Introduction

Surfactant–silicate mesophase composites self-assemble from dilute solutions containing surfactant micelles and a silica precursor to form a variety of mesoscale and macroscale morphologies, dependent on solution conditions. These materials contain ordered arrays of surfactant micelles within the silica matrix and are of interest for the production of high-surface-area mesoporous materials with pores that are very uniform, with controllable sizes and shapes for use as separation media, catalyst supports, in sensor arrays, and to produce nanocomposites. In acidic syntheses a range of well-defined secondary structures are produced ranging from thin films at interfaces, to monodisperse spheres to “single crystals” depending on synthesis conditions [1]. We are interested in understanding and controlling the growth of mesostructured films on solid substrates since this geometry raises possible applications of these materials for sensors and functional surface coatings. Growing the film onto a substrate from solution allows surfaces of arbitrary shape to be coated and allows alignment of the mesoscale structure [2] and patterning of film growth on larger scales [3].

Previously one study was carried out on the in situ growth of mesostructured silica–surfactant films at solid interfaces using a single concentration of silica precursor/surfactant and the growth of the film at hydrophilic and hydrophobic interfaces was observed. In that work, despite the difference in interface structure causing observable differences in the initial surfactant–silica interactions with the substrate, the structure of the final film was unchanged [4]. In the current paper we report on results from experiments where films were grown from solution onto a hydrophilic interface using a range of silica precursor concentrations, at two different values of solution pH.

Experimental

The experiments were carried out using neutron reflectivity on the beamline SURF at ISIS (UK). A solid-solution cell was used consisting of a silicon block clamped against an O-ring sealed facing disk machined out of polyetheretherketone with a fluid...
reservoir 5-mm deep. The cell was temperature-controlled by circulating water at 28 °C through the top and bottom clamp sections. Silicon is relatively transparent to neutrons so the neutron beam can be transmitted through a silicon block to impinge upon the horizontal silicon–solution interface from above. The silicon block was pretreated to form a hydrophilic silica interface (by immersion in H2SO4–H2O2, followed by rinsing in water) and the reacting solution was injected into the cell underneath the block. The solution was a dilute acidic solution (0.2 M HCl in D2O) of a silica source, tetramethoxysilane (TMOS) and the surfactant template cetyltrimethylammonium bromide (CTAB) in D2O. Molar ratios of TMOS to CTAB to HCl to D2O of 1:3.66·10−3:3.66·10−2 were used and the TMOS molar ratio was varied between 1.66·10−2 and 2.76·10−2 (i.e. 0.80 and 0.133 M solution concentration). In a separate set of experiments the TMOS molar ratio was held constant at 1.10·10−2, while the ratio of HCl was varied from 3.66·10−3 to 1.10·10−2 (0.2 M–0.6 M HCl). Time-resolved specular neutron reflectivity data were collected in 15-min shots to follow the formation of the first-order peak from the ordered mesostructure. Film growth occurs over 30 min to 1 h after a lengthy induction period of several hours, so 15-min intervals were sufficient to provide time-resolved information on the processes occurring at the silica-solution interface. The data were scaled against the pattern of D2O collected in the same cell prior to injection of the reacting solution.

It is possible to compare the peak positions of different runs and the time required for the peak to grow as a function of solution conditions. This though only accesses part of the available information; to understand the interfacial processes more fully it is necessary to fit a model to the measured reflectivity data. This was performed via the optical transfer method [5], as described in Ref. [6]. This method depends on dividing the interface into a series of slabs parallel to the interface typically with three adjustable parameters: layer thickness (d/angstroms), scattering length density (SLD/per square angstrom) and a Gaussian roughness between layers. From an initial starting point the calculated reflectivity is compared with the dataset and a least-squares minimisation method is the used to find the best fit to the data. In all cases the simplest model which adequately described the data was chosen. This method is best suited to systems with a smaller number of layers; it has therefore been used primarily to study the interfacial structure prior to film growth.

Results and discussion

The time evolution of a typical set of reflectivity profiles is shown in Fig. 1. From this it can be seen that from the earliest patterns collected a broad fringe appears in the data which changes little over the first 2–3 h of the reaction during the induction period. At the end of the induction period, a diffraction peak, positioned on top of the fringe, grows in rapidly, reaching a constant intensity after roughly 30 min. The fringe is due to the formation of surfactant and silica layers at the solid interface during the induction period, while the peak is similar to that observed in silica–surfactant films grown at the air–water interface. In the air–water interface case the composite film which develops has been shown to have a structure composed of elongated cylindrical micelles arranged in a hexagonally close-packed array with the long axis aligned parallel to the air–solution interface [7, 8]. It is likely that in the present case a similar structure has formed, although from the specular reflectivity patterns, which give information only on the film structure in the direction perpendicular to the substrate, we can only say that a layered structure forms at the interface with a repeat unit of 46.5 Å. From the peak width, which is limited by instrumental factors, using a Scherrer analysis we have at least 16 layers of alternating silica and surfactant in the film which deposits rapidly at the end of the induction period. From our current solid–liquid cell data we can obtain both direct information on the length of the induction period (i.e. the time until the peak appears) under a given set of experimental conditions.