ESRF	**Experiment title:** Structural mechanisms of casein micelle dispersions during tangential ultrafiltration process.	**Experiment number**: SC 1954
Beamline: ID02	**Date of experiment**: from: 19/04/2006 to: 20/04/2006	**Date of report**: 27/07/2007
Shifts: 6	**Local contact(s)**: T. NARAYANAN, M. SZTUCKI	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Christopher DAVID*, Frederic PIGNON*, Albert MAGNIN

Laboratoire de Rhéologie, Domaine Universitaire, B.P. 53, F-38041 Grenoble cedex 9, France

Theyencheri NARAYANAN*, Michael SZTUCKI*

E.S.R.F., 6 rue Jules Horowitz, B.P. 220, F-38043 Grenoble Cedex, France

Geneviève GÉSAN-GUIZIOU*, Anne JIMENEZ*

INRA-Agrocampus Rennes, UMR 1253, Science & Technologie du Lait et de l'Oeuf, 65 rue de Saint-Brieuc, F-35042 Rennes Cedex, France

Report: On one hand, the aim of this proposal was to further explore the internal structure of casein micelles at all relevant length scales. We therefore investigated the micro and nano structure of casein micelles as function of physico-chemical conditions (pH, charge, hydrophobicity, hydratation), and temperature. On the other hand, we wished to extend the study to the structural organization of the casein micelles in accumulated layers on the membrane surface during ultrafiltration. Both frontal and crossflow filtration mode were probed using filtration cells developed at the "Laboratoire de Rhéologie, Grenoble" to combined filtration and SAXS on ID02 at the ESRF.

The first set of experiments has been performed with suspensions at rest. It permitted to visualize that casein micelle internal structure was not affected by the mean size of the micelle. It also confirmed the model which describes the casein micelles as a relatively uniform matrix containing disordered calcium phosphate clusters. No effect of the temperature was observed. The pH decrease in suspension from 6.7 to 5.2 highlighted the dissociation of colloidal calcium phosphate by the disappearance of the shoulder of I(q) around $q = 7\times10^{-1}$ nm^{-1}. Finally, the dissociation of the caseins and minerals from the casein micelles induced by the addition of EDTA (Calcium chelating) was verified. All these results have been emphasized in literature. [1].

[1] Marchin S., Putaux J.-L., Pignon F., Léonil J., J.Chem. phys., **126,** 045101 (2007).

The second set of experiments has been performed with casein micelles and sepiolite fibers clay suspensions under filtration. The use of SAXS on ID02 permitted to follow the accumulation of matter *in*-situ with a 70 µm accuracy (Fig. 1). Several colloids concentration profiles between 280 µm and 2460 µm from membrane surface were obtained for the first time over the five first hours of casein micelles' frontal ultrafiltration. Structural information at length scales going from 1 to 420 nm inside of accumulated layers of matter were also obtained. This evolution correlated with the corresponding structural modifications and with permeation flux has given precious information on mechanisms responsible for output losses.

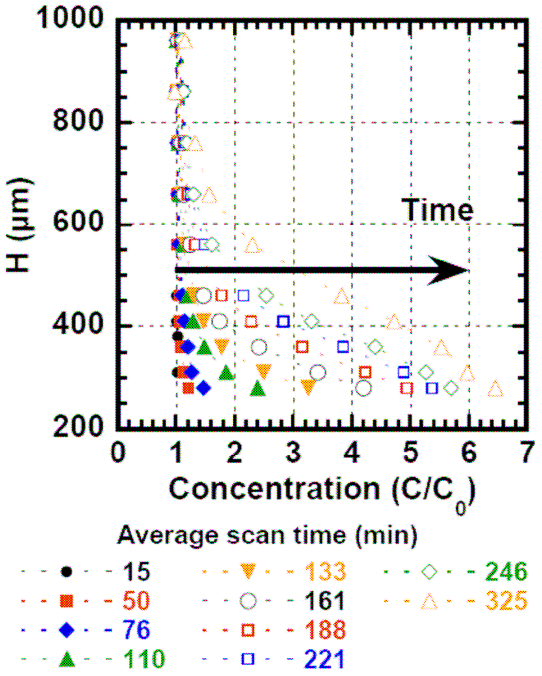

Fig 1. Evolution of the polarization concentration profile during frontal filtration of casein micelles suspensions at initial concentration C_0 = 29 g/L and pH = 7.2

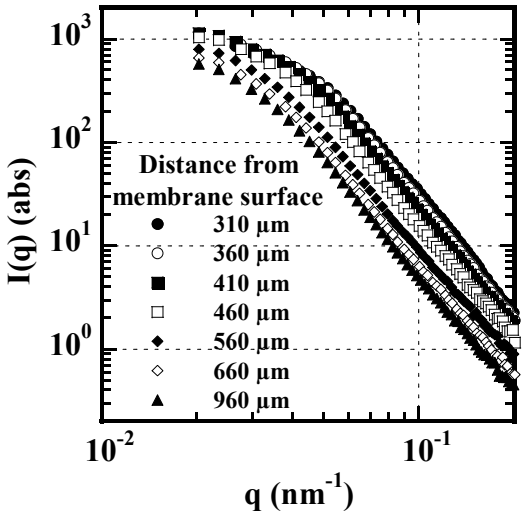

Fig. 2: Scattering curves obtained in accumulated matter at different distances H from the membrane surface after 325 min of casein micelle suspension frontal filtration. Initial casein micelle concentration was C_0 = 29 g/L

Casein micelles suspensions:

The high reduction of permeation flux in the early stage of frontal mode filtration is associated to an exponential increase of the concentration during time followed by a slowing down of this rise above a critical concentration of about C_c = 157 g of casein per liter. The corresponding scattering intensities exhibit a modification of the interaction between casein micelles (fig. 2). Cross flow ultrafiltration of casein micelles suspensions has then been probed by SAXS and demonstrated that the polarization layer involved was at least smaller than 280 µm even when permeation flux was highly reduced.

Sepiolite fibers suspensions:

Sepiolite suspensions were also filtered under crossflow conditions and SAXS measurements showed that suspensions rapidly concentrated near the membrane surface (fig.3). A transmembrane pressure of 1.10^5 Pa was applied at t = 12 min. The lower retentate tangential flow Q (0.03 L/min) imposed at t = 24 min initiated the growth of the deposit layer. With successive higher applied Q, a continuous increase in thickness, anisotropy and concentration of the deposit layer was observed. Simultaneously the permeation flux gradually decreased with time.

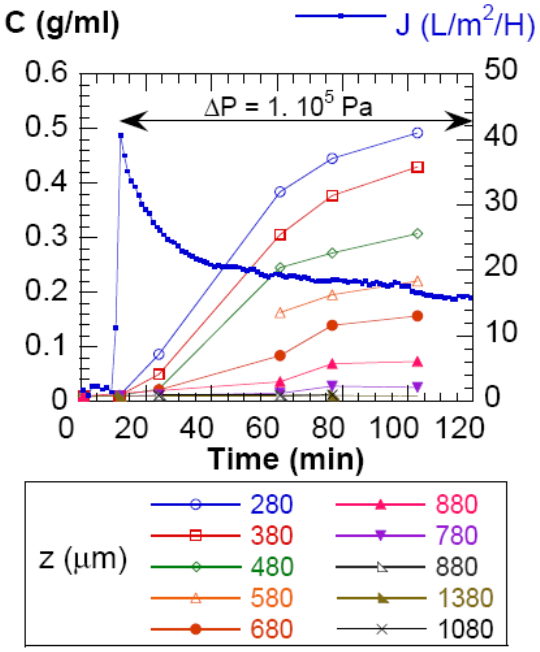

Fig. 3: Permeation flux (J) versus time and temporal evolution of concentration at different distance z to the membrane surface deduced from SAXS during ultrafiltration of sepiolite suspensions at initial concentration C_0 = 0.01 g/ml, for various cross flow conditions.

Those results proved the possibility to obtain pertinent structural information in the vicinity of membrane surfaces during ultrafiltration, and opened new opportunities in the understanding of the mechanisms responsible for the separation process efficiency. It would bring essential experimental data necessary for improvement in theoretical and numerical modelling.