Understanding of casein micelles concentrated layers properties during cross flow ultrafiltration by *in-situ* small-angle X-ray scattering (SAXS)

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Keywords: cross-flow ultrafiltration; fouling; SAXS; casein micelles; colloid; operating conditions

Short 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. Some precedent results on the possibly effect of operating conditions 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 is to elucidate the local structure and time dependant organization of casein micelles fouling layer under various operating conditions thanks to *in-situ* small-angle X-ray scattering SAXS during cross-flow ultrafiltration. This allowed to (i) distinguish the thickness and local solid concentration profiles in flowing (sol) and stagnant (gel) parts of the fouling layer; (ii) discriminate the effect of time, transmembrane pressure TMP, shear and temperature on the sol-gel transition; (iii) study the reversibility of the sol-gel transition under the moderate laminar cross flow.

Material and Methods

Dispersion with initial casein micelle concentration of 54.7 g.L⁻¹ (2.1 C0 with C0 = 26 g.L⁻¹) was prepared from casein micelle powder (Promilk 802 B, Ingredia, Arras, France) dispersed in preliminary obtained milk ultrafiltrate (Qu et al., 2012). The dispersions were prepared by thoroughly mixing the casein powder in a UF permeate for 15h at 35°C. SAXS experiments were performed at ID02 High Brilliance beamline of ESRF (Grenoble, France) with the help of specially developed SAXScross-flow ultrafiltration cell (Jin et al., 2014). Polyethersulfone ultrafiltration membrane with nominal MWCO of 100 kDa (Pleiade, Orelis Environnement, France) was used for filtration. Those experiments allowed to access to the structural organization at nanometer length scales and concentration profiles at the vicinity of the membrane surface. The profiles of casein micelles concentration in the fouling layer (local casein concentration versus distance to membrane) were obtained with spatial resolution of 20 µm. The impact of transmembrane pressure (10 and 110 kPa), cross-flow velocity (0.03, 0.05 and 0.15m.s⁻¹) and, notably, temperature (12, 25 and 44°C) on the local structure of fouling layer was studied during different stages of filtration (layer formation \rightarrow relaxation \rightarrow erosion).

Results and Discussion

Filtration run in figure 1 was carried out at v = 0.03m.s⁻¹ and TMP = 110 kPa. A second step of relaxation was performed by reducing the TMP at 10 kPa. Finally, erosion step at 10 kPa and 0.15m.s⁻¹ was applied to try to eliminate the fouling layer. Such conditions allow to build a thick casein micelle layer of around 125 µm (Fig. 1) with a maximal concentration of 7.5 C0 (around 195 g.L⁻¹) close to the membrane (z = 30 µm) above the sol- gel transition (180g/L), according to Bouchoux *et al.* (2009) and Jin *et al.* (2014). The SAXS analysis revealed that this highly concentrated layer is mostly reversible since it lasts a 50-70 µm of casein micelles layer reaching 3.5 C0 (around 91 g.L⁻¹) close to the membrane.

The effect of temperature on the concentration profile and its reversibility has been studied for three independent filtrations (Fig. 2). Concentrated layer thickness increased with temperature: from ~100 μ m at 12°C to 150 μ m at 25°C and 200 μ m at 44°C (after 183 ± 9min of filtration) and decreased with shear. However, the concentration distribution profile did not evolve with layer thickness. A maximal concentration is observed for filtration performed at 25°C. Irreversibility is similar for all the temperatures since a 3.5 C0 (around 91 g.L⁻¹) fouling layer close to the membrane is lasting after pressure relaxation.

Conclusion

In-situ SAXS measurements during cross-flow ultrafiltration of casein micelles allowed to follow the formation and reversibility of concentration polarization layers as a function of time, TMP, cross-flow and



Figure 1. Concentration profiles within the accumulated casein micelles over steps of filtration protocol at 25°C. F: Filtration step at 110 kPa and 0.03 m.s⁻¹; R: Relaxation step at 10 kPa and 0.03m.s⁻¹; E: Erosion step at 10 kPa and 0.15 m.s⁻¹



Figure 2. Evolution of concentration profiles within the accumulated layer over temperature during casein micelle crossflow ultrafiltration. F: after filtration step at 110 kPa, 0.03 m.s⁻¹ during 183 ± 9 min, R: after relaxation step at 10 kPa, 0.03 m.s⁻¹ during 57 ± 10min

temperature conditions. It leads to identify sol-gel transition of casein micelles near the membrane surface and to distinguish which part was reversible and eliminated by TMP relaxation. Those results are important for understanding the mechanisms of concentration during cross-flow filtration and they could be used to adjust the filtration parameters to avoid the formation of an irreversible fouling layer at the membrane.

References

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