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ESRF

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.

ESRF

Experiment title:
Effect of surfactant structure on formation of mesophase silica-surfactant composites from acidic solution

Experiment number:
CH-1285

Beamline:
BM26B

Date of experiment:
from: 3rd May 2002 to: 5th May 2002

Date of report:
29/08/02

Shifts:
9

Local contact(s):
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Report:

Porous inorganic materials have wide application in areas including catalysis, encapsulation, sensing, and separations. One route to materials with well-defined pore sizes with diameters greater than those of conventional materials such as zeolites involves cooperative interactions between surfactant micellar templates and inorganic precursor molecules in solution, to produce mesostructured hybrid composites. For example, when silica monomers are added to surfactant solutions, co-assembly results in mesophases that contain wall regions comprising amorphous silica, and ordered liquid crystalline channels filled with surfactant molecules. The size and uniformity of the template micelle controls the ordering and dimensions of porous channels produced in silica replicas created by calcination of the hybrid mesostructures. Pore sizes can be varied typically from 3 to 30 nm, yielding materials with surface areas around 1000 m^2 g^{-1}.

Mesostructured surfactant-templated materials have been made in lamellar, hexagonal and a variety of cubic phases as well as more disordered forms. In acidic syntheses, in addition to well-ordered mesostructures, a variety of well-defined shapes such as toroids, fibres and spirals form spontaneously and under certain conditions self-supporting thin films will grow at the air/water interface.[1,2] Thin films and membranes of mesoporous silica should have important industrial applications and so we are studying the formation processes occurring in the subphase of film-forming solutions during the assembly of the silica-surfactant mesophase. In the current experiment we investigated the effect of using nonionic surfactants such as P123 and Brij56 as templates rather than the cationic surfactant used previously. These surfactants are cheaper and more environmentally friendly than the cationic surfactants studied previously and have been shown to produce templated silicates with a rich variety of both mesoscale and macroscale structures. We looked at the effect of changing the silica and acid concentration on the mesostructure development.

The two graphs below show the development of mesostructure in two solutions using the triblock copolymer surfactant Pluronic P123 ($(EO)_{20}(PO)_{70}(EO)_{20}$, a gift from BASF) or the nonionic surfactant Brij56 ($C_{16}(EO)_{10}$, Aldrich) as the micellar template and tetramethoxysilane (TMOS) as the silica source. In the both graphs the reaction is catalysed by 0.6M HCl. Initially both graphs show the broad hump due to micelles in solution. After about 400 min in the first graph but only 70 min in the second graph, a sharper mesostructure diffraction peak grows in. In the case of P123 at this point the intensity from the micelle scattering decays, however in the case of Brij56 the micellar peak remains, with roughly the same intensity. The Brij56 template also causes the reaction to occur more quickly, and the peak is more well defined and narrower indicating a less disordered mesophase in this case. In the P123 case the shaper peak then decays and a lower intensity broad peak remains – probably due to growth of the mesostructured surfactant-silica particles so that they precipitate out of the beam, leaving small, less well-ordered nanoparticles in suspension. (The solutions change from initially clear to cloudy as the structure forms.)

In previous experiment on BM26B (CH-1182), using a small molecule surfactant, cetyltrimethylammonium bromide (CTAB), we were able to map the evolution of solution mesostructure onto variations in the mesostructured film growth mechanism observed at the surface of the solution during experiments on Tröika II (beamline ID10B, ESRF).[3] The combined SAXS and off-specular reflectivity experiments showed a strong variation in formation mechanism with concentration of the silica precursor.[4] The experiments reported here allow both comparison between solution-phase mesostructure development for the nonionic Brij56 and polymeric nonionic P123 surfactant with the small molecule surfactant, CTAB and will also help to determine formation mechanisms for emergent larger scale structures found in the nonionic surfactant/TMOS system.

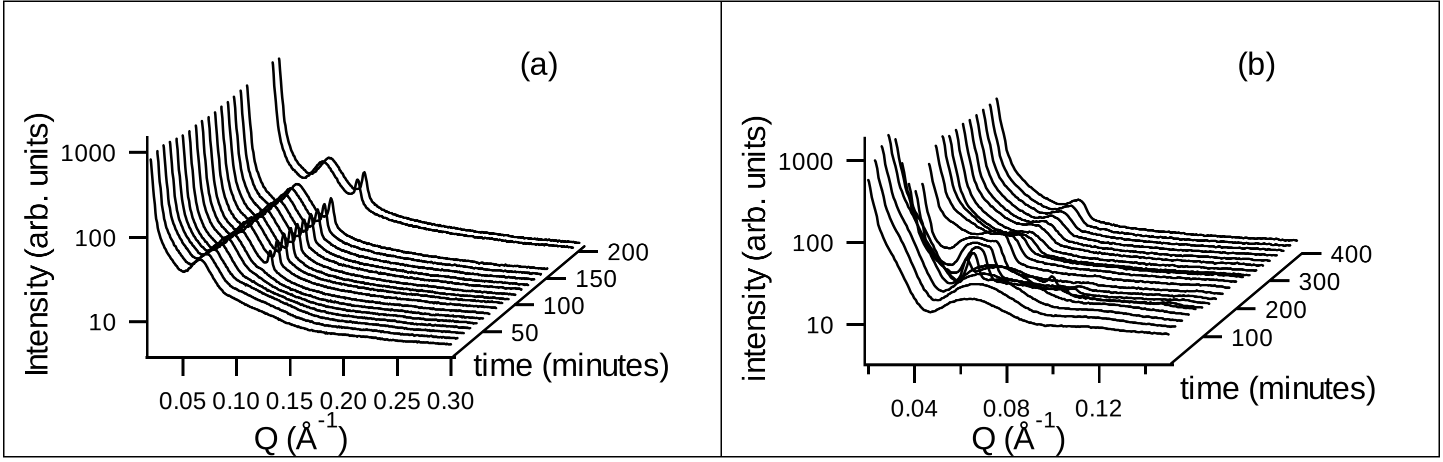

Figure 1: Time resolved SAXS patterns from (a) Brij56 templated TMOS solution and (b) P123 templated TMOS solution (data shown for 20 min time periods for clarity), both grown in the presence of 0.6M HCl.

References:

(1) Edler, K. J.; Roser, S. J. *Intl. Rev. Phys. Chem.* **2001**, *20*, 387.

(2) Edler, K. J.; Goldar, A.; Hughes, A. V.; Roser, S. J.; Mann, S. *Microporous Mesoporous Mater.* **2001**, *44-45*, 661.

(3) Edler, K. J.; Brennan, T.; Mann, S.; Roser, S. J. *manuscript in preparation.*

(4) Brennan, T.; Hughes, A. V.; Roser, S. J.; Mann, S.; Edler, K. J. *Langmuir* **2002**, *submitted.*