

Small-Angle X-Ray Scattering (SAXS) analyses of build-up, relaxation and erosion of casein micelles fouling layer during cross-flow ultrafiltration

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Abstract

The aim of this work is to understand the influence of operating conditions (time, transmembrane pressure (TMP), cross-flow velocity (v)) on the casein micelles fouling layer properties (build-up, sol-gel transition and reversibility behaviour during TMP relaxation) during cross-flow filtration. Small-Angle X-Ray Scattering (SAXS) has been coupled to cross-flow ultrafiltration to determine the behaviour of casein micelles concentrated layers at the membrane surface. Concentration profiles have been deduced from the scattering intensities registered *in-situ* in the course of the cross-flow ultrafiltration of casein micelles dispersions. SAXS and filtration results for a reference experiment (TMP = 110 kPa, $v = 0.03 \text{ m}\cdot\text{s}^{-1}$, 2h30 of filtration, 25°C) show the formation of a thick fouling layer of 275 μm and reaching 307 $\text{g}\cdot\text{L}^{-1}$ at the membrane surface, which is above the sol-gel transition of casein micelles ($\approx 180 \text{ g}\cdot\text{L}^{-1}$). Furthermore, results show some reversibility of the outer fraction of fouling layer and irreversibility of its fraction close to the membrane surface. Those results are important for understanding the concentrated layer build-up of casein micelles during cross-flow ultrafiltration but more originally the TMP relaxation behavior of casein micelles fouling layer linked to different operating conditions.

Keywords. Membrane fouling – cross-flow ultrafiltration – casein micelles – SAXS – operating conditions dependence.

INTRODUCTION

Ultra- and microfiltration of skim milk are widely used in the dairy industry for concentration and the fractionation of milk proteins. However, their performances are limited by formation of a concentrated fouling layer of casein micelles at the membrane surface when critical conditions are reached. Some precedent results on the possible effect of operating conditions (time, transmembrane pressure, cross-flow velocity) have been highlighted by Qu *et al.* (2012) and Jin *et al.* (2014). Nevertheless, there is a lack of knowledge on the behaviour of concentrated layer (sol-gel transition and reversibility) at different operating conditions. Consequently, the aim of this work was to elucidate the local structure and time dependant organization of casein micelles fouling layer under various operating conditions with the help of *in-situ* SAXS during cross-flow ultrafiltration. This allowed to (i) distinguish the thickness and local solid concentration profiles in flowing (solution) and stagnant (gel) parts of the fouling layer; (ii) discriminate the effect of time, transmembrane pressure, shear flow on the sol-gel transition; (iii) study the reversibility of the sol-gel transition under the moderate laminar cross flow.

METHODS

Dispersion with initial casein micelle concentration of $49.0 \pm 2.2 \text{ g}\cdot\text{L}^{-1}$ was prepared from casein micelle powder (Promilk 802 B, Ingredia, France) dispersed in preliminary obtained milk ultrafiltrate (Qu *et al.*, 2012). The dispersion was prepared by thoroughly mixing the casein powder in a UF permeate for 15h at 35°C. SAXS experiments were performed at beamline SWING of synchrotron SOLEIL (Paris, France) with the help of specially developed SAXS-cross-flow ultrafiltration cell (Jin *et al.*, 2014). Polyethersulfone ultrafiltration membrane with nominal cut-off of 100 kDa (Pleiade, Orelis Environnement, France) was used for filtration.

The profiles of casein micelles concentration in the fouling layer (local casein concentration versus distance to membrane) were obtained with spatial resolution of 25 μm . The impact of TMP (50 and 110 kPa), cross-flow velocity, v (dead-end filtration, 0.03 and 0.15 $\text{m}\cdot\text{s}^{-1}$) on the local structure of fouling layer was studied during different stages of filtration (concentrated layer build-up \rightarrow relaxation \rightarrow erosion).

RESULTS

Figures 1 and 2 present results of filtration experiment carried out at cross-flow velocity $v = 0.03 \text{ m}\cdot\text{s}^{-1}$ and TMP = 110 kPa. A second step of relaxation was performed by reducing the TMP to 10 kPa. Finally, erosion step at 10 kPa and 0.15 $\text{m}\cdot\text{s}^{-1}$ was applied in order to eliminate the fouling layer. Such conditions of filtration allow to build a thick casein micelle layer of around 275 μm (solid curve a in Fig. 1) with a maximal concentration of 307 $\text{g}\cdot\text{L}^{-1}$ close to the membrane ($z = 20 \mu\text{m}$), which is above the sol-gel transition ($\approx 180 \text{ g}\cdot\text{L}^{-1}$), according to Bouchoux *et al.* (2009) and Jin *et al.* (2014). The SAXS analysis revealed that this highly concentrated layer was partially reversible, since its thickness decreased to 220 μm then 180 μm during the following pressure relaxation and erosion steps (Fig. 1). Nevertheless, in the vicinity of membrane surface its concentration decreased to 267 $\text{g}\cdot\text{L}^{-1}$, which is still above the sol-gel transition concentration. TMP relaxation allowed to eliminate a third of gel thickness (Fig. 2).

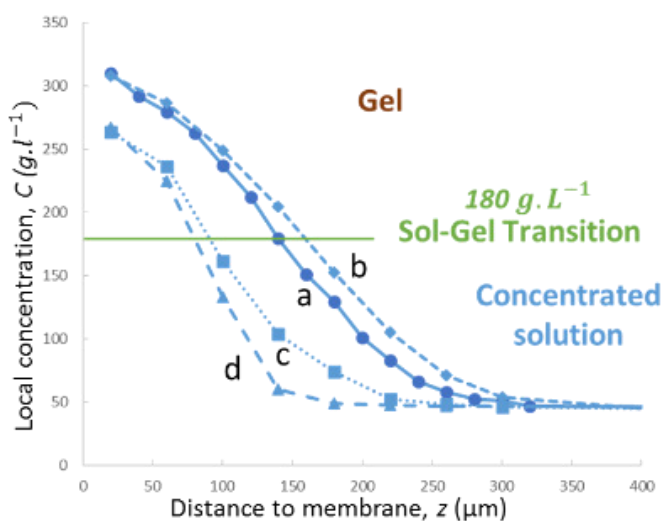


Fig. 1. Local casein micelles concentration versus distance to membrane surface at different steps of ultrafiltration cycle at 25°C:

- (a) end of filtration (TMP = 110 kPa, $v = 0.03 \text{ m}\cdot\text{s}^{-1}$);
- (b) beginning of relaxation (10 kPa, $0.03 \text{ m}\cdot\text{s}^{-1}$);
- (c) after 40 min relaxation (10 kPa, $0.03 \text{ m}\cdot\text{s}^{-1}$);
- (d) after 7 min of erosion (10 kPa, $0.15 \text{ m}\cdot\text{s}^{-1}$).

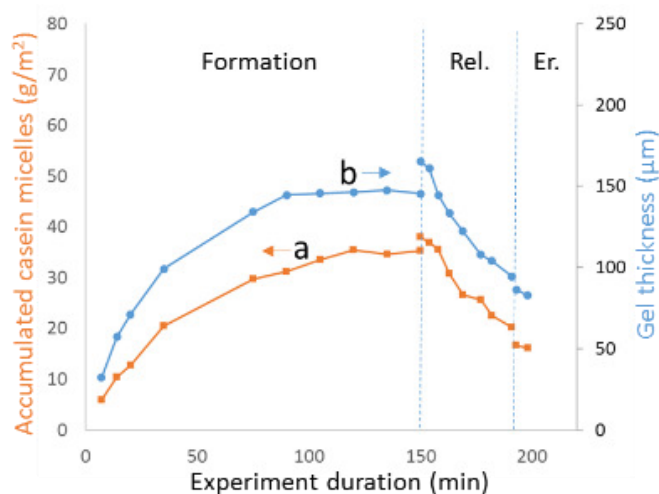


Fig. 2. Quantity of casein micelles accumulated as fouling (in concentrated solution and in gel) (a) and gel thickness (b) at different step of ultrafiltration cycle at 25°C:

- 1) layer build-up (TMP = 110 kPa, $v = 0.03 \text{ m}\cdot\text{s}^{-1}$);
- 2) pressure relaxation (10 kPa, $0.03 \text{ m}\cdot\text{s}^{-1}$);
- 3) erosion (10 kPa, $0.15 \text{ m}\cdot\text{s}^{-1}$)

CONCLUSION

In-situ SAXS measurements during cross-flow ultrafiltration of casein micelles allowed to follow the formation and the reversibility of concentration polarization layers as a function of time, TMP and cross-flow. This allowed to identify sol-gel transition of casein micelles near the membrane surface and to distinguish, which part was reversible and eliminated by TMP relaxation. Furthermore, those results are original for understanding of mechanisms of fouling layer removal during cross-flow filtration and could allow a better rinsing and cleaning membrane conduct (e.g. avoid to use a strong chemical cleaning).

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