere addition in the mixtures makes the distance between the clay platelets smaller whatever the clay concentration. This means that the concentration of clay platelets in the nematic phase becomes larger. Remarkably, we note that the distances in the coexisting isotropic phase

also decrease. This actually agrees with the observation that the amount of nematic phase decreases and the amount of isotropic phase increases upon addition of silica spheres. Finally, the dependence of $d_{ave}$ with clay volume fraction shows two regimes. At low $\phi_{clay}$, the interparticle distances tend to scale as $\phi^{-1/3}$, which can be assigned to the 3D swelling of freely rotating objects. At higher volume fractions, a crossover occurs to a $\phi^{-1}$ unidimensional swelling regime related to the local lamellar order of the clay particles. The crossover between these two regimes provides a good qualitative estimate of the position of the I/N phase transition. This position shifts to larger clay volume fractions upon silica addition, which is consistent with our optical observations.

Contrary to previous studies on the effect of silica particles on the liquid-crystal phase behavior of plate-like gibbsite colloids [3], we observe here a positive shift of the I/N transition line, i.e. the nematic phase is destabilized by silica addition. This is even to the extent that an initially biphasic I/N sample becomes completely isotropic. While it seems reasonable that depletion interactions could play a key role in changing the clay microstructure, and hence the bulk phase behavior and rheology, the precise microscopic mechanisms involved required further investigations. This experiment brought us many useful information that will soon be gathered in an article dealing with the evolution of the phase diagram of clay-silica mixtures. [5]

[1] L. Michot *et al.*, **PNAS**, 2006, 103, 16101
[2] B. Ruzicka *et al.*, **Nat. Mater.**, 2011, 10, 56
[3] D. Kleshchanok *et al.*, **Soft Matter**, 2011, 7, 2832
[4] E. Paineau *et al.*, **J. Phys. Chem. B**, 2009, 113, 15858
[5] J. Landman *et al.,* manuscript in preparation.