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X-ray diffraction study of the intermediate phases formed by sodium dodecylsulphate in aqueous mixtures of *N*-methylformamide

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We report the sequence of intermediate phases formed by sodium dodecylsulphate (SDS) in water on addition of *N*-methylformamide (NMF). Although only a single phase, L_α, is formed in the SDS/NMF system, the three sequences $H_\alpha \Leftrightarrow M_\alpha \Leftrightarrow R_\alpha$, $H_\alpha \Leftrightarrow M_\alpha \Leftrightarrow Q_\alpha$ and $H_\alpha \Leftrightarrow Q_\alpha$ (Ia3d) were observed with increase in concentration of NMF in the SDS/water/NMF mixtures. The sequences $H_\alpha \Leftrightarrow Q_\alpha$ and $H_\alpha \Leftrightarrow L_\alpha$ were identified in the water/NMF mixture, although they were not observed in the initial SDS/water system or in the SDS/NMF system. These results indicate that solvent mixtures could be profitably employed to investigate the conditions of formation of intermediate phases and to study the transitions of the $H_\alpha \rightarrow M_\alpha \rightarrow R_\alpha$ to the $H_\alpha \rightarrow M_\alpha \rightarrow Q_\alpha$ sequences.

1. Introduction

Considerable attention has been devoted to analysis of the complex liquid crystal lyotropic phases formed by certain ionic surfactants such as sodium dodecyl sulphate (SDS) [1–7] or hexadecyltrimethylammonium chloride (CTACl) [8, 9] in water. A succession of poorly identified intermediate phases is formed between the two-dimensional H_α and the lamellar L_α phases. The H_α phase is transformed into a deformed hexagonal phase symbolized as M_α, commonly called 'ribbon phase'. Hagslätt [10] has proposed four models for the straight cross-sections of rod-like micelles: rectangular-rod, ribbon-rod, elliptic-rod and hexagon-rod. Deformation of the straight cross-sections of the micelles disrupts the hexagonal symmetry and the observed structures tend to become centred rectangular (cmm) or monoclinic (p2) structures. These two space groups are not readily distinguished in view of the number of diffraction peaks observed. These ribbon phases are commonly characterized by the formation of complex three-dimensional phases on increase in surfactant concentration prior to formation of the L_α phase. Careful study of the SDS/water system has identified the following phases:

$H_\alpha \rightarrow M_\alpha$ (p2) $\rightarrow$ rhombohedral $R_\alpha \rightarrow$ centred cubic (Im3m) $\rightarrow$ centred tetragonal $T_\alpha \rightarrow L_\alpha$

[4, 6]. We have recently demonstrated the existence of a centred rectangular phase M_α,

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the cubic phase Im3m only being observed along a line in the R_α region. This cubic phase is a particular deformation of the rhombohedral phase with a lattice angle of 109·47° [7].

In contrast to the complexity of the intermediate lyotropic phases formed in water, simpler sequences of ordered lyotropic phases are observed in certain non-aqueous polar solvents [11–13] such as the SDS/formamide system [7]:

$$H_\alpha \rightarrow \text{body centred cubic } Q_\alpha \text{ (Ia3d)} \rightarrow L_\alpha.$$

Charvolin and Sadoc [14] have interpreted the sequence observed in non-aqueous polar solvents and with certain surfactants in water, such as the alkylpyridinium chlorides and bromides, on purely geometrical considerations [12, 15]. The intermediate phases so far lack an adequate interpretation. Micellization of cationic surfactants in aqueous mixtures of ethylene glycol, glycerol and formamide has been described recently [16]. In the present study, we examined the sequence of intermediate phases formed by SDS in water on addition of *N*-methylformamide, a solvent in which only the lamellar L_α phase is usually observed. The system was studied by X-ray diffraction, which has been profitably employed to investigate the SDS/water diagram [7] and a variety of binary surfactant/non-aqueous polar solvent systems [13]. The isoplethal method has also been used.

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2. Materials and methods

2.1. *Reagents*

Sodium dodecyl sulphate (SDS) (Merck, 99 per cent minimum purity) was used as supplied. *N*-methylformamide (Aldrich, 995) was kept over molecular sieves (3 Å). Water was twice distilled.

2.2. *Apparatus*

The X-ray study was carried out in a conventional small angle set-up: a quartz monochromator selected the 0·154 nm CuK_α wavelength and focused the beam 25·1 cm from the sample on a linear localization detector with a spatial resolution of 136 μm. The path between the sample and the counter was maintained under vacuum. A series of horizontal slits in front of the detector slit limited the effects of beam height and improved the signal/noise ratio. Reticular distances ranging from 10 nm to 1·5 nm could be measured in this set-up.

The cell was made of brass with Mylar windows; with a sample thickness of 1 mm, the weight of the sample was around 0·08 g. It was heated in a thermostated water bath regulated to the nearest 0·1°C. Temperature was checked with a thermocouple placed in the cell.

We used the method employed in our previous study of the SDS, CTAB and CPBr/polar solvent systems [7, 13]. A sample with a surfactant concentration of around 50–70 per cent by weight was prepared in a mixture of water and NMF at a given concentration. The sample was heated in the cell and the diffraction diagrams were recorded along the so-called T_c curve separating the ordered lyotropic phase regions from the crystal region. The time for the recording of diagrams was 2000 s. The diffraction diagrams of all the ordered phases from H_α to L_α with regions of existence bounded by the T_c curve were recorded as the temperature was raised. The temperatures at which an ordered phase appeared (T_0) or disappeared (T_1) along this curve for different concentrations of NMF were recorded. For each concentration of NMF, the reticular distances d_{hkl} derived from the characteristic peaks of the space groups of the ordered phases were plotted against temperature. If the initial concentration of the sample is below a certain value (around 50 per cent), there is a departure from the T_c curve before appearance of an intermediate phase, and the phase transitions are thus observed at constant concentration as a function of temperature, i.e. under isoplethal conditions. Sodium dodecyl sulphate crystals have three or four characteristic diffraction peaks corresponding to the three or four orders of the reticular distance peak ($d = 3{\cdot}82$ nm), which is in good agreement with the value (3·79 nm), reported by Kekicheff [4].

3. Results

Samples of fixed SDS concentration have often been used in these studies. The diffraction peaks of the SDS crystals allow one to confirm that the diffraction spectra of the lyotropic ordered phases are retained along the T_c curve.

3.1. *Experiments carried out along the T_c curve*

The temperatures at which the intermediate phases appeared and their ranges of existence were determined for the SDS/water system under the same conditions as for the SDS/water + NMF system (see figures 1 (*a*), (*b*) and (*c*)). The H_α phase appeared at 23°C and the changes in d_{10} are represented in figure 1 (*a*). At 36·5°C, there was a transformation of the H_α phase. Two strong peaks appeared on either side of peak 10 of H_α, characteristic of the M_α phase (peaks 20 and 11 of the centre rectangular phase, see figure 2 (*a*)). The phase R_α was observed between 47°C ns 50°C (see figure 2 (*b*)). The tetragonal phase T_α was only observed in this experiment over a range of a few tenths of a degree (see figure 2 (*c*)). The diffraction ring 002 of T_α is met with the ring 100 of L_α. The L_α phase was observed above 52°C. These transition temperatures were in agreement with those obtained in our previous study [7].

The H_α, M_α, R_α, T_α and L_α phases are observed in aqueous mixtures of NMF up to a concentration of 20 per cent (X-ray diffraction patterns: see figures 3 (*a*), (*b*), (*c*), and 1 (*b*),(*c*) and 4). The gap between the diffraction peaks 20 and 11 of the M_α phase decreases with increase in NMF concentration (see figures 1 (*b*), (*c*) and 3 (*b*)). The presence of NMF in water has relatively little effect on the temperatures of appearance of the H_α, T_α and L_α phases (see figures 1 (*b*), (*c*) and 4); the temperatures of formation of the M_α and R_α phases increase with increase in NMF concentration. The region of existence of the M_α and R_α phases are reduced. The NMF concentration of 20 per cent is a critical value (see figures 1 (*c*) and 4): the diffraction peaks characteristic of the M_α, R_α and T_α phases are always observed over a range of about 2°C and the R_α phase appears at an SDS concentration of around 63·5 per cent. The existence of a monophasic region in equilibrium with SDS crystal is doubtful. At concentrations of NMF above 20 per cent, the three phases M_α, R_α and T_α are simultaneously lost, and the transition $H_\alpha \leftrightarrow L_\alpha$ is observed (see figure 5). Over a range of some degrees, the two phases coexist. At a concentration of NMF of 23 per cent the H_α phase is observed between 28 and 53°C. The line separating the H_α region and the L_α region continues the one separating H_α and M_α (see figure 4).

3.2. *Experiments realized out of the T_c curve*

At NMF concentrations below 13–15 per cent, the regions of existence of the three phases M_α, R_α and T_α extend to over several degrees, indeed 10–15°. For example, with an NMF/water mixture of 8 per cent and at an SDS concentration of 62 per cent, the

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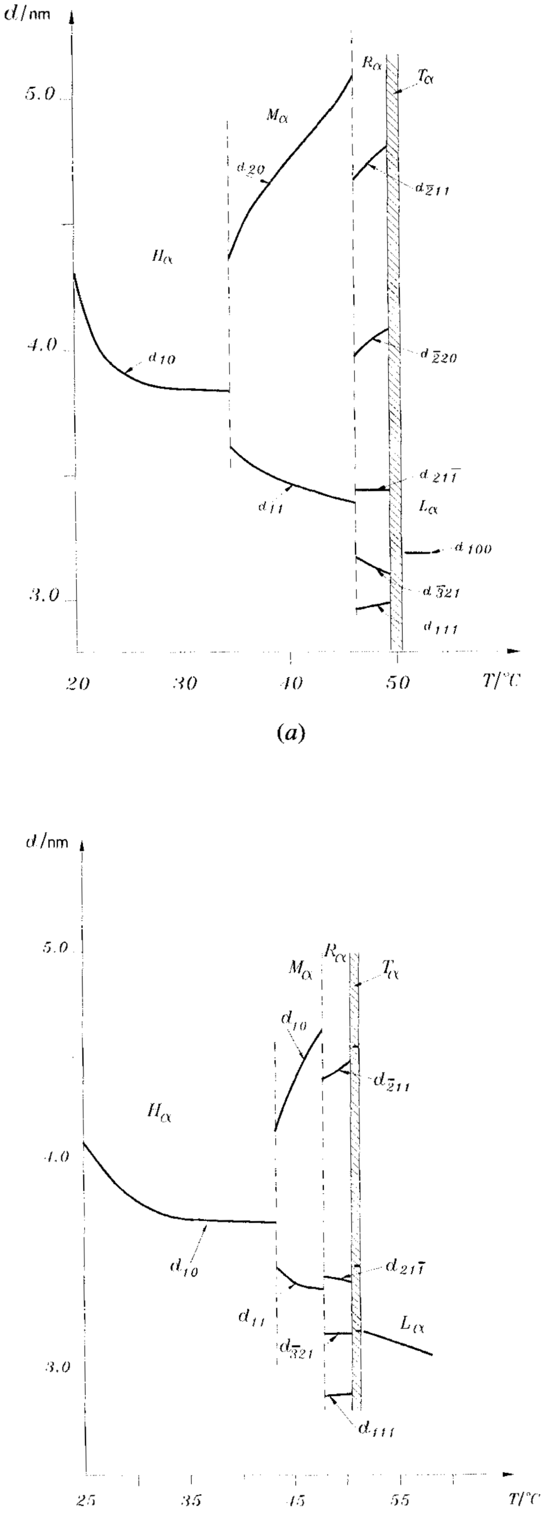

(a)

(b)

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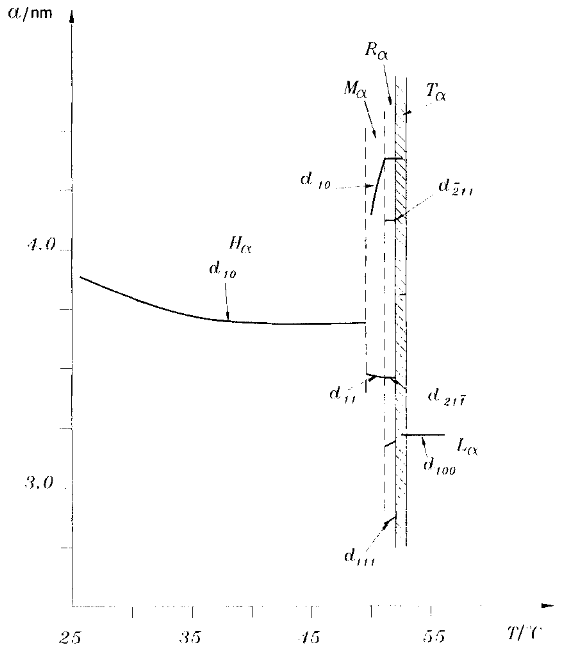

(*c*)

Figure 1. Reticular distances corresponding to the strongest diffraction peaks of the lyotropic phases between H_α and L_α along the T_c curve as a function of NMF concentration. Certain reticular distances of R_α are in the following ratios: $d_{1\bar{1}0}/d_{\bar{2}11} = \sqrt{3}$, $d_{1\bar{1}0}/d_{2\bar{2}0} = \sqrt{4}$ and $d_{1\bar{1}0}/d_{\bar{3}21} = \sqrt{7}$. The peak $\bar{2}20$ of the R_α phase conflicts with the peak of SDS crystals. The T_α region is hatched. (*a*) Reticular distances of ordered phases of the SDS/water system. The domain of existence of the centred tetragonal phase T_α between R_α and L_α is only around 0·5° along the T_c curve. Peak 200 of T_α is continuous with peak 100 of L_α [4]. (*b*) Reticular distances of ordered phases of SDS/water + 8 per cent NMF. (*c*) Reticular distances of ordered phases of SDS/water + 18 per cent NMF.

M_α phase is observed along the T_c curve as far as 47°C and the existence region extends to 51°C; R_α appears between 51°C and 66·5°C, and T_α between 66·5°C and 67·5°C. So the same sequences of ordered phases are observed either along the T_c curve or out of this curve. No metastability of intermediate phases is observed. At decreasing temperature, hysteresis of these phases is observed out of the T_c curve. The ranges of existence of M_α and R_α phases increase with decrease in NMF concentrations, at a fixed concentration of SDS. At the NMF concentration above 15 per cent the transition $M_\alpha \leftrightarrow Q_\alpha \leftrightarrow L_\alpha$ is observed (see figures 6 and 7 (*a*)). The deformation of the rectangular lattice has been stopped through lack of SDS crystals. The distance between the reticular planes (211) of the Q_α phase was very close to the distance between the planes (11) of the centred rectangular phase. Likewise the H_α phase is transformed into a phase with Ia3d symmetry (see figure 7 (*b*)). The bicontinuous cubic phase (Ia3d) forms between L_α and H_α or M_α, but out of the T_c curve; it is never in equilibrium with SDS crystals. This phase is not detected in either the SDS/water or the SDS/NMF systems.

4. Discussion

These results demonstrate the progressive evolution of intermediate phases between H_α and L_α in the SDS/water/NMF system as far as a concentration of NMF of 20 per

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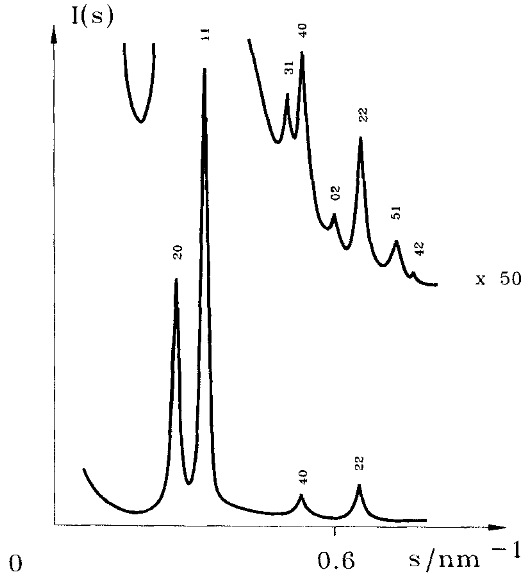

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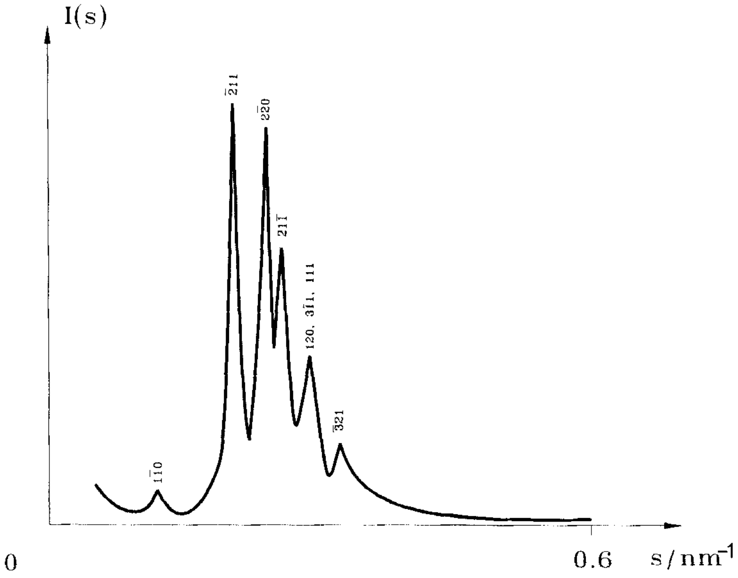

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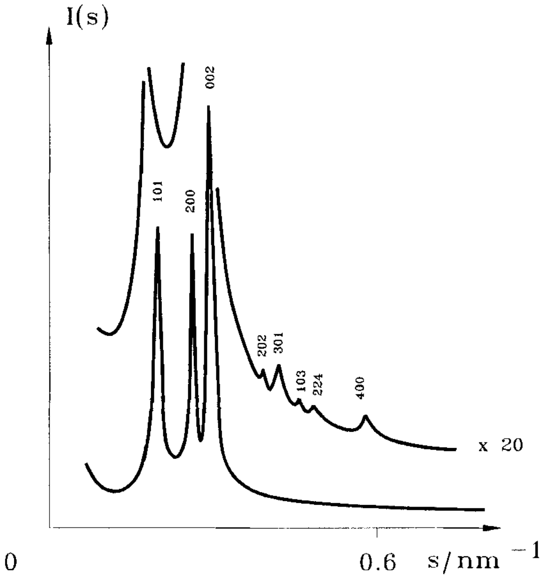

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Figure 2. X-ray diffraction diagrams of the intermediate phases for the SDS/water system: (*a*) M_α phase. (*b*) R_α phase. The diffraction peaks 120, $3\bar{1}1$, 111 form a large scattering band. (*c*) T_α phase.

cent (1 molecule of NMF for 13 of water) (see figure 4). Above a threshold c^*, about 20 per cent, no intermediate phases are detected along the T_c curve; the three phases disappear simultaneously over a range of SDS concentration of around 63–65 per cent (0·5 molecule of NMF, 7 molecules of water for 1 molecule of SDS). At NMF concentrations between 0 and 20 per cent the regions of existence of the H_α phase is increased along the T_c curve. At NMF concentrations of between 20 and 25 per cent, the H_α phase is transformed into a L_α phase at SDS concentrations of about 70 per cent. A biphasic region is observed over a range of 4°. In binary systems the $H_\alpha \leftrightarrow L_\alpha$ transition is rarely detected along the T_c curve. In nearly all the ionic surfactant/polar solvent systems, a micellar phase or a three-dimensional phase (3D) is formed between the 2D phase (H_α or M_α) and the 1D phase (L_α). The coexistence of H_α and L_α can occur when a co-surfactant is present, for example, sodium octanoate/decanol/water, where solid surfactant is also present. The SDS/NMF-water mixture system has a behaviour like a ternary system; the NMF concentration could be different in H_α and L_α phases.

The lattice parameters of the R_α and M_α phases as a function of the NMF content were calculated. The alternations in these parameters between the temperature of appearance T_0 and the temperature of disappearance T_1, in the presence of crystalline SDS could also be determined. The variations of parameters a_H and a_M of the H_α and M_α phases, respectively, against NMF concentration at T_0 and T_1 are shown in figures 8 (*a*) and (*b*). The parameter a_r and the angle α of the rhombohedral lattice at T_0 and T_1 are shown in figures 8 (*c*) and (*d*).

It can be seen that the presence of NMF reduced the values of these parameters as well as the difference between $a_{H,0}$ and $a_{H,1}$, which is also observed when water is replaced by a polar solvent such as formamide (in the SDS/formamide system a_H falls from 3·98 to 3·89 nm on an increase in surfactant concentration from 42 to 75 per cent

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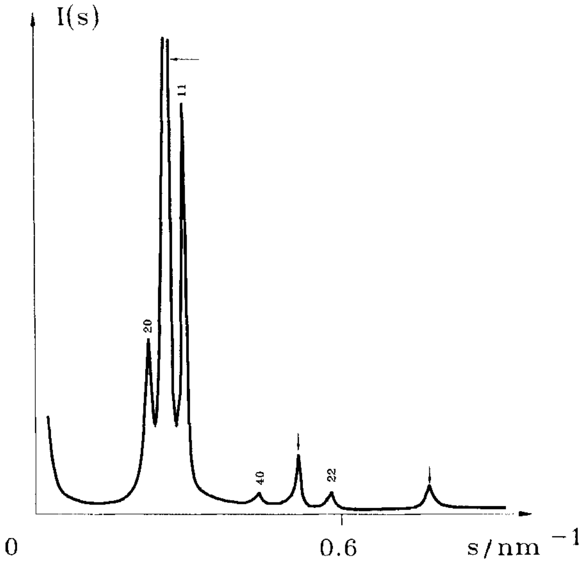

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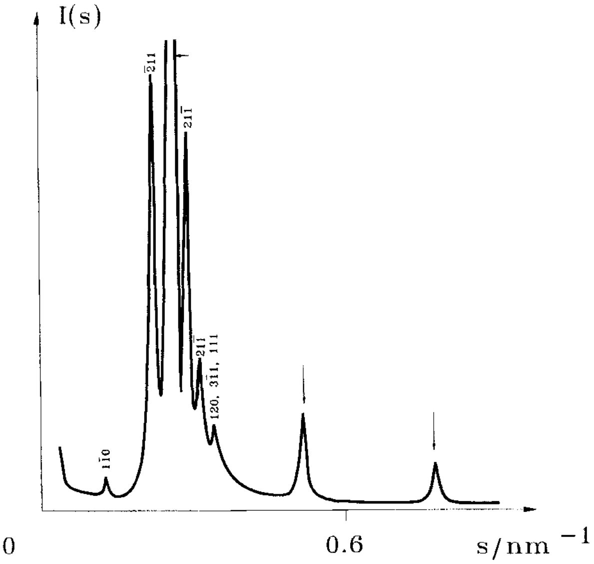

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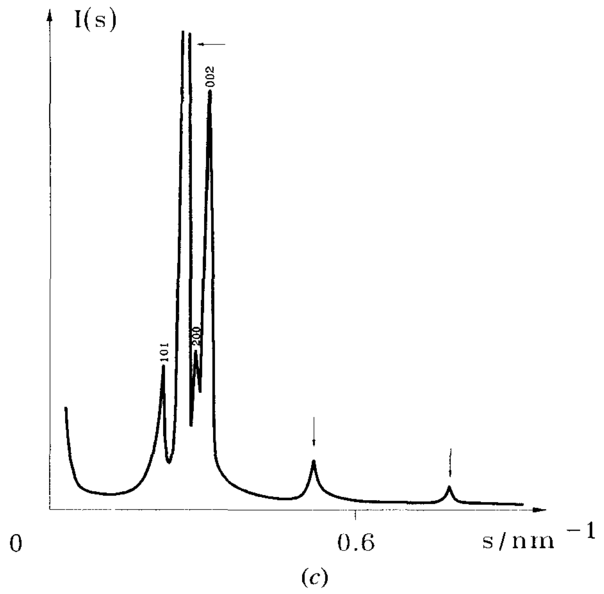

Figure 3. Strongest diffraction peaks of the intermediate phases for SDS/water + 8 per cent NMF along the T_c curve: (a) M_α phase. (b) R_α phase. The diffraction peak $2\bar{2}0$ coincides with the diffraction peak of the SDS crystals. (c) T_α phase. The arrows show the three diffraction peaks of the SDS crystals.

[7]). The parameter b_1 (3·66 nm) of the centred rectangular lattice is insensitive to the NMF concentration.

In our previous study of the SDS/water system [7], we found that the formation of the R_α phase and its parameters depended on the exact structure of the M_α phase which preceded it. The R_α phase only appeared if the difference between d_{20} and d_{11} of the M_α phase lay above a certain threshold; in fact this difference between d_{20} and d_{11} is related to the ratio between the parameters a and b of the M_α phase, i.e. to the deformation of the straight cross-section of the micelles (see figure 9). The sequence of ordered phases is $\mathrm{M}_\alpha \leftrightarrow \mathrm{R}_\alpha \leftrightarrow \mathrm{T}_\alpha \leftrightarrow \mathrm{L}_\alpha$; formation of the T_α phase is necessary between R_α and L_α phases. In case the concentration of SDS is such that the deformation of the cross-section of the micelles is low, either the M_α phase is stable to increasing temperature (the NMF concentration is lower than 13–15 per cent), or the M_α phase turns into a Q_α phase (see figure 7 (a)), always in the absence of SDS crystals, out of the T_c curve. In this case the reticular distances d_{11} of M_α and d_{211} of Q_α are equal; as a result, there is a relation between the lattice parameters a_M, b_M and a_c. Together with this purely geometrical condition, the concentration of surfactant also plays a part as the Q_α phase only forms over a relatively narrow range of concentration. In these conditions, the reticular distances between the planes (11) of M_α and (211) of Q_α, which contain all the cylindrical axes of the two labyrinths, are not only equal (see figure 7 (a); $a_\mathrm{c}/\sqrt{6} \approx 1/\sqrt{(1/a^2 + 1/b^2)}$), but also the intensities of the diffraction rings are equal. The arrangement of the planes and the distances are conserved during the $\mathrm{M}_\alpha \rightarrow \mathrm{Q}_\alpha$ transition. Furthermore, two other conditions are fulfilled:

(i) the minimal distance between the axes of the cylinders b_1 in M_α is close to the distance $(a_\mathrm{c}\sqrt{3})/4$ between the two centres of connection of the two labyrinths

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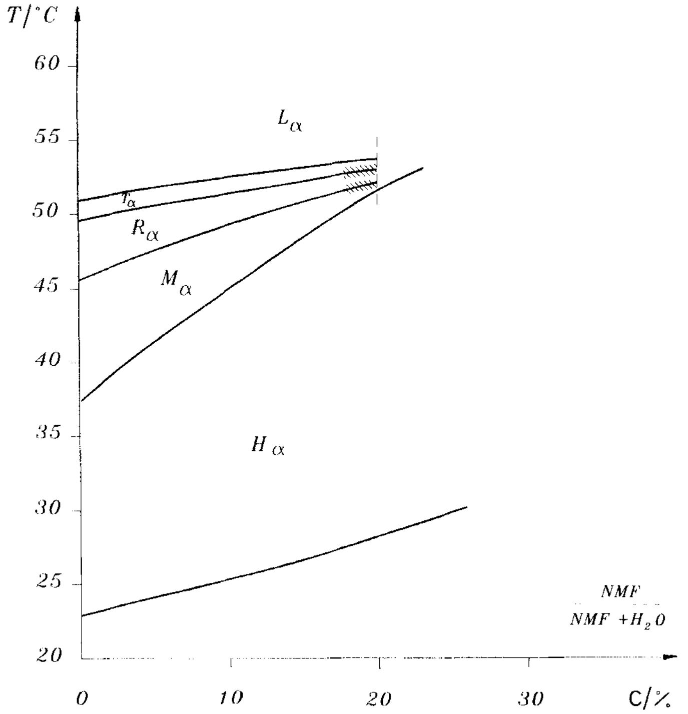

Figure 4. Diagram representing the temperatures T_0 and T_1 bounding the domains of existence of the ordered lyotropic phases along the T_c curve as a function of the concentration of NMF in water. The biphasic region is hatched.

in Q_α [7, 12] at a concentration of NMF of 18·6 per cent. $b_1 = 3{\cdot}66$ nm and $(a_c\sqrt{3})/4 = 3{\cdot}57$ nm.

(ii) the distance between the axes of the cylinders in the planes (11) of M_α: $(a_1^2 + b_1^2)^{1/2}/2$ (see figure 9) is close to the distance $D_{\max}$ between the points of the axes of the labyrinths whose opposing surfaces are furthest apart [7, 17] (for example, the points of coordinates (3/8, 1/2, 1/4) and (5/8, 1/2, 3/4): $D_{\max} = (a_c\sqrt{5})/4$. At 18·6 per cent NMF: $(a_1^2 + b_1^2)^{1/2}/2 = 4{\cdot}67$ nm $D_{\max} = 4{\cdot}61$ nm. The strict equalities between these distances, which were almost exactly those observed in the solution containing 18·6 per cent NMF gives rise to the following relationships:

$$(a_c\sqrt{3})/4 = b_1, \tag{1}$$

$$(a_c\sqrt{5})/4 = (a_1^2 + b_1^2)^{1/2}/2, \tag{2}$$

or

$$a_1 = b_1\sqrt{(17/3)} = 2{\cdot}38\,.\,b_1$$

However, if conditions (1) and (2) are fulfilled, d_{11} is not strictly identical to d_{211}: $d_{11}/d_{211} = 1{\cdot}023$. This ratio, a_1/b_1, was found to be 2·35 for the previous solution with 18·6 per cent NMF. This ratio tends toward 2·38 as R_α forms along the T_c curve and the NMF concentration is increased to about 20 per cent.

The phase L_α which forms is such that the distance d_{100} is equal to $\sqrt{2}\,.\,d_{213}$ of Q_α. This condition, which was nearly always fulfilled in our observations of cationic

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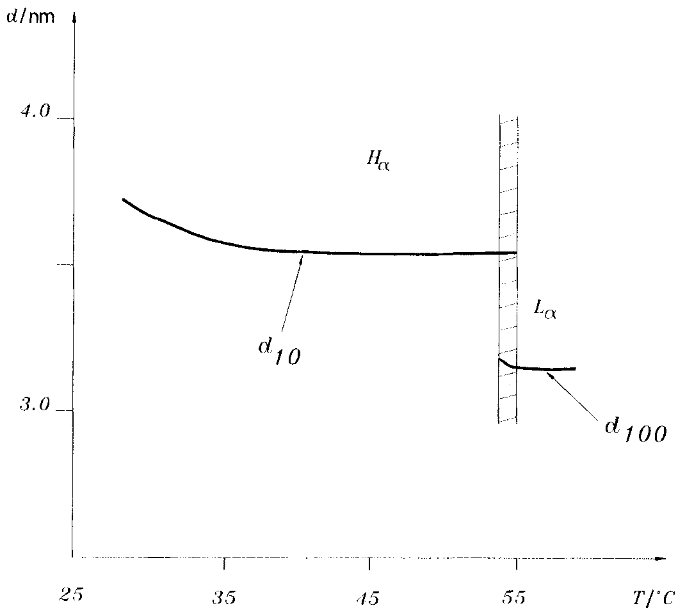

Figure 5. Reticular distances corresponding to the strongest diffraction peaks of the H_α and L_α phases along the T_c curve of SDS/water + 23 per cent NMF.

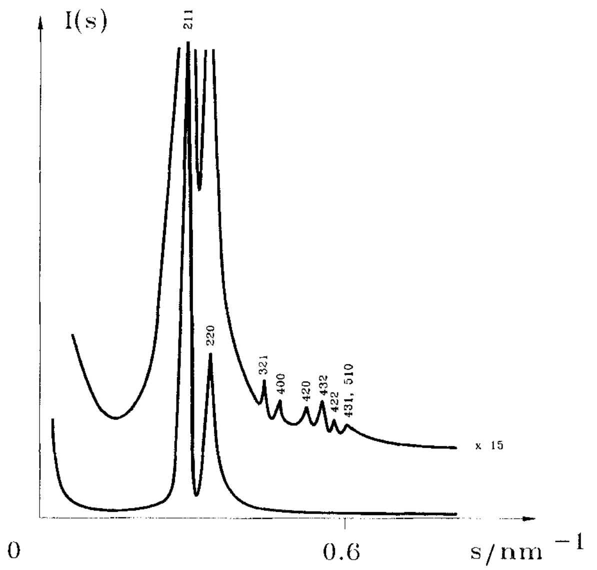

Figure 6. Strongest diffraction peaks of the Ia3d phase (Q_α) formed by SDS/water + 18·6 per cent NMF at 51°C with an SDS concentration about 70 per cent.

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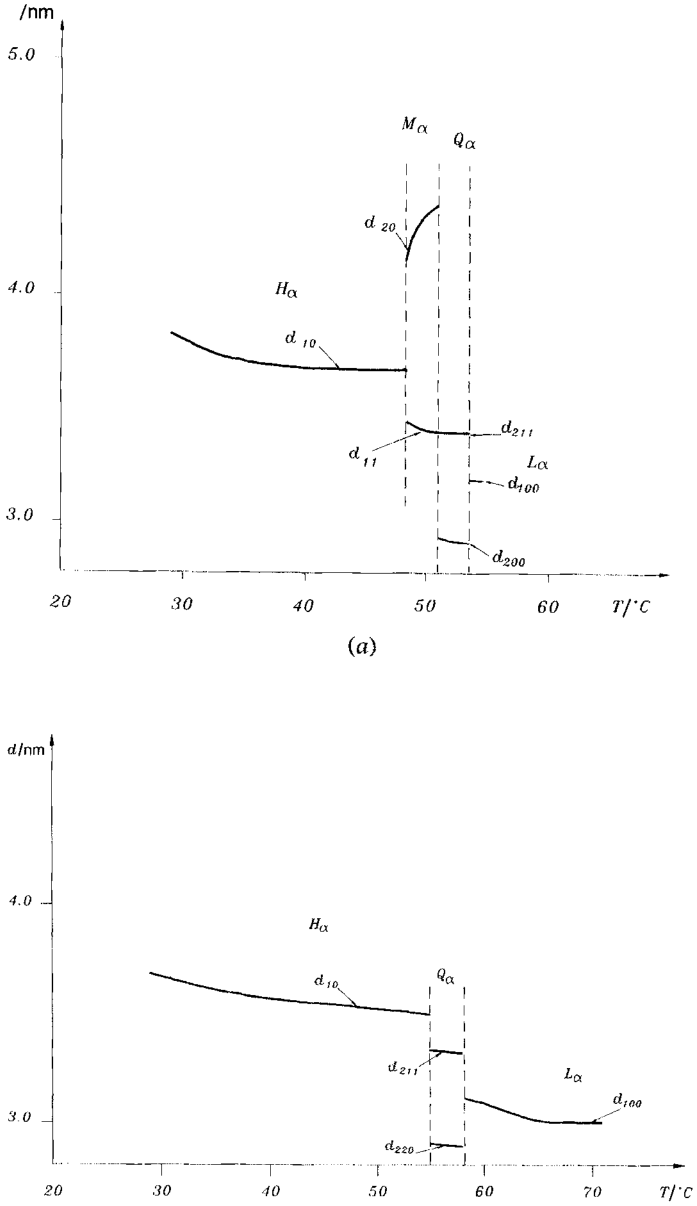

(*a*)

(*b*)

Figure 7. Reticular distances corresponding to the strongest diffraction peaks of the lyotropic phases between H_α and L_α out of the T_c curve, a function of NMF concentration: (*a*) Reticular distances of H_α, M_α, Q_α (Ia3d) and L_α phases for SDS/water + 18·6 per cent NMF. (*b*) Reticular distances of H_α, Q_α and L_α phases for SDS/water + 25 per cent NMF.

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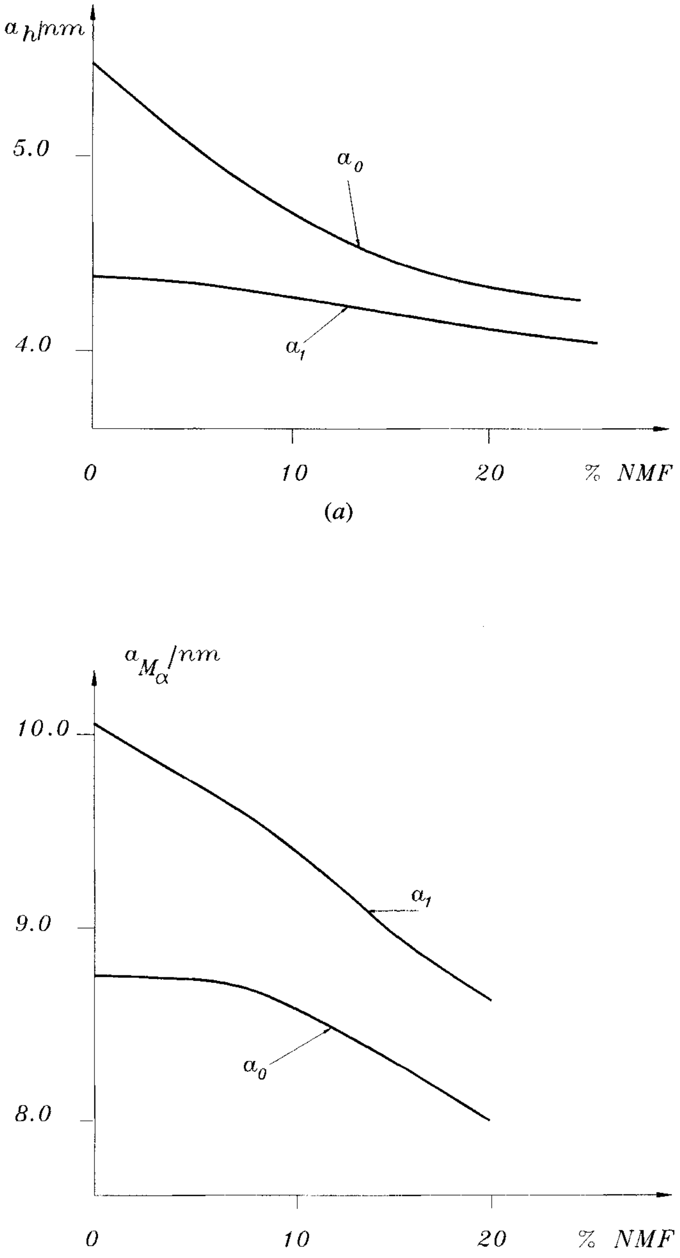

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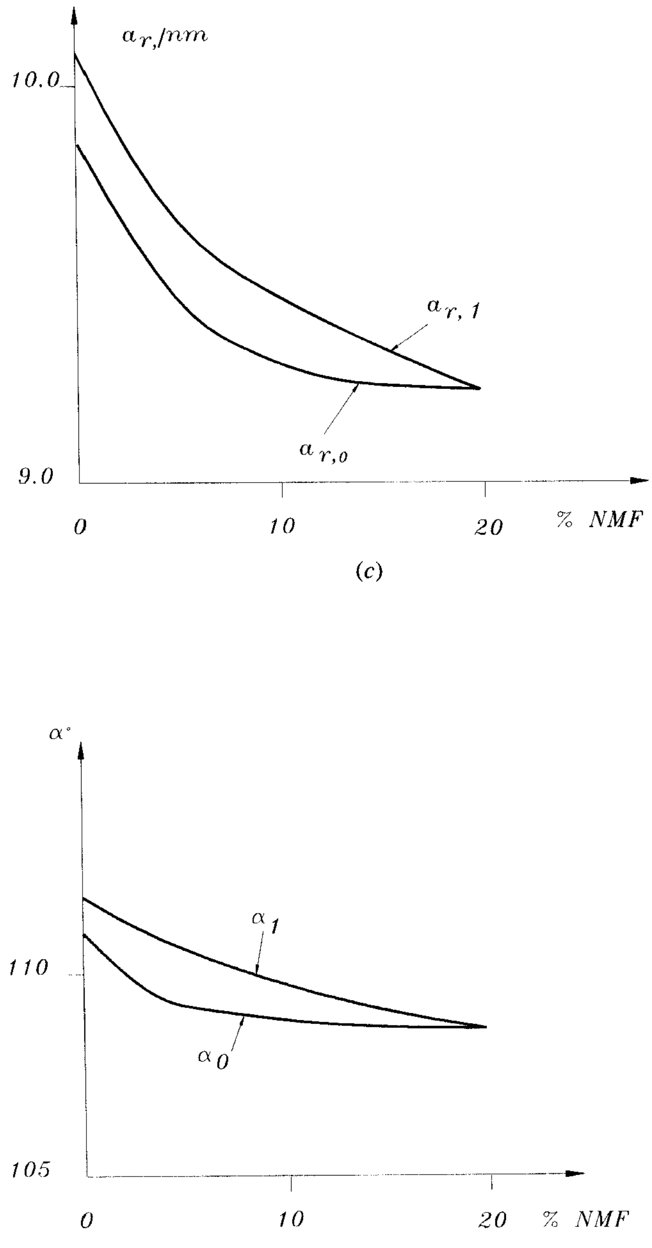

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(*d*)

Figure 8. Plot of parameters a_0 and a_1 of the ordered phases against NMF concentration at the temperatures of appearance T_0 and disappearance T_1 of these phases along the T_c curve. (*a*) Parameters $a_{H,0}$ and $a_{H,1}$ of the hexagonal phase. (*b*) Parameters $a_{M,0}$ and $a_{M,1}$ of the M_α phase. (*c*) Parameters $a_{R,0}$ and $a_{R,1}$ of the R_α phase. (*d*) Angles α_0 and α_1 of the rhombohedral lattice.

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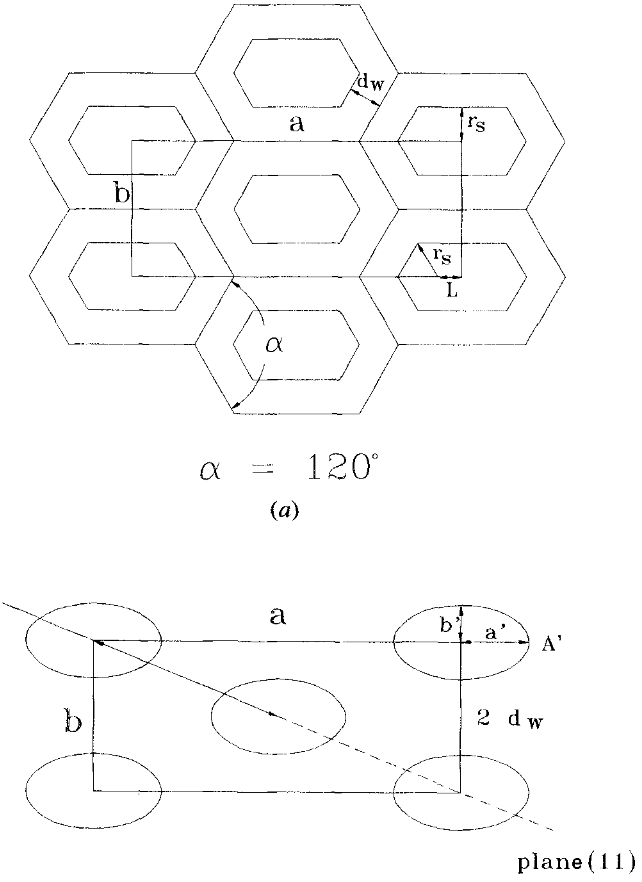

(*a*)

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Figure 9. Representation of a centred rectangular lattice [10]. (*a*) Hexagonal-rod model. (*b*) Elliptic-rod model.

surfactant/solvent (aqueous or not) systems and in SDS/formamide [7, 12, 13], was not observed by Rançon on the $L_\alpha \rightarrow Q_\alpha$ transition in the $C_{12}EO_6/H_2O$ system with fall in temperature [18]. In this case, d_{211} is equal to d_{100}, and the (211) planes of Q_α are parallel to the planes of the layers, although the experimental procedure employed was unable to discern any epitaxial relationships.

Recently Hagslätt [10] has described the structure of ribbon phases, and found that the centred rectangular phase was the most energetically favourable. He proposed a hexagon-rod model (see figure 9), in which the thickness of the water layer d_w was constant. This is not the case in the Q_α phase (the thickness of the solvent layer may vary by around 0·5 nm [7]). Hagslätt calculated the dimensions of the hexagon-rod close to the $M_\alpha \rightarrow R_\alpha$ transition for our SDS/water system:

$$r_s = 1{\cdot}14\,\text{nm}, \quad d_w = 0{\cdot}7\,\text{nm}.$$

The ratio ρ defined by $\rho = 1 + L/r_s$ is 1·85 with $L = 1/4(a - b\sqrt{3})$.

r_s is the smallest dimension of the micelle and is much smaller than the stretched out chain length l_e (around 1·6 nm). At 12·5 per cent NMF, the ratio a_1/b_1 is 2·52, and assuming r_s to be independent of the concentration of NMF, as b_1 is practically constant, the ratio ρ is 1·64 and the R_α phase forms. At 18·6 per cent NMF, the ratio a_1/b_1 is 2·35 out of the T_c curve and the ratio ρ is 1·50 (for a ratio $a_1/b_1 = \sqrt{(17/3)}$, $\rho = 1{\cdot}52$). Under these conditions, the Q_α phase is formed between M_α and L_α. A ratio ρ of 1·52 thus appears to be a critical value:

$$\rho < 1{\cdot}52, \quad M_\alpha \rightarrow Q_\alpha,$$

$$\rho > 1{\cdot}52, \quad M_\alpha \rightarrow R_\alpha.$$

The sequence $M_\alpha \rightarrow Q_\alpha$ (Ia3d) $\rightarrow L_\alpha$ is also observed for the CTAB/water system [10, 12] for a value of ρ of 1·30. In the dodecyltrimethylammonium chloride/water (DOTCl/water) system [19] ρ was 1·39. This criterion was also fulfilled in the CTACl/water system [20]. In the experiments on the CTACl/water system reported by Henriksson [9], this criterion could not be validated as the parameters of M_α were given at 45°C, which is far from the temperature of transition of the M_α to 3D phases. Anisotropy of the aliphatic cores is indicative of a change in curvature and a change in surface area per polar head σ at the paraffinic interface along the straight cross-section. The packing parameter $v/\sigma l$ is related to the mean curvature H by expression [21]:

$$v/\sigma l = 1 - Hl, \tag{3}$$

if the gaussian curvature is zero as in the H_α and M_α phases; v is the volume of the chains and l the distance between the chain end and the polar hydrophobic interface. In an elliptic-rod model of micelles, with a ratio of the axes $a'/b' = 1{\cdot}3:1$ as in the DOTCl/water system (model of Hagslätt [10]), a shift is produced in H from $b'/2a'^2$ to $a'/2b'^2$, with $b' = l = l_e$; consequently the packing parameter varies: $0{\cdot}35 \leq v/\sigma l \leq 0{\cdot}70$.

A packing parameter of 0·35 corresponds to that of a spherical micelle. The M_α phase between H_α and L_α implies that the packing parameter has values between 0·5 and 1. At the extremity of the axis of the ellipse equal to a' (point A', figure 9 (*b*)), $v/\sigma l$ is taken as 1/2, and the ratio l/b' as 0·77. In a elliptic-rod model, b' is the smallest dimension of the core and is smaller than $(b_0 - 2d_w)/2$ (see figure 9); b' is assumed to be the mean value of the radius of the hexagonal and the lamellar aggregates: about 1·5–1·4 nm ($l = 1{\cdot}1$ nm $= r_s$).

The product $\sigma . l$ varies along the surface of micelles. The chain must accommodate spatial alterations in the surface area per polar head which either fall or remain constant with increase in surfactant concentration [6]. The competition between chain flexibility and surface area per polar head can account for the formation of intermediate phases in water [8, 19], which are only observed for surfactants with chains containing 12 or more carbon atoms.

Calculation of the electron density showed that a spatial alteration in the surface area of the polar head also leads to a non-uniform distribution of $-OSO_3^-$ charges and counterions Na^+ [22]. Even in H_α there is a high concentration of counterions round the axes of symmetry of order 3, and the straight cross-section of the micelles resembles that of a hexagon-rod. The surface of micelles is an equipotential surface. The M_α phase can be formed if both these conditions—geometric and electric—are fulfilled.

The progressive blocking of deformation of the micelles by NMF molecules remains to be explained. The disappearance of the phases M_α phase along the T_c curve

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leads to the disappearance of the phases R_α and T_α; there is one molecule of NMF for only two molecules of SDS on disappearance of the M_α phase. NMF destructures water, reducing the interfacial tension between the solvent and the aliphatic medium. It thus favours large surface areas per polar head and hence small micelles. The non-uniform distribution of the NMF molecules may also alter the balance between chain packing and surface area per polar head. NMF has a high dielectric constant ($\varepsilon_r = 182{\cdot}4$ [14]) and so reduces the range of repulsive forces between surface charges. This could account for the denser stacking of rod-like micelles in the H_α phase, which is reflected by a decrease in the H_α lattice parameter. This closer stacking is energetically more favourable than deformation of the cross-section of micelles with rise in surfactant concentration. The 0·34 nm difference between d_{10} of H_α and d_{211} of Q_α shows that the distance between the planes containing the axes of the cylinders can be further reduced in the $H_\alpha \rightarrow Q_\alpha$ transition (the difference between d_{10} and d_{211} is 0·1 nm in SDS/formamide, and is much smaller or zero in other binary systems). Rançon [18] detected epitaxia between these two planes, which could account for the lack of formation of intermediate phases in ionic surfactant/non-aqueous polar solvent systems.

To account for the presence of intermediate phases in the SDS/water system, we propose a hypothesis based on two equilibria for SDS in water:

the acid-base equilibrium between the base $C_{12}H_{25}OSO_3^-$ and the conjugated acid $C_{12}H_{25}OSO_3H$;

the hydrolysis of SADS salt leading to dodecanol and sodium hydrogen sulphate [7].

The presence of these different compounds could explain the marked deformation of SDS micelles as in the SDS/decanol/water system. The presence of NMF in the water is assumed to block the decomposition of SDS.

These two accounts do not however rule out decomposition of surfactant or the presence of a molecule modifying solvation of ions. This would also affect the balance between chain packing and surface area per polar head between phases or within the same phase.

5. Conclusions

Our results have shown that the intermediate phases between H_α and L_α of the SDS/water system are abolished simultaneously by addition of *N*-methylformamide along the T_c curve, they disappear at NMF concentration of 20 per cent. The deformation of the M_α phase, distinguished by the ratio between the two lattice parameters, leads to the formation of the rhombohedral and tetragonal phases. In particular cases, the centred rectangular phase M_α may turn into a bicontinuous cubic phase of space group Ia3d if the ratio between the two lattice parameters does not exceed 2·38 at suitable surfactant concentrations. This initial study has also indicated that use of a mixture of solvents represents a simple method for investigating the conditions of formation of intermediate phases and for studying the transitions from a sequence to another sequence. The reasons why intermediate phases have not so far been observed in binary surfactant/non-aqueous polar solvent systems will be discussed subsequently.

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References

[1] Husson, F., Mustacchi, H., and Luzzati, V., 1960, *Acta crystallogr.*, **13,** 668.

[2] Leigh, I. D., McDonald, M. P., and Wood, R. M., 1981, *J. chem. Soc. Faraday Trans I*, **77,** 2867, 2876.

[3] Wood, R. M., and McDonald, M. P., 1985, *J. chem. Soc. Faraday Trans I*, **81,** 273.

[4] Kekicheff, P., and Cabane, B., 1978, *J. Phys., Paris*, **48,** 1571; 1988, *Acta crystallogr.* B, **44,** 395.

[5] Kekicheff, P., Grabielle-Madelmont, C., and Ollevon, M., 1989, *J. Colloid Interf. Sci.*, **131,** 112.

[6] Kekicheff, P., 1989, *J. Colloid Interf. Sci.*, **131,** 133; 1991, *Molec. Crystals liq. Crystals*, **198,** 131.

[7] Auvray, X., Perche, T., Anthore, R., Petipas, C., Rico, I., and Lattes, A., 1991, *Langmuir*, **7,** 2385.

[8] Blackmore, E. S., and Tiddy, G. J. T., 1990, *Liq. Crystals*, **8,** 131.

[9] Henriksson, U., Blackmore, E. S., Tiddy, G. J. T., and Soderman, O., 1992, *J. phys. Chem.*, **96,** 3894.

[10] Hagslatt, H., Soderman, O., and Jonsson, B., 1992, *Liq. Crystals*, **12,** 667.

[11] Warnheim, T., and Jonsson, A., 1988, *J. Colloid Interf. Sci.*, **125,** 627.

[12] Auvray, X., Perche, T., Anthore, R., Petipas, C., Marti, M. J., Rico, I., and Lattes, A., 1990, *J. phys. Chem.*, **94,** 8604.

[13] Auvray, X., Anthore, R., Petipas, C., Rico, C., and Lattes, A., 1988, *C. r. hebd. Séanc. Acad. Sci., Paris*, **306,** 695; 1989, *J. phys. Chem.*, **93,** 7458. Auvray, X., Perche, T., Anthore, R., Petipas, C., Marti, M. J., Rico, I., and Lattes, A., 1992, *Langmuir*, **8,** 2671.

[14] Charvolin, J., and Sadoc, J. F., 1987, *J. Phys. II, Paris*, **48,** 1559.

[15] Blackmore, E. S., and Tiddy, G. J. T., 1988, *J. chem. Soc. Faraday Trans II*, p. 84.

[16] Sjoberg, M., Henriksson, U., and Warnheim, T., 1990, *Langmuir*, **6,** 1205. Palepu, R., Gharibi, H., Bloor, D. M., and Wyn-Jones, E., 1993, *Langmuir*, **9,** 110.

[17] Gulik, A., Luzzati, V., De Rosa, M., and Gambacorta, A., 1985, *J. molec. Biol.*, **182,** 131.

[18] Rançon, Y., and Charvolin, J., 1988, *J. phys. Chem.*, **92,** 2646.

[19] Kang, C., Soderman, O., Eriksson, P. O., and Stael Von Holstein, J., 1992, *Liq. Crystals*, **12,** 71.

[20] Auvray, X., Perche, T., Petipas, C., Anthore, R., Rico, I., and Lattes, A. (to be published).

[21] Hyde, S. T., 1990, *J. Phys., Paris*, **C7,** 209.

[22] Vargas, R., Mariani, P., Gulik, A., and Luzzati, V., 1992, *J. molec. Biol.*, **225,** 137.

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