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Amphitropic liquid crystals

Two lamellar phases in a surfactant containing thermotropic and lyotropic mesogenic groups

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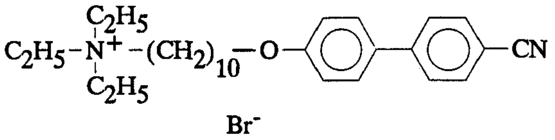
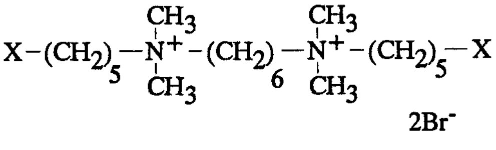
We have studied the lyotropic liquid-crystalline behaviour of cationic surfactants containing a potentially thermotropic moiety, a terminal cyanobiphenyloxy group. Both mono-alkyl and mid-chain substituted dialkyl surfactants have been examined using optical microscopy and NMR spectroscopy. Incorporation of the cyanobiphenyloxy group destabilizes the hexagonal and bicontinuous cubic phases, with only an extensive lamellar region being observed. For the dialkyl surfactant there is a range of compositions where two lamellar phases co-exist, one water-rich and the second surfactant-rich.

This preliminary communication describes an initial survey of the lyotropic liquid crystals formed by surfactants which contain a conventional thermotropic moiety in their molecular structure, in addition to the usual polar and hydrophobic units. We term these materials amphitropic because they offer the potential of combining lyotropic (amphiphilic) and thermotropic mesomorphism. The two compounds examined so far are 10-(4′-cyano-4-biphenyloxy)decyltriethylammonium bromide



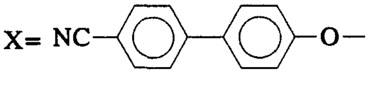
(I)

and *N*,*N*′-bis(5-(4′-cyano-4-biphenyloxy)pentyl)-(*N*,*N*,*N*′,*N*′)-tetramethyl hexane diammonium dibromide



$$X-(CH_2)_5-\overset{CH_3}{\underset{CH_3}{N^+}}-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{N^+}}-(CH_2)_5-X \quad 2Br^-$$

(II)



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Optical microscopy and nuclear magnetic resonance spectroscopy (^2H_2O) have been employed to monitor the phase behaviour. Conventional surfactants of this type would be expected to exhibit hexagonal and lamellar phases separated by cubic or intermediate phases [1]. For these compounds we observe only lamellar phases over a very wide range of compositions (20–80 wt% surfactant). In addition, compound (II) exhibits a biphasic region of co-existing lamellar phases.

The materials were synthesized in a two stage process. First the 4-hydroxy-4′-cyanobiphenyl was coupled with the appropriate α,ω-dibromoalkane (10 mole excess) with potassium carbonate in analar acetone (20 h). The product was filtered hot, recrystallized from ethanol and soxlet-extracted with methanol. For compound (I) the α-bromodecyl-ω-oxy-4,4′-cyanobiphenyl was reacted with excess triethylamine in dry toluene (40°C, 5 days). The filtered precipitate was purified by reprecipitation with dry toluene from absolute ethanol. For compound (II), α-bromopentyl-ω-4,4′-cyanobiphenyl (excess) was reacted in acetonitrile with *N*,*N*,*N*′,*N*′-tetramethyl-1,4-butane diamine (solution in dry acetonitrile added drop wise, 80°C, 2 days). The product precipitated on addition of petroleum ether (40–60°C), was filtered and recrystalized from ethyl acetate. Both compounds (I) and (II) were dried in a vacuum oven over P_2O_5. Purity was established by ^1H NMR at 300 MHz.

Normal water was deionized and double distilled. Deuterium oxide was obtained from Aldrich (>99·7 per cent).

To examine the phase equilibria, samples were prepared by weighing directly into glass tubes which were then sealed and the contents mixed by heating and centrifugation. NMR measurements were made using a Bruker AC 300 MHz spectrometer and variable temperature probe, operating at 46·07 MHz for ^2H resonance. To obtain some indication of the phase behaviour of the compounds, the penetration technique [1] was employed using a Carl Zeiss Jena JENAVAL polarizing microscope with a Linkam hot stage. Macroscopic visual observations were then made on the bulk samples by heating and cooling in a water bath at rates of 2–3°C min^{-1}. The samples were viewed continuously through illuminated crossed polaroid windows. Changes in sample birefringence, opacity or translucency were used to follow their phase behaviour. The temperatures of phase transitions were reproducible to within ±2°C. Surface tension measurements on the solutions of compound (II) were carried out on thermostatted samples using a torsion balance in conjunction with a platinum Du Nouy ring. Measurements were recorded after an equilibration period of 5–15 min.

Preliminary phase diagrams for compounds (I) and (II) are shown in figure 1. Compound (I) forms a large area of lamellar phase (identified by its low viscosity and the mosaic/oily streak optical textures [2]). The phase extends over the composition range of about 25–70 wt% surfactant and its lower surfactant concentration boundary is strongly dependent on temperature. As yet we have been unable to identify a nematic phase at the L_1/L_α boundary, despite the easy alignment of L_α phase samples in a magnetic field during NMR measurements. These have been used to monitor the ordering of water (^2H_2O) in the lamellar phase. Macroscopic alignment of samples with the director along the magnetic field occurs close to the L_1/L_α boundary. Figure 2 (*a*) shows that at 30°C the quadrupole splittings (Δ) are linearly dependent on the surfactant/water molar ratio, at least up to a concentration range of about 60 wt% surfactant. This is a good indication that Δ is determined by the fraction of water bound to the head groups, and that the number of water molecules bound to the head groups is invariant over this concentration range [3, 4]. There is also a marked decrease in Δ on

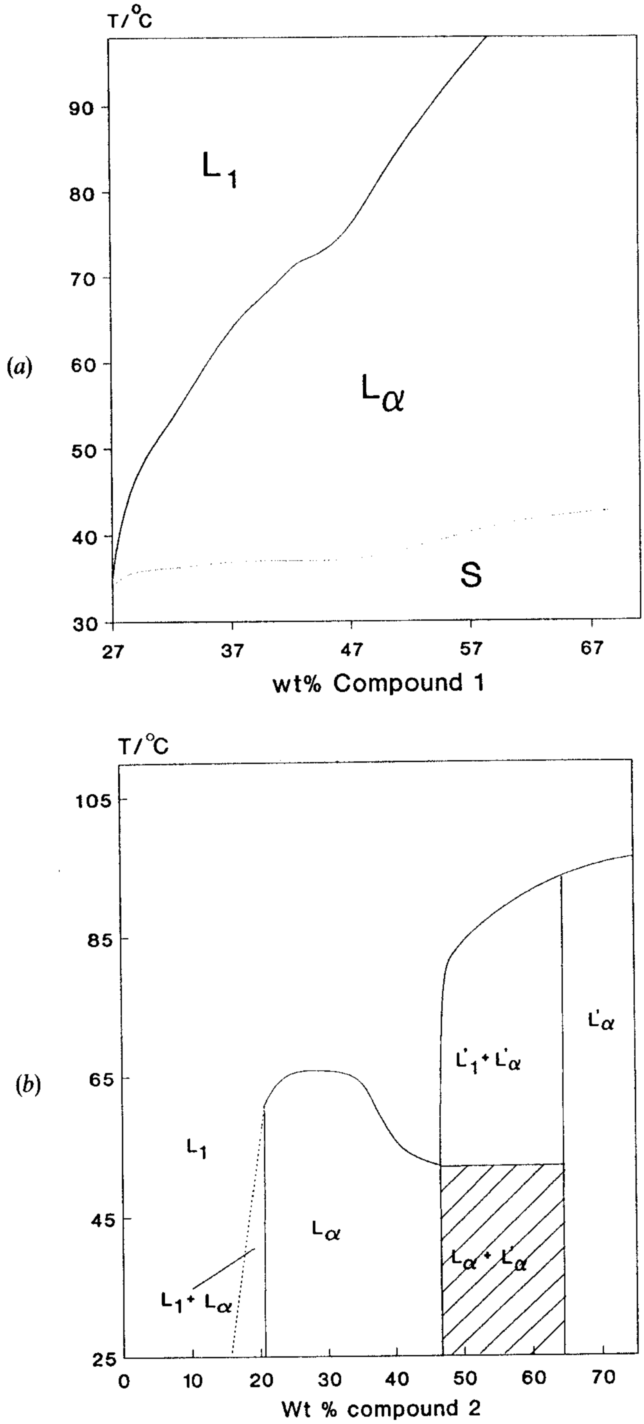


Figure 1. (*a*) Preliminary phase diagram of the compound (I)/^2H_2O system. Symbols are as follows: L_1, micellar solution phase; L_α, lamellar phase; S, solid. (*b*) Preliminary phase diagrams of the compound (II)/^2H_2O system. L'_α, lamellar phase; L'_1, re-entrant micellar solution phase. The shaded region shows where both L_α and L'_α co-exist. The boundary to the biphasic region $L_1 + L_\alpha$ is tentative (dotted line).

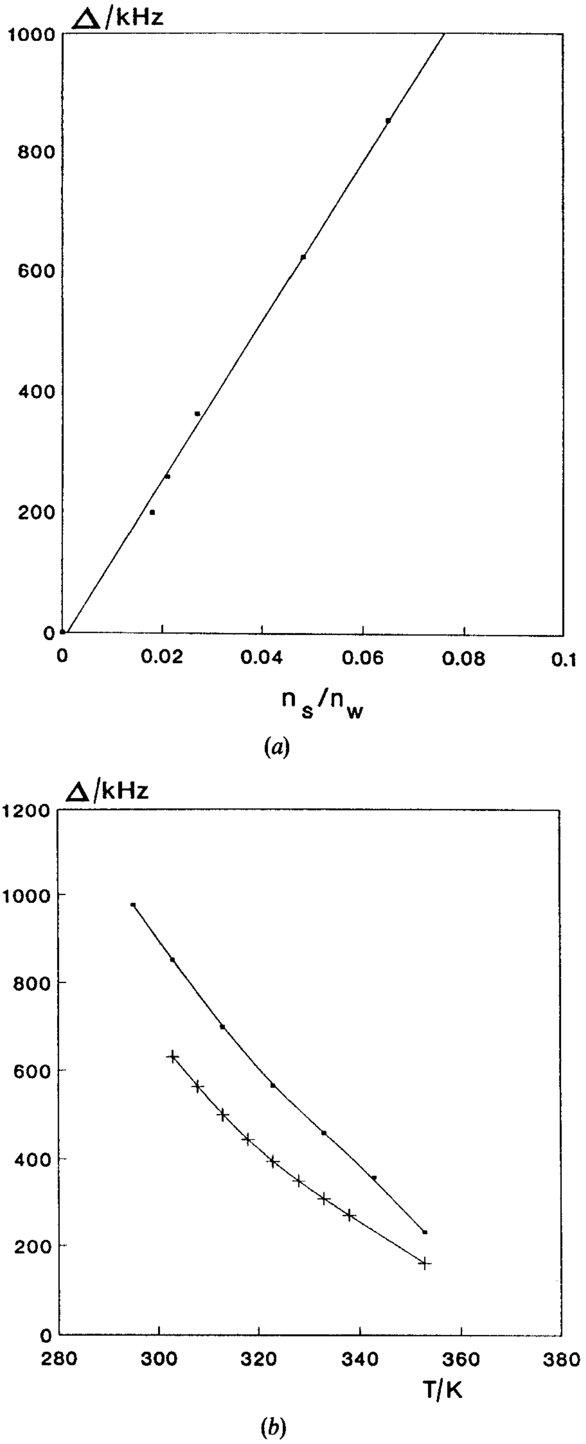


Figure 2. (*a*) ^2H NMR quadrupole splittings (Δ) for compound (I)/^2H_2O samples as a function of surfactant to water mole ratio at 30°C. (*b*) ^2H NMR quadrupole splittings (Δ) for compound (II)/^2H_2O samples as a function of temperature at two compositions. –□–, 58·7 wt%; +, 51·1 wt%.

increasing the temperature (see figure 2 (*b*)), the change for the more concentrated samples being a factor of 3–4 over a temperature range of approximately 60°C. This is quite unlike the behaviour of conventional ionic surfactants where Δ has a much smaller dependence on temperature.

Compound (II) is a relatively unusual type of surfactant, having two mid-chain polar groups and the aromatic polarizable ends. In order to verify that this compound does actually form micelles, the critical micelle concentration (cmc) was determined from the variation of the surface tension (γ) as a function of concentration. The du Nuoy ring technique was employed for surface tension measurements. A sharp break in the γ versus log (concentration) curve was observed at $C = 2 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ (25°C). This compares well with cmc values for other di-ionic surfactants (di-potassium alkyl malonates) [5], indicating that the cyanobiphenyl unit does not prevent micelle formation. Recognizing that the cmc of di-ionic surfactants decreases by a factor of about 2·7 for each additional two CH_2 groups added to the alkyl chain [5], we can roughly estimate the cmc expected for compound (II) if we assume that the cyanobiphenyl group is equivalent to approximately five CH_2 groups. The α-CH_2 group of alkyl trimethyl ammonium surfactants is normally assumed to reside in the aqueous region, thus compound (II) is roughly equivalent to a C_{22} surfactant. The measured cmc value is similar to that for a C_{18} surfactant [5]. This discrepancy is not serious, since the hydrophobic effect of an oxycyanobiphenyl group could be lower than that of aromatic rings with no polar substitutents. Also, the conformational restrictions on the molecule required for the mid-C_6 chain to loop into the micelle interior may prevent it from completely avoiding water. Hence the measured cmc value is a good indication that compound (II) does form conventional micelles, even with its non-conventional structure.

The liquid crystal behaviour of compound (II) is shown in figure 1 (*b*). Again, only a lamellar phase occurs with the composition varying from 18–80 wt%. A remarkable feature of figure 1 (*b*) is the weak dependence of the L_1/L_α transition temperature on composition over 20–45 wt%. Moreover, the sequence $L_1/L_\alpha/L_1'/L_\alpha'$ on increasing surfactant composition appears to occur in the temperature range 50–55°C (see figure 3). This implies that there may be a difference in the structure of the surfactant bilayers at high and low concentrations. As for compound (I), we were unable to identify any nematic textures in samples at the L_1/L_α transition region.

NMR spectra of samples containing ^2H_2O give powder or aligned (director parallel to magnetic field) patterns as for compound (I) according to their previous treatment (thermal history) and concentration. In the concentration region 45–65 wt% and below 50°C two overlapping spectra were observed (see figure 4). The relative intensities of the two spectra vary in a manner expected for two co-existing lamellar phases, one having a composition of about 45 wt% compound (II) and the second containing approximately 65 wt% compound (II). The spectra were reproducible on heating/cooling cycles, were unaltered by remixing and were invariant with time. Hence the observations are not due to incomplete mixing. Samples in this region of the phase diagram have an emulsion-like cloudy appearance, while optical microscopy shows two lamellar phase regions having distinctly different viscosities. Thus compound (II) forms two distinct L_α regions having different water concentrations. The NMR Δ values (see figure 5) in the two single lamellar phases fall on two separate lines passing through the origin, indicating that the water binding and head group orientation are somewhat different in the two phases. The Δ values do decrease with an increase in temperature, albeit less markedly than occurs for compound (I).

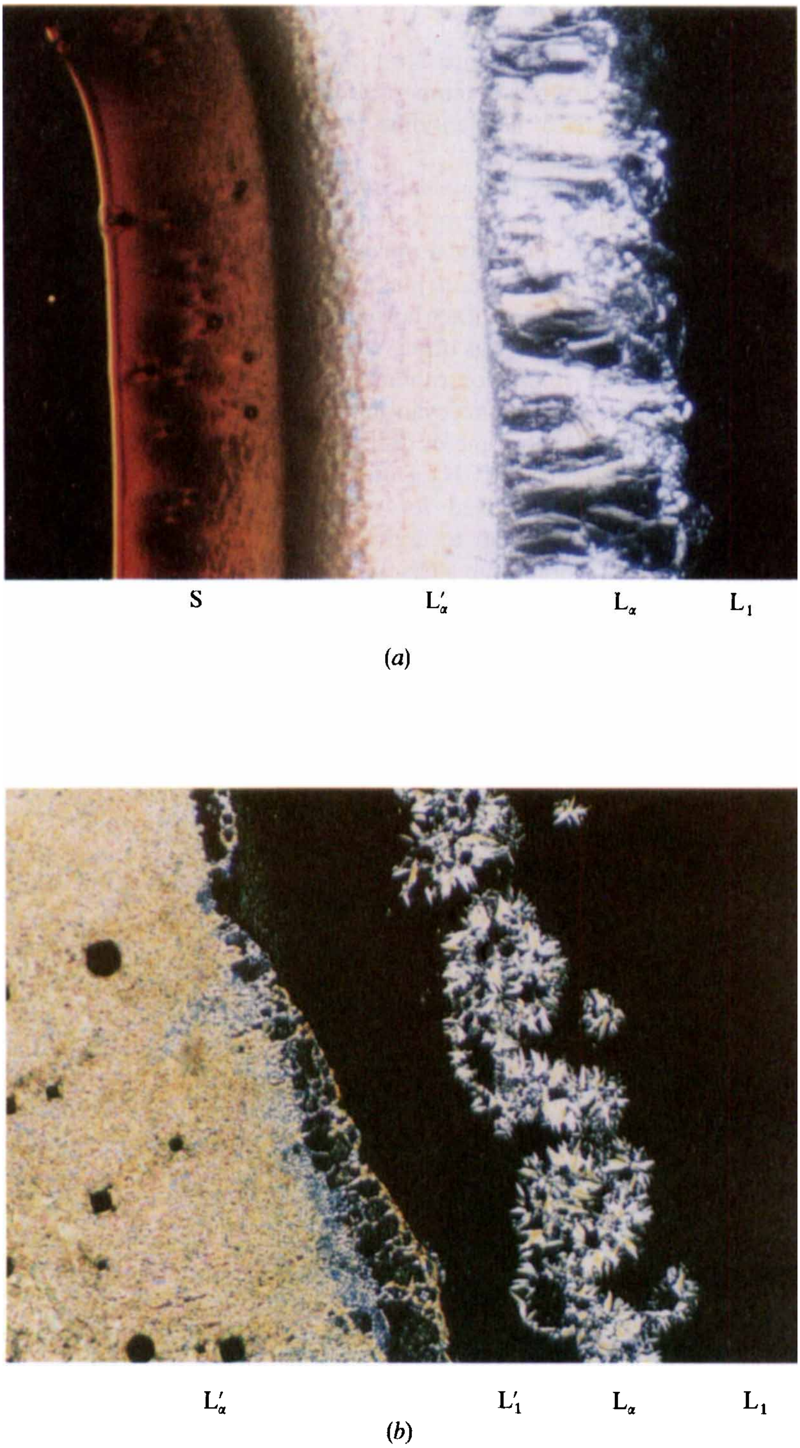


Figure 3. Photomicrograph of the phases formed by penetration of water into solid compound (II) (crossed polaroids; magnification ×85). (*a*) At 23°C. From right to left: L_1, micellar solution; L_α, low viscosity lamellar phase; L'_α, higher concentration lamellar phase; S, solid. The isotropic region on the left is a glassy or cubic phase which forms crystals on contact with water. (*b*) At about 55°C on cooling. L'_1, re-entrant micellar solution phase. On cooling L_α reappears in the form of bâtonnets.

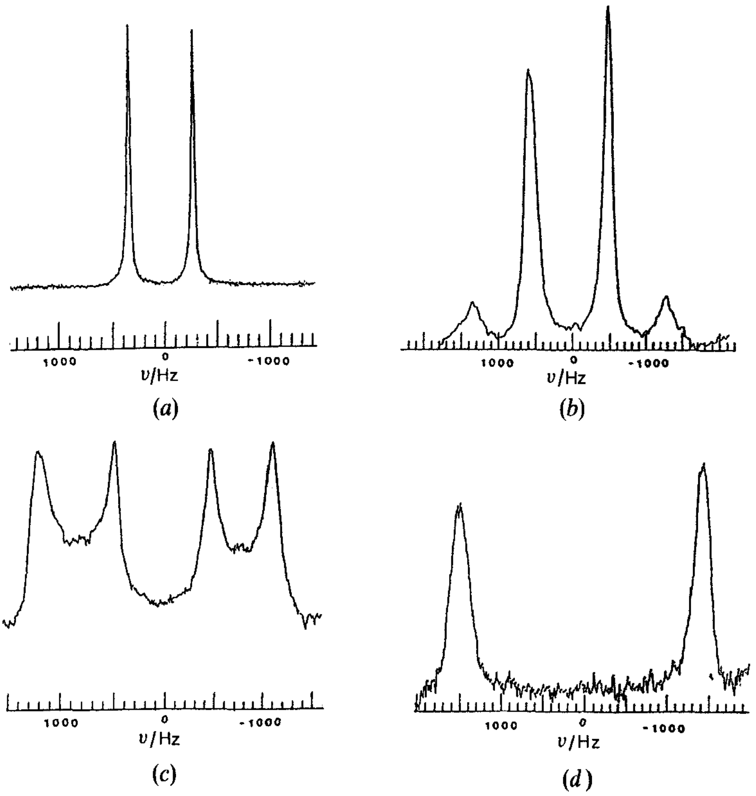
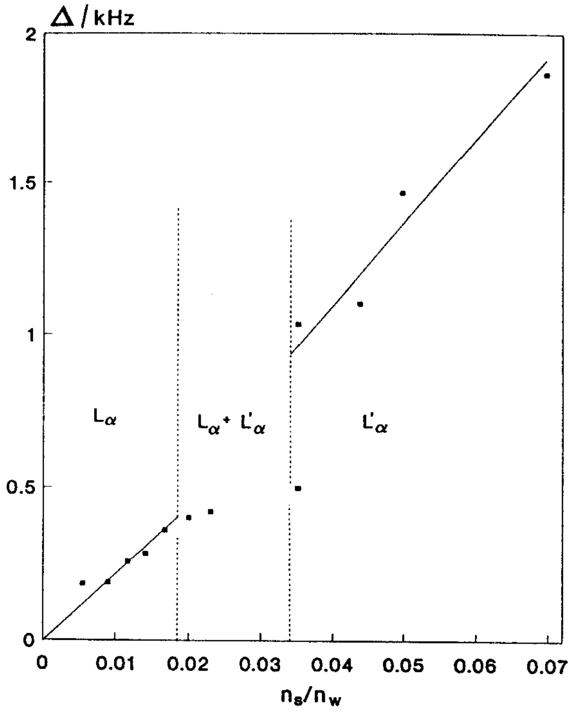
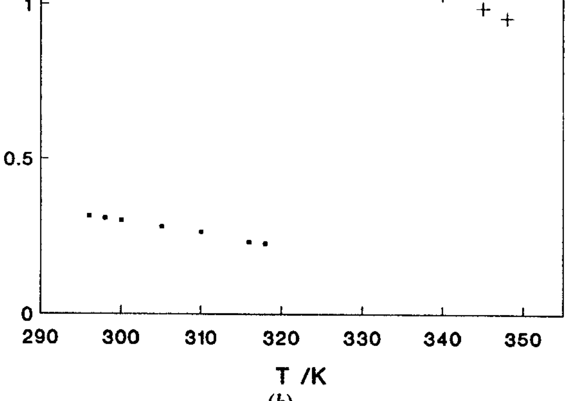


Figure 4. ^{2}H NMR spectra for compound (II)/${}^2H_2O$ samples at 25°C. (*a*) 37·7 wt% only L_2 present. (*b*) 49 wt% L'_α just formed as seen from the intensities of the outer small peaks; the sample consists predominantly of L_α. (*c*) 60·2 wt% (27°C) L_α and L'_α present in almost equal proportions. (*d*) 68 wt% only L'_α present. All of the samples were aligned with the director parallel to the magnetic field.

The absence of hexagonal (H_1) and bicontinuous cubic (V_1) phases [1] with compounds (I) or (II) shows that the substitution of the oxycyanobiphenyl groups has a large influence on lyotropic mesomorphism. This group has a length of about C_{11}, and so we should compare the behaviour of compounds (I) and (II) with $C_{21}H_{43}NEt_3Br$(III) and $C_{16}H_{33}NMe_2(CH_2)_6NMe_2C_{16}H_{33}Br_2$ (IV), respectively. Neither of these compounds are available. For compound (III) we can compare the behaviour of $C_{22}H_{45}NMEt_3Br$ [6], $C_{16}H_{33}NEt_3Br$ [1] and $C_{16}H_{33}NMe_3Cl$ [1]. All form the sequence H_1, V_1, L_α on increasing surfactant concentration, giving some confidence that (III) would show a similar mesophase pattern. For compound (IV) no data are available on like compounds hence we are currently synthesizing a range of compounds having this type of structure. However, it does seem likely from packing constraints [7] that H_1, V_1 and L_α phases will all occur here also. The destabilization of these high curvature mesophases (H_1, V_1) by the bulky oxycyanobiphenyl group obviously stems from the difficulty of packing to high density in a spherical or rod-like micelle interior. We might imagine an alternative where the polarizable oxycyanobiphenyl group exists preferentially at the micelle/water surface. However, recent studies [8] have shown that 4-*n*-pentyl-4′-cyanobiphenyl is located mainly in the hydrophobic interior of a non-ionic surfactant lamellar phase. In any case, if this group were to reside



(a)



(b)

Figure 5. (a) ^{2}H NMR quadrupole splittings in compound (II)/$^2H_20$ samples as a function of surfactant to water mole ratio at 30°C. (b) ^{2}H NMR quadrupole splittings in compound (II)/D_2O samples as a function of temperature at the two compositions. □, 37·7 wt%, +, 68 wt%.

at the micelle surface, the micelle radius would be reduced to that of a C_8 surfactant, giving a low melting hexagonal phase and more extensive L_1 region, as occurs, for example, with sodium ricinoleate [9].

The wide composition range of the L_α phase and the unusual temperature stability of the region below about 55 wt% surfactant may suggest that bilayers at high surfactant levels have a markedly different structure from those at low concentrations. This could involve a different orientation of the bulky end groups within the hydrophobic layers. It would certainly help to explain the co-existence of two L_α phases over the 45–65 wt% range. However, we note the (almost) linear dependence of Δ on the surfactant/water mole ratio for compound (I), while the two curves for compound (II) have different slopes. Hence the head group orientation is somewhat different in the two phases, an indication of differences in the hydrophobic region structure. However, the only other published case of two co-existing L_α phases in a binary system is for the related surfactant didodecyldimethyl ammonium bromide [10]. Here it is likely that a weak, specific counterion binding mechanism is responsible for the inter-bilayer attractive force required to produce this effect [11]. Thus before speculating further on the origin of this phenomenon we plan to measure the bilayer thickness using low angle X-ray diffraction. Such measurements are underway, as are investigations on the thermotropic mesophase behaviour and the solubilization of conventional thermotropic mesogens. In these studies we pursue the goal of obtaining materials with separate micro-domains of lyotropic and thermotropic mesomorphism, which will be truly amphitropic!

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