In situ SAXS study on cationic and non-ionic surfactant liquid crystals using synchrotron radiation

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In situ synchrotron small-angle X-ray scattering was used to investigate various surfactant/water systems with hexagonal and lamellar structures regarding their structural behaviour upon heating and cooling. Measurements of the non-ionic surfactant Triton X-45 (polyethylene glycol 4-*tert*-octylphenyl ether) at different surfactant concentrations show an alignment of the lamellar liquid-crystalline structure close to the wall of the glass capillaries and also a decrease in d-spacing following subsequent heating/cooling cycles. Additionally, samples were subjected to a weak magnetic field (0.3–0.7 T) during heating and cooling, but no influence of the magnetic field was observed.

Keywords: surfactants; lyotropic liquid crystals; SAXS; Triton X-45.

1. Introduction

Surfactant molecules in water form a variety of self-assembled structures, leading to lyotropic liquid-crystalline (LC) phases, such as lamellar and hexagonal-packed cylindrical micellar, cubic-packed spherical micellar and bicontinuous cubic structures, depending on the concentration of surfactant, temperature and the structure of the surfactant. These assemblies can be used as structure-directing agents to form ordered mesoporous materials with nanometer-scale periodicities (Beck *et al.*, 1992; Yanagisawa *et al.*, 1990; Zhao *et al.*, 1998). Different strategies have been used to align the hexagonal and lamellar LC structures in externally applied fields such as strong magnetic fields (Firouzi *et al.*, 1997; Tolbert *et al.*, 1997; Emsley *et al.*, 2000), shear flow (Melosh *et al.*, 2001; Müller *et al.*, 1999) or utilizing surface effects (Jager-Lezer *et al.*, 1999; Raimondi *et al.*, 1997).

Under ambient conditions the LC domains are randomly distributed and the high viscoelasticity of the LC aggregates usually counteracts externally induced orientational ordering. A strategy to overcome this is to increase the temperature. Subsequent cooling of the samples in the presence of an external field causes LC domains to reform, this time with a higher degree of orientational order.

Here we describe the temperature dependence of the LC structures of a selection of ionic and non-ionic surfactants upon heating and cooling with and without the presence of a weak magnetic field. It is well known that temperature plays a significant role in the aggregation behaviour of a lyotropic crystal. Using *in situ* small-angle X-ray scattering (SAXS) with synchrotron radiation, we show that the processing parameters also influence orientation and structural properties of the liquid-crystalline system.

2. Materials and methods

2.1. Sample preparation

All surfactants are commercially available from Aldrich and Fluka and were used as received, including the following: Triton X-45, polyethylene glycol 4-*tert*-octylphenyl ether (Fluka), Span 40, sorbitan monopalmitate (Fluka) and CTAB, cetyltrimethylammonium bromide (Aldrich). Aqueous surfactant solutions were homogenized for several hours to days at 323–333 K and sealed in 2 mm quartz capillaries. The system Triton X-45 in water was studied in various concentrations (20, 50 and 60 wt% surfactant).

2.2. *In situ* heating and cooling device

For *in situ* SAXS measurements during heating and cooling of the sample, an oven was built that could be placed in the beam. Fig. 1 shows a sketch of the oven design.

The temperature was controlled using a temperature sensor at the sample and a heating wire, both connected to an

Table 1
Investigated surfactant/water systems with the observed structure and effects owing to heating and cooling.

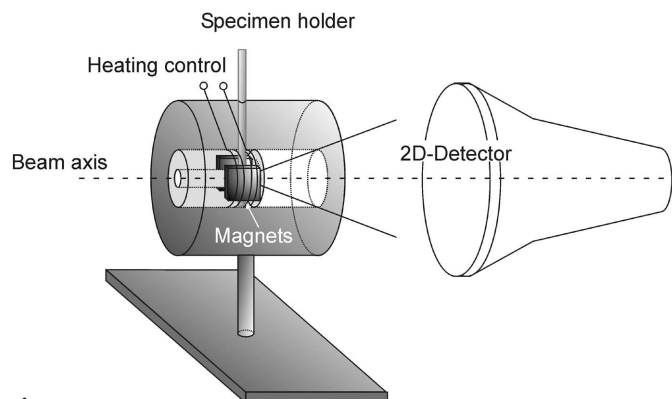| Surfactant	Molecular formula	Conc. [%]	Structure	Change in d-spacing after heating	Alignment (through shear or/and border effects)
Triton X-45	$C_8H_{17}C_6H_4EO_5$	20	Lamellar	No	Yes
Triton X-45	$C_8H_{17}C_6H_4EO_5$	50	Lamellar	Yes	Yes
Triton X-45	$C_8H_{17}C_6H_4EO_5$	60	Lamellar	Yes	Yes
Span 40	$C_{22}H_{42}O_6$	60	Lamellar/hexagonal	–	–
CTAB	$C_{16}H_{33}N(CH_3)_3Br$	30	Hexagonal	No	No

Figure 1
Schematic sketch of the oven design.

external temperature controller that could be operated from outside the experimental hutch. To study possible alignment effects in weak magnetic fields, permanent magnets consisting of Sm_2Co_{17} were placed inside the oven to either side of the sample. The gap between the magnets was 4 mm, resulting in a magnetic field at the sample position of 0.3 T (verified by Hall sensor measurements). The applied magnetic field was perpendicular to the beam axis.

2.3. Synchrotron measurement

Scattering experiments were carried out at the SAXS beamline (BL5.2L) at the synchrotron research centre Elettra/Trieste (Amenitsch *et al.*, 1997). The monochromatic X-ray beam (wavelength $\lambda = 0.154$ nm) was focused to a diameter of 0.5 mm. A two-dimensional detector was placed at a distance of 524 mm from the sample. The beamline optics consisted of a flat asymmetric-cut double-crystal monochromator and a double-focusing toroidal mirror. SAXS data were acquired using a two-dimensional CCD detector for small-angle scattering (Photonic Science).

The above-described oven for *in situ* measurements was mounted on a movable stage. Typically, samples were heated to 333 K (above the order/disorder transition temperature of the LC systems) and kept at this temperature for at least 10 min to equilibrate. Subsequently they were cooled down at a rate of 1 K min^{-1}, in order to allow the LC order to reform. SAXS patterns were recorded at several temperatures. Additional samples were heated and cooled in an external magnetic field of 0.7 T for comparison. The obtained data were analysed using the software *fit2d* (Hammersley, 1989).

3. Results and discussion

Table 1 lists systematically the investigated surfactant/water systems, the respective surfactant concentrations, the observed structure and effects owing to heating and cooling. With the exception of the CTAB/water system that shows a hexagonal order at 30% surfactant with a d_{100}-spacing of 6.74 nm in accordance with the literature (Auvray & Anthore, 1989; González-Gaitano *et al.*, 1999), all investigated systems exhibited a lamellar morphology at the investigated concentrations. For Span 40, a transition from hexagonal to lamellar was observed with decreasing temperature (in the temperature regime 333 K > T > 313 K the system exhibits a hexagonal structure with $d = 4.8$ nm and below a lamellar structure with $d = 6.4$ nm). No influence of the weak magnetic field resulting from the *in situ* magnetization (0.3 T) was observed in any of the studied LC systems. Most LC samples, however, proved to be very shear sensitive.

In the case of Triton X-45 in water, a change of d-spacing was observed following subsequent heating and cooling cycles. Moreover, the Triton X-45/water system exhibited strong preferential alignment of the LC lamellae at the sample/glass-capillary interface that grew even more pronounced upon heating and cooling. Results for 50 wt% Triton X-45 in water are depicted in Fig. 2(*a*), which shows the scattering intensity plotted *versus* q, obtained from an integration of the two-dimensional patterns over the azimuth, with $q = 4\pi/\lambda \sin\theta$ and 2θ being the scattering angle. The peak positions can be indexed according to a lamellar LC phase, with the d_{100} and d_{200} reflections clearly visible. The curves are ordered from bottom to top, with the lowest curve recorded at room temperature before heating and giving an initial d-spacing of 5.38 nm. Upon heating the sample to 333K, the long-range order vanished and the diffraction peaks disappeared (second curve from bottom) indicating that the order–disorder transition was passed at this temperature. Upon slow cooling of the system (1 K min^{-1}), the lamellar phase was restored, but with a smaller d-spacing of 4.41 nm (decrease by 18%). A second heating/cooling cycle resulted in a further decrease of the d-spacing by another 7% to $d = 4.01$ nm (four upper curves in Fig. 2a). In the case of 60 wt% Triton X-45 in water the observed decrease in d-spacing was around 13.5% from 5.03 nm to 4.35 nm. Since no additional peaks evolved, a formation of ripple phases could be excluded.

A possible explanation for the observed effect is that, upon heating and cooling several times, the surfactant molecules are given the opportunity to stack with their tails closer together, such that they start to partly overlap (see Fig. 2b). The length of a single Triton X-45 molecule (see Fig. 2c) is about 3.23 nm. If the molecules were to stack in a lamellar morphology with no overlap and no bending of the molecule (which is highly unlikely in practice), the d-spacing would be 6.46 nm, thus representing the theoretical maximum value. The re-ordering mechanism appears to be highly dependent on the processing
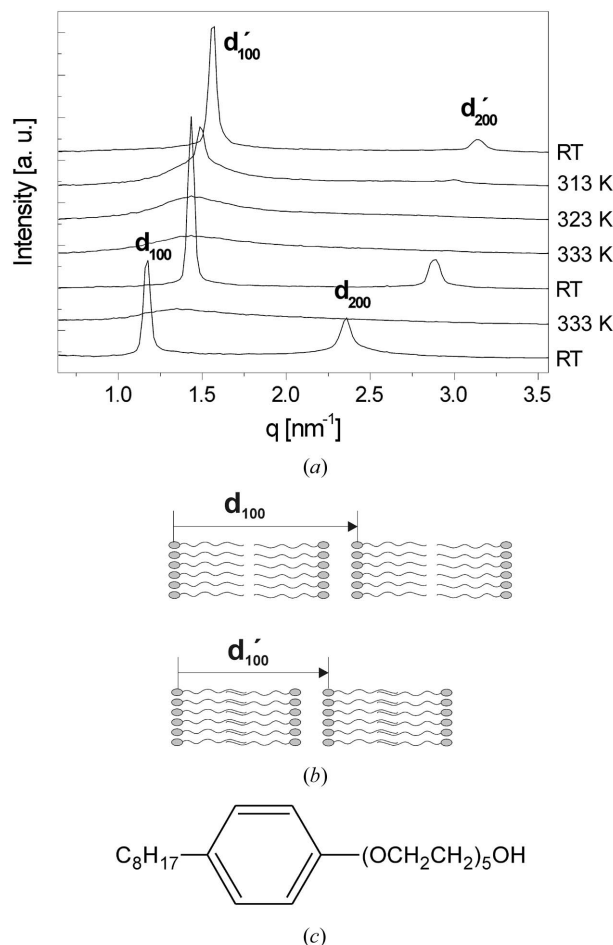
(a)

Figure 2
(a) Change in d-spacing after heating of the sample. (b) Model for the decrease in repeat distance: the long hydrophobic molecule tails of Triton X-45 stack with increasing degree of overlap. (c) Triton X-45 molecule.

Figure 3
50 wt% of Triton X-45 in water after heating to 333 K and subsequently cooling to room temperature without magnets. The lamellar crystalline domains close to the sample/glass interface tend to orient parallel to the capillary wall. (a) Two-dimensional scattering pattern from the middle of the capillary and (b) close to the glass wall. (c) Intensity of the 100 reflection integrated over 2θ and displayed *versus* the azimuth. I and III show signals close to the capillary wall (left and right, respectively), II from the centre. The individual curves have been displaced along the axis for better visibility. (d) Schematic representation of the preferential alignment at the interface. D is the director of the lamellar domains. The size of the beam was 0.5 mm and is shown schematically.

history as well as on the surfactant concentration. Whereas heating and slow cooling of 50% and 60% Triton X-45 in water showed a considerable decrease of the d-spacing, no decrease of the d-spacing upon heating and cooling was observed in the samples with 20% Triton X-45 in water. Here, the d-spacing was constantly as small as $d = 4.55$ nm from the beginning. Faster cooling of externally heated samples for comparison showed no decrease of the d-spacing (d is constant with a value of 5.2 nm).

Scanning of the 2 mm capillary through a 0.5 mm beam in steps of 0.1 mm allowed a clear distinction between the regions close to the capillary wall and the bulk material. In the bulk, no preferential orientation of the LC domains was observed (thus also excluding effects of the weak magnetic field applied to the sample), whereas the LC domains tended to align parallel to the walls of the glass capillary. The preferential alignment became much more pronounced after heating and cooling, most likely owing to re-ordering processes in the sample.

Typical scattering patterns of Triton X-45 in water are shown in Fig. 3. Whereas in the bulk the diffraction rings exhibit constant intensity (Fig. 3a), close to the sample/glass interface strong intensive spots were observed at the equator
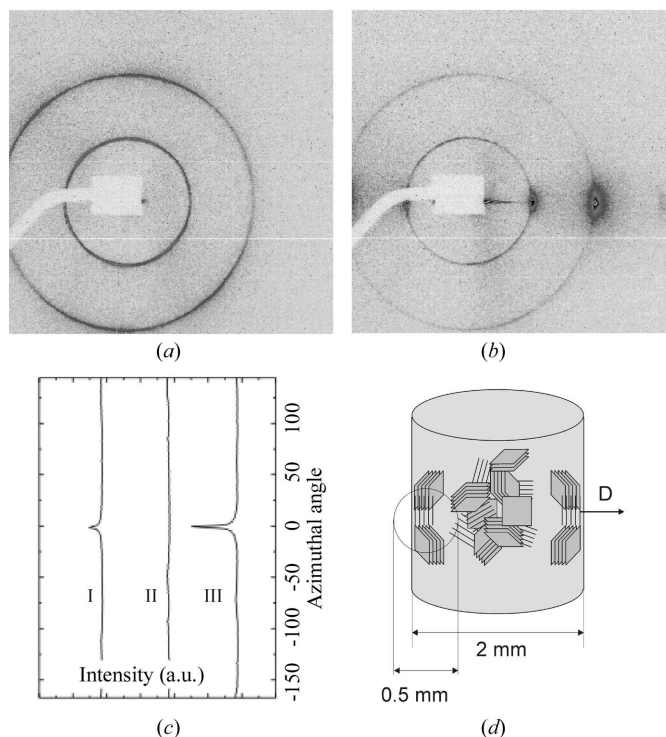
of the SAXS pattern, indicating a strict preferential orientation of the lamellae parallel to the walls (Fig. 3b). Integration of the 100-reflection ring over the scattering angle 2θ and plotting the intensity *versus* the azimuth gives a more quantitative picture of the intensity distribution: Fig. 3(c) shows SAXS intensity curves from either side of the capillary (I and III) exhibiting a strong peak at the equator with full widths at half-maximum (FWHM) of 2.7° and 2°, respectively, indicative of almost strictly parallel orientation of the lamellae. The scattering curve from the bulk (II) shows constant intensity (random orientation). After two heating/cooling cycles alignment was found in the region 0–0.6 mm from the wall of the capillary. Towards the centre the amplitude of the peak decreases by a factor of 1/3 and the FWHM increases by a factor of 3 but does not vanish entirely.

In Fig. 3(d) a model of the arrangement is displayed. The lamellar LC domains orient parallel to the capillary walls, since a parallel alignment is the energetically most favourable arrangement. D is the domain director which is perpendicular to the glass wall near the interface. Similar observations were reported by Jager-Lezer *et al.* (1999) and for hexagonal structures by Raimondi *et al.* (1997). Owing to the high viscosity of the system at room temperature, the system cannot

adopt this arrangement fully without heating (thus lowering the viscosity) and cooling slowly (providing time for re-ordering). The reason for the strong alignment of LC Triton X-45 in water may be the formation of particularly large lamellar domains, and therefore considerable lowering of energy for parallel alignment with the glass surface. The presence of large LC domains would also explain the shear sensitivity of Triton X-45 in water that often led to a weak preferential alignment of the system owing to the processing of the liquid when filling the capillary, often in different directions than the eventual alignment at the interface. The shear-induced orientation, however, vanished completely after heating, leading to the sharp parallel orientation along the walls. This interface-induced alignment does not seem to be as strongly dependent on the heating and cooling history of the sample as the change in the d-spacing, and was also observed in externally treated samples subjected to faster cooling.

In the case of 20 wt% Triton X-45 in water the lamellar domains were oriented parallel to the capillary wall from the beginning (see Fig. 4a, a scan across the 2 mm capillary in steps of 0.6 mm), presumably owing to lower viscosity of the mixture at lower concentration. Heat treatment, however, did have an influence in further enhancing the alignment (see Fig. 4b). The capillary was scanned in steps of 0.2 mm. Alignment was observed in a 0.4 mm region close to the wall before and after heating. The transition to the unaligned phase is very sharp (within 0.2 mm). The FWHM decreases by half and the amplitude approximately doubles after the first heating cycle, confirming the alignment tendency after heat treatment.

The lower viscosity of 20 wt% Triton X-45 in water as compared with higher concentrations may also account for easier re-arrangement of the molecules with respect to those already at room temperature, and therefore a closer stacking reflected by the small d-spacing observed in these samples right from the start.
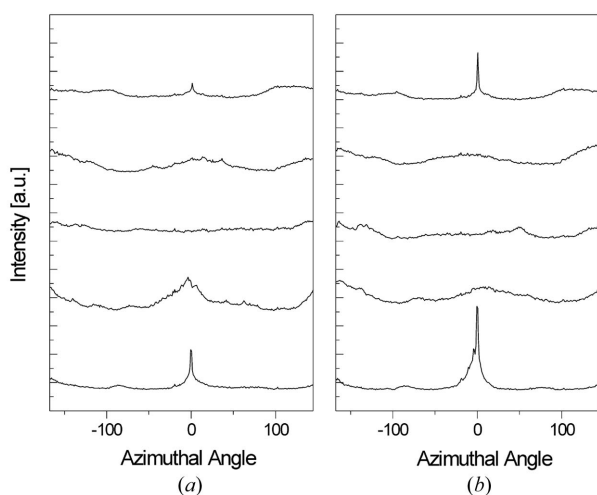

Figure 4
20 wt% Triton X-45. Scan across the 2 mm capillary in steps of $\Delta x = 0.6$ mm (a) before and (b) after heating to 333 K. The domains in the region close to the capillary walls are already aligned at the beginning of the experiment. After heat treatment the orientation has increased.

4. Conclusions

A selection of liquid-crystalline non-ionic and ionic surfactant systems in water were studied with *in situ* synchrotron SAXS measurements during heating and slow cooling in a weak magnetic field. For the lamellar structure of 20 wt% and between 50 and 60 wt% polyethylene glycol 4-*tert*-octylphenyl ether (Triton X-45) in water, a strong orientational ordering parallel to the walls of the quartz glass capillary could be observed. The distance of the lamellar layers was sensitive to the heating and to the cooling process. The d-spacing decreased after heating to 333 K and subsequent cooling (1 K min^{-1}) by 18% in the case of 50 wt% Triton X-45. Another run led to a further decrease of 7%. In the case of higher surfactant concentration this effect was slightly less pronounced (13.5%). For the analysed surfactants no measurable influence of a weak magnetic field could be observed during the involved exposure times.

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