Structure of casein micelles in filtered deposits investigated directly above the membrane

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Casein micelles (CMs) are used as raw material for processed food as well as in a number of technical applications such as blend fabrics, glues and coatings. A fast and cost-effective way of their preparation from skimmed milk is the micro-filtration of milk. During the micro-filtration a porous membrane enables the separation of CMs from smaller milk ingredients such as whey proteins, lactose and salts. This process is the most challenging one among all membrane processes because smaller proteins are meant to pass the membrane while deposited CMs form an additional mass transfer barrier. It is therefore of paramount interest to understand structural details of deposited layers in order to enable a more targeted process design. Recent X-ray scattering experiments showed that CMs deform when subjected to osmotic stress[1,2] or shearing forces[3]. These experimental results support the hypothesis that casein micelles behave as soft objects that structurally respond to changes in their environment.

We used a GISAXS-filtration setup (Figure 1) in order to investigate structural changes of CMs induced by a directed flow field through a membrane.

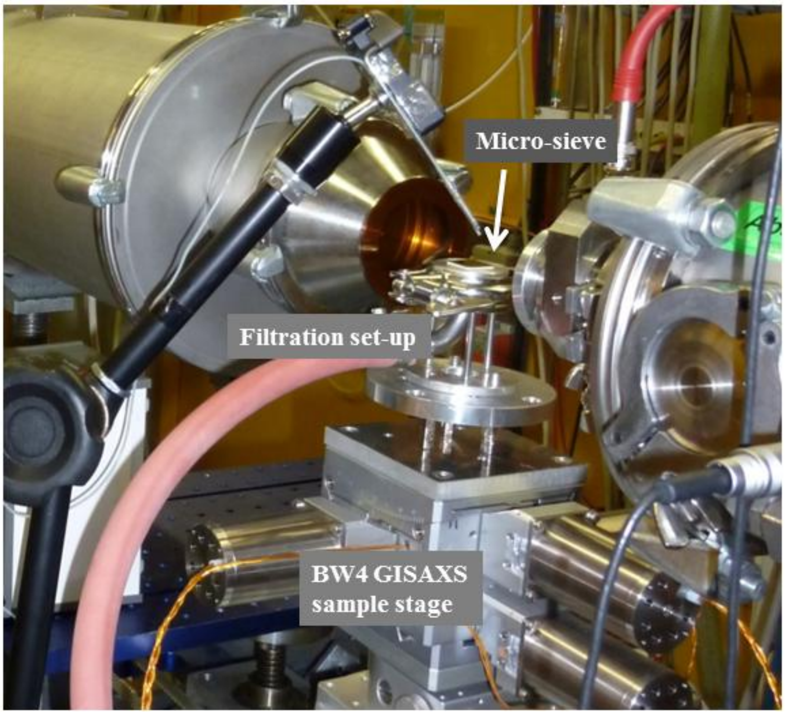

Figure 1: GISAXS-filtration set-up on the BW4 beamline, built-up for the investigation of membrane-near casein micelles in filtered deposits.

We used micro-sieves as membranes[4] since they contribute only a little to the scattering signal due to their low surface-roughness. After applying the liquid casein sample by a hydraulic pump or by a syringe on top of the micro-sieve, we started filtration. A pneumatic pump generated the trans-membrane pressure needed to drive the volumetric flow through the pores of the micro-sieve. Once the casein deposit layer was formed, we started the GISAXS measurements.

Lateral GISAXS scans across the micro-sieve were recorded with a resolution of 100 µm using a focused X-ray beam with a horizontal beam-size of 32 µm. The micro-sieve consists of membrane areas covered with pores, which are separated by impermeable spacer. Depending on where the CMs become deposited during filtration, different forces act on their structure. We extracted scattering functions from out-of-plane cuts of GISAXS patterns, which were measured either above the pores or beside the pores in the spacer regions. While the shoulder at $Q_Y = 0.01\ nm^{-1}$ belongs most probably to a deposited super-structure, the shoulder at $Q_Y = 0.04\ nm^{-1}$ can be assigned to the lateral size of CMs. Above the pores, this size is reduced as the shift of the second shoulder towards higher Q_Y-values indicates. A rough estimate of the radius of gyration (RG) in the Guinier region shows that the super-structures deposited above the pores have – compared to those beside the pores – a reduced lateral size by a factor of 0.8. Both observations point to a deformation of CMs in membrane deposits along the fluid flow direction, which is discussed in more detail elsewere[5].

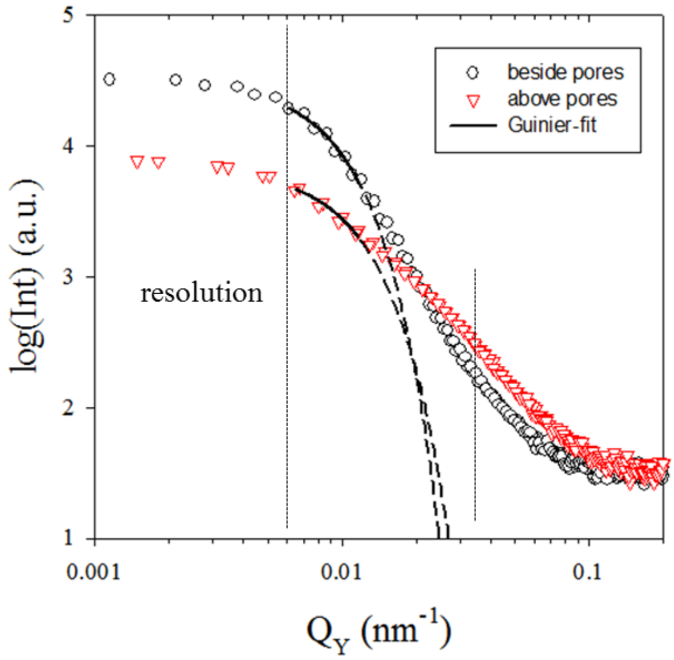

Figure 2: Scattering functions of CMs beside and above pores as obtained from out-of plane cuts of the corresponding GISAXS-patterns. CMs in the filtered deposit were subjected to a trans-membrane pressure of $\Delta P = 200$ mbar. Fits to the data in the Guinier-region are indicated by (—), the resolution limit and the shoulder, which belongs to the size of CMs, are indicated by (…).

References

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