The Lower-Temperature Phase of a Nematic Lyomesophase System

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Abstract

The system Na decyl sulfate/water/decanol/Na sulfate, which forms a nematic NL lyomesophase with planar micelles at 298 K, changes to a CG phase at 295 K on cooling. Phase CG studied by X-ray diffraction has a lamellar structure with repetition distance 31.4 Å. Comparison of observed and calculated intensities from a step-function model defines the CG phase as a coagel where anhydrous lamellar aggregates of extended tilted bilayers are dispersed in water. This result gives support to the model of aggregates of micelles in the NL phase previously proposed.

I. Introduction

X-ray diffraction results (Amaral, Pimentel, Tavares & Vanin, 1979; Charvolin, Levelut & Samulski, 1979; Figueiredo Neto & Amaral, 1981) on some specific nematic lyomesophases made of hydrocarbon amphiphile/water/additives (alcohol and/or salt) produced evidence that the so-called (Radley, Reeves & Tracey, 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) NL and NC, respectively, and there has been increasing interest in their study in recent 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 behaviour 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 \( \sim 25 \) 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 had been extensively studied in the type II nematic lyomesophase at room temperature (298 K) (Amaral et al., 1979; Amaral & Tavares, 1980) and because it shows a transition at a suitable Krafft temperature (295 K 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 diameter.

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 vertical, as well as a Debye–Scherrer camera (capillary horizontal), with Cu K\(_\alpha\) (Ni-filtered) radiation with wavelength \( \lambda = 1.542 \) Å and the X-ray beam perpendicular to the capillary axis. The ambient temperature was controlled within 1 K. Relative intensities of the diffraction peaks were obtained by a combination of microdensitometer curves and visual estimates of spot and line intensities using sets of intensity scales (series of exposure-calibrated blackening marks).

III. Results and discussion

Small-angle results obtained in the nematic NL phase at 303 K show a band at \( s^{-1} = 38 \) Å, partially oriented in the horizontal equator direction; the angular aperture defined by the two crescents is \( 40^\circ \) (scattering vector \( s = 2 \sin \theta / \lambda \), \( 2\theta \) being the angle between the...
directions of incidence and scattering). In the lower-temperature phase, which will be called the CG phase, at 291 K, three lamellar reflections appear in the small-angle region, defining a lamellar repetition distance \( d = 31.4 \text{ \AA} \); in a typical result the arcs are preferentially oriented in a direction deviating 10° from the horizontal equator and have an angular aperture of 50°, but the preferred direction and the aperture may vary and a situation of complete rings may occur. Fig. 1 shows microdensitometer curves of the small-angle diffraction lines. The widths of the lines are about the experimental resolution (10°).

Relative peak intensities of the second and third orders were obtained from these curves. The first order is much stronger and easily saturates; the relative intensity between the first order and the average between the second and third orders was obtained by visual estimate of calibrated line intensities. The relative intensities for the three lamellar reflections thus obtained are \( I^0 = 1000, I^2 = 36, I^3 = 31 \). Most of the usual correction factors are negligible for small angle and therefore the effects of peak width, polarization factor, Debye-Waller temperature factor and oblique incidence in the planar film need not be considered. Absorption is not negligible; however, for relative intensities no corrections due to different path lengths in the sample need to be considered because the sample is cylindrical and angles are small. The only important correction factor is the Lorenz factor, coming to \( 1/\sin^2 \theta \) (as for powder Debye–Scherrer diffraction rings). This is equivalent to considering as corrected intensities the values \( I^c = n^2 I^0 \).

Some results for the CG phase were obtained from a sample that was magnetically oriented in the nematic phase, with the magnetic field \( H \) perpendicular to the capillary axis. The lamellar reflections appear then oriented in the equatorial direction when the X-ray beam is parallel to \( H \) (geometry \( GII \)) and are absent when the X-ray beam is perpendicular to \( H \) (geometry \( G_\perp \)). 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 CG phase.

Laue and Debye–Scherrer results from the CG phase showed two strong and well defined rings at \( s^{-1} \) values 4.0 and 4.2 \text{ \AA}, besides weaker lines, a result typical of bidimensional packing of the extended carbon chains; the 002 and 003 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, so that \( I_4 = 0 \). In the higher-angle region for the type II nematic phase only a broad band at \( s^{-1} = 4.6 \text{ \AA} \) appears, typical of disordered paraffin chains.

The small number of lamellar reflections associated with the two high-angle reflections characterize the CG phase as either a gel or a coagel phase (Vincent & Skoulios, 1966). The gel phase is a 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, but there is a direct transition from lyomesophase to a coagel phase.

The area per polar head for the CG phase, assuming homogeneous distribution along the normal to the lamellar planes and infinite planes, can be obtained from (Luzzati, 1968) \( A = 2M_\phi v/N_0 \), where \( M, v \) and \( \phi \) 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 \text{ \AA}^2, extremely high for a gel phase; this indicates that probably a large fraction of the water is outside the lamellar structure, which gives support to the coagel hypothesis.

The length of the amphiphile molecule in the extended configuration (assuming for the polar head the ionic radius 2.3 \text{ \AA} of the sulphate anion) is expected to be about 18 \text{ \AA}. The components of the

Fig. 1. Microdensitometer curves of small-angle diffraction results: (b) CG phase at 391 K; (a) NL phase at 303 K.
system that are in the micelles (amphiphile plus alcohol) correspond to 37% of the volume. A homogeneous distribution of amphiphile and water along the normal to the lamellar plane, with the observed repetition distance, would require an amphiphilic layer thickness $l \approx 12 \, \text{Å}$, which 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 assumed that water is being excluded from the lamellar structure, it is possible to accept smaller $\gamma$ 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 $\gamma \approx 20^\circ$, since the repetition distance is smaller than the length of two extended molecules. Fig. 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.

It is virtually impossible to solve the structure by direct methods from the few reflections observed and without knowing the phases. Instead, a plausible structural model for the electron density profile $\rho(x)$ along the direction normal to the lamellar planes can be used. Expected intensities can then be compared with observed intensities to define the structure of the CG phase better as a function of a suitable parameter of the model. The adopted model for $\rho(x)$, shown in Fig. 3 and described in detail in the Appendix, corresponds to a three-step function, with different levels corresponding to the region where CH$_3$, CH$_2$, polar heads and water are located.

A two-step model simulating polar heads and CH$_3$ is physically meaningful, since electron densities of water and CH$_2$ are very similar. A preliminary analysis was thus performed with such a two-step model. 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. It is seen from the analysis made here that this intensity distribution characterizes the coagel phase as lamellar aggregates with almost anhydrous bilayers. In the case of monolayers with little water between layers, a monotonic decrease of the intensity with the order of reflection is also expected; depending on the amount of water between layers, there may be other intensity relations, as seen in Fig. 4.

The two-step model is already enough to choose between the two extreme possibilities discussed. Calculated intensities as a function of the parameter $r$ (see Fig. 3) can be seen in Fig. 5(a); the values adopted for the other parameters of the model are given in the Appendix.

Since it is not possible to arrive at absolute intensity values, calculated intensities $I_n$ have been normalized to corrected observed intensities $I'_n$ at the first-order reflection. Therefore, normalized calculated intensities $I'_n = KI_n$ were obtained, with $K = I'_1/I_1$. The degree of agreement between calculated and measured values can then be measured through the conventional $R$ discrepancy index considering the structure factors of the four reflections.

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**Fig. 2.** Lamellar structure in the two extreme possibilities: anhydrous bilayers (on the left) and monolayers with water (on 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 $2r/d$. 
With the two-step model, comparison of calculated and observed values requires simultaneously the presence of CH\textsubscript{3} groups at the layer centre and \( l = d \). The definition is rather sharp since, for the parameter \( r = 14 \) Å, \( R \) drops to 8%, while with 13.5 and 14.5 Å one gets \( R \) values of 30 and 16%. Further change in \( r \) leads quickly to \( R \) values as high as 50–60%. The best \( r \) value corresponds to completely anhydrous bilayers (even with small interpenetration of polar heads of adjacent layers) and tilted carbon chains. From the very simple two-step model it is already possible therefore to eliminate the possibility of monolayers with large quantities of water between layers and to define the CG phase as a coagel phase.

To obtain a better adjustment of the layer thickness, calculations have been performed with a three-step function. Fig. 5(b) shows intensities of the four first orders as a function of \( r \). The best value \( r = 14.25 \) Å (also corresponding to \( l = d \)) leads to \( R = 0.07 \). Deviations of 0.25 Å lead to \( R \) values of 14–16% and again further changes in \( r \) increase \( R \) values to 50–60%. Slightly different values (given in the Appendix) for the several fixed parameters of the model have been used in the fitting of two- and three-step functions to test the sensitivity of the fitting to such parameters. The fact that the best values of \( r \) for the two functions are so close give us confidence in the adopted model. It is interesting to remark that the use of a plausible model allows a rather sharp definition of the bilayer thickness, while by direct methods only a very low resolution profile could be expected.

One layer of water between lamellae would mean an \( l \) value at least 3 Å smaller than \( d \), which is not compatible with the results obtained in the comparison of calculated and observed values. It may therefore be concluded that the CG phase is a coagel phase where anhydrous lamellar aggregates of amphiphile are dispersed in water.

In view of these results, an attempt is being made to determine the structure of the pure amphiphile; preliminary results for the pure amphiphile in powder form gave (Bittencourt & Amaral, 1984) \( d_{1001} = 34 \) Å, compatible with the conclusion for the CG phase. The difference in \( d_{1001} \) values might be due to differences in the tilt angle.

In the transition from coagel to nematic phase the repetition distance of 31.4 Å changes to an average distance of 38 Å. 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 by 15 to 20% (Seelig, 1977). These two effects together lead to the expectation of a small decrease (2–9%) in the layer thickness in the \( N \) phase. The observed difference in the distance between lamellae may be attributed to the presence of a water layer between bilayers in the nematic phase.

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

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**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 done by direct methods (see Worthington, King & McIntosh, 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, Tardieu & Taupin, 1972).

The adopted form for the \( \rho(x) \) function shown in
Fig. 3 has the following parameters: $\rho_0$ electron density of the matrix (water), $\rho_1$ electron density of polar heads, with thickness $R_1$, $\rho_2$ electron density of CH$_2$ groups, with thickness $R_2$, $\rho_3$ 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, Blaurok & Engelman, 1971).

The structure factor for one isolated centrosymmetric lamella of thickness $l$ as a function of the scattering vector $s$ is

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

With the adopted electron density there results

$$F(s) = \frac{1}{n^2} \left[ \rho_3 \sin 2\pi R_3 s \right.$$ 

$$+ 2\rho_2 \sin \pi R_2 s \cos \pi(2R_3 + R_2)s \right.$$ 

$$+ 2\rho_1 \sin \pi R_1 s \cos \pi(R_1 + 2R_2 + 2R_3)s].$$

The intensity scattered by $N$ lamellae is

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

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

Calculations performed with the adopted model showed that for $N = 10$ the distortion due to $FI(s)$ is already negligible and the scattered intensity curve shows the typical Bragg peaks. Since the width of observed diffraction peaks indicate $N > 80$, it is enough to calculate $F^2(s)$. The calculated intensities $I_n$ will then simply be $F^2(n/d)$.

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 envelope decays with $R_1$. Fig. 4 shows the expected intensities $I_1$, $I_2$, $I_3$ and $I_4$ as a function of the ratio $2r/d$ assuming $R_1 = 4.6$ Å.

(b) Effect of CH$_3$ groups: two-step model ($\rho_1 = 1$, $\rho_3 = -0.5$, $\rho_0 = 0$). The parameters $R_1 = 4.6$ Å and $r = 16.45$ Å (obtained from the estimated length of an extended molecule) were fixed and 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 $F^2$ become more intense than even orders, and this effect increases with $R_3$. This characteristic has already been discussed 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-step model, can test both the presence of CH$_3$ at the layer center and the layer thickness. Calculated intensities for the first four reflections in the case $R_3 = 2$ Å can be seen in Fig. 5(a).

For the calculations with a three-step function, more exact values for the relative electron densities have been used. The presence of salt is expected to increase $\rho_0$ from 0.33 to 0.35 e Å$^{-3}$; $\rho_2 = 0.27$ e Å$^{-3}$; $\rho_3$ is expected to have a contrast with water three to seven times bigger than $\rho_2$; $\rho_1$ oscillates between 0.3 and 1.5 e Å$^{-3}$ depending on the particular polar head. With $\rho_1 = 0.2$, $\rho_2 = -0.05$, $\rho_3 = -0.27$, $\rho_0 = 0$, and with $R_1$ and $R_2$ fixed, $R_1 = 4.5$ and $R_3 = 2$ Å, calculations have been performed varying $R_3$ and consequently $r$. Results can be seen in Fig. 5(b). As it is not very meaningful to try to adjust so few intensities by changing more than one parameter, no further improvement was tried.

References


