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THE LOWER TEMPERATURE PHASE OF A NEMATIC
LYOMESOPHASE SYSTEM

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ABSTRACT

The system Na decyl sulphate/water/decanol/Na sulfate, which forms a nematic N_L lyomesophase with planar micelles at 25°C , changes to a G phase at 22°C on cooling. Phase G studied by X-ray diffraction has a lamellar structure with repetition distance 31.4 \AA . Comparison of observed and calculated intensities from a step function model defines the G phase as a coagel where lamellar aggregates of extended tilted bilayers, with only one layer of solvation water between lamellae, are dispersed in water. This result gives support to the model of aggregates of micelles in the N_L phase, previously proposed.

I. INTRODUCTION

X-ray diffraction results (Amaral et al, 1979; Charvolin et al, 1979; Figueiredo Neto & Amaral, 1981) on some specific nematic lyomesophases made of hydrocarbon amphiphile/water/additives (alcohol and/or salt) evidenced that the so-called (Radley et al, 1976) type II phases (with diamagnetic anisotropy $\Delta\chi < 0$) have micelles with planar symmetry while the type I phases (with $\Delta\chi > 0$) have micelles with cylindrical

symmetry. These phases have also been called (Yu & Saupe, 1980) respectively N_L and N_C and there has been increasing interest in their study in the last years.

Although these phases have been characterized as nematic mesophases by their spontaneous orientation in the presence of magnetic fields and by observation of their optical textures in a polarizing microscope (Radley & Saupe, 1978; Charvolin et al, 1979), evidence has been reported on the existence of positional correlations not present in usual nematic mesophases (Amaral & Tavares, 1980; Figueiredo Neto & Amaral, 1983). Also the analysis of the interactions between micelles showed (Amaral & Figueiredo Neto, 1983) that the systems are in flocculation conditions, with behavior determined by the interplay of the net attractive interaction, thermal agitation and the amount of bound water giving the length of the excluded volume interaction; flocculation in an irreversible way is avoided by thermal agitation but aggregates of micelles may be formed in a fluctuating mode. The widths of the diffraction peaks indicate aggregates of 10-20 planar micelles for type II (Amaral & Tavares, 1980) and ~25 cylindrical micelles for type I (Figueiredo Neto & Amaral, 1983).

In order to have more information about these aggregates of micelles in the nematic lyomesophase, it was found interesting to study the structure of the phase occurring below the Krafft melting point of the hydrocarbon chains. The system SDS (Na decyl sulfate/water/decanol/Na sulfate) was chosen because it has been extensively studied in the type II nematic lyomesophase at room temperature (25°C) (Amaral et al, 1979; Amaral & Tavares, 1980) and because it shows a transition at a suitable Krafft temperature (22°C on cooling), making the

lower temperature phase easily observable without the need of special cooling systems.

II. EXPERIMENTAL

Samples were prepared by usual methods (Radley et al, 1976; Amaral et al, 1979) with weight composition Na decyl sulfate 36% / water 54% / Na sulfate 5% / decanol 5% , and were sealed in lindemann glass capillaries 0.7 mm thick.

X-ray diffraction was obtained by photographic techniques, using a small angle Rigaku-Denki diffractometer and a Laue camera, both in transmission geometry with the capillary in vertical position, as well as a Debye-Scherrer camera (capillary in horizontal position), always with $\text{CuK}\alpha$ (Ni filtered) radiation and the X-ray beam perpendicular to the capillary axis. The ambient temperature was controlled within 1°C . A microdensitometer was used to obtain relative intensities of the diffraction peaks.

III. RESULTS AND DISCUSSION

Figure 1 shows small angle results obtained at 18°C and 30°C , showing the band at $s^{-1} = 38 \text{ \AA}^{-1}$ in the N_L nematic phase and three lamellar reflections with repetition distance $d = 31.4 \text{ \AA}$ in the lower temperature phase, which will be called G phase. Results with the microdensitometer gave $I_{100} = 100$, $I_{200} = 10$ and $I_{300} = 8$. The width of the lines are about the experimental resolution, showing that the crystalline

approach may be adopted.

Some results for the G phase were obtained from a sample that was magnetically oriented in the nematic phase, with the magnetic field \vec{H} perpendicular to the capillary axis. The lamellar reflections appear then oriented in the equatorial direction when the X-ray beam is parallel to \vec{H} (geometry G_{II}) and are absent when the X-ray beam is perpendicular to \vec{H} (geometry G_I). This result is analogous to the results obtained for the oriented nematic phase (Amaral et al, 1979) and evidence that the orientation is not necessarily lost in the transition from the nematic to the G phase.

Laue and Debye-Scherrer results of the G phase showed two strong and well defined rings at s^{-1} values 4.0 \AA^{-1} and 4.2 \AA^{-1} , besides weaker lines, a result typical of a bi-dimensional packing of the extended carbon chains; the 200 and 300 lamellar reflections appear also (the first order is under the beam stopper). In some results the rings due to the hydrocarbon chains are partially oriented and indicate that they might be inclined and not perpendicular to the lamellar plane, but it was not possible to obtain the tilt angle. Also in some Laue results higher order lamellar reflections appear very weakly, but the 400 reflection is absent, indicating that $I_{400} = 0$. In the higher angle region for the type II nematic phase only a broad band at s^{-1} value 4.6 \AA^{-1} appears, typical of the disordered paraffin chains.

The small number of lamellar reflections associated with the two high angle reflections characterize the G phase as either a gel or a coagel phase (Vincent & Skoulios, 1966). The gel phase is an homogeneous phase made of amphiphilic monolayers or bilayers, while the coagel is inhomogeneous,

corresponding to a mixture of two phases (crystallites of amphiphile and water); the gel phase may be metastable, transforming into the coagel phase. In binary systems with Na and Li soaps the gel phase does not occur, with a direct transition from lyomesophases to a coagel phase.

The area per polar head for the G phase, admitting homogeneous distribution along the normal to the lamellar planes and infinite planes, can be obtained from (Luzzati, 1968):

$A = \frac{2Mv}{N_0 d \phi}$, where M , v and ϕ are the molecular weight, the partial specific volume and the volume concentration of the amphiphile and N_0 is Avogadro's number. The calculation gives a value of 51 \AA^2 , extremely high for a gel phase; this indicates that probably a large fraction of the water is outside the lamellar structure, what gives support to the coagel hypothesis.

The length of the amphiphile molecule in the extended configuration (admitting for the polar head the ionic radius 2.3 \AA of the sulphate anion) is expected to be about 18 \AA . The components of the system that are in the micelles (amphiphile plus alcohol) correspond to 37% in volume. An homogeneous distribution of amphiphile and water along the normal to the lamellar plane, with the observed repetition distance, would require an amphiphilic layer thickness $l \approx 12 \text{ \AA}$, what would correspond to a monolayer of amphiphilic molecules with the chain axis making an angle $\gamma \approx 48^\circ$ with the normal direction. As long as it is admitted that water is being excluded from the lamellar structure, it is possible to accept smaller γ values and larger l values. The extreme possibility would correspond to $l = d$, or an anhydrous lamellar phase; in this case the lamellae correspond to bilayers with a tilt angle $\gamma \approx 29^\circ$, since the repetition distance is smaller than the length of two

extended molecules. Figure 2 shows these two extreme possibilities. Any model intermediate to these two would be possible, implying partial interpenetration of the chains and/or partial exclusion of water from the lamellar structure.

To better define the structure of the G phase, expected intensities have been calculated from a structural model, shown in figure 3 and described in detail in the appendix. In this model the electron density profile $\rho(x)$ along the direction normal to the lamellar planes is approximated to a step function with different levels, corresponding to the regions where CH_3 , CH_2 , polar heads and water are located.

As discussed in the Appendix, the existence of a central CH_3 group in a bilayer leads to odd order peaks more intense than even order peaks in the scattering factor of one isolated lamella. If the period d of the lamellar structure is close to the thickness l of the layer (little or no water between layers) this leads to odd lamellar reflections stronger than even lamellar reflections. In the study of gel and coagel phases by Vincent & Skoulios (1966) it was verified that the coagel phase is characterized by higher intensities of the odd reflections, what does not occur in the gel phase. It is seen from the analysis here made that this intensity distribution characterizes the coagel phase as lamellar aggregates with almost anhydrous bilayers. In the case of monolayers, a monotonic decrease of the intensity with the order of reflection is expected, also for little water between layer; depending on the amount of water between layers other intensity relations may occur, as seen in figure 4.

A two steps model simulating polar heads and CH_3 is physically meaningful, since electron densities of water

and CH_2 are very similar; such a model is already enough to choose between the two extreme possibilities discussed. Calculated intensities as a function of r can be seen in figure 5a. Comparison with observed intensities requires simultaneously the presence of CH_3 groups at the layer centre and $\ell = d$. It is possible therefore to eliminate the hypothesis of monolayers with large quantities of water between layers and to define the G phase as a coagel phase.

To obtain an adjustment of the layer thickness ℓ , calculations have been performed with a three steps function. Figure 5b shows the intensities of the four first orders as a function of r ; best agreement with experiment is obtained for a bilayer thickness $\ell = 28 \text{ \AA}$, what corresponds to one single water solvation shell between layers and a tilt angle of 39° for the extended carbon chains.

It is therefore concluded that the G phase is a coagel phase where lamellar aggregates, probably with only one layer of water solvation shell between lamellae, are dispersed in water. This result of one water solvation shell is in agreement with studies of gel phases in systems amphiphile/alcohol, that showed the necessity of existence of at least one layer of solvation water (4 \AA) to promote the dissolution of alcohol in the amphiphile (Vincent & Skoulios, 1966).

In the transition from coagel to nematic phase the repetition distance of 31.4 \AA changes to an average distance of 38 \AA . In the nematic phase disordered chains are expected to have an average direction perpendicular to the planes, without defined tilt angles; the contraction due to the disordered state is expected to decrease the thickness of the hydrocarbon bilayer in 15%-20% (Seelig, 1977). These two effects together

lead to about the same thickness ℓ in the two phases, (within 10%), and the observed difference in the distance between lamellae may be attributed to differences in the thickness of the water layer.

The transition G to N_L would then imply, besides the fusion of the hydrocarbon portion, the transition from a situation of one solvation shell between lamellae to the situation of one-two water solvation shells per micelle. These micelles would be more flexible and would no more form crystallites, but the attractive interaction would keep the micelles in aggregates (with three-four water solvation shells between micelles), so that no homogeneous distribution of micelles in water would occur in the nematic phase.

APPENDIX

STRUCTURAL MODEL

The problem of the determination of $\rho(x)$ from the observed diffracted intensities has been considered extensively in the study of membranes as well as of lipid bilayers. This can be made by direct methods (Worthington et al, 1973, for a review) or by alternative methods that utilize models for $\rho(x)$, with parameters determined by a fitting of observed and calculated intensities (Pape & Kreutz, 1978; Luzzati et al, 1972).

The adopted form for the $\rho(x)$ function shown in figure 3 has the following parameters:

- ρ_0 - electron density of the matrix (water),
- ρ_1 - electron density of polar heads, with thickness R_1 ,
- ρ_2 - electron density of CH_2 groups, with thickness R_2 ,
- ρ_3 - electron density of CH_3 groups, with thickness R_3 .

The matrix electron density can be considered zero, since what counts is the electron density contrast between the parts, and therefore $\rho(x)$ may be considered in arbitrary units.

Such a model is a reasonably good physical approximation often used in the study of both lipid bilayers and membranes (Wilkins et al, 1971), particularly when there are few reflections, making the determination of $\rho(x)$ by direct methods almost impossible.

The structure factor for one isolated centro-symmetric lamella of thickness l as a function of the scattering vector s is:

$$F(s) = 2 \int_0^{l/2} \rho(x) \cos(2\pi x) dx$$

The intensity scattered by N lamellae is:

$$I_N(s) = N^2 |F(s)|^2 FI(s)$$

where $FI(s)$ is an interference function, that reduces to sharp peaks at the Bragg positions for N sufficiently large.

Calculations performed with the adopted model showed that for $N=10$ the crystalline approach is already a good one; it is therefore enough to calculate $F^2(s)$.

A study was first made of the effect of each parameter independently:

a) effect of polar heads: one step model ($\rho_1=1, \rho_0=\rho_2=\rho_3=0$). This model simulates monolayers. The variable parameters are R_1 and $r = R_3 + R_2 + R_1/2$. The function F^2 oscillates with period $1/2r$ and the envelop decays with R_1 . Figure 4 shows the expected intensities I_1, I_2, I_3 and I_4 as a function of the ratio $2r/d$ admitting $R_1 = 4.6 \text{ \AA}$.

b) effect of CH_3 groups: two steps model ($\rho_1=1, \rho_3=-0.5, \rho_0=\rho_2=0$). Fixing the parameters $R_1 = 4.6 \text{ \AA}$ and $r = 16.45 \text{ \AA}$ (obtained from the estimated length of an extended molecule) the parameter R_3 was varied. The depression of the electron density in the central part of the layer introduces an oscillation in the peak intensities: odd orders in F^2 becomes more intense than even orders in F^2 , and this effect increases with R_3 . This characteristic had already been commented in the study of membrane bilayers with step-function models (Wilkins et al, 1971).

Variation of the two parameters R_3 and r , in the two steps model, can test both the presence of CH_3 at the layer middle and the layer thickness. Calculated intensities

for the first four reflections in the case $R_3 = 2\overset{\circ}{\text{Å}}$ can be seen in figure 5a. Comparison with observed intensities give $r = 14\overset{\circ}{\text{Å}}$ and $R_3 = 2\overset{\circ}{\text{Å}}$ as reasonable values. This corresponds to completely anhydrous bilayers (even with interpenetration of polar heads of adjacent layers) with tilted carbon chains.

For the calculations with a three steps function, more exact values for the relative electron densities have been used. The presence of salt is expected to increase ρ_0 from $0.33\text{ e}/\overset{\circ}{\text{Å}}^3$ to $0.35\text{ e}/\overset{\circ}{\text{Å}}^3$; $\rho_2 = 0.27\text{ e}/\overset{\circ}{\text{Å}}^3$; ρ_3 is expected to have a contrast with water 3 to 7 times bigger than ρ_2 ; ρ_1 oscillates between $0.3\text{ e}/\overset{\circ}{\text{Å}}^3$ and $1.5\text{ e}/\overset{\circ}{\text{Å}}^3$ depending on the particular polar head. Using $\rho_1 = 0.2$, $\rho_2 = -0.05$, $\rho_3 = -0.27$, $\rho_0 = 0$, fixing $R_1 = 4.5\overset{\circ}{\text{Å}}$ and $R_3 = 2\overset{\circ}{\text{Å}}$, calculations have been performed varying R_2 and consequently r . Results can be seen in figure 5b. The intensities I_1 , I_2 and I_3 show agreement with experiment for $R_2 = 7.4\overset{\circ}{\text{Å}}$ (and $r = 11.65\overset{\circ}{\text{Å}}$), but I_4 is not zero in this condition. As it is not very meaningful to try an adjustment of so few intensities changing more than one parameter, no further improvement was tried.

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FIGURE CAPTIONS

- Fig. 1 - Small angle X-ray diffraction results in N_L phase (upper figure) and G phase (down figure).
- Fig. 2 - Lamellar structure in the two extreme possibilities: anhydrous bilayers (to the left) and monolayers with water (to the right).
- Fig. 3 - Adopted model for the electron density profile $\rho(x)$ along the direction normal to the lamellar planes.
- Fig. 4 - Calculated intensities for the four first lamellar reflections in the case of monolayers as a function of $2r/d$.
- Fig. 5 - Calculated intensities for the four first lamellar reflections in the case of bilayers as a function of r :
- (a) two steps model for $\rho(x)$.
 - (b) three steps model for $\rho(x)$.

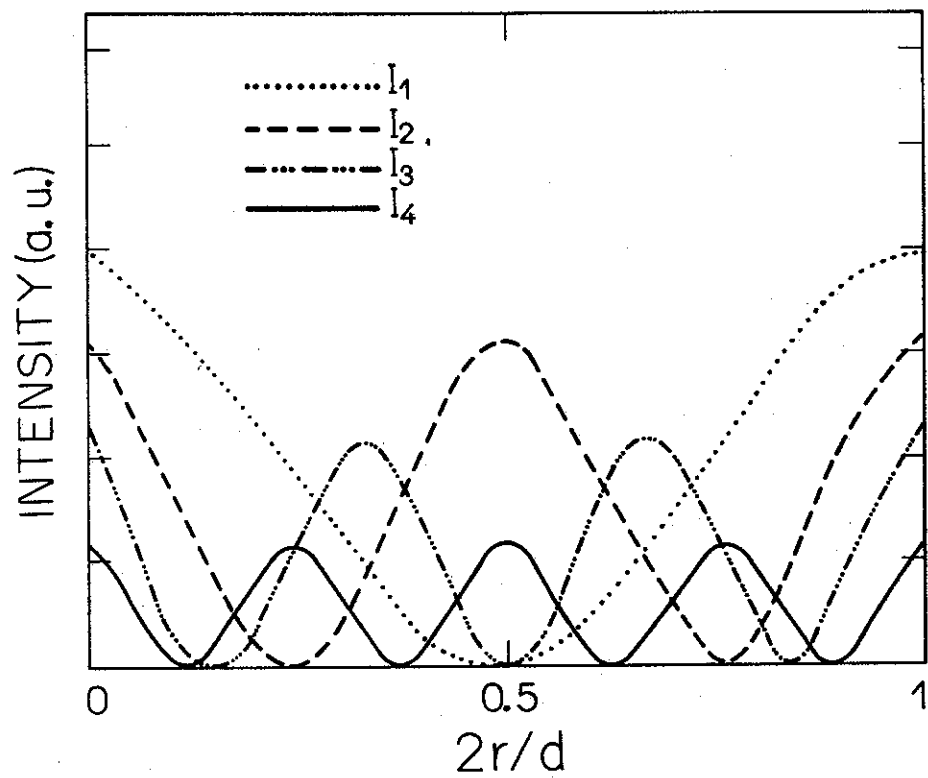


FIGURE 4

INTENSITY (ARBITRARY UNITS)

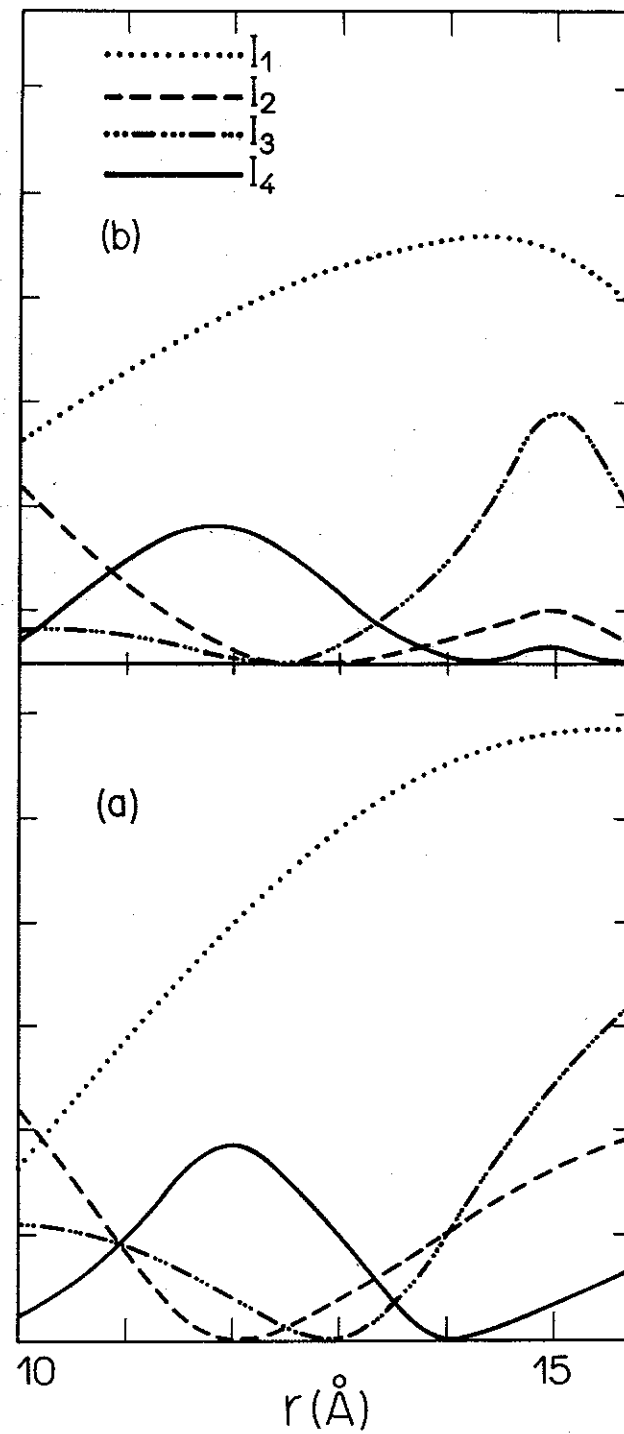


FIGURE 5