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Lyotropic Mesophase Behaviour of n-$C_{16}H_{33}EO_3$ - Evidence for Two "V_2" Phases

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LYOTROPIC MESOPHASE BEHAVIOUR OF n-$C_{16}H_{33}EO_3$ - EVIDENCE FOR TWO "V_2" PHASES.

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Nonionic surfactants of the alkyl polyoxyethylene ether variety commonly form hexagonal (H_1) or lamellar (L_α) lyotropic mesophases with water[1]. Less well-known is the frequent occurrence of I_1 or V_1 cubic mesophases.* No reports exist to date of the occurrence of reversed phases with these materials. While the surfactants are known to form several solid complexes with water, their melting points are below those of the anhydrous surfactants[2]. In an optical microscope study of the liquid crystals formed by water penetration into n-hexadecyl trioxyethylene glycol ether ($C_{16}EO_3$) we have observed a solid complex with a melting point above that of the pure surfactant. We also observe a cubic region which we classify as a reversed structure (V_2). Moreover, the occurrence of a refractive index discontinuity within this region strongly suggests that two different phases are present. The cubic region

*Footnote: Phase labelling according to ref. 1, I_1, V_1 refer to cubic structures occurring at compositions between micellar solution (L_1) and H_1 phases, or between H_1 and L_α phases resp. Subscripts 1 or 2 refer to mesophases where the alkyl-chain/water interface has curvature of the same sign to that of normal or reversed micelles.

coexists with water for part of the temperature range over which it occurs. When water droplets form within the cubic region on heating, they adopt angular shapes which suggest that a single, long-range structure exists, rather than a "powder" orientation of domains.

EXPERIMENTAL

The surfactant was synthesised by reacting hexadecyl bromide with the sodium salt of triethylene glycol. Purity estimated by g.l.c. was >98%. Optical microscopy was carried out using a Reichert "Neopan" polarising microscope with a Koffler hot-stage. Temperatures (^{o}C) are accurate to $\pm$ 1^{o}.

PENETRATION EXPERIMENT

This is a simple, rapid technique that allows the range of mesophases occurring in a given system to be determined. A sample of the pure surfactant is sandwiched between a microscope slide and cover-slip. Contacting the cover-slip with a drop of water results in the spreading of water around the surfactant. Thus a surfactant/water concentration gradient occurs at the edge of the surfactant sample, where any mesophases form as distinct bands. Different mesophases are distinguished by their microscope textures (using cross-polars), and by their differing flow properties (monitored by gently pressing on the cover-slip). The temperature of measurement can be altered by using a microscope hot-stage. If the surfactant is a liquid, spacers placed between slide and cover-slip are usually required to obtain a layer sufficiently thick for the easy observation of birefringence.

RESULTS AND DISCUSSION

The solid anhydrous surfactant $C_{16}EO_3$ melts at 31^{o} to form a liquid (L_2). On cooling, the solid re-forms only very slowly. On contact with water, a region of "grainy" appearance occurs at the liquid surfactant (L_2)/water boundary above 31^{o}, which changes to an L_α phase at 39.5^{o}. The L_α phase was identified from its optical texture and relative viscosity. It forms myelins which extend into water (Fig. 1a). On cooling below 39.5^{o} the myelins adopt an angular configuration (Fig. 1b), lose water and the L_α phase becomes rigid. On re-heating, normal L_α phase re-forms at 39.5°. Thus we conclude that the "grainy" appearance corresponds to a solid-like phase. Since the material does not form without water it is termed a "solid complex". Whether it is a type of gel structure (L_β) with liquid-like water and rigid surfactant layers is currently under investigation.

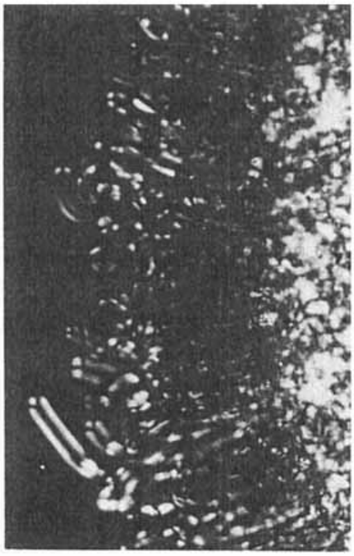

FIGURE 1(a)

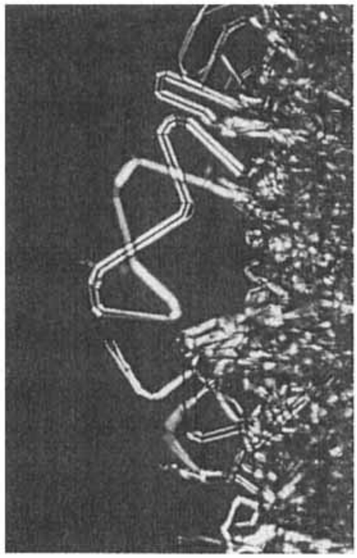

FIGURE 1(b)

(a) Myelin formation at L_α/water boundary (40°).

(b) "Angular" configuration of myelins indicating solid complex (38°). [Magn. x 75, crossed polars].

Above 39.5° the L_α phase persists to 50°. It is replaced by a cubic region, which is observed first at the water-rich boundary (46.5°) and has fully melted (to L_2) by 61.5°. The cubic region is detected by its very high viscosity and the absence of birefringence. Within the cubic region there is a refractive index discontinuity (Fig. 2). It occurs on increasing or decreasing the temperature, and is similar in appearance to mesophase/mesophase boundaries observed in other systems. We tentatively suggest that it represents a boundary between two different cubic mesophases. At least two different "bicontinuous" structures are thought to be possible with the "V" cubic phases[3], but this is the first report with evidence for two structures in a single surfactant/water system.

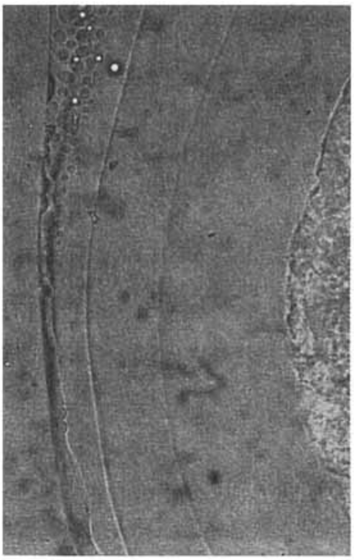

FIGURE 2

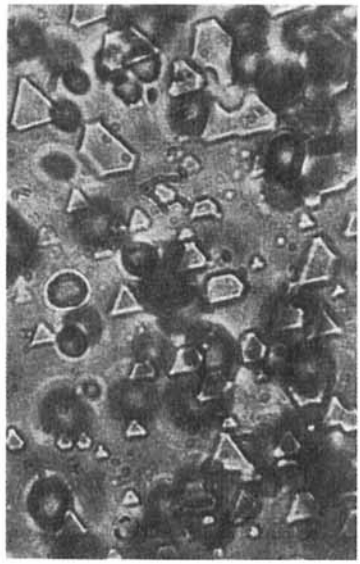

FIGURE 3

FIGURE 2: Succession of phases at $\sim 48^{\circ}$. (Right to left, phases are $L_{\alpha}/V_2(1)/V_2(2)/L_3$/Water.) Only L_{α} phase is birefringent. [Magn. x 75].

FIGURE 3: Water droplets formed at cover-slip surface in $V_2(2)$ region ($\sim 61^{\circ}$). [Magn. x 400].

The behaviour of compositions between water (containing dissolved surfactant monomer) and the water-rich mesophase boundary is complex. A third liquid (L_3) with intermediate surfactant content occurs over the temperature range 43-50°. The L_3 region was first reported[4] for $C_{12}EO_5$ and has since been observed for several compounds[5,6]. N.m.r. and conductivity measurements suggest[5] that in $C_{12}EO_4$ it is a micellar solution containing oblate spheroid micelles. There are tie-lines between L_3 and L_α or the cubic region, and between water and L_3. Above the L_3 phase the cubic region coexists with water. This behaviour is typical of V_2 rather than V_1 phases. Also, the V_1 phases of other poly-EO surfactants occur within this temperature range for derivatives having EO numbers greater than six. Thus we assign the region a V_2 structure. This is the first "reversed" mesophase reported for a surfactant of this type.

Observation of the V_2/water boundary over the temperature range 50-61.5^o shows that more and more water droplets are formed in the water-rich V_2 phase as temperature is increased. When they occur at the glass/mesophase surface, these droplets have an unusual angular shape (Fig. 3). Note that only three directions, at 60^o or 120^o to each other, occur for the boundaries. Thus the droplets form triangular or related shapes at the surface. No special cleaning or surface treatment of the glass was used. Thus if a powder arrangement of cubic domains were present we would expect no regular pattern of droplets to occur. The observation of a regular pattern indicates that the water-rich cubic region consists of a "single-crystal" structure, unlike the poly-domain powders observed for L_α or H_1 phases. This is consistent with a micelle network ("bicontinuous") structure[1,3] for this region, which might be expected to form large "single-crystals".

To summarise, using optical microscopy we have evidence for the occurrence of a solid complex, an L_α and two V_2 cubic phases in $C_{16}EO_3$ water mixtures. An unusual pattern of water droplets in the water-rich V_2 phase is consistent with a network structure for this region.

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