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| | Experiment title: “Crystalline phase behaviour of surfactant monolayers on liquid substrates cooled down to -50°C” | Experiment number: SI/1247 |
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Report:

Ordered phases of monolayers of most amphiphilic molecules at the liquid/air interface are so-called rotator phases, characterised by a hindered or even free rotation of the molecules along their length axis. For bulk systems of alkane molecules the various rotator phases are known to be intermediate phases between the isotropic liquid and the crystalline phase. For these bulk systems the crystalline phase is achievable upon moderate cooling or even above room temperature, depending on the length of the alkanes [1]. For a quasi two-dimensional system like a Langmuir monolayer however, the transition from a rotator to a crystalline phase is expected to appear at much lower temperatures. The reasons for this phase shift in two-dimensions is twofold: in general the molecular interactions are weaker in two dimensions (the number of neighbour molecules is smaller) and in addition the liquid surface is always decorated with thermal fluctuations (capillary waves), which diminish the net molecular interactions. An obvious way to overcome these hinderances is the cooling of the system, which would both damp the capillary waves present on the liquid subphase and strengthen the molecular interactions. To date virtually all investigations of surfactant monolayers at the liquid/air interface used water as a subphase, restricting the accessible temperature range to temperatures above 0°C, consequently rendering the investigation of the rotator-crystalline phase transition impossible.

We have investigated the behaviour of Langmuir monolayers upon cooling from 22°C to -50°C by means of GIXD. The subphase was a mixture of H₂O and DMSO at the eutectic mixing ratio [2], a low viscosity water-like liquid subphase with a freezing point of about -63°C. Starting from a rotator phase at ambient temperature, low temperature phases with values for the area per molecule similar to equivalent bulk systems were achieved at lower temperatures.

The investigated surfactant molecules were two model systems for biological surfactants: a phospholipid (dipalmitoyl-phosphatidic-acid, DPPA, (C₃₅H₆₈O₈PNa)) and a saturated fatty acid (arachidic (eicosanoic) acid, CH₃(CH₂)₁₈COOH). Monolayers of these surfactants were prepared by spreading from chloroform

solutions at a typical concentration of 0.2g/L using a Hamilton Microsyringe. The surface pressure of the monolayers during the preparation process was monitored *in-situ* using a conventional tensiometer (Nima ST 9005).

Samples were prepared in a chamber specially designed for cooling liquid samples under a helium atmosphere. The sample environment is made up of an inner chamber, housing the liquid sample under an helium atmosphere, and an outer chamber under vacuum, which provides the thermal insulation against the ambient environment. The sample was prepared on an aluminum trough of 68mm diameter, which was cooled by four peltier elements with a total cooling power of 250W at its bottom side. The hot side of the peltier elements is sitting on an aluminium block which is cooled (down to -30°C) by circulation of a liquid cooling agent from an external chiller. The temperature of the aluminum block, the liquid sample and the helium atmosphere are monitored by Pt 100 temperature sensors. A PID controller, reading the temperature of the sample, was used to drive the power supply of the peltier elements. This setup allowed for changing the sample temperature by programmed smooth temperature ramps. To avoid underpressure caused by imperfect encapsulation against the vacuum, the inner cell is flushed with helium instead of just containing a static atmosphere. In order to avoid turbulences on the liquid surface, convection inside the cell is guided by an aluminum cap. This cap is in thermal contact with the trough containing the sample and therefore thermalizes the helium to the sample temperature. To minimize the heat load, the helium is pre-cooled before entering the cell by circulating through a copper spiral that is immersed in liquid nitrogen.

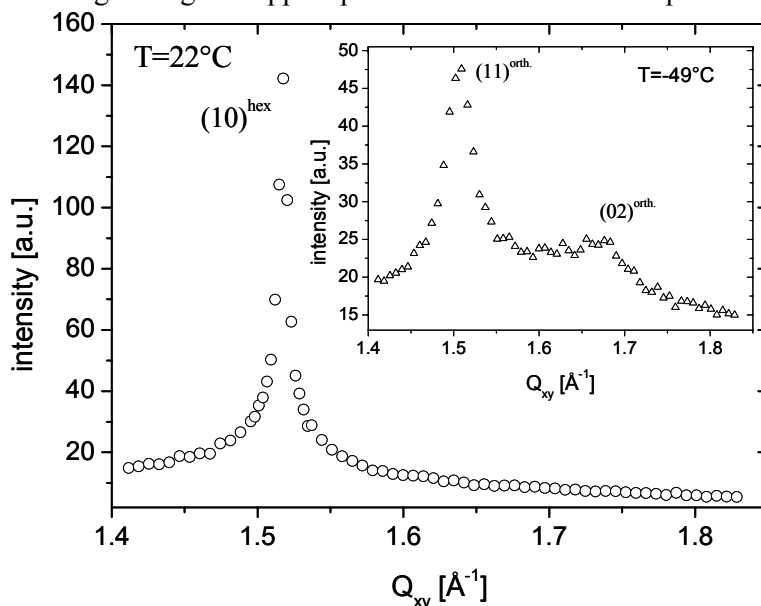


Fig. 1 In-plane Bragg peaks for DPPA monolayer at temperatures of 22°C and -49°C (inset). Upon cooling the 2d lattice changes from a hexagonal to a centred rectangular configuration. This reorientation process is accompanied by a strong decrease of one lattice spacing and consequently by a reduction of the area per molecule.

Figure 1 shows the scattering pattern integrated over Q_z for a DPPA monolayer prepared at a surface pressure of 30mN/m. At a sample temperature of 22°C only one diffraction peak can be observed, indicating that the monolayer is in a hexagonal phase. This finding is consistent with experimental data from DPPA monolayers on water subphases at similar surface pressures [3]. After cooling the sample down to -49°C, a second diffraction peak at a higher in-plane wavevector transfer Q_{xy} is observed. The corresponding 2d lattice was identified as centred rectangular. The appearance of a second reflection at larger Q_{xy} is indicative of a strongly reduced lattice spacing in one direction as compared to the hexagonal lattice at room temperature. Consequently, the corresponding area per molecule is also drastically reduced, from 39.6 \AA^2 at 22°C to 38.0 \AA^2 at -49°C. At the low temperature phase, the areas per molecule become hence comparable with those of bulk alkane systems [4] in the crystalline phase. In contrast, the starting value of 39.6 \AA^2 at 22° is more comparable with values found for the rotator phase of bulk alkanes. As shown in Figure 2, the so-called Bragg rods provide information about the alignment of the alkane chains of the DPPA molecule in the unit cell. From Bragg rod analysis the tilt angle of the molecules with respect to the surface normal was determined to be zero at both temperatures. It is noteworthy, that the observed structural changes are only induced by the reduction of temperature. In contrast to the majority of Langmuir studies the monolayer is not laterally compressed to reduce the area per molecule and to induce phase transitions. In our case, the

structural reorientation can hence be attributed to a change in the net effective molecular interactions upon cooling.

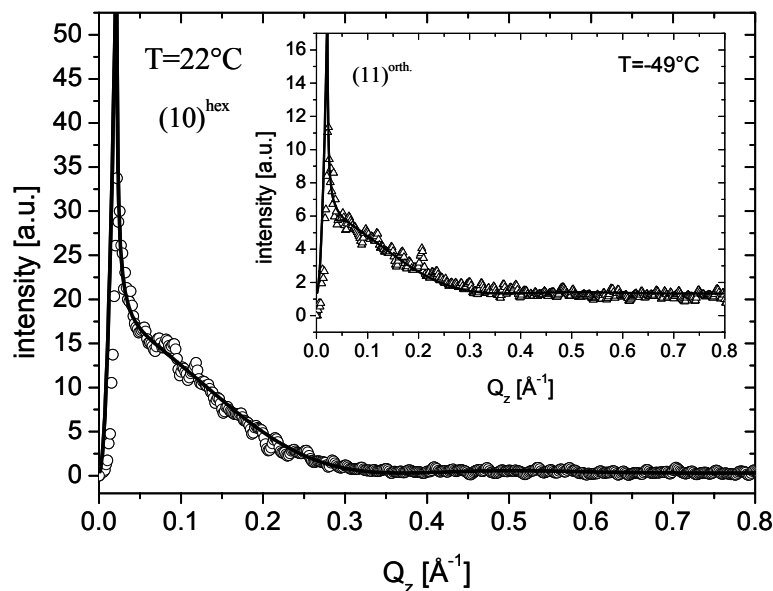


Fig. 2 Bragg rods of the (10) reflection of the hexagonal lattice at 22°C and of the (11) reflection of the centred rectangular lattice at -49°C (inset). The fitting of the Bragg rods with a cylinder model [5] (solid lines) reveal a upright chain conformation with zero tilt angle with respect to the surface normal over the whole investigated temperature range.

Figure 3 shows the scattering pattern in reciprocal space (Q_z - Q_{xy} plots) and integrated intensities along Q_z for a monolayer of arachidic acid prepared at a surface pressure of 4mN/m. Unlike DPPA, the structure adopted at 21°C is centred rectangular as indicated by the presence of two diffraction peaks.

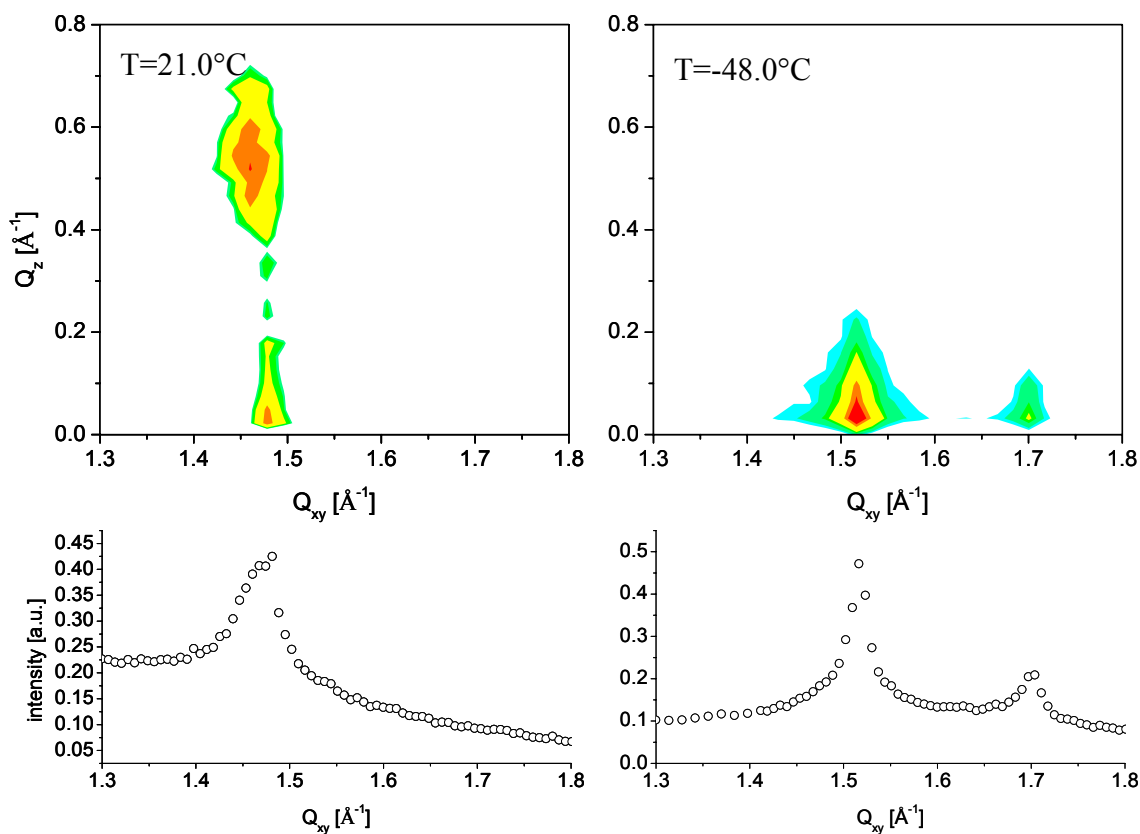


Fig. 3 Intensity distribution in reciprocal space (upper panels) and integrated over Q_z (lower panels) for a monolayer of arachidic acid at temperatures of 21°C and -48°C.

The smearing out of the scattered intensity along the Q_z direction points towards a tilt angle of the alkane chains larger than zero. Bragg rod analysis revealed at a temperature of 21°C a tilt angle of 21.2° with respect to the surface normal and a tilt direction towards the nearest neighbour, while the tilt angle was found to be reduced to zero at -48°C. Again, the observed distinct structural reorientations were only driven by the changing molecular interactions upon cooling. For a DPPA monolayer undergoing a structural transition from a hexagonal lattice to a centred rectangular one, one lattice spacing remains almost unchanged. In contrast, for an arachidic acid monolayer both lattice spacings change quite noticeable. This different behaviour could be a consequence of the glycerol backbone of the DPPA molecule acting like a ‘spacer’ in one direction.

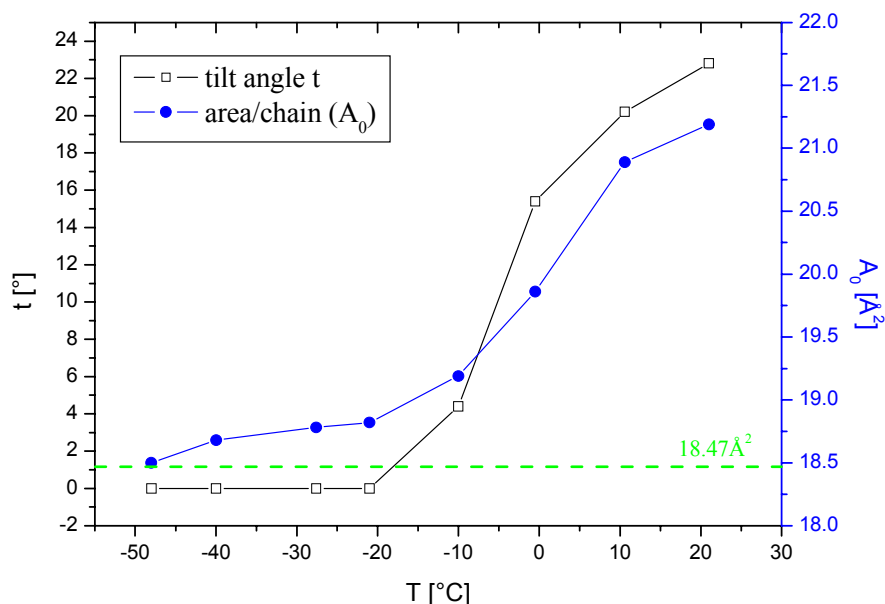


Fig. 4 area/molecule and tilt angle (relative to the surface normal) for arachidic acid on H₂O/DMSO as obtained by GIXD upon cooling. The dashed line indicates a bulk crystal value [6].

Figure 4 displays the area per alkane chain and the tilt angle for arachidic acid monolayer as a function of temperature. At temperatures below -20°C the values for the area per molecule become comparable to those found for alkane bulk systems in the crystalline phase or even in bulk single crystals of fatty acids [6] (dashed horizontal line).

In conclusion, we have for the first time observed the fundamental phase transition from a rotator to a crystalline phase for the investigated organic model surfactants. The phase transition was purely induced by a temperature reduction and the accompanied increase in the net effective molecular interactions. The temperature range of the phase transition requires undoubtedly the use of subphases with freezing points distinct lower than that of water.

Further data analysis and a manuscript for peer review are in progress.

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