STRUCTURAL FEATURES OF THE CUBIC PHASE OF A TERNARY SURFACTANT SYSTEM


To cite this version:
STRUCTURAL FEATURES OF THE CUBIC PHASE OF A TERNARY SURFACANT SYSTEM


* Cavendish Laboratory, Madingley Road, GB-Cambridge CB3 0HE, Great-Britain
**AFRC Institute of Food Research, Colney Lane, GB-Norwich NR4 7UA, Great-Britain
***MRC Laboratory of Molecular Biology, Hills Road, GB-Cambridge CB2 2QH, Great-Britain
****LANSCE, Los Alamos National Laboratory, Los Alamos NM 87545, U.S.A.
*****Department of Physics, University of Lisbon, P-1700 Lisbon, Portugal

Abstract - We have studied the cubic phase formed by the ternary system water/didodecyldimethylammonium bromide/octane using small-angle x-ray and neutron scattering. We have observed the existence of more than one symmetry in this cubic region, with a transition from primitive to body centred cubic symmetry on increasing the water content of the system. Our results are consistent with a bicontinuous periodic structure of constant mean curvature. We also report rheological measurements which indicate that the ringing behaviour of the cubic samples is associated with a sharp increase in the quality factor as audible frequencies are approached.

Introduction

Cubic liquid crystalline phases formed by amphiphilic molecules in the presence of water have been studied extensively, and transitions between cubic structures of different symmetries have been observed in the phase diagrams of some binary systems /1-4/. Theoretical work on cubic phases has established the importance of periodic minimal surfaces and more generally periodic constant mean curvature (CMC) surfaces in the description of their microstructure /5-10/. More recently, strong interest has emerged in cubic phases of ternary surfactant systems /8, 11-14/. These consist of bicontinuous periodic labyrinths of water and oil conforming to a cubic symmetry. Ternary systems have more complex phase behaviour and a greater microstructural diversity arising from the extra degrees of freedom due to the presence of a third component. In the present paper we report a structural study of the cubic phase of the ternary system water/didodecyl dimethylammonium bromide (DDAB)/octane. Ternary mixtures of water, DDAB, and oil exhibit a large bicontinuous microemulsion region which has been studied in detail /15,16/ and is now well-characterised. The cubic phase is opposite this microemulsion region and exists over a wide range of aqueous content.

Experimental

The samples were prepared by thorough mixing of the three components in a sealed container at ca.100°C and were then allowed to cool to room temperature. The small-angle X-ray scattering (SAXS) measurements were carried out using a point-collimated beam from a Cu-Kα line of λ = 1.54 Å. The sample was placed between two mica sheets and rotated in the beam at about 1 r.p.m. A sample thickness of 0.7 mm was maintained by means of a Teflon O-ring. A two-dimensional position-sensitive detector /17/ was used to measure the scattered intensity. The sample-detector distance was 75 cm, and measurements were carried out at 22±1°C. The samples were
subjected to cycles of heating and rapid cooling prior to the measurements, as this was found to reduce the size of large crystallites and produce homogeneous powder diffraction rings.

The small-angle neutron scattering (SANS) experiments were performed on D17 at the ILL Grenoble with a monochromatic wavelength of 12 Å, and at the low-Q diffractometer of the Los Alamos National Laboratory using a pulsed source and time of flight methods /18/. The samples were kept at 22±1°C and contained in 0.8mm or 1mm path length quartz cells. They were subjected to heating and cooling cycles before the measurements. The Bragg spacings obtained from SAXS and SANS measurements on a given sample were equal to within ±3Å. The rheological measurements were performed on a Rheometrics RMS 800 rheometer using the cone and plate geometry and a variable temperature.

Results and Discussion

The phase diagram of the system D₂O/DDAB/octane is characterised by a large cubic region (Fig. 1), which extends from ca.35% to 77% D₂O. The high-octane side of this cubic phase is adjacent to the L₂ microemulsion, while the low octane side faces a lamellar phase. We have used SAXS and SANS to investigate the structure of the cubic phase as a function of composition, and in particular, along a water dilution path (Fig. 1). The results clearly show a symmetry transition at an aqueous volume fraction close to 0.5 (Fig. 2). At low water content the SAXS patterns can be indexed to a diamond (D) structure. This structure is related to the Schwarz-D minimal surface with space group F4 3m for a monolayer and Pn3m for a bilayer structure respectively /19/. As the aqueous volume fraction is increased, a transition occurs to a structure of body-centred cubic (bcc) symmetry. The space group is Im3m, and possible structures are the P-bilayer based on the Schwarz-P surface or the I-WP monolayer surface /8, 10/.

![Figure 1](image_url)

*Fig. 1. Phase diagram of the system D₂O/DDAB/octane at 22°C showing the cubic region. The broken line is a D₂O dilution path. The sample compositions given in Table I are indicated by the points within the cubic region, (*) diamond symmetry, and (*) bcc symmetry.*
Fig. 2. Two-dimensional plots of the detector showing the SAXS patterns of samples with composition by weight (A) DDAB: 40.10%, D2O: 51.70%, octane: 8.20%, and (B) DDAB: 36.22%, D2O: 56.36%, octane: 7.42%, which index to diamond and bcc symmetries respectively.

To gain further insight into this symmetry transition, we consider the variation of the lattice parameter with the aqueous volume fraction. Let $A$ denote the interfacial area per unit cell of lattice constant $\xi$. We introduce a dimensionless area $A^* = A \xi^{-2}$. It is easy to check that

$$A^*(\phi) = c_s a_s \xi^2$$  \hspace{1cm} (1)

where $\phi$ is the volume fraction, $c_s$ is the surfactant concentration in molecules per unit volume, $a_s$ is the area per surfactant molecule at the interface, and $\xi$ is related to the magnitude of the scattering vector $Q_{\text{max}}$ for a Bragg reflection $(hkl)$

$$\xi = \frac{2\pi}{Q_{\text{max}}} \sqrt{h^2 + k^2 + l^2}$$  \hspace{1cm} (2)

The value of $A^*(\phi)$ depends on the symmetry and topology of a given CMC surface. For bicontinuous CMC surfaces of cubic symmetry

$$A^*(\phi) = A^*(\phi_0) - \frac{1}{c} (\phi - \phi_0)^2$$  \hspace{1cm} (3)

where $\phi_0$, $A^*(\phi_0)$ and $c$ are symmetry-dependent constants whose values have been computed by Anderson /8-10/ for various surfaces.

It follows from equations (1), (2), and (3) that $c_s Q_{\text{max}} = A^*(\phi)/a_s$. Since $A^*$ changes according to the symmetry and topology of a given cubic structure, a plot of $c_s Q_{\text{max}}$ against $\phi$ can reveal such structural changes. This is shown in Fig. 3, where a transition is clearly seen between the two families of points corresponding to the D and bcc structures. The data indicate a change in $c_s Q_{\text{max}}$ of about 20% between the two symmetries, in close agreement with the theoretical difference in $A^*$ between the D-bilayer and the P-bilayer at $\phi = 0.55$ and at constant $a_s /8-10/$. 


Fig. 3. Plot of $c_s/Q_{\text{max}}$ against the aqueous volume fraction (including the surfactant head group). $c_s$ is in units of mol l$^{-1}$. $Q_{\text{max}}$ corresponds to the position of the first observed Bragg reflection and has the units of Å$^{-1}$. The symmetry of each sample is indicated by different symbols: Diamond (o) and bcc (□). The broken line is a theoretical fit to a D bilayer (Pn3m).

If the data points in Fig. 3 are fitted using the theoretical $A^*$ values for these structures, with $a_s$ as the only adjustable parameter, both the D and P-bilayers yield a value of 64±3 Å$^2$ for $a_s$. This is in good agreement with the area per surfactant measured in the L2 microemulsion phase /8, 14, 15/. Thus a D-bilayer to P-bilayer transition is strongly supported by the data. A similar transition has recently been reported by Barois et al/19/ in the system water/DDAB/cyclohexane. However, the SANS profiles of samples 8 and 9 in Table 1, which have bcc symmetry and an aqueous volume fraction close to 0.55, show three Bragg reflections whose intensities are in the order strong, medium, weak for the (110), (200) and (211) reflection respectively (see Fig. 4).

Fig. 4. SANS profile of a sample with composition DDAB: 36.22%, $D_2O$: 56.36%, octane: 7.42% showing bcc symmetry.
The theoretical "bulk" scattering amplitudes (i.e. for a contrast between the aqueous and paraffinic regions of the structure) for the P-bilayer at $\phi = 0.5$ have been computed by Anderson /8-10/ and a very weak second peak is predicted for the (200) reflection, followed by a moderately strong (211) peak. This is clearly inconsistent with the result shown in Fig. 4. On the other hand, the observed profile is both qualitatively and quantitatively consistent with the predicted intensities for a monolayer decorating an I-WP minimal surface ($\phi = 0.536$) /8-10/. If the bcc points in Fig. 3 are fitted to the I-WP model, a value of $55\pm3 \text{ Å}^2$ can be extracted for $a_0$. It appears therefore, that the I-WP monolayer structure cannot be ruled out, at least in part of the bcc region of the cubic phase, although it must be borne in mind that the aqueous volume fraction of these samples is ca. 0.55 and thus differs from the volume fraction of 0.50 for which theoretical intensities are at present available for the P-bilayer.

The physical properties of the cubic samples such as their texture, rigidity, and "melting point" show considerable variation between the two symmetries and generally change dramatically with composition. The "melting point" (i.e. the temperature at which the cubic liquid crystals "melt" into a random microemulsion) is lowest at the low-water edge of the cubic region, but increases rapidly with aqueous content. The cubic samples are also characterised by the property of "ringing" (i.e. they ring like a bell when tapped gently). As the temperature is raised the ringing ability of the samples is lost but can be restored reversibly on cooling. If equal volumes of sample are placed in the same type of container (e.g. a glass tube), the frequency of ringing is found to decrease with increasing water content, in parallel with the decreasing rigidity of the samples. Thus samples with Pn3m symmetry ring at a considerably higher pitch than their Im3m counterparts. We have carried out rheological measurements on Sample 1 (see Table 1), which melts at about $40^\circ\text{C}$, using the cone and plate geometry. As the frequency $\omega$ approaches the audible range, the storage modulus, $G'(\omega)$ and the loss modulus $G''(\omega)$ are seen to diverge, so that their ratio, the quality factor $G'(\omega)/G''(\omega)$ increases sharply at room temperature (see Fig. 5).

**Fig. 5.** Plot of the quality factor $G'(\omega)/G''(\omega)$ as a function of frequency at different temperatures (+) $22^\circ\text{C}$, (x) $27^\circ\text{C}$, (*) $32^\circ\text{C}$, (o) $36^\circ\text{C}$, and (o) $40^\circ\text{C}$.

This is consistent with the condition for ringing, since the quality factor defines the ratio of the energy density stored to the energy density dissipated per cycle, with $G'(\omega)/G''(\omega) >> 1$ at the frequency at which ringing is
heard. As the temperature is raised, structural changes take place in the sample which reduce the quality factor and result in the loss of ringing. It appears that ringing is associated with cooperative effects involving the cubic microcrystallites, and cannot be sustained when long-range order is lost and the crystallites begin to melt.

Table 1. \( D = \text{diamond, } \text{bcc} = \text{body-centred cubic. The composition of each sample is given in } \% \text{ weight: DDABID}_2\text{O/ooctane. } d = 2\pi Q_{\text{max}} \text{ is the spacing of the first observed Bragg reflection.} \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>Symmetry</th>
<th>( d(\text{Å}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48.21/36.44/15.34</td>
<td>D</td>
<td>59</td>
</tr>
<tr>
<td>2</td>
<td>47.73/37.22/15.04</td>
<td>D</td>
<td>61</td>
</tr>
<tr>
<td>3</td>
<td>44.82/40.95/14.23</td>
<td>D</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>43.84/46.12/10.03</td>
<td>D</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>40.10/51.70/8.20</td>
<td>D</td>
<td>69</td>
</tr>
<tr>
<td>6</td>
<td>38.18/54.0/7.82</td>
<td>D</td>
<td>70</td>
</tr>
<tr>
<td>7</td>
<td>36.95/57.35/5.70</td>
<td>D</td>
<td>76</td>
</tr>
<tr>
<td>8</td>
<td>36.22/56.36/7.42</td>
<td>\text{bcc}</td>
<td>93</td>
</tr>
<tr>
<td>9</td>
<td>35.23/54.84/9.93</td>
<td>\text{bcc}</td>
<td>97</td>
</tr>
<tr>
<td>10</td>
<td>34.94/57.90/7.16</td>
<td>\text{bcc}</td>
<td>95</td>
</tr>
<tr>
<td>11</td>
<td>32.98/60.26/6.75</td>
<td>\text{bcc}</td>
<td>108</td>
</tr>
<tr>
<td>12</td>
<td>29.80/64.10/6.10</td>
<td>\text{bcc}</td>
<td>118</td>
</tr>
<tr>
<td>13</td>
<td>29.29/64.71/6.00</td>
<td>\text{bcc}</td>
<td>113</td>
</tr>
</tbody>
</table>

Conclusions

Our results demonstrate the existence of more than one symmetry in the cubic phase of a ternary system, whose structure is well-described by a bicontinuous periodic CMC surface model. Analysis of the volume fraction variation of the lattice parameter is particularly useful as an indicator of structural change and a guide to the topological features of the cubic structure. The "ringing" ability of the gels is shown to be consistent with their rheological behaviour and is associated with their long-range crystalline order.

Acknowledgments

The authors are grateful to Dr. D.M. Anderson, University of Lund and Dr. T. McLeish, University of Sheffield for helpful discussions. We also thank the AFRC for support to L.D. This work was supported by a NATO grant (No. 880589). This work benefitted from the use of the Low-Q diffractometer at the Manuel P. Lujan, Jr. Neutron Scattering Center at the Los Alamos National Laboratory which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, and other Department of Energy programs under Contract W-7405-ENG-32 to the University of California.

References