



**Experiment title: Dynamical transition from fluid to gel of anisotropic colloids in concentration polarization layers during cross-flow membrane separation process**

**Experiment number:**  
SC 2894

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**Report:**

Membrane separation processes are widely used in industrial applications (bio-industries, agro-industries, or sludge treatment) for concentrating and purifying nanoparticle dispersions. Under the action of transmembrane pressure and cross-flow velocity, the particles accumulate near the membrane and their concentration can rise above the sol-gel transition, leading to a catastrophic loss in permeability.

The focus of this project is to investigate the structure and organization in the polarisation layer during cross-flow ultrafiltration of anisotropic clay dispersion. Dedicated SAXS cross flow ultrafiltration cells (Fig. 1) have been used to access to the *in-situ* concentration profile as described in details in precedent work [1].

Three different aqueous colloidal clays have been studied, to explore the consequences of changes in size, form and mutual particles interaction on their macroscopic filtration reversibility properties and structural organization in the concentration polarization layers:

(1) Natural plate-like Na-Wyoming montmorillonite [2]. Two size have been explored WyT2 S3 (1 nm in thickness, 75 nm in lateral averaged size) and WyT2 S2 (1 nm in thickness, 250 nm in lateral averaged size).

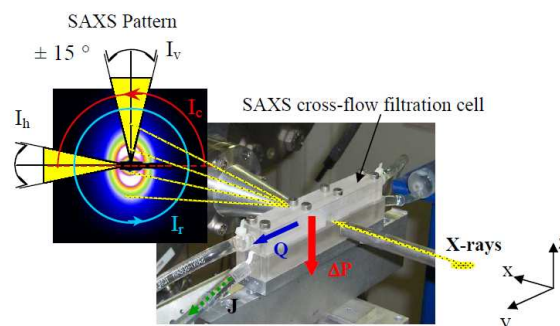


Fig. 1: Picture of the set-up on ID02 Beamline.

- (2) Synthetic disk-like Laponite clay (1 nm in thickness, 30 nm in mean diameter) in the presence or absence of an added polyphosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) at a concentration  $C_p$ .
- (3) Natural disk-like beidellite clay dispersions (1 nm in thickness, 286 nm in mean diameter) [3].

The reversibility of the concentration polarization layers and permeation flux evolutions have been associated to the changes in particle size, mutual particle interaction and osmotic pressure of the dispersions.

### Effect of particle size and osmotic pressure on the concentration profile and permeation flux:

In figure 2 is presented the evolution of the volume fraction as a function of the distance  $z$  from the membrane surface, for two different particle size of montmorillonite dispersions submitted to the same cross-flow filtration conditions (Fig. 2a) and a comparison for Laponite and montmorillonite at different filtration conditions (Fig. 2b). The concentration profiles for montmorillonite  $\phi_v(z)$  have been obtained from the scattered intensities in the concentration polarization layers, the deduced interparticle distance  $d$  from the kratky plot (Fig 2c) and the already known swelling laws  $d(\phi_v)$  [2]. For the Laponite dispersions the volume fractions were deduced as already detailed in precedent work [1].

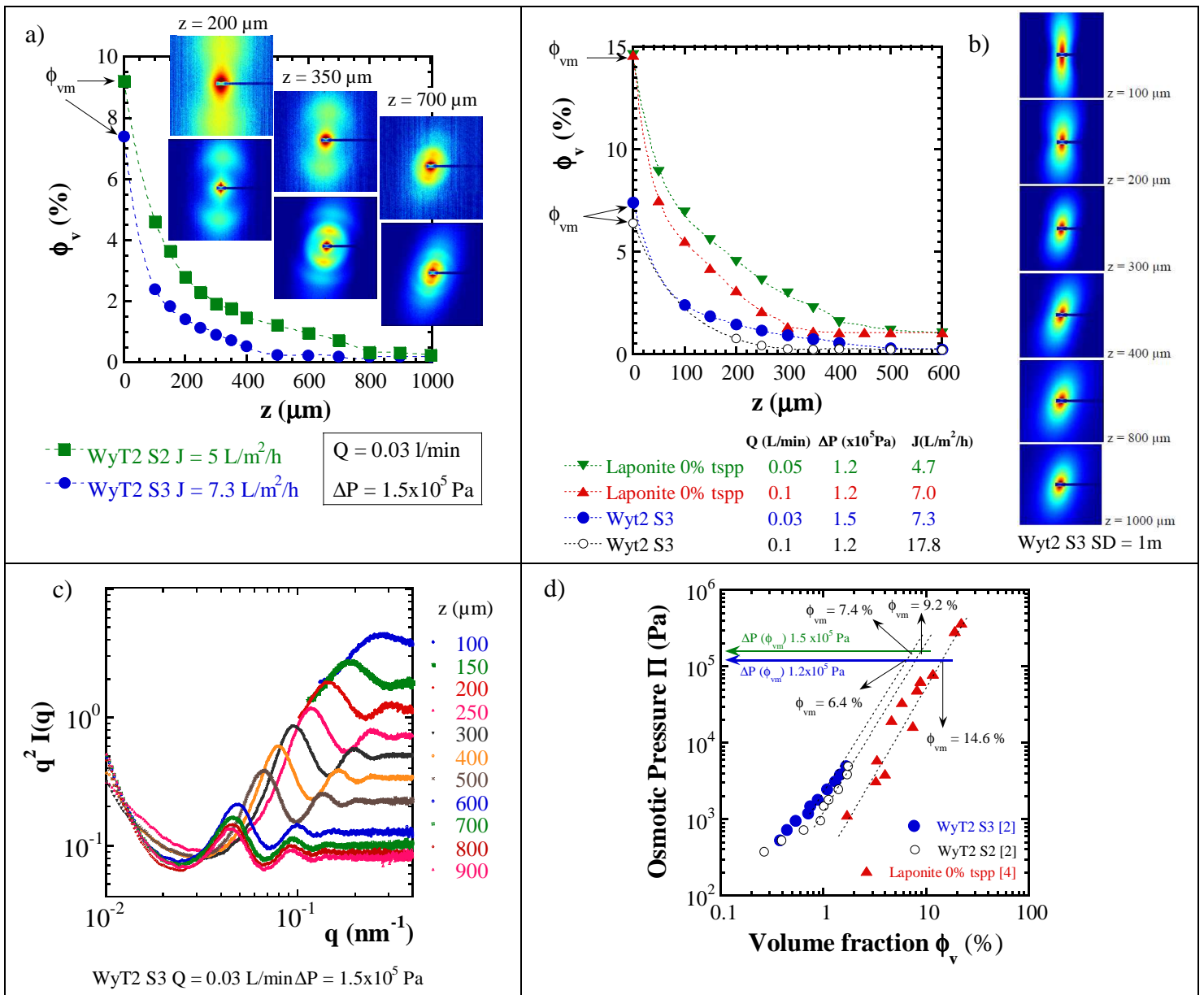


Fig. 2: Structural organization (2D-SAXS patterns and concentration profiles versus distance  $z$ ), deduced from in-situ SAXS during cross flow separation process of a) Na-Wyoming montmorillonite and b) comparison with Laponite dispersions, c) structure factor  $q^2 I(q)$  at different distances  $z$ , d) osmotic pressures and deduced extended volume fraction ( $\phi_{vm}$ ) at the membrane surface.

The extended volume fraction ( $\phi_{vm}$ ) at the membrane surface ( $z = 0 \mu\text{m}$ ) has been evaluated from the osmotic pressure  $\Pi(\phi_v)$  data [2,4] (Fig. 2d) and considering in a first approximation, that the osmotic pressure of the filtered dispersions  $\Pi_m(\phi_{vm})$  equilibrate the transmembrane pressure  $\Delta P$  at the membrane surface, as discussed in ref [1]. The results show that the filtered dispersions with the biggest sized particles (WyT2 S2) build a more concentrated and thicker polarization layer than the smaller sized one (WyT2 S3), in accordance with a lower permeation flux  $J$ . For the same filtration conditions ( $Q = 0.1 \text{ L/min}$  and  $\Delta P = 1.2 \times 10^5 \text{ Pa}$ ), the system having a lower osmotic pressure (Laponite) build a higher concentrated polarization layer in accordance with a lower permeation flux. This result is well in accordance with the osmotic pressure model, for which the permeation flux is proportional to the effective pressure difference  $\Delta P_{eff} = (\Delta P - \Delta \Pi_m) = \Delta P - (\Pi_m(\phi_{vm}) - \Pi_{permeat})$ .

The 2D-SAXS patterns exhibit an increase in anisotropy when approaching the membrane surface (Fig. 2a and 2b), indicating an orientation of the plate like particles with their normal aligned along the direction of applied pressure. The angular orientation of the SAXS pattern flip regularly at increasing distance from the membrane surface denoting a change in the orientation angle of the particles in the polarization layers.

### Effect of shear and transmembrane pressure on the structural organization of Laponite dispersions:

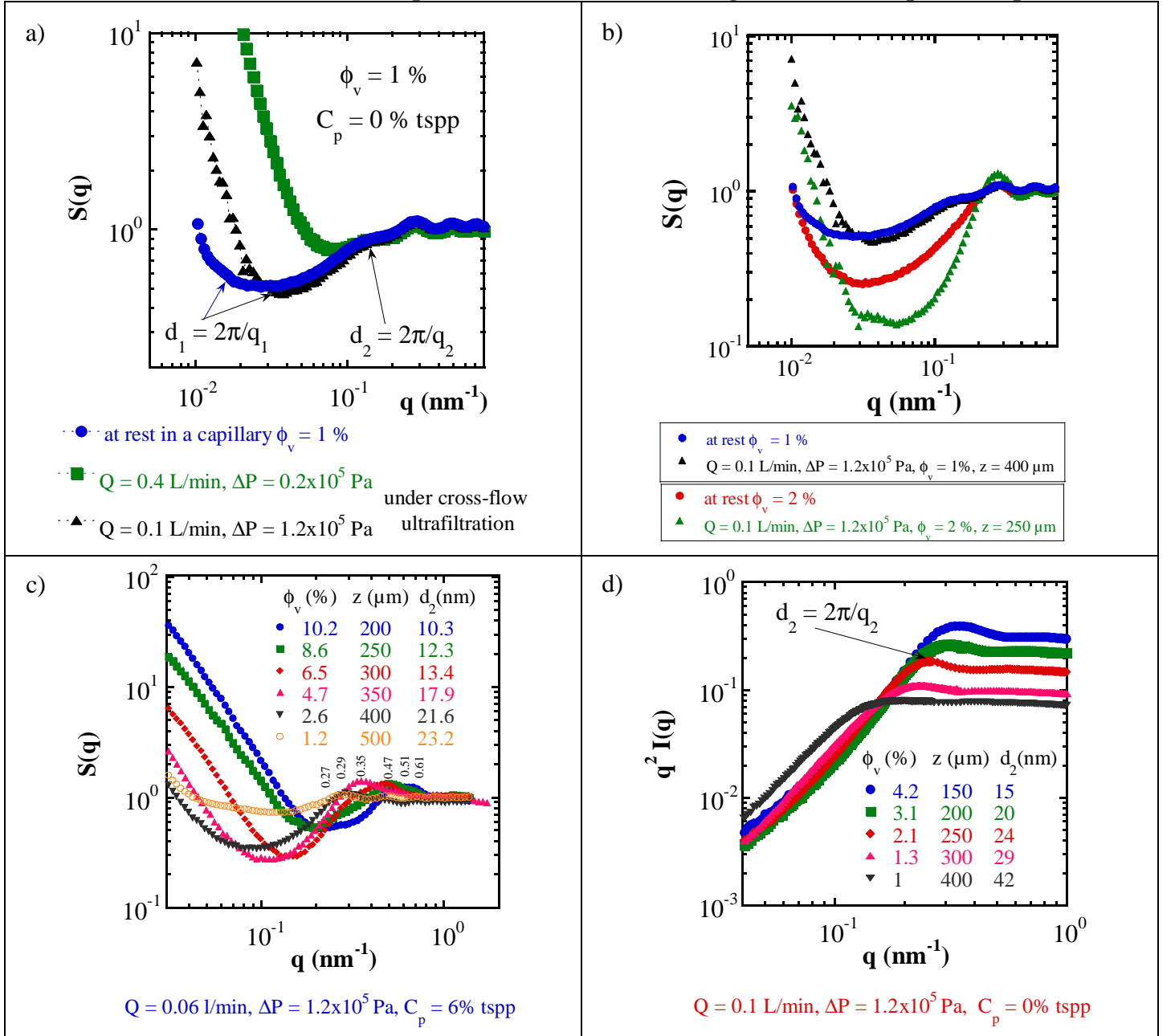


Fig. 3: Structural organization deduced from *in-situ* SAXS during cross flow separation process of Laponite dispersions, a) and b) comparison of the structure factor for different conditions, c)  $S(q)$  for different position  $z$  in a concentrated polarization layer, d) structure factor  $q^2 I(q)$  and deduced interparticle distance  $d_2$ .

From the scattered intensities of particles in the polarization layers, the concentration profiles and associated structure factor  $[S(q)]$  can be deduced for the laponite dispersions under cross-flow ultrafiltration (Fig. 3). In order to evaluate the effect of shear and/or pressure on  $S(q)$ , different conditions were compared for the same volume fraction in particles: firstly in a capillary for the dispersion at rest, secondly under a cross-flow ( $Q = 0.4$  L/min) without any applied transmembrane pressure, thirdly in a concentration polarization layer under simultaneous cross-flow and transmembrane pressure ( $Q = 0.1$  L/min and  $\Delta P = 1.2 \times 10^5$  Pa).

For the dispersions at rest, at  $q$  values below  $1.5 \times 10^{-1} \text{ nm}^{-1}$ , there is a strong depression of  $S(q)$ . This depression originates from inter-particle repulsions that eliminate fluctuations particles concentration in the range extended from  $q_1$  to  $q_2$ . This means that the dispersion appears homogeneous over scales extended from  $d_2$  (distance between neighboring particles) to  $d_1$  (size of elementary heterogeneities: aggregates). For one equivalent volume fraction  $\phi_v = 1\%$ , this depression is almost suppressed under the predominant effect of shear (Fig. 3b). This can be attributed to a break-down of the initial aggregated particles by the shear strength which provides a more homogeneous dispersion at these length scales. On contrary, under cross-flow ultrafiltration, the structure factor in the concentration polarization layers (Fig. 3b and 3c) exhibit a deeper depression at low  $q$  than the  $S(q)$  of the dispersion at rest. Therefore, the combined effect of shear flow and transmembrane pressure allows forming smaller aggregates ( $d_1 \downarrow$ ) with a more homogeneous dispersion and reduced inter-particle distances ( $d_2 \downarrow$ ) between the neighboring particles than the dispersion at rest (fig. 3c and 3d). At increasing volume fraction in the polarization layers (Fig. 3c), the extent in  $q$  range of the depression is reduced which correspond to an increasing homogeneous dispersion of smaller sized aggregates. In conclusion the cross-flow ultrafiltration process has the effect to change the initial heterogeneous open structure to a more homogeneous closed structural organization of denser and smaller aggregates of particles.

#### Références:

- [1] Pignon F. *et al.*, Langmuir, 28, 1083-1094, 2012.
- [2] Paineau E. *et al.*, Langmuir, 27, 5562-5573, 2011.
- [3] Paineau E. *et al.*, J. Phys. Chem. B, 113, 15858-15869, 2009.
- [4] Martin C. *et al.*, Langmuir, 22, 4065-4075, 2006.