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The Structure of Neat Mesomorphic Phase

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Abstract—Optical microscopy, low-angle X-ray diffraction, and electron microscopy have been used to study the lamellar mesomorphic phase (neat phase) given by the sodium 2-ethyl hept-6-enyl sulphate + water system. Good agreement for the interlayer spacing has been obtained from X-ray diffraction measurements and the electron microscopy techniques of surface replication and thin sectioning. Comparable surface replicas have been obtained from anhydrous neat phase and from the quench-frozen mesomorphic phase containing 20% water.

Introduction

In many surface-active agent + water systems, neat mesomorphic phase exists at low water concentrations over a limited concentration range (10–30% H_2O), and can be transformed reversibly into other lyotropic mesomorphic phases on further dilution.[1] Polarization microscopy[2–4] has shown that neat phase belongs to the smectic class[5, 6] of mesomorphic phases and low-angle X-ray diffraction[1, 7] patterns from neat phase samples have been interpreted in terms of a lamellar structure composed of extensive bimolecular layers of surface-active molecules interleaved with layers of water of variable thickness.

Direct confirmation of the layered structure has been obtained from electron micrographs of anhydrous surface replicas,[8] osmium tetroxide fixed sections,[9] or negatively stained specimens.[10] However, electron microscopy techniques require the examination of anhydrous specimens which may contain appreciable amounts of staining reagent. Misleading artifacts may therefore be introduced, and so it is highly desirable to confirm phase structure on a single,

well-defined system using several different electron microscopy techniques.

At room temperature, sodium 2-ethyl hept-6-enyl sulphate exists as neat phase in the anhydrous condition and forms only one mesomorphic phase, neat phase, on addition of water. The surface replication technique can be applied to this anhydrous neat phase with confidence, since no pseudomorphs of any precursive mesomorphic phase should result on drying dilute aqueous-solution droplets. In addition, the presence of an ethylenic double bond in the molecule permits the use of the well-known technique of osmium tetroxide fixation.[11]

Experimental

Materials

2-Ethyl hept-6-enyl alcohol, $CH_2{=}CH\cdot(CH_2)_3\cdot CH(C_2H_5)\cdot CH_2OH$, shown to be pure by gas–liquid chromatography, was sulphonated with chlorosulphonic acid. After neutralizing with sodium hydroxide, unreacted alcohol was removed by solvent extraction. The product, obtained as an anhydrous neat phase, gave a correct elemental analysis and iodine value.

Phase Diagram

The condensed binary phase diagram for the sodium 2-ethyl hept-6-enyl sulphate + water system was constructed using polarization microscopy, and confirmed at room temperature by low-angle X-ray diffraction, using the vacuum camera described previously.[1]

Electron Microscopy

Specimens for electron microscopy were examined in a Siemens Elmiskop I at 80 kV, with magnifications in the range 10^4–$10^5\times$.

Surface replicas of the anhydrous neat phase were prepared from dilute ($\sim 5\%$) aqueous solutions of the surface-active agent. Suitably sized droplets of these solutions were deposited on mica

surfaces and allowed to dry slowly at room temperature. Replicas were prepared by shadowing *in vacuo* at 15 or 30° with platinum/carbon, or platinum alone followed by carbon backing. The replicas were stripped from the mica at a water surface.

Surface replicas were also prepared from quench-frozen neat phase containing 20 % water. A dilute (~5 %) aqueous solution of the surface-active agent was deposited onto a mica surface held in a closed vessel at constant relative humidity (0·85) so that the solution became slowly concentrated over a period of 24 hours. The equilibrated neat phase (on its mica support) was quench-frozen by immersion in liquid nitrogen and then quickly transferred to a "Speedivac" coating unit which contained a specially designed specimen holder pre-cooled with liquid nitrogen to −130° C. The work chamber of the coating unit was then evacuated and the specimen was shadowed in the usual way.

Thin sections were prepared from neat phase fixed with osmium tetroxide (OsO_4). The nearly anhydrous surface-active agent reacted very slowly unless the temperature was raised to 50° C. However, if the neat phase contained 20 % water, then fixing was possible at room temperature although prolonged exposure to OsO_4 vapour was necessary (7–14 days). After extracting with water to remove any unfixed material, the remainder was dehydrated and embedded in Araldite using normal techniques.[11] Sections ~300 Å thick were cut using a Porter-Blum MT-1 ultramicrotome, and were picked up on grids covered with "holey" carbon films.[11] For each section a through-focal series of electron micrographs was taken.

Results

Phase Behaviour

In the polarizing microscope, the sodium 2-ethyl hept-6-enyl sulphate + water system shows only neat phase and isotropic solution (Fig. 1). At room temperature neat phase extends from 0–30 % water. From 30–36 % water there is a region where neat and fluid isotropic phases coexist. These can be separated in a centrifuge

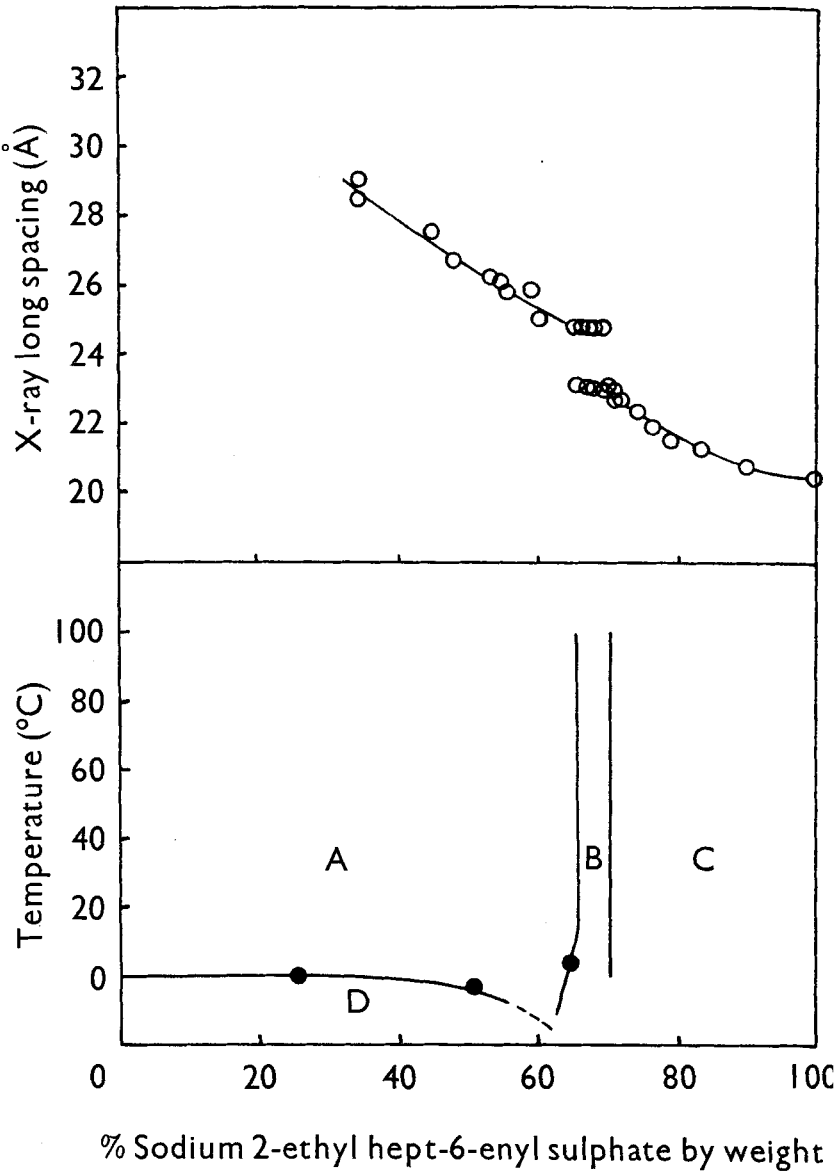

Figure 1. X-ray long spacing versus concentration (○), and partial phase diagram (●), for sodium 2-ethyl hept-6-enyl sulphate + water. (A) Isotropic phase, (B) Isotropic phase + neat phase, (C) Neat Phase, (D) Isotropic phase + ice.

at 3000 rev./min. Within the two-phase region the relative proportions of the conjugate phases are governed by a tie-line relationship.

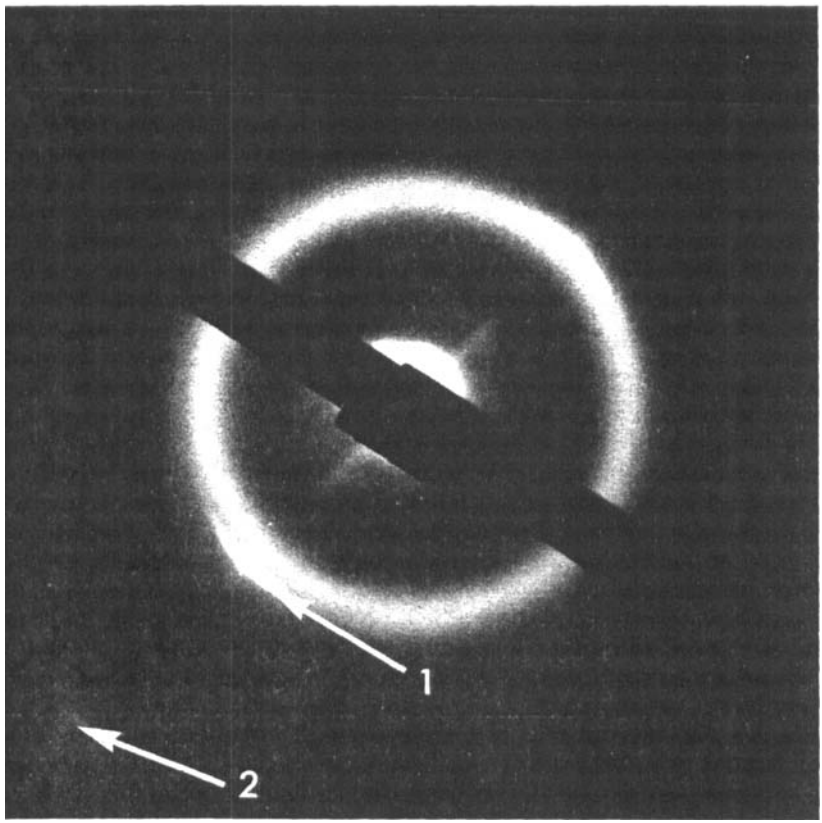

Figure 2. X-ray diffraction pattern obtained from the region where neat and isotropic phases coexist. Enlarged 3.3×. Arrows (numbered 1 and 2) indicate first and second order diffraction maxima of neat phase.

All X-ray diffraction patterns from neat phase can be indexed as a series of (00l) reflections, typical of a layered structure. They show pronounced orientation parallel to the capillary axis. Relatively large oriented mesomorphic domains could be prepared by centrifuging neat phase specimens back and forth in a capillary

tube at 70°C, followed by slow cooling to room temperature. These gave diffraction patterns showing an equatorial row of spots normal to the capillary axis, implying a cylindrical orientation of the neat phase layers as predicted by Mabis[12] for the SSR structure type of Hermann.[13] In the graph of X-ray long spacing versus concentration at room temperature (Fig. 1) distinct discontinuities occur at the boundaries of the two-phase region, where the low-angle X-ray photographs show a superposition of two patterns (Fig. 2) viz. sharp lines from the neat phase, and a single diffuse ring characteristic of micellar solution from the isotropic phase. Within the region of two-phase coexistence, the X-ray long spacings for both neat and isotropic phases are invariant with composition and the relative intensities of the two sets of reflections change in proportion to the amounts of each phase present.

Electron Microscopy

Surface replicas prepared from the anhydrous neat phase showed the typical stepped drop arrangement with scalloped edges, described previously.[8] Single step-heights, measured from platinum replicas prepared at a shadowing angle of 15°, were 20 ± 5 Å showing good agreement with the results obtained by X-ray diffraction.

Surface replicas obtained from quench-frozen specimens were similar to those obtained from the anhydrous mesomorphic phase, either flat droplets with steps (Fig. 3) or, more commonly with thicker specimens, massed focal conic arrangements (Fig. 4), indicating that the low-temperature technique had neither disrupted the structure nor introduced any new artifacts. Accurate step height determinations however were hampered by the high incidence of multiple steps. Nevertheless this freeze-replication technique may provide a general method for electron microscopical investigation of lyotropic mesophase structures, the only limitation being the possible crystallization of the surface-active agent during freezing.

Electron micrographs obtained from thin sections of osmium tetroxide-fixed neat phase show a cross-section of a structure with an interlayer spacing of 20 Å (average over 25 lines) (Fig. 5). The

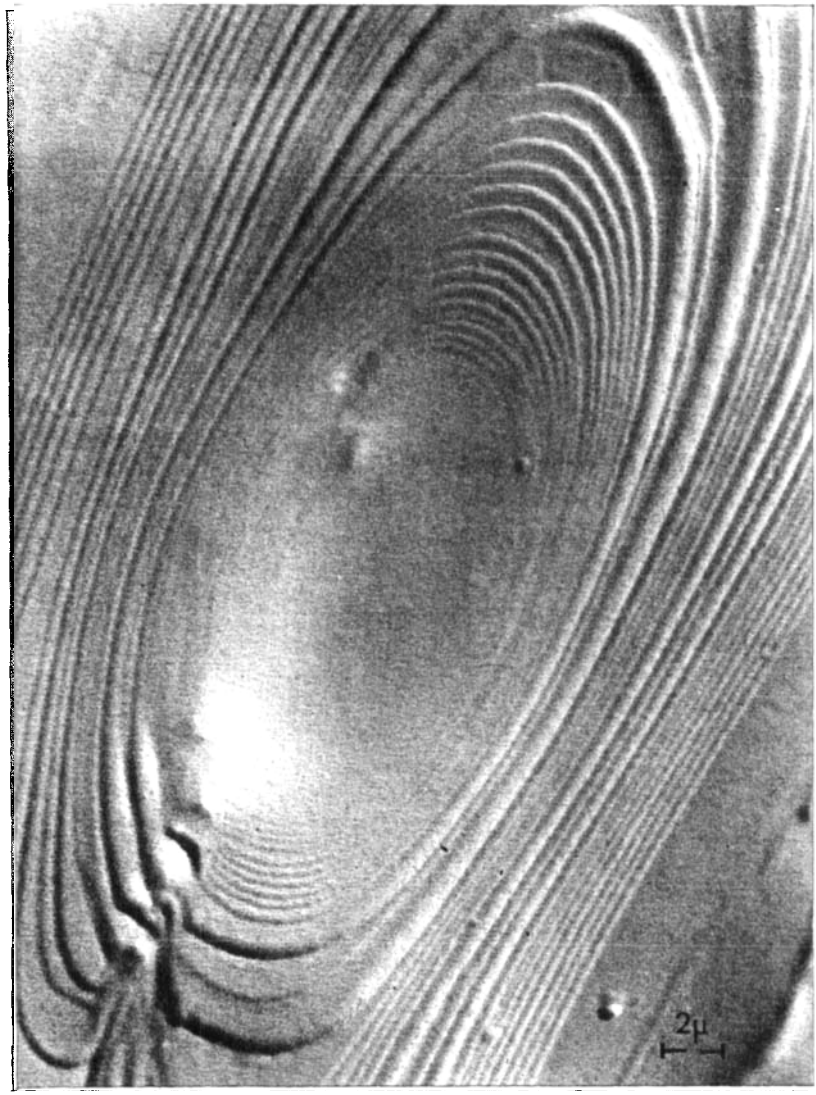

Figure 3. Electron micrograph of a replica of quench-frozen neat phase containing 20% water. Magnification 56,000×.

Figure 4. Electron micrograph of a replica of quench-frozen neat phase containing 20% water. Magnification 36,000×.

best resolution was obtained when viewing locally-thin areas of the sections through holes in the carbon support film.

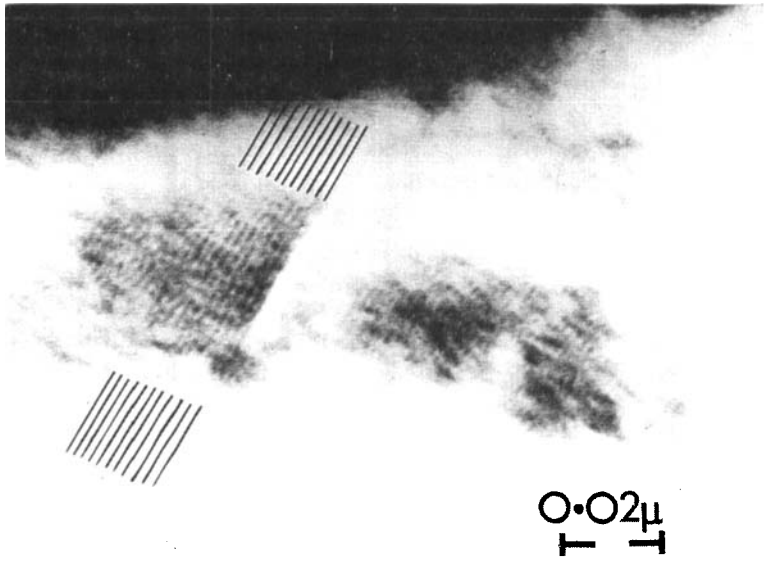

Figure 5. Transverse section of neat phase fixed with osmium tetroxide. Magnification 630,000 ×.

Discussion

Phase Behaviour

The occurrence of only one mesomorphic phase, neat phase, which persists even when all the water has been removed, is unusual. The lack of crystallinity presumably arises from steric effects associated with the 2-ethyl branching.[8] The presence of a region in which the neat and fluid isotropic phases coexist as conjugate solutions is the type of behaviour expected for a first order phase transformation in a two-component system.[14]

Following Luzzati,[15] the bimolecular layer thickness (d_1), the aqueous layer thickness (d_2) and the area per long-chain ion (A) at the aqueous interface may be calculated from the X-ray long

spacing (d_{001}) and the mesophase density (ρ) measured as described previously.[1] At the neat⇌isotropic phase boundary, $d_{001} = 22.7$ Å and $\rho = 1.146$ g cm^{-3} and so $d_1 = 15.6$ Å, $d_2 = 7.1$ Å and $A = 52$ Å^2. Any structural interpretation of the neat⇌isotropic phase change in terms of the break-up of the neat phase layers must be highly speculative at the present time since the micellar structure in the isotropic phase is unknown. The volume fraction (0.63) at the phase boundary is consistent with either randomly packed spherical micelles[16] or disc-shaped micelles.

Electron Microscopy

The three specimen preparative techniques clearly illustrate the lamellar structure of neat mesomorphic phase. The individual bimolecular layers of neat phase form flat sheets when immediately adjacent to a flat orienting surface[6] (Fig. 3) while the "stepped drop" or "goutte à gradins" of Grandjean[17] that can be observed in the optical microscope consists of numerous parallel layers fringed by a chain of focal conic structures.[5, 8] Not only do the surface replicas from both anhydrous and frozen structures illustrate the equilibrium surface forms of neat phase droplets, but the anhydrous replicas have also given step heights in good agreement with those obtained from OsO_4-fixed thin sections and from low-angle X-ray diffraction.

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