



Experiment title:
**Formation of Titania-Surfactant Mesostructured
Films at the Air-Water Interface**

**Experiment
number:**
CH-1652

Beamline: ID10B	Date of experiment: from: 13 th to: 19 th July 2004	Date of report: 24 Aug 2004
Shifts: 18	Local contact(s): Dr Leide Cavalcanti	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

*Dr. Karen J. Edler (Chemistry Department, University of Bath)

*Dr. Ben O'Driscoll (Chemistry Department, University of Bath)

*Ms Cristina Fernandez-Martin (Chemistry Department, University of Bath)

Report:

This experiment is one of a series we have done on ID10B in order to study the formation mechanisms of mesostructured surfactant-templated inorganic thin films that grow at the air-water interface. In this experiment we extended our work beyond silica to study surfactant-templated mesostructured films of titania. These films have also very recently been shown to grow at the air-solution interface¹ from dilute solutions containing a titania precursor and the appropriate surfactant species. Free-standing mesostructured titania films have potentially important applications not only as membranes but also for photocatalysis, semiconducting layers and photochromic devices. We aimed to try to observe the film formation process using off-specular scattering in the same way as we have previously done for silica-surfactant films and also to identify the film structures using specular reflectivity and grazing incidence diffraction.

Films were prepared by first dissolving the surfactant template in water and the titania precursor, titanium (IV) tetrabutoxide (TBOT), to concentrated HCl solution. These two solutions were mixed and poured into a teflon trough mounted on a temperature controlled base, on the beamline. The temperature was maintained at 25°C. Most of the experimental time was spent investigating the use of sodium dodecylsulphate (SDS) as the surfactant template however we also carried out some preliminary experiments using the nonionic surfactant octaethyleneglycol cetyl ether (OEGC). Significant time was lost due to computer and attenuation problems so restricted the scope of the planned experiments. In the TBOT-SDS films we systematically investigated the effects of changing both the surfactant concentration and the acid concentration. The molar ratios used were TBOT: HCl: water: SDS 0.001706: 0.02867: 1: X where X was varied between 2.43×10^{-4} and 7.28×10^{-4} for the surfactant experiments and TBOT:HCl:water:SDS 0.001706:X:1:0.000282 where X was varied between 4.94×10^{-3} and 4.94×10^{-2} for the acid experiments.

In the case of SDS templated syntheses, film growth proved to occur too quickly to obtain useful time-resolved off-specular data so we restricted data collection on these films to grazing incidence diffraction and specular reflectivity patterns. The mesoscale organisation of

the surfactant filled channels within the films proved to be highly dependent on both acid concentration and concentration of the templating surfactant. At low acid concentrations although a film is visible to the eye, the mesostructure did not develop. Above a threshold acid concentration, several orders of well developed diffraction peaks were visible in the films. The d-spacing of the first order peaks was dependent on acid concentration, moving from 35.5 Å to 37.0 Å (ie to smaller Q values) as the concentration increased. The in-plane structure of the film as revealed by GIXD shows a series of different phases for increasing acid concentration at a constant surfactant concentration (Figure 1). These have not yet been fully assigned.

As the SDS concentration is changed at a given acid concentration a similar change in d-spacing is noted. As the concentration of SDS increases the first order diffraction peaks move from 35.9 Å to 34.5 Å ($Q = 0.175$ to 0.182 \AA^{-1}), however the in-plane structure observed in the films surprisingly appears to be relatively unchanged. At lower acid concentrations the in-plane structure tends to show partially oriented rings of diffraction whereas at higher acid concentration scattering is more confined to the specular ridge or, in some cases, to sharp diffraction spots. This suggests that the ordering in the film is more powder-like at lower acid concentrations, while higher acid concentration improves the overall mesophase ordering.

In previous work on silica films, surfactant concentration has had a much larger effect on film mesostructure than acid concentration.² Clearly the association between surfactant and titania is governed by different factors to that of the silica-surfactant system despite the growth of similar nanostructured films in both cases. Further work is needed to determine whether a different mechanism is operating in the case of the titania surfactant film to that which causes silica-surfactant film growth.

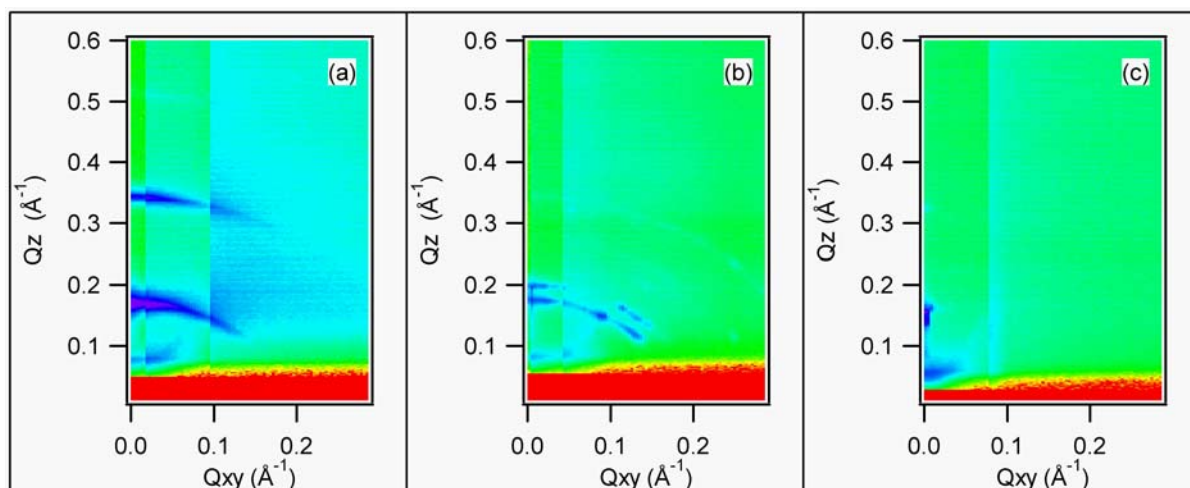


Figure 1: GIXD patterns at incident angle $\mu = 1.3^\circ$ for films grown at a constant SDS concentration with varying HCl concentration. The molar ratios used were TBOT: HCl: water: SDS 0.001706: 0.02867: 1: X (a) X = 0.024, (b) X = 0.037, (c) X = 0.049.

References:

1. Henderson, M. J.; King, D.; White, J.W. *Aust. J. Chem.* **2003**, *56*, 933.
2. K.J. Edler, T. Brennan, S.J. Roser, S. Mann, R. M. Richardson *Microporous Mesoporous Mater.*, **2003** *62*, 165-175.