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Intermediate phases in the dodecyltrimethylammonium chloride/water system

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Two intermediate phases have been found in the concentration range between the hexagonal and concentrated cubic phases in the binary system dodecyltrimethylammonium chloride ($C_{12}TACl$)/water. This region in the phase diagram was studied by means of ^2H NMR of specifically deuteriated surfactant as well as by ^{14}N NMR. Below 35°C, an intermediate phase with non-cylindrical aggregates is formed in the concentration range 80 to 84 wt% surfactant, X-ray data from this phase can be indexed to a centred rectangular lattice. In addition, there is a uniaxial phase with a reduced quadrupole splitting. The aggregates comprising the centred rectangular phase were analysed by means of bandshape analysis of the NMR spectra and by small angle X-ray scattering.

1. Introduction

Within the study of lyotropic liquid crystals, considerable attention has recently been drawn to the so-called intermediate phases [1]. These are generally formed between the hexagonal H_1 and lamellar L_α phases. So far, the most studied system in this regard is the sodium dodecylsulphate/water system [2, 3], where no less than four different phases (including a cubic phase) were observed in this region of the phase diagram. It is an important task to unravel under which conditions, such as surfactant chain length, type of head group and so forth, these intermediate phases are formed. Other important questions pertain to their structure and the driving force behind their formation. To date intermediate phases have been found for charged surfactants, both cationic and anionic, and for non-ionic and zwitterionic surfactants. It would appear that a certain minimum chain length is required for their formation. Thus surfactants with twelve or more carbons in the hydrocarbon chain tend to form intermediate phases while shorter chain surfactants tend to form cubic phases instead. This observation may have implications as to why these phases are formed.

In the present work we report on the intermediate phases formed in the dodecyltrimethylammonium chloride/water system. The classic phase diagram for this system, presented in figure 1, is due to Balmbra *et al.* [4], and shows, in order of increasing surfactant concentration, an isotropic micellar region, a cubic, a hexagonal, a second cubic and finally, a lamellar liquid-crystalline phase. We have examined the

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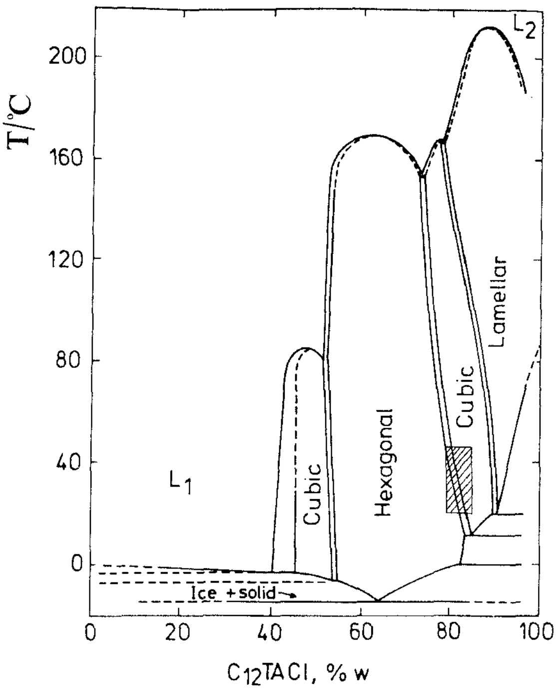

Figure 1. Phase diagram of the dodecyltrimethylammonium chloride/water system from [4]. L1 denotes an isotropic micellar solution. The hatched region has been investigated in detail in this work.

region close to the border between the hexagonal and the cubic phase (cf. figure 1) at low water content by means of nuclear magnetic resonance and X-ray scattering. The results of the NMR studies have been analysed by means of a model due to Quist and Halle [5], pertaining to the NMR bandshapes for quadrupolar nuclei in biaxial lyotropic structures.

2. Experimental

Materials: Dodecyltrimethylammonium chloride (C_{12}TACl) was obtained from Tokyo Kasei Int., Japan, and was used without further purification. Dodecyltrimethylammonium chloride, C_{12}TACl-d_9 with three deuteriated methyl groups in the head group, was purchased from Syntestjänst AB, Lund. The atomic enrichment of deuterium was better than 99 per cent as judged from ^{1}H NMR. The water used was triply distilled.

Sample preparation: The samples were prepared by weighing all components into glass ampoules that were immediately flame sealed. The samples were equilibrated by repeated centrifuging back and forth under mild heating. They were left for at least two weeks, often longer, before any measurements were performed. In the samples used for ^{2}H NMR measurements, 30 per cent of the C_{12}TACl was replaced with C-TACl-d_9. The compositions of these samples are converted so that they refer to C_{12}TACl/H_2O.

NMR studies: ^{2}H NMR experiments were performed at 15 MHz (2·3 T) on a Bruker MSL 100 spectrometer, while a Bruker AM 500 was used for the ^{14}N studies, in both cases the quadrupolar echo sequence was used [6]. Typical experimental parameters were: 90° pulse lengths; 9 μs for ^{2}H and 56 μs for ^{14}N, number of transients: 400 for ^{2}H and 8000 for ^{14}N; signal length: 0·03–0·14 s for ^{2}H and 0·08–0·16 s for ^{14}N; number of points: 2048 for ^{2}H and 4096 for ^{14}N; spectral width: 40 000 for ^{2}H and 125 000 for ^{14}N; total waiting time between pulses, 0·2–0·5 s for both ^{2}H and ^{14}N.

The control of the temperature was judged to be better than ±0·5°C.

Small angle X-ray scattering: X-ray scattering experiments were performed at 24°C according to a procedure described in [7].

3. Results and discussion

The disposition of this section is as follows. We start by covering some background material necessary for the interpretation of the NMR results. Then we describe the phase diagram for the region between the hexagonal and cubic phases and analyse the NMR spectra in terms of the aggregate shape. The X-ray scattering data is discussed in the next section, and finally, we give some concluding remarks.

3.1. *Quadrupole NMR spectra in uniaxial and biaxial liquid crystals*

Both ^{2}H and ^{14}N possess spin quantum numbers equal to one. Thus their NMR spectra in an anisotropic molecular system is determined by the coupling between the nuclear quadrupole moments and the electric field gradient at the nucleus. For an oriented liquid crystal, two absorption bands of equal height centred around the Larmor frequency are obtained. For a powder sample, in which all orientations between the static magnetic field and the symmetry axis of the liquid crystal are present, the characteristic Pake pattern is obtained, of which a simulated example is presented in figure 2. There are several accounts in the literature that provide the theoretical framework of this bandshape [5, 6, 8], and so we only give the necessary background material here. As a starting point consider the simulated NMR spectrum in figure 2. From the spectrum, two experimental parameters, important for the present work may be extracted (see figure 2); these are the quadrupolar splitting, Δ, and the asymmetry parameter, η. In the present study we shall be concerned with uniaxial and biaxial phases. To the former class belongs the hexagonal phase of infinitely long rods with circular cross-section, for which η is zero, while an example of a phase belonging to the latter case is constituted by phases consisting of aggregates of infinitely long rods with non-circular cross-section. For this case, η is related to the axial ratio of the cross-section of the rods. The exact relation depends on the particular model chosen to describe the cross-section. In the ribbon model (RM) of Chidichimo *et al.* [9], the cross-section is modelled as a semicircle capped rectangle, while the elliptic model (EM) of Quist and Halle is based on an elliptic cross-section [5]. In both models, for small deviations from circular cross-sections (for the EM, the ratio between the major and minor axes must not exceed 1·585, assuming a uniform surface distribution of spin bearing molecules), the quadrupolar splitting is equal to that obtained in the hexagonal phase; $\Delta = \Delta_{hex}$, provided that other factors, such as chain packing, are equal in the two phases.

As should be clear from this, we can use quadrupolar NMR on two levels in the study of liquid crystals. First, the spectrum can be used as an aid, together with other methods, in determining the phase diagram, as the values for Δ and η vary between different phases. In addition, the spectrum may be used to infer information about the structure of the surfactant aggregates comprising the phase.

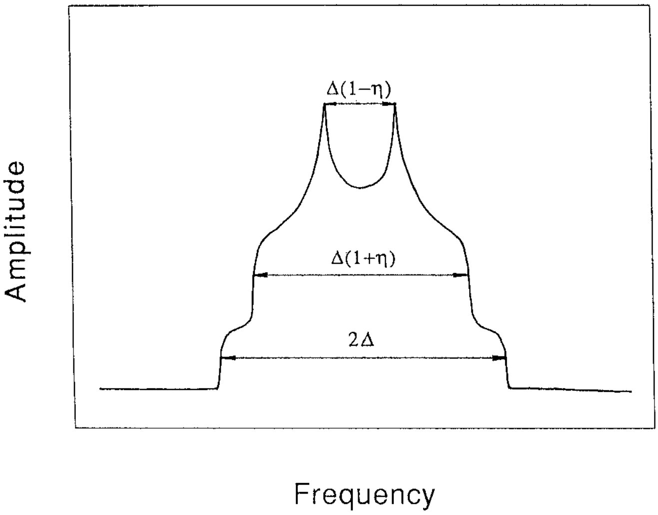

Figure 2. A simulated anisotropic quadrupole NMR spectrum for a powder sample. The experimentally obtained parameters Δ, the quadrupolar splitting and η, the asymmetry parameter, are indicated in the figure. The values used in the simulation were: $\Delta = 2100$ Hz, $\eta = 0{\cdot}5$ and a lorentzian line broadening of 10 Hz.

3.2. *The phase diagram of the $C_{12}TACl$/water system*

The temperature/composition diagram of the $C_{12}TACl$/water system, reported in [4] is presented in figure 1. Up to about 40 wt% $C_{12}TACl$, there is an isotropic micellar solution, followed by a discrete cubic phase of type I_1'' [10]. The cubic phase is followed by a normal hexagonal phase H_1, a bicontinuous cubic phase I_1', and finally, a lamellar phase L_α is formed. For some surfactant/water systems, one or more intermediate phases in the region between the normal hexagonal and lamellar phases are found. We decided, therefore, to examine this region in the $C_{12}TACl$/water system in detail and the results, corresponding to the shaded region in figure 1, are shown in figure 3.

Figure 3 shows the partial phase diagram for the $C_{12}TACl$/water system with the phase boundaries determined by ^2H NMR. Because of the length of time required to establish equilibrium, the difference in the transition temperatures when heating or cooling the samples is about 1°C for reasonable rates of temperature change. The boundaries given in figure 3 correspond to those occurring on slow heating. The intermediate phase region is distinguished clearly by the ^2H and ^{14}N NMR spectrum. Experimental ^2H NMR spectral patterns from the deuteriated methyl site of $C_{12}TACl$ are shown in figure 4 for three different phase situations.

For concentrations below 82 per cent, the uniaxial pattern ($\eta = 0$) shown in figure 4 (*a*) is observed. This bandshape is characteristic of a hexagonal phase. The value of the quadrupole splittings Δ is 1·95 kHz. This value remains rather invariant as the concentration is increased and also as the temperature is increased within the hexagonal phase. Presented in figure 5 are the results of analysing the ^2H NMR bandshapes obtained at 24°C. The ^{14}NMR data parallel those of ^2H, giving approximately the same values of η and a splitting that is around 13 kHz. This is to be expected, since the value of η is related to the phase structure, while Δ, in addition to the type of phase, also depends on the particular nucleus studied.

At around 82 per cent (see figure 3), an intermediate phase is formed and at 24°C a biaxial pattern is observed. The asymmetry parameter, as determined from the

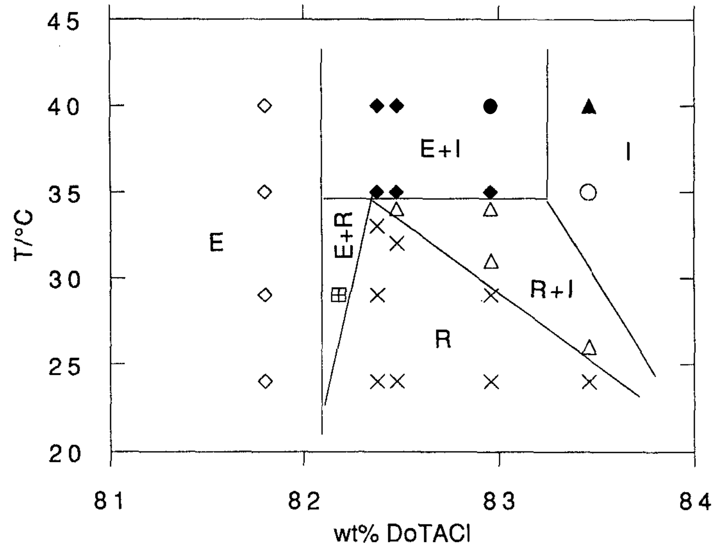

Figure 3. Partial phase diagram of the dodecyltrimethylammonium chloride/water system: (E) normal hexagonal liquid crystal, (I) bicontinuous cubic liquid-crystalline phase, (R) intermediate phase with non-cylindrical aggregates. The symbols in the figure refer to the concentrations and temperatures investigated. The concentration and temperature marked O give rise to the spectrum in figure 4(*c*).

spectrum is about 0·4 and increases slightly to 0·5 as the intermediate phase region is passed (cf. figure 5). The quadrupole splittings of the biaxial patterns are slightly higher than those of the hexagonal phase. However, the difference is marginal. As the temperature increases, some samples give a two phase spectrum of the biaxial intermediate phase and the isotropic bicontinuous cubic phase. At 35°C, all the intermediate phase signals disappear. Instead, hexagonal and cubic two phase spectra were recorded. This means that the phase transforms from intermediate phase to hexagonal and cubic phases between 34°C to 35°C. According to the phase rule, there must then be a three phase line around that temperature, which is indicated in the figure.

For one sample of concentration 83·5 wt% $C_{12}TACl$, at 24°C a biaxial spectrum was observed. At 26°C, the system enters the two phase region of intermediate and cubic phases in equilibrium. As the temperature reaches 35°C, the spectrum shows a cubic phase and a uniaxial phase with a value of the quadrupole splitting reduced to approximately one third of that in the hexagonal phase. When the temperature is increased to 40°C, a cubic phase spectrum was obtained. We shall return to this observation later.

Of special interest is the spectrum shown in figure 6(*a*). This corresponds to the two phase region hexagonal/intermediate phase. That the spectrum is indeed a superposition of two spectra, can be seen from figure 6(*b*), which displays the sum of experimentally obtained spectra from the hexagonal and intermediate phases at the same temperature. Thus the transition from the hexagonal to the intermediate phase is a first order transition.

It should be pointed out, that the phase boundaries determined by ^2H NMR shift to higher compositions by about 2 wt% as compared to those determined by ^{14}N NMR. We attribute this difference to the different batches of $C_{12}TACl$ used for the two different nuclei.

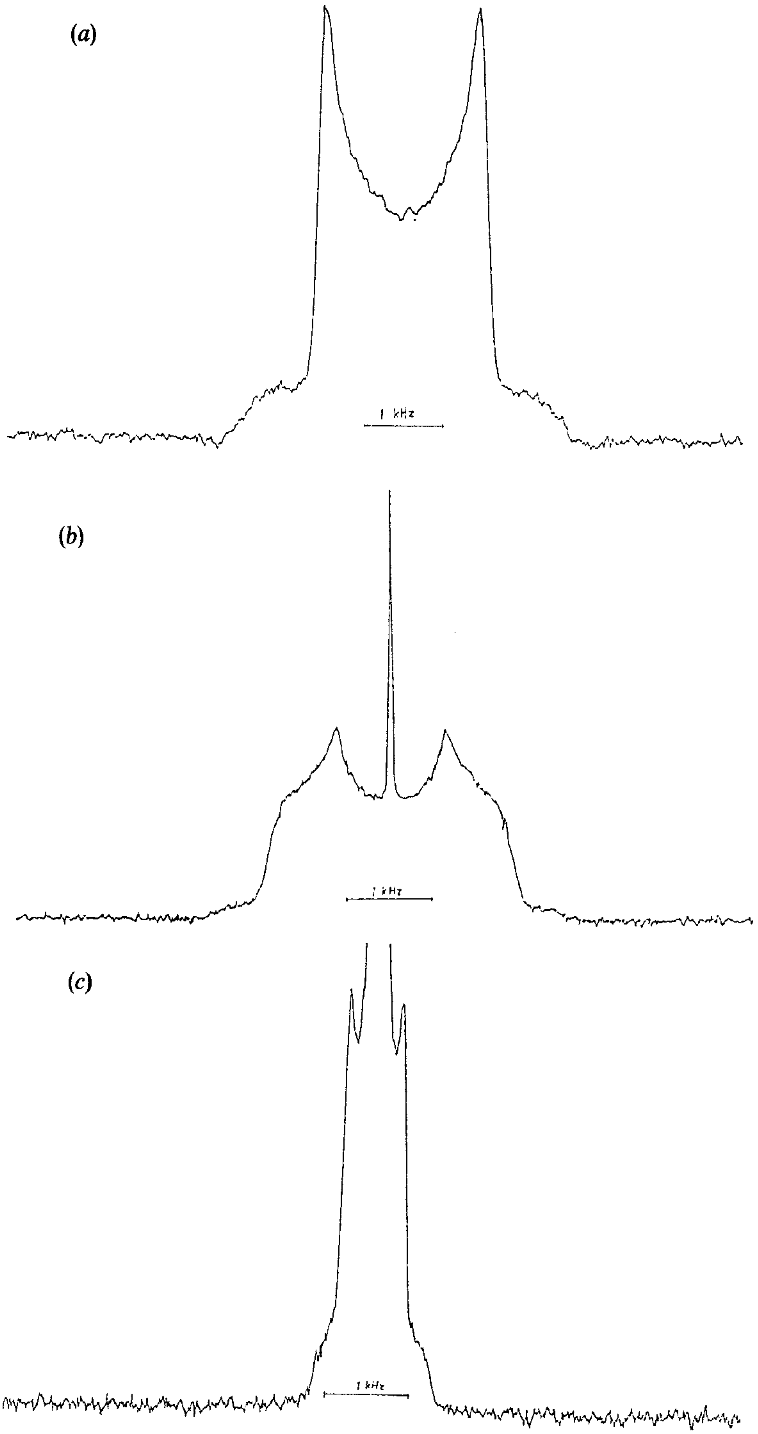

Figure 4. The recorded deuterium NMR spectra for deuteriated $C_{12}TACl\text{-}d_9$. (*a*) Corresponds to a 65·06 wt% sample in hexagonal phase, (*b*) to a 82·96 wt% sample in the intermediate and cubic two phase region and (*c*) for a 83·5 wt% sample in the cubic and uniaxial two phase area.

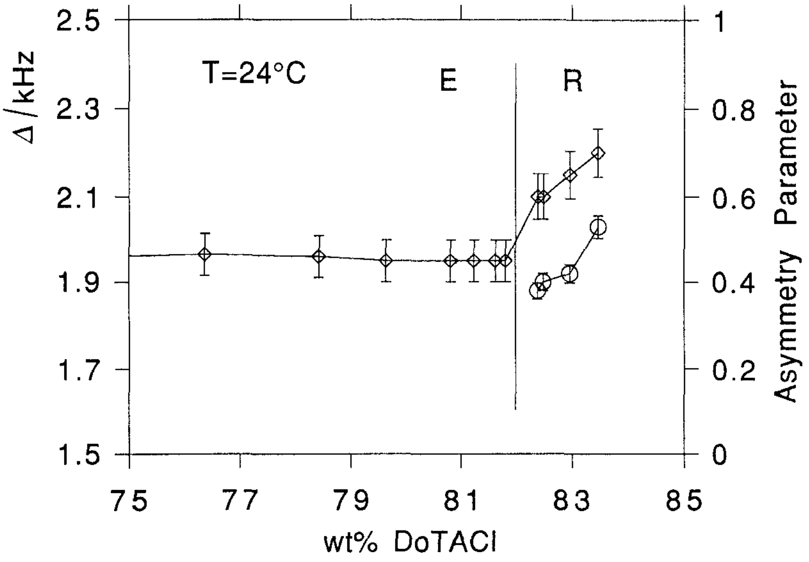

Figure 5. Experimental quadrupole splittings (◇) and asymmetry parameters (○) obtained from the deuterium NMR spectra as functions of the composition for $C_{12}TACl$/water mixtures at 24°C. Indicated in the figure is the transition from hexagonal to intermediate phase.

3.3. *Phase structure from NMR results*

As we have noted, the values of Δ and η can be used to infer information about the aggregate structure. For the spectrum corresponding to the intermediate phase, we note that the values of Δ are almost the same as those in the hexagonal phase while η is about 0·4 (cf. figure 5). This points to a phase structure of long rods with non-circular cross sections. As we discuss later, this phase structure is also compatible with the X-ray data. We are then in a position to determine the axial ratio of the surfactant aggregates. In doing so, we shall use the elliptic model of Quist and Halle [5] in which the rods are assumed to have an elliptic cross-section. To begin with, we note that the values of Δ indicate that the axial ratio, r, defined as the ratio between the major and minor axes, is rather close to unity; in the language of Quist and Halle we are in the small deformation region. In order to compute r we shall make two assumptions. First, we shall assume that the local residual anisotropy is uniform over the surface, and secondly, we shall assume that the spin bearing molecules have a uniform surface distribution (see later). This specifies the model and from the results [5] at 24°C we obtain the axial ratios given in table 1; as can be inferred from these the axial ratio remains fairly constant at approximately 1·2. When analysing the ^{14}N data in the same way slightly higher values of r are obtained. At 26°C they vary from 1·18 to 1·27 over the intermediate phase. This difference can be attributed to the different batches of $C_{12}TACl$ used.

We end this section with some remarks concerning the spectrum in figure 4 (*c*). This is a two phase spectrum of a cubic phase and a phase giving a uniaxial spectrum. The latter component in the spectrum has a quadrupolar splitting of 0·6 kHz, i.e. the splitting is reduced to approximately one third of that in the hexagonal and intermediate phases. Thus this spectrum comes from a second intermediate phase. A similar spectrum has recently been observed in the C_{16} analogue of $C_{12}TACl$ [11]; here, it is suggested that the structure of the phase is bicontinuous, and that the

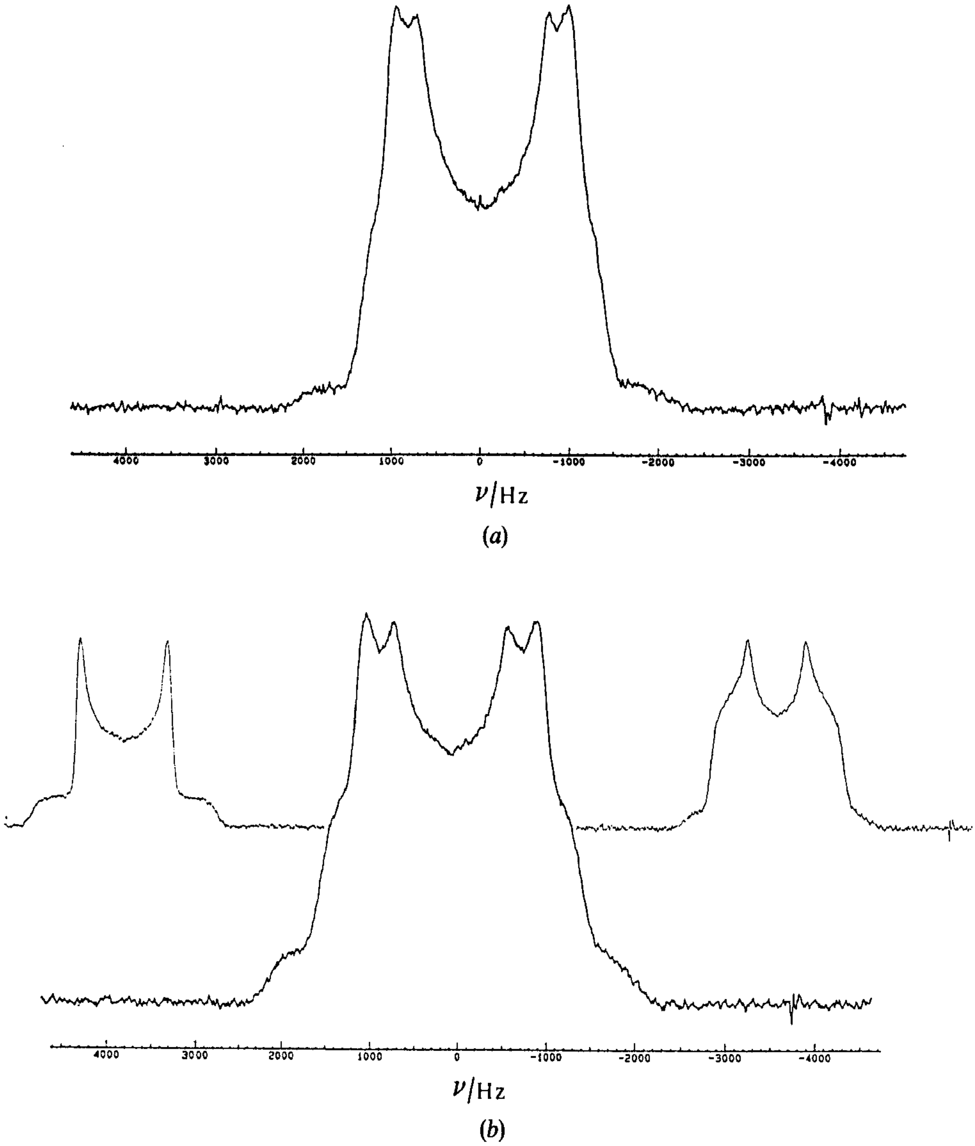

Figure 6. The experimental ^{2}H NMR spectrum for a sample in the hexagonal and intermediate two phase region at 29°C and (*b*) the spectra for samples in hexagonal and intermediate one phase region and the sum of the two spectra. The sum has been obtained by adding 50·7 per cent of the hexagonal phase spectrum and 49·3 per cent of the rectangular spectrum.

Table 1. Axial ratios of the aggregates in the intermediate phase at 24°C, as determined from the ^2H NMR results.

wt% C_{12}TACl	r
82·38	1·18 ± 0·01
82·48	1·18 ± 0·01
82·96	1·22 ± 0·01
83·46	1·23 ± 0·01

structure can be described in terms of infinite periodic minimal surfaces. This type of surface has long been used in the description of bicontinuous cubic phases [12]. The reduction of the quadrupolar splitting as compared to the hexagonal phase would then be the result of surfactant lateral diffusion over this surface, where the cubic phase represents the extreme case where the splitting is averaged to zero. It is a reasonable assumption that the same holds for the system presently under study.

3.4. *Analysis of X-ray data*

Two of the samples used in the ^{14}N experiments were studied by small angle X-ray diffraction. As judged by the ^{14}N spectra, one of these was in the hexagonal phase and had a composition of 79·95 wt% C_{12}TACl. This sample gave only one X-ray diffraction line at $d = 33{\cdot}9$ Å. The other sample, giving a ^{14}N spectra indicative of the intermediate phase with a value of $\eta = 0{\cdot}534$, had a composition of 81·61 wt% C_{12}TACl and gave four diffraction lines at 42·5, 33·7, 21·1 and 18·7 Å. In order to analyse the diffraction patterns further the group volumes for the constituents of the C_{12}TACl molecule given in table 2 were used.

For the hexagonal phase the radius of the hydrocarbon core, R_{HC}, of the aggregates can be computed from

$$R_{HC} = \left[\frac{2d^2\Phi_{HC}}{\pi\sqrt{3}}\right]^{1/2}. \tag{1}$$

In this equation, Φ_{HC} is the volume fraction of the hydrocarbon core and d is the value of the first order Bragg spacing. We assume that the hydrophobic core is made up of the C_{12} alkyl chains. This choice is dictated by the fact that the trimethylammonium head group is hydrated (at least to some extent), while the number of water molecules penetrating into the hydrocarbon core is certainly very small. With this assumption Φ_{HC} can be computed from table 2 and the density of water. From equation (1) we then obtain for the sample in the hexagonal phase a value of $R_{HC} = 15{\cdot}8 \pm 0{\cdot}5$ Å. This value can be compared with that for an all-trans C_{12} alkyl chain which is 16·7 Å. Thus the radius of the hydrocarbon core in the hexagonal phase is close to the length of an all-trans chain.

For the sample in the intermediate phase, the diffraction lines can be indexed to a centred rectangular lattice. The interplanar distances are for this case given by [15]

$$d_{hk} = \left[\frac{h^2}{a^2} + \frac{k^2}{b^2}\right]^{-1/2}, \tag{2}$$

with conditions limiting possible reflections to $h + k = 2n$ and where a and b are the dimensions of the unit cell. The indexing of the diffraction is given in table 3.

Table 2. Group volumes (in Å^3) for the different parts of the $C_{12}TACl$ molecule.

$-CH_2-$	$-CH_3-$	$(-CH_3-)_3N^+$	Cl^-
26·6 [13]	53·2 [13]	102·3 [14]	28·9 [14]

Table 3. X-ray experimental and calculated interplanar distances for a sample in the intermediate phase at 81·91 wt% $C_{12}TACl$ at 24°C. The calculated distances are for a centred rectangular lattice with $a = 84{\cdot}9$ Å, $b = 36{\cdot}9$ Å.

d_{obs}/Å	d_{calc}/Å	hk
42·5	42·45	20
33·7	33·84	11
21·1	21·22	40
18·7	18·45	02

In the analysis of the NMR results, the surfactant rods comprising the centred rectangular phase were assumed to have an elliptic cross-section. If it is assumed that the length of the minor semiaxes is equal to 15·8 Å, i.e. the length of the hydrocarbon chain in the hexagonal phase close to the phase boundary to the intermediate phase, then the axial ratio of the elliptical cross-section can be computed from

$$r = \frac{\Phi_{HC}ab}{2\pi 15{\cdot}8^2}. \tag{3}$$

The result obtained is $r = 1{\cdot}21$, which can be compared with the value obtained from the ^{14}N NMR experiment of η which, if analysed in the same way as for the ^2H NMR spectra, yields $r = 1{\cdot}27$. We note that if we allow for a non-uniform distribution of the spin bearing molecules in the analysis of the asymmetry parameter, the axial ratios, determined by means of NMR and X-ray, can be made to agree (within the EM the axial ratio, r, would be reduced if the density of surfactant molecules is higher in regions of low curvature). However, due to the fact that the difference is small as well as to the uncertainty in the evaluated parameters, we shall not pursue this matter further.

4. Conclusion

In conclusion, we have shown that in the $C_{12}TACl$/water two component system, an intermediate phase exists in the range of 80 to 84 wt% surfactant when the temperature is lower than 35°C. This phase can be identified with the so-called centred rectangular phase and can be seen as a deformed hexagonal phase built up of rods with non-circular cross-sections. This structure is in agreement with the X-ray scattering data. The deviation from a circular cross-section is quite small; analysis of the NMR spectra and the X-ray data indicate that the ratio between the major and minor semi-axes is about 1·2–1·3.

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References

[1] Bleasdale, T. S., and Tiddy, G. J. T., 1990, *The Structure, Dynamics and Equilibrium Properties of Colloidal Systems*, edited by D. M. Bloor and E. Wyn-Jones (Kluwer Academic), pp. 397–414.

[2] Kekicheff, P., Gabrielle-Madelmont, C., and Ollivon, M., 1989, *J. Colloid Interface Sci.*, **131,** 112.

[3] Kekicheff, P., 1989, *J. Colloid Interface Sci.*, **131,** 133.

[4] Balmbra, R., and Clunie, J., 1969, *Nature, Lond.*, **222,** 1159.

[5] Quist, P.-O., and Halle, B., 1988, *Molec. Phys.*, **65,** 547.

[6] Davis, J. H., 1983, *Biochim. biophys. Acta*, **737,** 117.

[7] Lindblom, G., Larsson, K., Johansson, L., Fontell, K., and Forsen, S., 1979, *J. Am. chem. Soc.*, **101,** 5465.

[8] Seelig, J., 1977, *Q. Rev. Biophys.*, **10,** 353.

[9] Chidichimo, G., Golemme, A., Doane, J. W., and Westerman, P. A., 1985, *J. chem. Phys.*, **82,** 536.

[10] Fontell, K., 1990, *Colloid Polym. Sci.*, **268,** 264.

[11] Henriksson, U., Blackmore, E. S., Tiddy, G. J. T., and Söderman, O., *J. phys. Chem.* (in the press).

[12] Lindblom, G., and Rilfors, L., 1989, *Biochim. biophys. Acta*, **988,** 221.

[13] Cabane, B., 1987, *Surfactants in Solutions: New Methods of Investigation*, edited by R. Zana (Dekker).

[14] Hayter, J. B., and Penfold, J., 1983, *Colloid Polym. Sci.*, **261,** 1022.

[15] Henry, N. F. M., and Lonsdale, K., 1952, *International Tables for X-ray Crystallography*, Vol. I (The Kynoch Press).