

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Solution processes occurring during formation of surfactant-templated mesoporous silica films	<b>Experiment number:</b> SC-740
<b>Beamline:</b> BM26B	<b>Date of experiment:</b> from: 26 Feb 2001 to: 2 March 2001	<b>Date of report:</b> 21 Aug 2001
<b>Shifts:</b> 9	<b>Local contact(s):</b> Dr. Igor Dolbnya	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

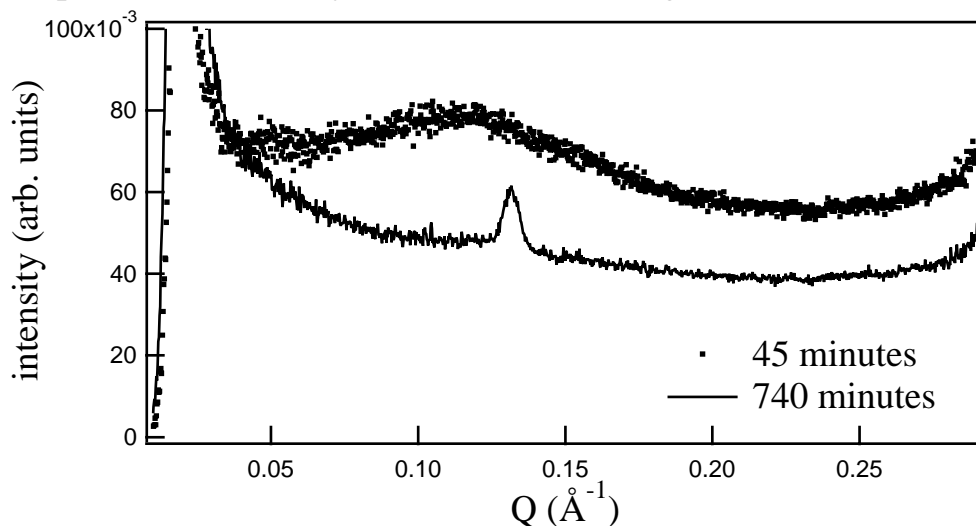
<b>Dr. Steve J. ROSER</b>	] Department of Chemistry, University of Bath Claverton Down, Bath, BA2 7AY, U.K.
Dr. Karen EDLER*	
Mr. Arach GOLDAR*	
Dr. Arwel V. HUGHES	
Mr Barry STIDDER*	
Dr. Roberto FELICI	Ist. Nazionale Fisica della Materia, Operative Group in Grenoble ESRF, 6, rue J. Horowitz, BP220, F-38043 Grenoble, France.

**Report:**

Surfactant templated silicate materials are formed by the polymerization of silica around surfactant micelles in solution to form composite solids containing a channel system that has the dimensions and connectivity of a surfactant liquid crystalline phase.<sup>1,2</sup> These materials can be grown as powders, or as monoliths and under some conditions will spontaneously form thin solid films at the air/solution interface.<sup>3</sup> The formation mechanisms for these materials are currently not well understood, and the experiments reported here were designed to investigate solution processes that are involved in formation of thin films at the air/water interface. During a time-resolved reflectivity study on ID10B on the formation of surfactant-templated silica films, the details of film formation were observed for the first time. Instead of the expected reflectivity from domains that nucleated at the surface and slowly grew to form a continuous film, we observed patterns that were more consistent with a solution-driven formation mechanism. In the model proposed from these reflectivity measurements, particles which eventually form part of the film, nucleate in the bulk solution, during the induction period and grow to aggregates of more than 30 repeat units of the channel system before diffusing to the interface where aggregation occurs.<sup>4</sup> We therefore carried out small angle X-ray scattering experiments in order to study the time-dependence of the nucleation and growth of these particles in solution.

We were able, in the time available, to carry out experiments on the silica-surfactant composite nucleation at three concentrations and two camera lengths, using 5 minute data collection times. Two of these concentrations corresponded to conditions under which we found solution-driven formation mechanisms for film growth in the reflectivity experiment and in the third experiment we heated the solution to 40°C. In the first experiment we clearly saw a correlation peak due to the presence of the surfactant micelles from the earliest pattern taken 30 minutes after mixing of the silica precursor and the templating surfactant solution.

This broad peak grew in intensity with time, over the next 200 minutes but then started to loose intensity. The diffraction peak corresponding to the first order peak from the ordered hexagonal mesostructure observed in films grown from this synthesis solution started to grow in at approximately 550 minutes and became sharper with time, although the second order of diffraction was not observed. This is the first direct evidence for silica-surfactant mesostructure formation in the bulk of the film forming solution. An early pattern and the final pattern from this system are shown in Figure 1.



**Figure 1**  
Development of the SAXS signal from the reacting solution with time.

In the second solution, at a lower silica precursor concentration, the initial correlation peak from the surfactant was less intense and broader, and it too gradually lost intensity, although in this solution no diffraction peak was observed to grow in, despite the ordering observed in films grown from solutions with this concentration. In the 40°C synthesis the initial correlation peak from the surfactant micelles was less intense than that observed in the room temperature preparation, however a broad peak at the diffraction peak position started to grow in much faster than in the room temperature experiment. Interestingly this peak remained much broader than the peak observed in the room temperature experiment, implying that the degree of long range ordering at the higher temperature was lower than at room temperature.

An initial attempt has been made to fit the scattering from the first room-temperature data set to a dilute spherical core-shell particle composed of a surfactant micelle surrounded by polymerising silica. This model fits the time-resolved data reasonably for the first 200 minutes of the experiment, however after this it is not possible to fit the data to this model, indicating that at this point in the self-assembly process the shape of the micelle begins to change or that intermicelle interactions become increasingly important to the shape of the scattering. Attempts to fit the data to more complex models that incorporate changes with time are continuing.

#### References:

- (1) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* 1992, *114*, 10834.
- (2) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* 1992, *359*, 710.
- (3) Yang, H.; Coombs, N.; Sokolov, I.; Ozin, G. A. *Nature* 1996, *381*, 589.
- (4) Edler, K. J.; Goldar, A.; Hughes, A. V.; Roser, S. J.; Mann, S. *Microporous Mesoporous Mater.* 2001, *44*, 661.