ESRF	**Experiment title:** Simultaneous reflection and surface diffraction from secondary templated mesoporous silica at the air/water interface	**Experiment number**: SC-630
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Report:

The aim of this experiment was to study the growth of surfactant templated silicate films at the air/water interface. These silicate films form through a spontaneous aggregation process where long cylindrical silica-coated surfactant micelles in solution accumulate at the surface. These cylindrical micelles pack with their long axis parallel to the surface, and silica polymerization then "freezes in" the structure, resulting in a thin solid film at the air/solution interface. Previous work has described the growth process as a gradual accumulation of layers of silicated micelles at the surface, [1] and has suggested that it may be possible to influence this process by the presence of an insoluble monolayer at the air/solution interface.[2] In this experiment we carried out the first short time-scale measurements on the in situ growth of a surfactant-silicate film at the air/water interface, allowing direct observation of the formation processes in order to investigate this mechanism. The intensity available at the ESRF allowed patterns to be collected in 60 seconds, permitting direct observation of the development of the diffraction peaks which corrsespond to ordered structures in these films.

Figure 1 shows the specular reflectivity patterns from the air/solution interface during the lengthy induction period prior to film formation, and also the pattern observed from the final film. The initial pattern can be fitted to a one layer model corresponding to a layer of surfactant at the interface, 36Å thick. The final pattern corresponds to a layered system consisting of more than 30 alternating silica and surfactant layers of 35 and 12 Å thick respectively. However, the appearance of the diffraction peaks occurs over a very short timescale and the specular reflectivity measurements proved to be too slow to observe the kinetics of this system.

To overcome this problem we used an alternate experimental geometry in which the incident angle was fixed, and the linear position sensitive detector was positioned perpendicularly to the plane of the sample so that many reflected angles could be measured simultaneously.

The detector was positioned so that the reflectivity peak appeared near the centre of the detector, flanked by the first order and second order diffraction peaks. The Yoneda wing was also visible at the bottom edge of the detector. Using this configuration it was possible to collect data in 60s time steps and to monitor the appearance and growth of the diffraction peaks during the growth of the film. Figure 2 shows the increase in the intensity of the first order diffraction peak, and the Yoneda wing with time, and the simultaneous decrease in the reflectivity intensity. The second order peak behaviour followed that of the first order, but with lower overall intensity. The observed increase in first order diffraction peak intensity could be fitted to an exponentially increasing surface coverage of diffracting species within the film with time. The same relationship between surface coverage and time was then shown to also fit to the increasing roughness of the surface demonstrated by the fall-off in reflectivity intensity and the increase in intensity in the Yoneda wing.[3] The fits to the data are also shown in Figure 2. Significantly, however the expected growth mechanism described above was not observed. Gradual accretion of silica-coated micelles at the surface was expected to produce domains which slowly increase in size, and so cause the width of the diffraction peaks to decrease. No change in the diffraction peak width was observed, so this model cannot be correct. The data suggest instead formation of large layered particles in solution which then pack at the interface to form the film.

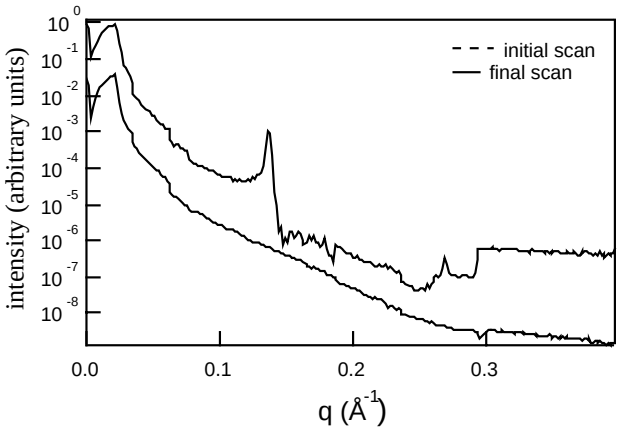

Figure 1: Specular reflectivity from a spontaneous film forming solution during the induction period and after formation of the final film.

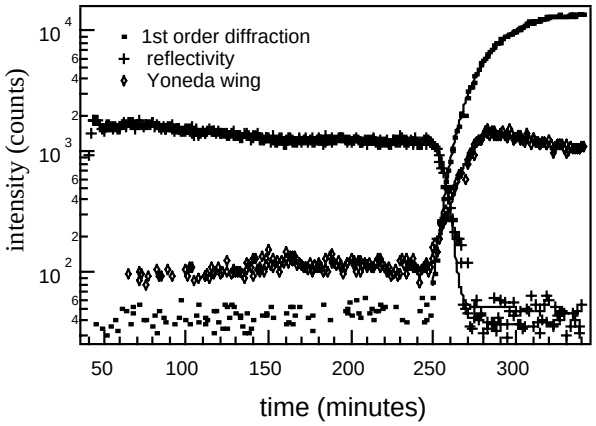

Figure 2: Changes in intensity of the first order diffraction peak, the reflectivity and the Yoneda peak with time.

Several days were spent attempting GISAXS on these film forming systems to observe the development of in-plane structure. Unfortunately these were not successful due to problems with alignment of the instrument. This left us with little time for the experiments described above so that only two synthetic conditions at one set of angles were measured.

1. A. S. Brown, S. A. Holt, T. Dam, M. Trau and J. W. White, Langmuir 13 (1997) 6363.
2. S. Roser, H. M. Patel, M. R. Lovell, J. E. Muir and S. Mann, Chem. Commun. (1998) 829.
3. K. J. Edler, A. Goldar, A. V. Hughes, S. J. Roser and S. Mann, Microporous Mesoporous Mater. submitted (2000) .