ESRF	**Experiment title:** **Off-specular time resolved studies of the formation of surfactant-templated silicate thin films at the air/water interface**	**Experiment number**: CH-912
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Shifts: 18	**Local contact(s)**: Dr Oleg Konovalov	*Received at ESRF:*

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Report:

This experiment was a continuation of experiment SC-630, in order to investigate in more detail the *in situ* growth of mesoscale composite silica-surfactant films at the air-solution interface. These experiments make use of the intensity available at the ESRF to carry out time-resolved off-specular X-ray reflectivity measurements on the growing films, giving us time resolution of 1 minute. Structure on the mesoscale develops over a period of about 30 minutes after an induction period which varies in time with solution concentration. For the purposes of the X-ray reflectivity measurements the induction period is defined as the period up until the appearance of the diffraction peaks. Using a vertically mounted linear detector which is stationary during the measurements allows us to observe the growth of the diffraction peaks during film formation and also the development of surface roughness through the variation in the Yoneda wing scattering.

In the earlier experiment we collected data on a solution containing 0.075M cetyltrimethylammonium bromide (CTAB) /0.54M tetramethoxysilane (TMOS). The film which developed in this experiment showed no width variation in the diffraction peaks which developed over time, only an increase in peak intensity. This was modelled as the adsorption of pre-formed mesophase composite particles at the air-solution interface[1] that formed the film by packing together to cover the surface. This type of film growth also was responsible for the increasing roughness as the increase in Yoneda wing scattering and decrease in specularly reflected intensity could also be fitted using this model. In the current experiment we looked at several different incident beam angles for the original CTAB/TMOS concentration and also at several CTAB/TMOS ratios by holding the CTAB concentration

constant while varying the TMOS concentration. Using a longer linear detector also enabled us to see a third order of diffraction that was previously unobserved. The experiments at different incident beam angles were fitted to the same model as was used previously and confirmed our earlier results.[2] The concentration experiments presented several intriguing results.

Unexpectedly, increasing the TMOS concentration caused a large increase in the induction period, while decreasing it caused the induction period to become much shorter. Owing to shutter problems it was not possible to collect a complete data set on the film growth which exhibited the longer induction period. Data for the lower TMOS concentration showed distinctly different behaviour than that of the initial TMOS concentration investigated previously. While it was still possible to fit the increasing intensity in the diffraction peaks, and the decreasing intensity of the specularly reflected beam to the same model as used previously, the characteristic exponent in the fit increased in value from *ca* 1.5 to *ca* 2.[2] The value of the exponent in this fit is related to the diffusion and interaction of the mesophase composite particles which fuse to form the film on the solution surface. Also the diffraction peaks which grew in from this solution concentration showed a decreasing full-width half-maximum as they increased in intensity, indicating that the diffracting areas near the surface were initially small and increased in size, rather than arriving at the interface fully formed as was the case for the original TMOS concentration. This corresponds with Brewster angle microscope images which show the initial formation of a smooth, thin film at the solution/air interface for the lower TMOS concentrations which later undergoes a rapid roughening transition which looks visually similar to that observed for the original TMOS concentration. Such an intial smooth film is not observed for the original TMOS concentration. Further experiments using small angle scattering and Brewster angle microscopy are underway to investigate the different film growth regimes that we observe at different concentrations.

Off-specular scattering in the horizontal as well as the vertical direction was also investigated, confirming that the films consisted of a hexagonally close-packed cylindrical surfactant phase. Time losses due to loss of communication with motors and detector owing to network congestion as well as the shutter problems mentioned above reduced the number of experiments possible in the time allocated, preventing investigation of the slower film growth from high concentration solutions and further horizontal off-specular scattering experiments.

References:

[1] K. J. Edler, A. Goldar, A. V. Hughes, S. J. Roser and S. Mann, Microporous Mesoporous Mater. in press (expected publication date: March 2001) .
[2] K. J. Edler, A. Goldar, S. J. Roser and S. Mann, Langmuir, in preparation (2001) .