



Beamline: ID-10B	Experiment title: <i>In-Situ</i> Characterization of ZnS Nanowire and Nanorod Assemblies at the Air-Water Interface	Experiment number: SC-2098
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In our previous experiment SI-1157, we used grazing incidence small-angle x-ray scattering (GI-SAXS) to study the formation of 2D superstructure assemblies of ZnS nanorods coated with octadecylamine (ODA) or tetradecylamine (TDA) surfactants at the air-water interface. There is a strong mutual interaction between the ZnS nanorods and the surfactant molecules, suggesting that the assembly of the ZnS nanorods into ordered superstructures is strongly mediated by the surfactants.

One of the aims of this experiment was to study the crystal structures of the pure ODA and TDA surfactant molecules in 2D Langmuir films (LF) at the air-water (or air-solution) interface. ODA and TDA surfactants dissolved in chloroform were spread on the surface of an NaOH aqueous solution at pH=10.5 on the Langmuir trough in Beamline ID-10b and compressed to a close-packed structure. Grazing incidence x-ray diffraction (GIXD) measurements were performed directly at the air-water interface without transferring the films onto a solid support.

From the diffraction intensity maps of q_z vs. q_{xy} obtained in a GIXD experiment at the air-NaOH aqueous solution at pH=10.5 from ODA compressed to $\Pi=50\text{mN/m}$ at 22°C (Figure 1a), a doublet peak was observed with high intensity at $q=1.528\text{\AA}^{-1}$ ($d=4.112\text{\AA}$) and low intensity at $q=1.612\text{\AA}^{-1}$ ($d=3.898\text{\AA}$), indicating a distorted hexagonal (centered rectangular) structure. On the other hand, TDA compressed under the same conditions showed one peak at $q=1.505\text{\AA}^{-1}$ ($d=4.174\text{\AA}$) (Figure 1c), indicating an undistorted hexagonal structure. This result points to that not only the nanorods form ordered 2D structure at the air-water interface, but also the surfactants do. The difference between the structure of chains longer and shorter than C_{16} is not surprising and is in fact expected from the literature. Furthermore, no appreciable chain tilt was observed for any of the two monolayers.

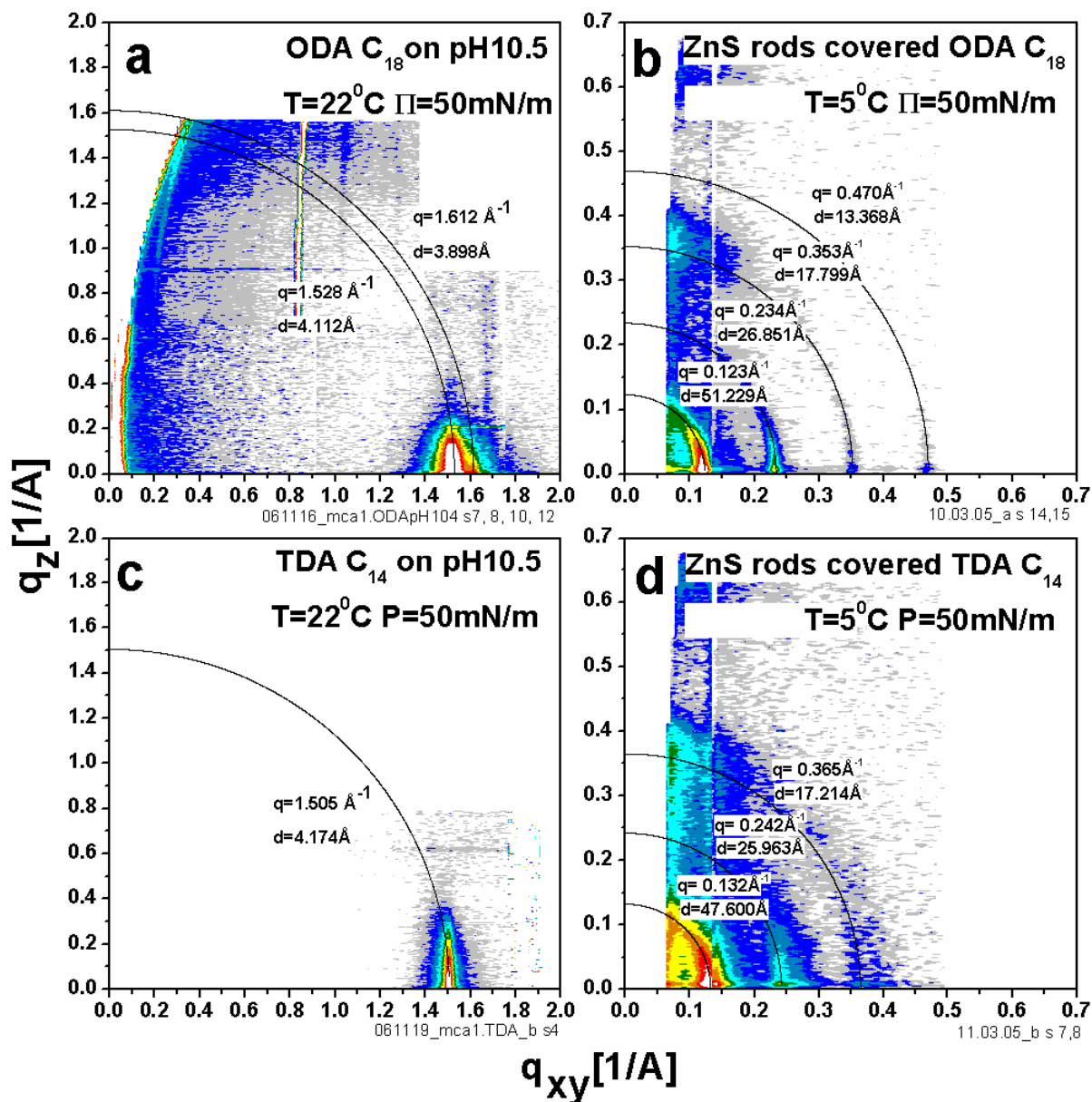


Figure 1: GIXD diffraction intensity maps of q_z vs. q_{xy} obtained at the air-NaOH aqueous solution interface (pH=10.5) at $T=22^\circ\text{C}$ and $\Pi=50\text{mN/m}$ from (a) ODA and (c) TDA surfactants. GI-SAXS diffraction intensity maps of q_z vs. q_{xy} obtained at the air-water interface at $T=5^\circ\text{C}$ and $\Pi=50\text{mN/m}$ from ZnS nanorods capped with (b) ODA and (d) TDA.

TDA (C_{14}) has a shorter hydrocarbon chain length than ODA (C_{18}), so the small difference in the d -spacing between them indicates that the interactions largely depend on the van der Waals forces between the chains. Studying the 2D structure of the surfactants at the air-water interface provided important information for our efforts to elucidate the three dimensional structure of ODA and TDA powders and the superstructure formed by assembly of surfactant coated ZnS nanorods in 2D (air-water interface) and 3D (powder form).

By comparing the data obtained in this experiment with powder XRD and SAXS data, we were able to identify and assign the in-plane peaks which correspond to the lateral ordering of the lamellae in the lamellar structure of pure ODA powder. Not surprisingly, the position of these peaks in 3D powder form and in the Langmuir films was essentially the same. This was an important breakthrough in our attempts to elucidate the 3D structure of alkylamine surfactant molecules (TDA [C₁₄NH₂], HDA [C₁₆NH₂], ODA [C₁₈NH₂]) which has not been solved to date.

The GI-SAXS intensity maps from ZnS nanorods capped with ODA and TDA at the air-water interface, compressed to a surface pressure of 50mN/m at a temperature of 5°C are shown in Figure 1b and 1d, respectively. The data indicates that the inter-particle spacing scaled with the length of the surfactant molecule and larger spacing is obtained between ODA (C₁₈)-coated ZnS nanorods compared to TDA (C₁₄)-coated ZnS nanorods, due to their shorter carbon chains. Hence, this demonstrates that the inter-rod spacing in the nanorod superlattices can be continuously tuned simply by using different hydrocarbon chain lengths of the amine surfactant molecules used.

Another aim of this study was to investigate the crystallographic selectivity in the formation of these surfactant assisted synthesis. For this purpose, GIXD “snapshots” were taken while compressing the ODA molecules in the presence of divalent metal ions (Zn²⁺) in the subphase or by injecting the ZnCl₂ solution under ODA LF compressed on water. Subsequently, formation of ZnS nanoparticles was induced *in-situ* exposing the ODA monolayer at the interface to controlled amounts of H₂S gas in the presence of Zn²⁺ ions in the subphase. In this part of the experiment, our goals were to monitor not only the formation of the ZnS mineral but furthermore, to study the effect of the nucleating mineral on the structure of the ODA LF. The preliminary results obtained suffered from a high background noise and did not show well-defined ZnS mineral peaks, while TEM images of samples taken from the interface during this experiment showed that nanoparticles were indeed mineralized underneath the ODA monolayer films. More in-house TEM imaging coupled with additional synchrotron GIXD experiments will be needed in order to obtain conclusive information on the mineralization of ZnS in the presence of alkylamine Langmuir films.