



**Experiment title: Structure and aggregation mechanisms of nano-particles dispersions during cross-flow ultrafiltration.**

**Experiment number:**  
SC 2409

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## Report:

The performance of the separation process is mainly governed by the accumulation of colloidal particles on a filtrating media. The development of new “SAXS cross-flow filtration cells” at the "Laboratoire de Rhéologie" combined with *in-situ* time resolved SAXS, has allowed to characterize the colloids structural organization inside the concentration polarization layer during cross-flow separation process. The concentration profile of colloids has been deduced reliably as a function of the distance from the membrane. Major fouling mechanisms have been identified: the formation of a reversible polarization layer in a first regime and the transition to irreversible deposit formation above a critical flux.

The filtration of different types of colloids (hard and soft particles) has been performed. Membrane porosity was also changed in order to perform ultrafiltration (nanometer pore size) or microfiltration (0.01 micrometer pore size). The hard nano-particles used were fiber sepiolite particles (10x1000 nm) and plate-like clay Laponite particles (1x30 nm). The soft particles were casein micelles (average size 100 nm) from model phospho caseinate powder (promilk 852B, Ingredia).

The “SAXS cross-flow filtration cell” used for these measurements is made of polycarbonate and contains a flat filtration membrane. In the retentate channel, the Q cross-flow and  $\Delta P$  transmembrane pressure are imposed and measured constantly. Permeate flux J is recovered in a recipient and its mass is registered. The beam (50  $\mu\text{m}$  vertically x 250  $\mu\text{m}$  horizontally) crosses the deposited particles allowing to probe multi-level structures and interactions as a function of the height z above the membrane (Figure 1). Additionally static SAXS measurements were performed in a temperature controlled

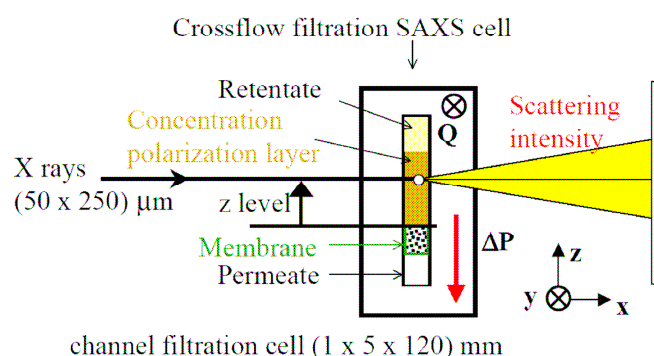


Figure 1: Schematic diagram of *in-situ* SAXS under cross-flow separation process.

Additionally static SAXS measurements were performed in a temperature controlled

flow-through capillary cell and permitted to establish a calibration curve to correlate the level of absolute scattering intensity to  $C$  particle concentration or  $\phi_v$  volume fraction. Consequently from the SAXS pattern measured during time in the filtration SAXS cell, the particle concentration or volume fraction can be deduced reliably. For the first time, concentration profiles have been measured along filtration time at distances  $z$  from the membrane surface, above 100 or 200 micrometers for ultra- and micro- filtration respectively. An anisotropy parameter  $I_z/I_x$ , has been calculated by integrating the scattering intensity over a sector of 25 degrees around the vertical ( $z$ ) and horizontal ( $x$ ) axes, respectively.

#### I- Microfiltration of fibers sepiolite suspensions:

The transition from stable to unstable filtration and irreversible deposit formation, has been demonstrated in the results presented in (figure 2) [1]. Initially, the concentration near the membrane was equal to the initial concentration  $C = 0.01$  g/ml at all distances  $z$  above 200  $\mu\text{m}$  from the membrane surface. In the first step, at increasing pressure conditions under a constant cross-flow  $Q$  of 0.5 L/min, no increase of concentration was detected. In the second step after  $t = 160$  min when the cross-flow was reduced from 0.5 to 0.15 L/min, the related reduction of hydrodynamic forces initiated the growth of a deposit and an increase of anisotropy parameter. Simultaneously a high reduction of permeation flux was registered. These results underline the critical and unstable character of the filtration process and show that the origin of these instabilities is due to the colloidal nature of the particles interactions. Indeed, above a critical concentration for which the colloidal interactions are sufficiently high compared to the hydrodynamic forces generated by the cross-flow, a shear induced oriented structure is initiated.

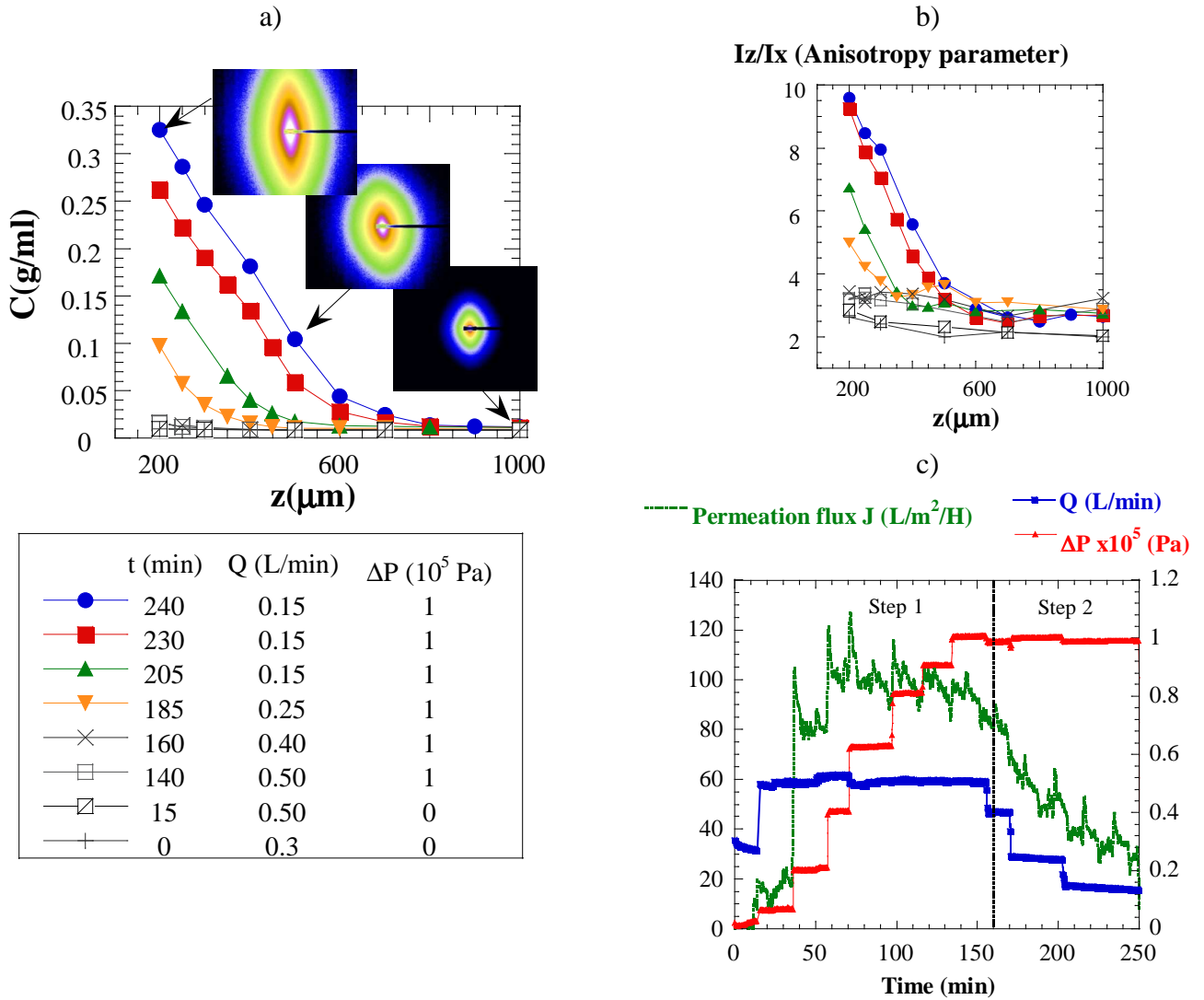


Figure 2: Cross-flow separation process of sepiolite suspensions (microfiltration). a) concentration profile deduced from *in-situ* SAXS and corresponding 2D SAXS patterns. b) anisotropy parameter versus distance  $z$  from the membrane. c)  $Q$  Cross-flow,  $\Delta P$  transmembrane pressure and corresponding  $J$  permeation flux measured simultaneously with scattering measurements during time. pH = 8,  $T = 30 \pm 1^\circ\text{C}$ .

## II- Ultrafiltration of plate-like Laponite dispersions:

The reversibility of the concentration polarization layer in agreement with permeation flux measurements, has been demonstrated in the results presented in figure 3. In step (1), no change of the concentration is detected above 100  $\mu\text{m}$  from the membrane whatever the change in  $\Delta p$  for a sufficient cross-flow  $Q$  of 0.45 L/min. When the cross-flow is reduced to 0.2 L/min (step (2)) the concentration in the polarization layer start to increase and stabilize after a few minutes of ultrafiltration. At  $z = 100 \mu\text{m}$ , the volume fraction is equal to 4 which correspond to the gel state of these dispersions in the phase diagram. Furthermore, 2D SAXS Patterns exhibit an important increase in orientation of the plate-like particles. A further increase of the cross-flow to 0.45 L/min (step (3)), induce the disruption of this high concentrated polarization layer. The corresponding permeation flux reaches then the same level as the one at the end of step (1). For the first time, the evolution of the volume fraction as a function of the distance from the membrane has been measured in a dynamic concentration polarization layer during the cross-flow separation process.

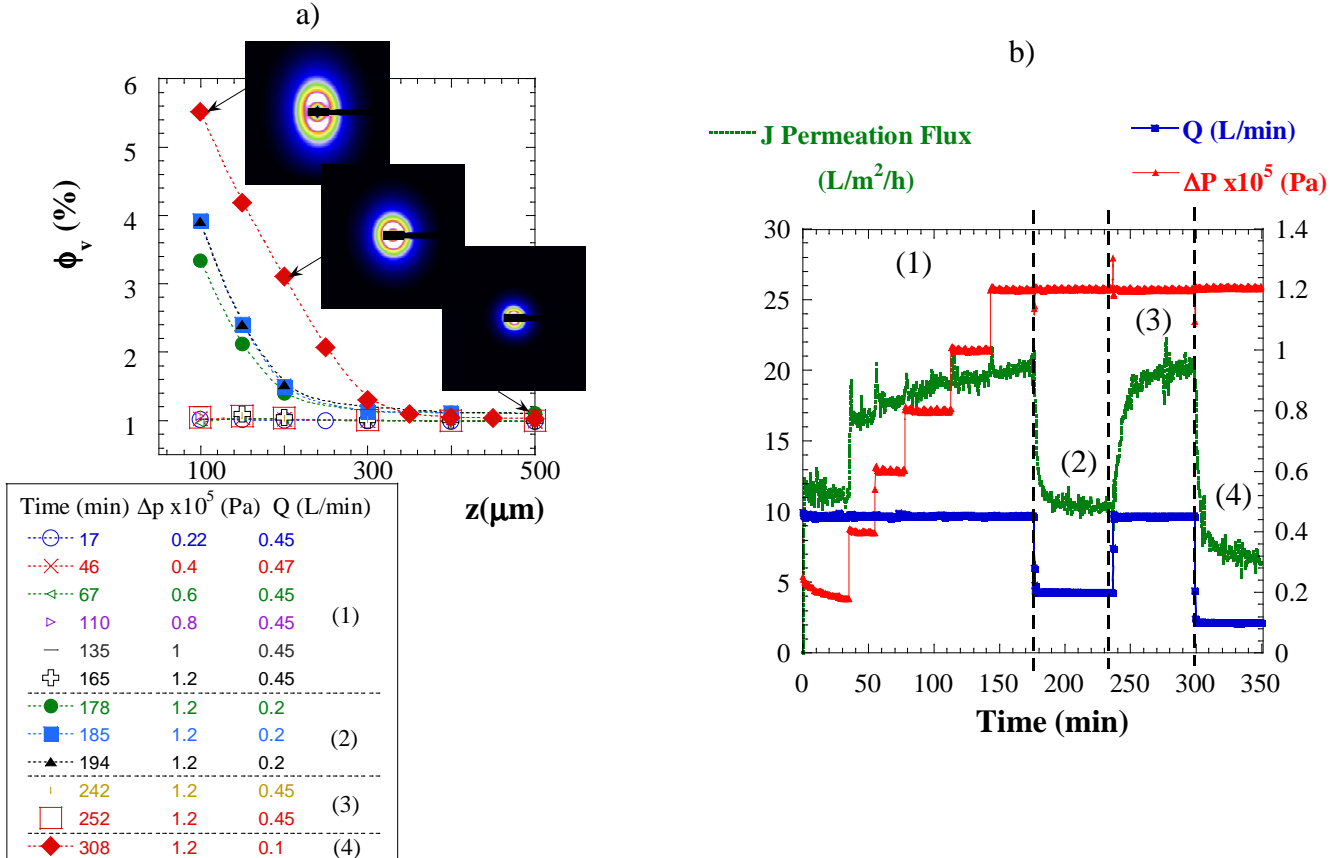


Figure 3: Cross-flow separation process of Laponite dispersions (Ultrafiltration). a) concentration profile versus distance  $z$  deduced from *in-situ* SAXS and corresponding 2D SAXS pattern. b)  $Q$  Cross-flow,  $\Delta P$  transmembrane pressure and corresponding  $J$  permeation flux measured simultaneously with scattering measurements during time. Ionic strength  $10^{-3}$  M [NaCl], pH = 10,  $T = 29 \pm 1^\circ\text{C}$ .

## III- Microfiltration of casein micelle dispersions:

The microfiltration of a skimmed milk (casein micelles suspended in microfiltrat), has been explored in frontal mode. The time dependance of the concentration profile has been established [2] and shows the same features in terms of concentration levels, profile evolution and thickness of the deposit than the one of casein micelles suspended in deionized water. This result exhibits the importance of the concentration parameter as compare to others parameters like ionic strength, or soluble protein content in the mechanisms which governs the frontal filtration process of casein micelles dispersions.

## References:

- [1] Pignon F., David C., Magnin A. and Sztucki M., XV<sup>th</sup> International Congress on Rheology, The Society of Rheology, 80<sup>th</sup> Annual Meeting, Book Series: AIP Conference Proceedings, **1027**, 120-122 (2008).
- [2] C. David, "Compréhension et Maîtrise des Mécanismes de Structuration des Dépôts, lors de la Filtration Tangentielle de Produits Laitiers" PhD thesis of the "Grenoble Institut National Polytechnique" October 2008.