Shear Melting and Orientation of a Lyotropic Cubic Phase

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(Received 13 December 1994, revised 28 February 1995, accepted 13 March 1995)

Abstract. — A bicontinuous lyotropic cubic phase, composed of the nonionic surfactant pentaoctyl allyl ether (C12E5), heavy water (D2O) and tetradecane (C14H30), was investigated by small angle neutron scattering (SANS). The cubic phase is stable only in a narrow temperature and composition range. Upon increasing the oil content the phase melts to an L3 phase and at higher temperature it is in equilibrium with a lamellar (Lα) phase. The scattering function of the powder cubic sample is dominated by a strong correlation peak at \( q = 0.057 \) Å\(^{-1}\) in addition to a small hump at \( q \approx 0.11 \) Å\(^{-1}\). From the known area per C12E5 molecule at the polar/apolar interface the lattice parameter is calculated for different minimal surface model structures. The position of the dominating reflection from the cubic phase is found to be consistent with the spacing between the 211 planes of the Gyroid minimal surface structure. The effect of shear on the scattering pattern was investigated using a Couette shear cell. Under shear a weakly anisotropic scattering pattern was obtained. From a separate rheology experiments it was concluded that shearing the sample has the effect of melting the long range cubic order, presumably into a fluid disordered L3 phase. When turning off the shear, the cubic phase recrystallises with a preferred orientation. The diffraction pattern is consistent with the diffraction from 211 planes with one major and one minor population in the orientation of the \( <111> \) axis. A major population having the \( <111> \) axis parallel to the shear velocity (i.e. the tangent direction), and a minor component having the \( <111> \) axis parallel to the velocity gradient.

1. Introduction

Surfactants and lipids in solution can form phases of fluid surfaces, with monolayer or bilayer films extending over macroscopic distances. One phase which has attracted particular attention in recent years is the L3 ('sponge') phase [1–3]. Here a bilayer film forms a disordered multiply connected dividing-surface between two interwoven subvolumes containing the same solvent. At higher concentrations, the bilayer film may crystallise into a cubic lattice. Here the order-disorder transition occurs while retaining the topology of the bilayer film, as seen by the self-diffusion of surfactant and solvent [4,5].

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Recently the phase behaviour and phase structures of a ternary surfactant system: pentaoxyethylene dodecylether (C₁₂E₅)-water-tetradecane, at a constant C₁₂E₅/water weight ratio of 3/2, was reported [6]. In this section of the composition- temperature phase prism a bicontinuous cubic phase, \( V_1 \), is formed close to room temperature for oil volume fractions in the range \( \Phi_0 = 0.4 - 0.5 \). The cubic phase is stable only in a narrow temperature range (\( \approx 6 \) °C) and transforms upon heating to a lamellar phase, \( L_\alpha \). At lower temperatures, it is in equilibrium with a normal hexagonal phase. Upon dilution with oil, the cubic phase 'melts' and transforms to a liquid, oil-rich \( L_3 \) phase. We note also that the cubic phase here contains simultaneously relatively large amounts of water and oil, which is a less common feature.

Lyotropic cubic phases often form relatively large microcrystallite domains, which makes small angle X-ray (SAXS) studies, using thin capillaries, of these materials difficult. Samples often possess a finite and unknown distribution of microcrystallite orientations rather than a uniform powder. This is a problem also in the present system, where all attempts to prepare a powder sample of the cubic phase in the X-ray capillary failed [6].

In small angle neutron scattering (SANS) experiments, it is less of a problem, since one here often work with larger sample sizes (path lengths up to several mm can be used). In the present paper we report on a SANS study of a sample containing C₁₂E₅/D₂O/C₁₄H₃₀ with the relative weight fractions 0.362/0.268/0.370 in the cubic and lamellar phases. In a first set of experiments, powder samples were prepared in normal quartz cells, and the scattering from the lamellar and cubic phases were recorded. In a second set of experiments, we investigated the influence of shear on the lamellar and cubic phases, using a Couette shear cell. Finally, we also report on a stress-sweep experiment on the cubic phase using a cone and plate rheometer. As mentioned above, a phase diagram has been published in [6].

2. Experimental

2.1. Sample Composition. — The sample composition in weight fraction and volume fraction, respectively, is presented in Table I. In this table are also given the densities of the various compounds as used in the calculation of volume fractions from weight fractions.

<table>
<thead>
<tr>
<th></th>
<th>Weight fraction</th>
<th>Volume fraction</th>
<th>( \rho / \text{g cm}^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂E₅</td>
<td>0.362</td>
<td>0.341</td>
<td>0.96</td>
</tr>
<tr>
<td>D₂O</td>
<td>0.268</td>
<td>0.220</td>
<td>1.105</td>
</tr>
<tr>
<td>C₁₄H₃₀</td>
<td>0.370</td>
<td>0.439</td>
<td>0.763</td>
</tr>
</tbody>
</table>

2.2. SANS Studies. — SANS experiments were performed using the Risø-SANS facility. The shear cell, of the Couette type has been described in details elsewhere [7]. The gap size was \( b = 0.5 \) mm and the inner radius of the outer cylinder (rotator) was \( R = 30 \) mm. Although we anticipate the possibility of non-laminar flow in the liquid crystalline samples, we still, for simplicity, represent the applied shear in terms of a single effective shear rate \( \dot{\gamma}_{\text{eff}} = R \omega / b \), where \( \omega \) is the angular velocity.
3. Powder Scattering Experiment

Figure 1 shows the radial averaged scattered intensity in arbitrary units from the lamellar \((T = 34.8 \, ^\circ C)\) and cubic \((T = 24.4 \, ^\circ C)\) phases. A single first order reflection is observed from the lamellar phase. In the cubic phase sample we observe in addition to a strong correlation peak the appearance of a small hump at higher \(q\)-values. The appearance of only low number of reflections is a common feature of lyotropic liquid crystals and is mainly due to a combination of two factors. i) The ‘softness’ of the materials broadens the reflections. ii) The size of the building blocks of the structure is only slightly smaller than the unit cell size, and higher order reflections in the structure factor are often very weak due to a rapidly decaying formfactor at higher \(q\)-values.

3.1. The L\(_\alpha\) Phase. — In the L\(_\alpha\) phase only a first order peak, with the position \(q_1 = 0.065 \, \text{Å}^{-1}\), is observed. This corresponds to a repeat distance of \(D = 2\pi/q_1 = 96.7 \, \text{Å}\). Neglecting the area correction associated with the film undulations, the repeat distance can be written as

\[
D = \frac{2l_s}{\Phi_s}
\]  

Here, \(l_s \equiv v_s/a_s\) is the surfactant length, where \(v_s = 702 \, \text{Å}^3\) [6] is the surfactant molecular volume and \(a_s\) is the area per molecule at the polar-apolar interface, and \(\Phi_s\) is the surfactant volume fraction. \(\Phi_s/l_s\) is the monolayer interfacial area per unit volume. With \(\Phi_s = 0.341\), we obtain with equation (1) \(l_s = 16.5 \, \text{Å}\). This is in good agreement with the value obtained previously in a SAXS study of the same system [6].

The C\(_{12}\)E\(_5\) surfactant can be considered as a short AB block copolymer, where two blocks, the dodecyl (C\(_{12}\)) and the pentaethylene oxide (E\(_5\)) blocks, have approximately the same volume. Defining the polar-apolar interface as a surface in the monolayer film separating the
C_{12} from the E_5 block, we can define the bilayer volume fraction, \( \Phi_b = \Phi_w + \Phi_s / 2 \), where the bilayer half thickness, \( L \), is given by

\[
L = l_s \left( \frac{\Phi_w}{\Phi_s} + \frac{1}{2} \right)
\]  

Using the value \( l_s = 16.5 \ \text{Å} \), we obtain \( L = 18.9 \ \text{Å} \).

3.2. The Cubic Phase. — The scattering function of the powder cubic sample is dominated by a strong correlation peak at \( q_m = 0.057 \ \text{Å}^{-1} \). This corresponds to a lattice parameter \( \alpha = 2\pi \sqrt{m}/q_m \approx 110 \sqrt{m} \ \text{Å} \), where \( m = h^2 + k^2 + l^2 \). In addition we can also identify a weak reflection around \( q \approx 0.11 \ \text{Å}^{-1} \).

Self-diffusion measurements [6] have shown that the cubic phase is bicontinuous. From its relative position in the phase diagram, between the lamellar and normal hexagonal phases, we expect the monolayer to have a mean curvature on the average towards oil, i.e. intermediate between that in the lamellar phase and that in the normal hexagonal phase.

There are two commonly accepted and complementary descriptions of bicontinuous cubic phases. In the interconnected-rod model [8] the structure is described as two infinite networks of interconnected cylinders. In the bilayer model [9,10], the structure is described as a multiply connected bilayer decorating a minimal surface (corresponding to the mid-plane of the bilayer) of cubic symmetry. The two descriptions are complementary in the sense that the two cylinder networks in the first description are associated with the skeletal graphs of the two interwoven sub-volumes separated by the minimal dividing surface in the bilayer description. Here we will consider the bilayer description which appears to be the most appropriate. In particular if we also consider the disordered L_3 phase structure at higher oil-content. Note that a bilayer structure here implies a reverse, water-swollen bilayer separating two interwoven oil labyrinths.

The area per surfactant molecule, \( a_s \), evaluated at the polar/apolar interface defined above, was found to be almost identical in the lamellar and hexagonal phases of the present system [6]. Assuming \( a_s \) to be the same also in the cubic phase, we can calculate the cubic lattice parameter, for minimal surface cubic phase model structures, using the parallel surface formalism [1,11]. Here, the bilayer midplane is modelled as a minimal surface, and the polar/apolar interface a parallel surface at a distance \( L \). The area, \( A \), of the parallel surface is related to that of the base minimal surface, \( A_0 \), according to:

\[
dA = (1 + KL^2) dA_0
\]  

Here, \( K \) is the Gaussian curvature of the base surface and \( L \) is the distance from the base surface. Integrating equation (3) over one unit cell, we obtain

\[
A^u = A_0^u + 2\pi \chi^u L^2
\]  

where \( A^u \) and \( A_0^u \) are the parallel surface and base surface areas per unit cell, respectively, and \( \chi^u \) is the surface Euler characteristic per unit cell, which is given by

\[
\int \int \text{d}A_0 K \pi \chi^u
\]  

unit cell

\[
2A^u/\alpha^3 = \Phi_s / l_s \], where \( \alpha^3 \) is the unit cell volume, is the polar/apolar interfacial area per unit volume. Noting further that \( A_0^u = \alpha^2 \), we obtain

\[
\Phi_s = \frac{2\alpha^4}{\alpha} \left( 1 + \frac{2\pi \chi^u}{\frac{L}{\alpha}} \left( \frac{L}{\alpha} \right)^2 \right)
\]  

(6)
Table II. — Properties of the G, D and P minimal surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>space group</th>
<th>$\chi^u$</th>
<th>$\zeta$ [14]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>Ia3d</td>
<td>-8</td>
<td>3.091</td>
</tr>
<tr>
<td>D</td>
<td>Pn3m</td>
<td>-2</td>
<td>1.919</td>
</tr>
<tr>
<td>P</td>
<td>Im3m</td>
<td>-4</td>
<td>2.345</td>
</tr>
</tbody>
</table>

Table III. — Calculated and experimental values for the lattice parameter of the cubic phase.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\alpha_{\text{calc}}$/Å</th>
<th>$\alpha_{\text{exp}}$/Å</th>
<th>m</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>279</td>
<td>269</td>
<td>6</td>
<td>211</td>
</tr>
<tr>
<td>D</td>
<td>172</td>
<td>156</td>
<td>2</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td>191</td>
<td>3</td>
<td>111</td>
</tr>
<tr>
<td>P</td>
<td>209</td>
<td>156</td>
<td>2</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220</td>
<td>4</td>
<td>200</td>
</tr>
</tbody>
</table>

(a) Calculated according to equations (6) and (9).
(b) Calculated from the observed reflection at $q_m = 0.057$ Å$^{-1}$ in the cubic phase, according to $\alpha = 110\sqrt{m}$ Å.
(c) Assumed value of $m = h^2 + k^2 + l^2$, where $h$, $k$ and $l$ are the Miller indices.

The effective bilayer half-thickness, $L$, can be obtained in a similar way by considering the volume fraction constraint:

$$\frac{V_b^u}{\alpha^3} = \Phi_b = \Phi_w + \Phi_s/2$$  \(7\)

where $V_b^u$ is the bilayer film volume per unit cell, and can be written as

$$V_b^u = 2 \int \int_{\text{unit cell}} dA_0 \int_0^L dL \frac{dA}{dA_0}$$  \(8\)

Using equations (3) and (7) in (8) we obtain
\[ \Phi_b = \frac{2cL}{\alpha} \left( 1 + \frac{2\pi \chi^u}{3\zeta} \left( \frac{L}{\alpha} \right)^2 \right) \]  

(9)

The most commonly found bicontinuous cubic phase structure corresponds to the Gyroid minimal surface with the space group Ia3d [12, 13]. In some occasions structures corresponding to the D (Pm3n) and the P (Im3m) minimal surfaces, have also been reported. In Table II are given the space group, values for the Euler characteristic and the dimensionless constant \( \zeta \) [14], for the three minimal surfaces.

Using equations (6) and (9), we have calculated the lattice parameter, \( \alpha_{\text{calc}} \) for the various minimal surface structures, assuming \( l_b = 16.5 \, \text{Å} \) as determined from the lamellar phase. These values are presented in Table III where we also compare with a lattice parameter, \( \alpha_{\text{exp}} \), calculated from the observed reflection at \( q_m = 0.057 \, \text{Å}^{-1} \), by assuming a value for \( m \). As is seen, the best agreement is found with the G-surface, assuming that the strong reflection corresponds to the [211] planes. Possibly, the weak reflection at \( q \approx 0.11 \, \text{Å}^{-1} \) corresponds to \( [hkl] = [332] \). As will be shown below, the indexation of the strong reflection to \( [hkl] = [211] \) is consistent with the results obtained in the shear cell experiments. We note also that the 211-reflection normally is much stronger than other reflections from the Ia3d cubic phase [15, 16], which supports our indexation.

4. Shear Cell Experiments

Scattering experiments in the shear cell were performed at various temperatures and effective shear rates. The geometry of the experimental set up is illustrated in Figure 2, defining the directions of the \( x \), \( y \), and \( z \) axis. The primary beam we define in the \( y \)-direction which also defines the direction of the velocity gradient in the Couette flow. The velocity vector is parallel with \( x \)-axis while the \( z \)-axis defines the cylindrical symmetry axis of the Couette.

4.1. The Lamellar Phase. — The lamellar phase showed no indication of a preferred orientation in the shear field except very close to the lower phase boundary. The situation is illustrated in Figure 3 where we show the two-dimensional scattering pattern from the lamellar phase at three different temperatures approaching the lower phase boundary towards the cubic phase \( \approx 30.5 \, \text{°C} \) for a shear rate of \( \dot{\gamma}_{\text{eff}} = 150 \, \text{s}^{-1} \). At 33.3 \, \text{°C} no orientation effects are observed. However near the phase boundary the scattering function becomes strongly anisotropic. At higher temperatures in the lamellar phase, the scattering similar patterns as at 33.3 \, \text{°C} was observed, with no preferred orientation. The Bragg-spots in the \( q_z \) direction at 30.9 \, \text{°C} originates from lamellae oriented with the normal direction parallel with the \( z \)-axis. However, the scattered intensity along \( q_z \) at 30.9 \, \text{°C} is very similar to that observed in the powder lamellar phase at higher temperatures, showing that this is not the main orientation in the shear flow. This can be seen more clearly in Figure 4 where we compare the radially averaged intensity and angular dependence of the scattered intensity for the sample at 30.9 \, \text{°C} and 33.3 \, \text{°C}, respectively. In (a) we have plotted the radially averaged scattering intensity, \( I \), vs. \( q = (q_x^2 + q_z^2)^{1/2} \) and in (b) we show the azimuthal angular dependence \( \left( \tan \{q \} = q_z/q_x \right) \) of the scattered intensity, integrated from \( q = 0.04 \, \text{Å}^{-1} \) to 0.09 \, \text{Å}^{-1}. In Figure 4a we see that the total scattering intensity in the \( (q_z, q_x) \)-plane is strongly reduced at 30.9 \, \text{°C} compared to powder situation at 33.3 \, \text{°C}, and in Figure 4b, we see that the intensity in the two Bragg spots at 30.9 \, \text{°C} has the same magnitude as in the powder ring at 33.3 \, \text{°C}. From these results, we can conclude that the main orientation at 30.9 \, \text{°C} is with the normal direction, \( n \), of the lamellae parallel with the \( y \)-axis (gradient direction) which does not give any scattering in the
Fig. 2. — Schematic illustration of the scattering and shear cell geometry. The primary neutron beam is defined in the y direction parallel with the velocity gradient of the Couette shear geometry. The cylindrical symmetry axis of the shear cell is defined in the z direction. In the scattering volume, the velocity vectors are parallel with the x-axis.

C12E5 Shear=150/sec

Fig. 3. — Two dimensional scattering patterns recorded at three different temperatures within the lamellar phase for an effective shear rate $\dot{\gamma}_{\text{eff}} = 150 \, \text{s}^{-1}$. The various temperatures are indicated in the figures.
Fig. 4. — a) The radially averaged scattering intensity plotted as a function of \( q = (q_x^2 + q_z^2)^{1/2} \), and b) the angular dependence of the scattered intensity in the \( q \)-band \( 0.04 \leq q \leq 0.09 \text{ Å}^{-1} \), for two temperatures, 30.9 °C and 33.3 °C, respectively, and \( \gamma_{\text{eff}} = 150 \text{ s}^{-1} \) in the lamellar phase. The corresponding two-dimensional scattering patterns are shown in Figure 3.

\( (q_x, q_z) \)-plane. While other orientations in the powder have flipped to \( n//y \), the residual \( n//z \) orientation remains since the resulting torque on this orientation is zero. The same behaviour of a lamellar phase in a Couette cell was recently observed by Diat et al. [17]. The reason why the lamellar phase here orients only very close to the phase boundary with the cubic phase, and not at higher temperatures, is not yet understood. One possibility is the formation of liposomes (onions) [17] at higher temperatures which become unstable at lower temperatures close to the phase boundary. Further experiments are needed however to clarify this issue.
Fig. 5. — Two dimensional scattering pattern from the cubic phase at 25.4 °C. a) \( \dot{\gamma}_{\text{eff}} = 300 \text{ s}^{-1} \) b) Shortly after the shear had been turned off.

4.2. The Cubic Phase. — Under shear, the sample scatters almost uniformly on a ring, although with a weak azimuthal dependence. However, turning off the shear results in a preferred orientation. The situation is illustrated in Figure 5 for a temperature of 25.4 °C. In Figure 5a we show the scattering pattern obtained with a shear rate of \( \dot{\gamma}_{\text{eff}} = 300 \text{ s}^{-1} \). Figure 5b shows the scattering pattern obtained shortly after the shear has been turned off. In Figure 6 (a and b, respectively) we have plotted the radially averaged intensity (a) and the azimuthal angular dependence of the scattered intensity (b), the latter as obtained in the \( q_\parallel \) band \( 0.04 - 0.07 \text{ Å}^{-1} \), for the two situations with \( \dot{\gamma}_{\text{eff}} = 300 \text{ s}^{-1} \) and \( \dot{\gamma}_{\text{eff}} = 0 \), respectively. Six sharp peaks at \( q = 0.057 \text{ Å}^{-1} \) are observed in the oriented sample. Two peaks correspond to scattering vectors \( q_{\text{XX}} = (q_x, q_z) = (0, q_m) \), and \( (0, -q_m) \) respectively, and hence to a scattering plane with its normal direction parallel with the \( z \)-axis. The angles between this scattering plane and the two additional planes are close to ± the tetrahedral angle, 109.5°. This angle is indeed present between certain planes in the \{211\} family of reticular planes, namely between the \{211\} and \{211\} planes, and permutations of this combination. The observation of peaks at \( q_{\text{XX}} = (0, q_m) \) and \( (0, -q_m) \) suggests that the \( <111> \) direction is parallel to the \( z \)-axis.

In addition to the six strong peaks, four peaks of lower intensity can be resolved. They are located on either side of the two peaks on the \( q_y \)-axis. Presumably, these peaks stem from an additional orientation of the unit cell, where the \( <111> \) direction is parallel to the \( y \)-axis. In this case we expect two additional peaks to lie on the \( q_z \)-axis, which are not resolved between the stronger peaks. Close to the \( q_x \) axis additional intensity appear at \( q \approx 0.11 \text{ Å}^{-1} \), probably revealing scattering from \{332\}-type of reflections (These reflections are not visible in Fig. 5, which has been experimentally optimised to resolve the \{211\} reflections).

We now turn to the question if the observed orientation corresponds to only a minor part of the sample, as was the case for the lamellar phase, or if it corresponds to a major part and hence a preferred orientation of the sample. These plots in Figure 6 can be compared with the analogous plots for the lamellar phase in Figure 4, and if we do, we see that the situation for the cubic phase (Fig. 6) is different. In Figure 6a we see that when the sample orients, after the shear is turned off, we are not losing intensity in the \((q_x, q_z)\)-plane, as we did in the case of the lamellar phase. The integrated scattering intensity is similar for \( \dot{\gamma}_{\text{eff}} = 300 \text{ s}^{-1} \) and
\[ \gamma_{\text{eff}} = 0, \text{ respectively. Also, if we compare the angular dependence of the scattered intensity (Fig. 6b) we see that the intensity of the Bragg spots in the oriented sample (} \gamma_{\text{eff}} = 0 \text{) now has an intensity which is higher than the average intensity under shear. This indicates that the observed orientation of the cubic phase after the shear has been turned off indeed corresponds to a major part of the sample, and hence to a preferred orientation. However we do not expect to have a monocrystal situation. Rather, we probably orient only one axis of the cubic structure, namely that the} <111> \text{ direction orients parallel to the velocity} (x-\text{axis}). \text{ Hence, we expect a 2D powder of the} <211> \text{ directions in the} yz-\text{plane. (Unfortunately it was not possible to shift the Couette cell sideways in order to detect the} (q_y, q_z)-\text{plane).} \]
Single crystals of the Gyroid cubic phase have been obtained previously in both surfactant and block copolymer systems [16,18,19]. In those studies, however, the cubic phase crystals were grown from oriented lamellar or hexagonal phases with epitaxial relationships. Here, the mechanism is different. Under shear we observe a weak orientational order in the xz-plane as can be seen in the angular dependence of the scattered intensity in Figure 6b. The angular dependence at $\gamma_{\text{eff}} = 300$ s$^{-1}$ is qualitatively similar to that at $\gamma_{\text{eff}} = 0$, indicating a similar structure in the two cases. One possibility is that the cubic phase melts in the shear field into a disordered liquid L$_3$ phase, and that the cubic phase recrystallises after the shear has been turned off. The disordered structure shows only a weak orientation in the shear field, however sufficient enough to produce a strong orientation effect when the cubic phase recrystallises. This possibility is supported by the fact that the present cubic phase is very close in composition to the first order melting transition to the L$_3$ phase when diluting with oil [6], and as we will see below, a stress-sweep experiment performed on the cubic phase indicate that it indeed may undergo a melting transition under shear.

As mentioned above, the observed orientation of the recrystallised cubic phase corresponds to the (111) axis parallel with the velocity direction (y-axis). This three-fold $<111>$ symmetry axis of the Gyroid structure contains straight ‘cylindrical’ pores (see, e.g., Ref. [20]). While the properties of bicontinuous structures in a shear field is at present unknown, we note here that the observed orientation seems understandable, considering the cylindrical pores in the 111-direction.

If indeed the high shear phase corresponds to an L$_3$ phase, it is interesting to note that the position of the major correlation peak (the 211-peak in the cubic phase) remains unchanged under shear, since a particularly interesting question in L$_3$ phases concerns the average bilayer topology or coordination number. Self-diffusion measurements have demonstrated previously, for this system [6], as well as for the AOT-brine system [4,5], that the bilayer topology in the L$_3$ and cubic phases (Gyroid in both systems) are essentially identical. In other words the corresponding minimal surface of which the L$_3$ phase is the disordered or melted analogue, is indeed the Gyroid minimal surface, which also appears to be the most commonly observed cubic phase structure in surfactant systems. Since the conclusions from the self-diffusion measurements are partly based on an observed continuity of the diffusion constant across the order-disorder transition the question of the average topology in the disordered L$_3$ phase has only been addressed in systems which do show such a transition, and it is not yet clear if a low average coordination number (= 3 in the Gyroid case) is a general property of L$_3$ phases. This property could possibly be addressed also by small angle scattering experiments. What the present results indicate is that the correlation peak in the L$_3$ phase which only reports on nearest neighbour correlations, is related to the 211-reflection from the crystalline Gyroid structure. It would certainly be interesting with a more systematic study in this area, on systems with well controlled area to volume ratios. Also the ongoing debate on how ordered the disordered L$_3$ phase in fact is, may benefit from such a study. For this however, the present system is less suitable, due to the strong temperature sensitivity of the nonionic surfactants, but we hope to return to this question in a future publication.

5. Stress-Sweep Experiment

The rheological properties of the cubic phase were further investigated with a controlled stress cone-and-plate rheometer (Carri-Med CSL 100). In Figure 6 we present the results of a stress-sweep experiment on the cubic phase sample at 24 °C. In this experiment, a variable stress is applied to the sample and the resulting shear-rate is recorded. As seen in Figure 7, the sample has essentially the characteristics of a yield-stress. At low stress, the sample behaves
Fig. 7. — Applied stress versus shear rate recorded in the cubic phase at 24.0 °C in a stress-sweep experiment (increasing stress) on a cone and plate rheometer.

essentially as a solid. When the stress is increased above a particular (yield-stress) value the sample turns fluid and the shear-rate increases dramatically, indicative of a melting of the cubic phase. The results of Figure 7 should be considered only qualitatively since we do not control the cubic phase orientation and size distribution of the microcrystallites (a repeated experiment resulted in a similar curve however with a (≈ 20%) smaller yield stress). The results nevertheless indicate a melting transition when the cubic phase is exposed to a sufficiently high shear stress. Completely parallel scattering and rheology experiments could not be carried out, since in the Couette shear cell used in the scattering experiments only the shear rate, and not the shear stress, could be controlled.

The cubic phase here is stable only in a narrow range of oil concentrations. Upon dilution with oil, the cubic crystalline order 'melts', at a weak first order (order-disorder type) phase transition, to a liquid L3 ('sponge') phase, retaining the bilayer topology [6]. This type of phase transition has been addressed by Bruinsma [21] who showed that the bicontinuous cubic phase cannot be diluted infinitely. The shear modulus decrease upon dilution and vanishes at a finite concentration, where the cubic structure is expected to 'melt' [21]. The results presented here indicate that a melting transition also can occur under shear.

Acknowledgments

We are grateful to Krister Thuresson for his assistance with the stress-sweep experiment. A grant from Nils and Dorthi Troëdsson Research Foundation, financing the rheometer, is kindly acknowledged. This work was financially supported by the Swedish (NFR) and Danish Natural Science Research Council.
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