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Short Communication

Symmetry transition in the cubic phase of a ternary surfactant system

S. Radiman ⁽¹⁾, C. Toprakcioglu ^(1,2) and A.R. Faruqi ⁽³⁾

⁽¹⁾Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, G.B.

⁽²⁾AFRC Institute of Food Research, Colney Lane, Norwich NR4 7UA, G.B.

⁽³⁾MRC Laboratory of Molecular Biology, Hills Road, Cambridge CB2 2QH, G.B.

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Abstract. — We report a small-angle X-ray and neutron scattering investigation in the cubic phase of the ternary system water/didodecyldimethyl ammonium bromide (DDAB)/octane. We have observed a systematic variation in the lattice parameter as a function of water content, which can be related to the change in interfacial area per unit cell with the aqueous volume fraction. Our results are consistent with a bicontinuous periodic constant mean curvature structure, and show a transition from diamond to body-centred cubic symmetry on increasing the water content of the system.

Introduction.

The existence of cubic phases in binary lipid-water systems has been firmly established by the pioneering work of Luzzati *et al.* [1]. More recently, cubic phases of ternary systems have received much attention [2-5]. These systems can be described in terms of periodic constant mean curvature (CMC) surfaces which are solutions to the problem of area minimization under the constraint of constant enclosed volume fraction [3, 6, 7].

The resulting structure consists of bicontinuous periodic labyrinths of water and oil conforming to a cubic symmetry. In recent years, several authors have reported transitions between cubic structures of different symmetry in the phase diagrams of certain binary systems [8, 9]. Theoretical models have been proposed to account for such transitions [9-11].

It is thus of interest to explore the possibility of a symmetry transition in a *ternary* cubic system, where the additional degrees of freedom afforded by the introduction of the third component are likely to lead to a richer variety of microstructures. Furthermore, the transition from a cubic phase to a neighbouring microemulsion merits closer attention, since it is possible to regard the latter

as a molten liquid crystal. In the present paper we report a structural study of the cubic phase of the system D_2O /didodecyltrimethylammonium bromide (DDAB)/octane. Ternary mixtures of DDAB, water and oil are characterized by an extensive cubic domain and a large microemulsion phase, which has been the subject of much work recently [12, 13].

Experimental.

The samples were prepared by thorough mixing of the three components in a closed container at $\sim 100^\circ C$, and were then allowed to cool to room temperature.

The small-angle X-ray scattering (SAXS) measurements were carried out with a point-collimated beam from a $Cu-K\alpha$ line of $\lambda = 1.54 \text{ \AA}$. A two-dimensional position sensitive detector [14] was used at a distance of 75cm from the sample, which was placed between two mica sheets and rotated in the beam at about 1 r.p.m.. A sample thickness of ca. 0.7mm was maintained by means of a Teflon O-ring. The temperature of the sample was $22 \pm 1^\circ C$. The samples were subjected to several cycles of heating and quenching prior to the measurements as this reduces the size of large crystallites and gives rise to much improved powder diffraction patterns.

The small-angle neutron scattering (SANS) experiments were carried out on D17 at the ILL, Grenoble with a monochromatic wavelength of 12 \AA and a variable sample-detector distance 1.4-2.8 m. The samples were contained in 1mm path length quartz cells and subjected to heating and cooling cycles before each measurement. The spacings obtained from the SAXS and SANS measurements on a given sample were equal to within $\pm 3 \text{ \AA}$.

Results and discussion.

The phase diagram of the system D_2O /DDAB/octane exhibits a large cubic domain extending from ca. 35% to 77% D_2O (Fig.1). The high-octane side of this cubic region faces the L_2 microemulsion phase, while the low-octane side is opposite a lamellar region. Within the cubic phase itself, there is considerable variation in the physical properties of the system as a function of composition. Notably, the rheological properties change significantly, with increased rigidity being observed at low water content. Moreover, the "melting point" of the cubic samples (i.e. the temperature at which long-range order is lost and the cubic liquid crystal "melts" into a microemulsion) varies dramatically with composition, being lowest (ca. $40^\circ C$) in the low-water extreme of the cubic region. These cubic phases are further characterised by the property of "ringing" (i.e. they ring like a bell when tapped gently). Rheological data associated with this interesting effect will be reported elsewhere. The frequency of ringing also depends on composition and decreases at high water content. Furthermore, some of these properties appear to change rapidly with composition in certain regions of the cubic domain. These observations strongly suggest the possibility of structural changes within the cubic region as a function of composition. Measurements of specific heat in a similar ternary system were recently reported by Radlinska *et al.* [15], which also suggested a transition between two cubic phases.

We have used SAXS and SANS to investigate the microstructure of the cubic phase along a water dilution path (Fig.1). The results clearly indicate a symmetry transition at an aqueous volume fraction close to 0.5 (Fig.2). At low water content the SAXS profiles can be indexed to a diamond (D) structure⁽¹⁾. As the water content is increased, there is a transition to a structure of body-centred cubic (bcc) symmetry⁽²⁾.

⁽¹⁾ The structure invoked here is related to the Schwarz-D minimal surface. The space group is $F\bar{4}3m$ for a monolayer and $Pn3m$ for a bilayer structure respectively (see Ref.[6]).

⁽²⁾ Possible structures are the P-bilayer based on the Schwarz-P surface or the I-WP monolayer surface, both space group $Im3m$ (see Ref.[3], and note ⁽⁴⁾).

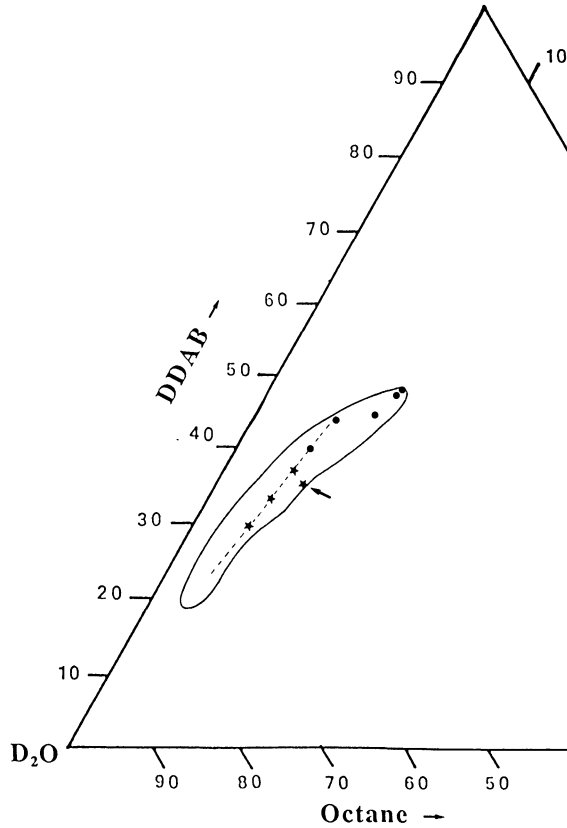


Fig. 1. — Phase diagram of the ternary system $D_2O/DDAB/octane$ at $22^\circ C$ showing the cubic region. The dashed line is a D_2O dilution path. The sample compositions are given by the points within the cubic domain: (●) diamond symmetry, and (*) body-centred cubic symmetry. The point indicated by an arrow corresponds to a sample for which SANS data suggest an I-WP monolayer structure.

If ξ is the lattice constant of the cubic structure with an interfacial area A per unit cell, it is useful to define a dimensionless area $A^* = A\xi^{-2}$, with

$$A^*(\phi) = c_s a_s \xi \tag{1}$$

where ϕ is the volume fraction, c_s is the surfactant concentration in molecules per unit volume, and a_s is the area per surfactant at the interface. The value of $A^*(\phi)$ depends on the symmetry and topology of a given CMC surface, and has been computed for various surfaces by Anderson [3]. For bicontinuous periodic CMC surfaces of cubic symmetry, he found

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

where ϕ_0 , $A^*(\phi_0)$, and c are symmetry-dependent constants. The lattice constant ξ is related to the magnitude of the scattering vector, Q_{max} , for a Bragg reflection (hkl)

$$\xi = \frac{2\pi}{Q_{max}} \sqrt{h^2 + k^2 + l^2} \tag{3}$$

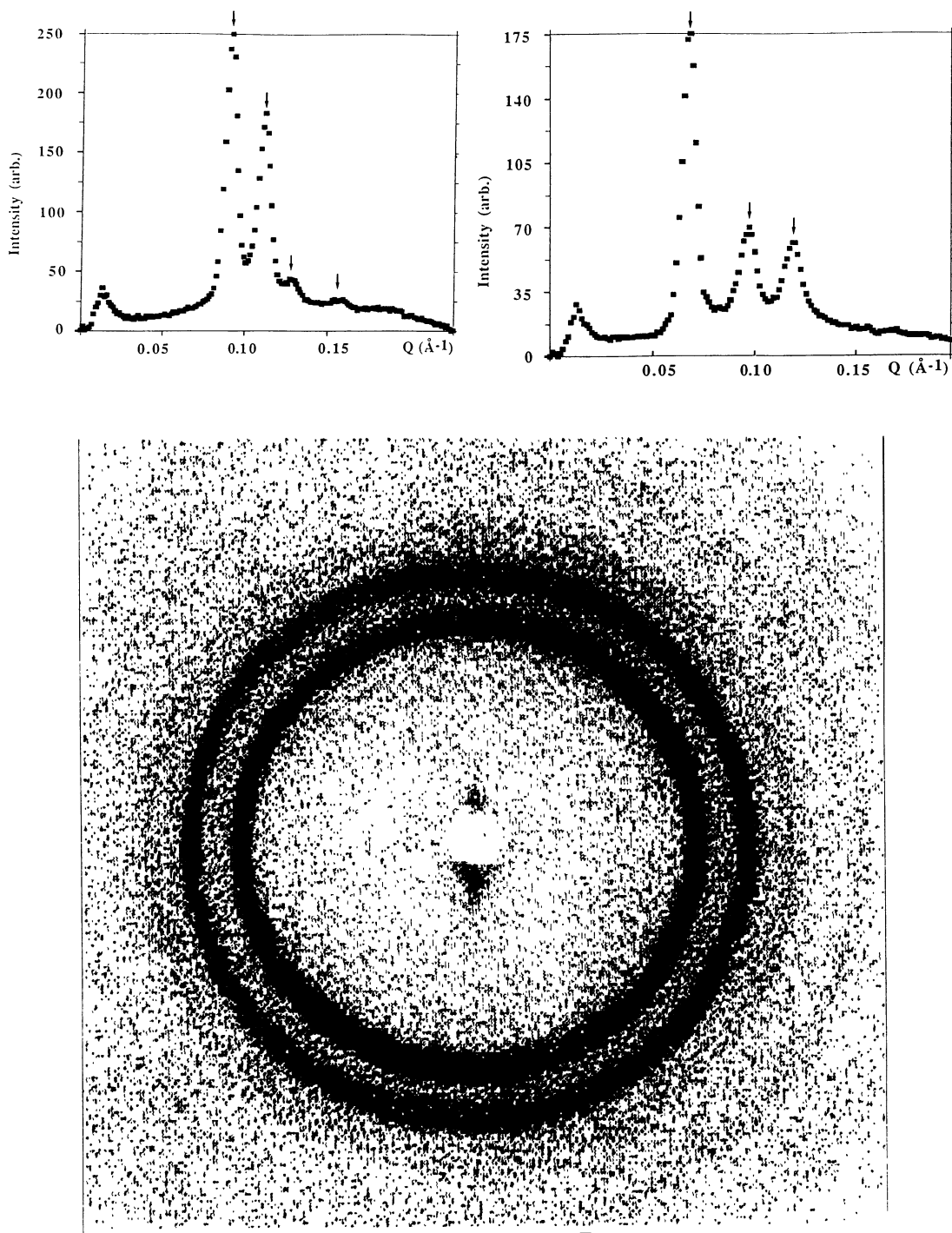


Fig. 2. — SAXS profile of samples with composition by weight (A) D_2O :51.7% , DDAB:40.1% , octane:8.2% and (B) D_2O :56.36% , DDAB:36.22% , octane:7.42% showing diamond and bcc symmetry respectively. (The feature at very low Q is due to the beam-stop, and is not a Bragg reflection). (C) Two-dimensional plot of the detector showing SAXS scattering from the sample in figure 2A. Five orders of reflection can be seen which index to a diamond structure ($1, \sqrt{3/2}, \sqrt{4/2}, \sqrt{6/2}, \sqrt{8/2}$, relative to the first peak).

It follows from (1), (2) and (3) that a plot of c_s/Q_{\max} against ϕ should be sensitive to changes of symmetry and topology, as these would manifest themselves in the ϕ -dependence of A^* . Figure 3 shows such a plot, and the transition from a D to a bcc structure is clearly indicated. There is also some evidence of a further transition above ca.68% D_2O , but more measurements are required before this can be shown conclusively.

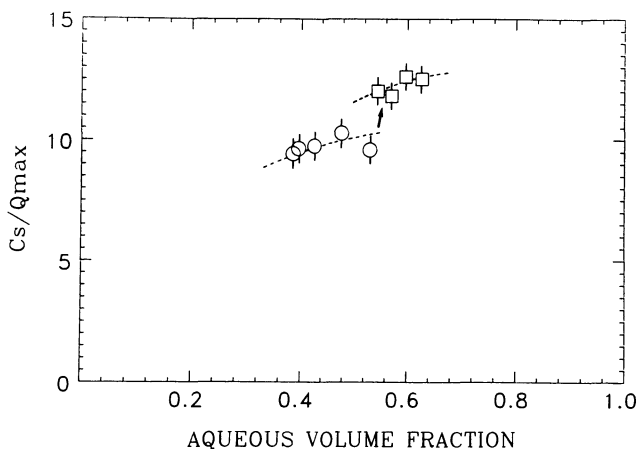


Fig. 3. — Plot of c_s/Q_{\max} against the volume fraction of the aqueous phase (including the surfactant head-group). c_s has the units of mol l^{-1} . Q_{\max} corresponds to the position of the principal reflection and has the units of \AA^{-1} . The symmetry of each sample is indicated by different symbols: diamond (o) and bcc (). The arrow indicates the transition between the two symmetries. The dashed lines are theoretical fits to the diamond bilayer (Pn3m) and P-bilayer (Im3m). The only adjustable parameter is a_s , yielding a value of $65 \pm 2 \text{\AA}^2$ for both symmetries (see Eqs. (1) - (3)).

Since A^* values for the bcc and diamond symmetry have been computed [3, 6] it is possible to extract values for a_s for the two regimes described in figure 3. (Conversely, if one *assumes* a value for a_s , an A^* value follows which can be compared to theory for various symmetries and topologies). In determining a_s , however, the question arises whether one should assume a monolayer or bilayer arrangement. This issue can only be resolved conclusively by careful measurement of peak intensities in a scattering experiment with “bulk” contrast (e.g. a SANS measurement with D_2O and the other components unlabelled) as opposed to the combination of the “bulk” and “film” scattering that is normally observed with X-rays. At present, we have insufficient SANS data to address the problem directly. However, the transition shown in figure 3 indicates a change of ca. 17% in c_s/Q_{\max} which is very close to the theoretical difference in A^* between the D-bilayer and the P-bilayer⁽³⁾. We have thus assumed a transition from a diamond bilayer (space group Pn3m) to a P-bilayer (space group Im3m)⁽⁴⁾ and the dashed curves in figure 3 are based on A^* values for these topologies. This allows determination of a_s which is found to be $65 \pm 2 \text{\AA}^2$ both for the D and P bilayers. While these values are reasonable and in good agreement with those obtained in the

⁽³⁾ It follows from equations (1), (2) and (3) that $c_s/Q_{\max} \sim A^*$. Since the A^* values for the D and P bilayers at $\phi = 0.55$ are ca. 3.4 and 4.1 respectively, a transition between these structures implies a change of about 20% in c_s/Q_{\max} at constant a_s .

⁽⁴⁾ Pn3m and Im3m are the space groups of highest symmetry among the possible ones, in each case.

L_2 microemulsion phase [3, 12, 13], it should be noted that there is no *a priori* reason why a_s must have the same value in the cubic phase as in the microemulsion. It might be reasonable to expect somewhat tighter packing of the surfactant molecules in the cubic phases in comparison with the microemulsion. Anderson [3] found a_s to vary with water content from ca.40 Å² to ca.60 Å² in the water/DDAB/decane microemulsion system. A similar variation might occur in the cubic phase, and it may thus be misleading to assume a constant a_s over the entire compositional range of the cubic phase. Nevertheless, our data are in good agreement with a D-bilayer to P-bilayer transition at an a_s value of ca.65 Å². If monolayers were assumed, the a_s values corresponding to the diamond and bcc symmetries would be 35 Å² and 55 Å² respectively. The a_s for the D-monolayer would seem unreasonably low⁽⁵⁾.

Table I. — $D = \text{diamond}$, $\text{bcc} = \text{body-centred cubic}$ (see notes ⁽¹⁾, ⁽²⁾ and ⁽⁴⁾), $d = 2\pi/Q_{\text{max}}$ is the spacing of the first observed Bragg reflection. The composition of each sample is given in % weight: DDAB/D₂O/octane.

Sample	Composition	Symmetry	$d(\text{Å})$
1	48.21/36.44/15.34	D	59
2	47.73/37.22/15.04	D	61
3	44.82/40.95/14.23	D	65
4	43.84/46.12/10.03	D	69
5	40.10/51.70/8.20	D	69
6	36.22/56.36/7.42	bcc	93
7	35.23/54.84/9.93	bcc	97
8	32.98/60.26/6.75	bcc	108
9	29.80/64.10/6.10	bcc	118

Finally, it is appropriate to comment on the possible mechanism of the observed transition. In recent years Hyde *et al.* [9, 10] have propounded the interesting argument that transitions related by the Bonnet transformation (a conformal, isometric, and curvature-invariant topological transformation that can occur between certain surfaces) might play an important role in cubic phases, since Bonnet-related transitions would occur smoothly, without any change in curvature, and would thus require a negligible enthalpy. Our results, however, are consistent with a first-order transition, and our data suggest that in a certain region within the cubic domain, samples can be prepared which appear to contain two coexisting cubic phases. This observation seems to be supported by the results of Radlinska *et al.* [15]. In addition to the transition between the diamond and bcc symmetries, assuming this to occur within a bilayer topology, there may be a monolayer to bilayer transition within the bcc domain, for SANS data [5] from a sample at the high-octane edge

⁽⁵⁾ We note, however, that the SAXS pattern of sample 5 ($\phi = 0.53$) is compatible with a D-monolayer structure. At $\phi = 0.5$ in the D-monolayer the bulk amplitudes vanish, and only film scattering is observed (see ref.[3]). The amplitudes extracted from the SAXS spectrum of sample 5, for the first three reflections are 1, 1.12, 0.47 (normalized to the first reflection), in good agreement with the theoretical values of 1, 1.02, 0.55 for a *monolayer* decorating a D-minimal surface. However, this might be due to a fortuitous combination of *bilayer* bulk and film scattering giving rise to intensities that resemble those of a monolayer. At present we do not have the theoretical values for the *bilayer* structure and cannot test this.

of the cubic phase (see Fig.1) are in much better agreement with the I-WP monolayer than the P-bilayer. This would further support our view that symmetry transitions between ternary cubic phases need not be confined to the Bonnet transformation, and may involve topologically more disruptive processes. In fact, many lyotropic transitions occur without any possibility of a topologically smooth transformation, and the mechanism of surface deformations responsible for these transitions remains an open question.

In conclusion, our analysis shows that the structure of ternary cubic phases is well-described by a periodic minimal or CMC surface model, and that the dependence of lattice spacing on aqueous volume fraction is a useful indicator of structural changes in such systems. Furthermore, our results clearly confirm the existence of more than one symmetry within the cubic domain of a ternary system. The transformation mechanism between the observed symmetries, and the transition from the cubic phase to the neighbouring microemulsion are not well-understood. More work is in progress to address these issues.

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Note added.

The cubic phase of a similar ternary system has been investigated by Barois *et al.*, Langmuir, in press, using small-angle X-ray scattering. These authors have used the same surfactant (DDAB), but a different oil (cyclohexane as opposed to octane employed in our study). In agreement with our results, they also find a symmetry transition from a diamond to a bcc structure as a function of water content. Assuming a value of 68 \AA^2 for the area per surfactant, Barois *et al.* calculate the expected topology of the diamond and bcc structure, and find in favour of a bilayer cubic phase for both symmetries. Contrary to the calorimetric data of Radlinska *et al.* (see Ref.[15]), they find no evidence of a further topological transformation within the bcc regime in their system. They point out, however, that in the bcc region their data are subject to some scatter which precludes a more definite conclusion.

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