ESRF	**Experiment title:** The near-surface behavior of low-hydrated monoacylglycerols at high hydrostatic pressure	**Experiment number**: SC-4581
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Report:

We conducted a high energy XRR and SAXS study on the near surface behavior of monoolein at low hydration at high hydrostatic pressure. Depending on temperature, solvent conditions, and pressure, monoolein molecules form different liquid crystalline structures, such as layers, tubes and spheres or even more complex configurations like cubic liquid-crystalline phases. The temperature- and water-content-dependent behavior of monoolein was vastly studied in literature [1-2] and also pressure-dependent phase diagrams are already available for bulk systems [3]. We investigated how monoolein/water mixtures assemble at hydrophilic and hydrophobic interfaces.

The XRR technique enables to resolve the vertical electron density profile of the sample system with sub-Ångström resolution, thus, it provides direct insight in the structure of monoolein layers that form at a solid substrate. Additionally, we recorded SAXS patterns in transmission and under grazing incidence before and after every reflectivity scan. The transmission geometry yields information on the bulk phase of the monoolein/water mixtures, while the grazing incidence scans provide a high surface sensitivity and, thus, contain further details on the behavior of the lipids in the near-surface region.

The measurements were performed in a custom-made high hydrostatic pressure cell [4] and at a photon energy of 70 keV. The beam size was approximately 5 µm (vertical) × 40 µm (horizontal). Pressures between 50 and 4000 bar in steps of 500 bar and a temperature of 25 °C were applied. A silicon wafer was introduced into the cell and the cell volume was filled with a mixture of monoolein and 40 %wt water. The silicon wafers were

either hydrophilized or coated with Octadecyltrichlorosilane (OTS) or 1H,1H,2H,2H-peruorodimethyl-decyl-chlorosilane (pF-DDMCS) to obtain a hydrophobic surface. A precharacterization of the substrates revealed a contact angle of approximately 107° for the OTS wafers and 95° for the pF-DDMCS wafers.
The SAXS data show that the monoolein/water mixtures undergo a phase transition between 2000 and 3000 bar from a cubic structure into a lamellar phase. At 50 bar, the cubic phase is the Pn3m phase. At higher pressures, we observed a coexistence of the Pn3m phase with the Im3m phase. The precise nature of the lamellar phase cannot be determined in this setup, as we have no access to the wide-angle scattering of the chain packing. However, due to the fact that the spacing of the lamellar phase barely changes at further pressurization up to 4000 bar, it can be concluded that the lamellar phase is not the liquid crystalline L_α phase. Instead, this indicates that the system is in the gel-like L_β or crystalline L_c phase, which are characterized by an all-trans conformation of the hydrocarbon chains of monoolein with maximum extension.
The surface sensitive measurements show that in case of a hydrophilic substrate, there is a formation of ordered lamellar layers at the interface already at 1000 bar, which is below the critical pressure of the phase transition from cubic to lamellar in the bulk. This early phase transition is suppressed when the substrates are hydrophobic. In case of a pF-DDMCS coated substrate, we also observed an alignment of the lamellar phase parallel to the surface once the bulk transition was reached. In contrast, the orientation of the lamellar phase at an OTS surface seemed to be more random. *Figure 1* shows SAXS scans conducted under grazing incidence at 3500 bar for all three substrates. A high intensity at the top of the fringes indicates an orientation of the lamellar phase parallel to the surface. Further data treatment including the fitting of the reflectivity curves is still in progress.

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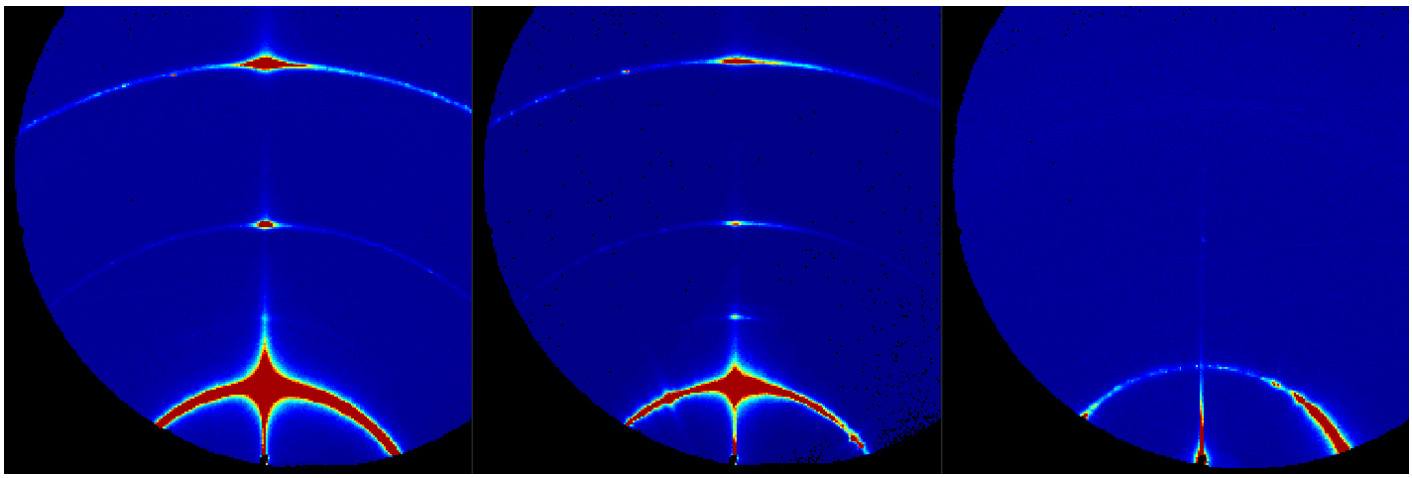

Figure 1: SAXS patterns taken under grazing incidence at 3500 bar at a hydrophilic surface (left), a pf-DDMCS surface (center) and an OTS surface (right). A strong signal at the top of the fringes indicates an alignment of monoolein crystallites parallel to the surface.