

## On the Existence of Micellar Positional Correlations in a Type I Nematic Lyomesophase: an X-ray Diffraction Experiment

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### Abstract

The nematic type I lyomesophase of K laurate/KCl/water is studied by X-ray diffraction and optical microscopy. X-ray diffraction patterns of samples in very thin capillaries and chemically surface-treated capillaries indicate the existence of a hexagonal array of cylindrical micelles. In normal conditions, where only one oriented band is observed, it is possible to describe the lyomesophase structure as nematic. An analysis of the band width is made by comparing the experimental scattering curves with theoretical expressions obtained from different models. This analysis indicates that micellar positional correlations have to be introduced to explain the experimental results.

### I. Introduction

Lyomesophases that orient spontaneously in the presence of a magnetic field  $H$  have been classified as types I and II depending on whether the phase director orients itself in a direction parallel or perpendicular to  $H$  (Radley, Reeves & Tracey, 1976; Fujiwara, Reeves, Suzuki & Vanin, 1979). They have been characterized as nematic mesophases by observation of their optical textures in a polarizing microscope (Radley & Saupe, 1978*a,b*; Charvolin, Levelut & Samulski, 1979; Charvolin & Hendriks, 1980*a,b*).

When the diamagnetism comes from the hydrocarbon portion of the amphiphile, this classification corresponds to a structure of finite planar micelles for type II and finite cylindrical micelles for type I (Amaral, Pimentel & Tavares, 1978; Amaral, Pimentel, Tavares & Vanin, 1979; Charvolin *et al.*, 1979).

The usual assumption of a homogeneous distribution of micelles in water (Luzzati, Mustacchi, Skoulios & Husson, 1960; Luzzati, 1968) was questioned by Amaral & Tavares (1980) in view of small-angle diffraction studies of a type II lyomesophase. This commonly made hypothesis can be misleading for systems with excess water (the nematic lyomesophases have at least 50 wt% of water). This hypothesis is known to be wrong, for instance, for dilute gel phases, where the measured repetition distance between amphi-

philic bilayers remains constant with increasing amounts of water (Vincent & Skoulios, 1966). Also, phospholipid/water systems are known to incorporate only up to 40 wt% of water between the bilayers; further water addition leads to lamellar aggregates dispersed in the excess water (Ladbroke & Chapman, 1969).

In a previous paper (Figueiredo Neto & Amaral, 1981) (hereafter called paper I), we discussed small-angle X-ray scattering results and optical microscopy observations made with two type I lyomesophases of potassium laurate (called LK) and cesium decylsulfate. These experimental results confirm the model of long cylindrical micelles previously proposed (Fujiwara *et al.*, 1979; Charvolin *et al.*, 1979) (length greater than 500 Å). They suggested also the formation of aggregates of micelles. A typical photographic result (presented in paper I) obtained with mesophase LK (Ni-filtered Cu radiation) had two broad bands with characteristic distances of about 40 Å (outer band *OB*) and 80–190 Å (inner band *IB*).

The results obtained by Charvolin *et al.* (1979) in another type I mesophase with a Laue camera and monochromatic radiation did not exhibit an *IB*. Although the tests carried out to identify the nature of the *IB* (variation of Ni-filter thickness and tube voltage) indicated that the possible contribution of white radiation was not dominant, it was found necessary to repeat the small-angle results with monochromatic radiation.

The non-homogeneous distribution of micelles in water proposed in paper I was strongly supported by the existence of an *IB*. There is, however, other supporting evidence which must be considered. Application of the classical theory of Derjaguin, Landau, Verwey and Overbeek (DVLO) (Verwey & Overbeek, 1948) for the stability of colloids to mesophase LK indicates that (Amaral & Figueiredo Neto, 1982) the cylindrical micelles tend to flocculate. The results obtained by Fujiwara & Reeves (1980) by means of nuclear magnetic resonance in mesophase LK, where a long-range hexagonal micellar ordered phase was identified, could also indicate the existence of intermicellar positional correlations.

In this paper we study mesophase LK under different experimental conditions; capillaries of various thickness and chemically treated surface by means of X-ray diffraction techniques using monochromatic and filtered radiation. Experimental results were obtained using photographic and counter methods. The different interpretations of the diffraction curves are discussed in terms of the usual nematic models and the model of aggregates of micelles.

## II. Theoretical part

For the purpose of this discussion we define an axis  $Z$  at the sample, which is perpendicular to the incident beam and parallel to the photographic-plate plane. The plane which contains the incident beam and is perpendicular to the  $Z$  axis is called the equator.

All the scatterers considered here (rods or lines) are positioned parallel to the  $Z$  axis and the scattering is observed along the equator. It is usually assumed in the literature that the molecules (or micelles) which are parallel to the  $Z$  axis give the principal contribution to the scattering at the equator. This hypothesis was, however, questioned by de Vries (1972), particularly when used to obtain the molecular cylindrical distribution function (m.c.d.f.) of thermotropic nematic liquid crystals from X-ray data. The shape of the m.c.d.f. curves obtained with the usual approach becomes much less acceptable in many situations, especially for the absolute intensity analysis of the scattering data. This deformation is accentuated more at large values of the scattering vector  $s$  (de Vries, 1972). So, in the small-angle limit, this deformation is expected to be not so drastic. Besides this, for the calculation of the m.c.d.f. it is necessary to know the average scattering factor of the scatterers (in our case the micelles) (Falgueirettes & Delord, 1974), which depends on the particular model adopted.

Taking into account the difficulties discussed above for the calculation of the m.c.d.f., the scattered intensity has been calculated theoretically from models and afterwards their characteristic parameters (width and angular position of the principal maximum) compared with those obtained from the experiment. As the position of the equatorial oriented band ( $OB$  - paper I) is in the small-angle region and the analysis is made in terms of relative intensities, the usual procedure was adopted (the scatterers parallel to  $Z$ ). The basic conclusions of the peak diffraction width discussion, from our point of view, are not essentially modified by this assumption.

### Model A

The usual procedure in the analysis of nematic thermotropic diffraction results was proposed by de

Vries (1970). It can be shown (James, 1948) that the diffracted intensity produced by a pair of long lines separated by a distance  $d_A$ , free to move around the  $Z$  axis, is

$$I_A = \alpha[1 + J_0(Hd_A)], \quad (I)$$

where  $H = 2\pi s$ ,  $\alpha$  is a constant related to the number of scatterers in each line and  $J_0$  is a Bessel function of the first kind of zero order. The position of the first maximum is given by the relation

$$2d_A \sin \theta = 1.117\lambda, \quad (II)$$

where  $\theta$  is half of the diffraction angle of the peak and  $\lambda$  the radiation wavelength. The parameter  $d_A$  is interpreted (de Vries, 1970, 1973) as the average distance between the long axes of neighboring parallel molecules.

### Model B

This model (Oster & Riley, 1952) considers a system composed of long particles of cylindrical shape whose dimensions are greater than  $\lambda$ .

Each cylinder is composed of a core of radius  $cR$  ( $0 \leq c \leq 1$ ) of a certain scattering material and a cylindrical shell of thickness  $(1 - c)R$  with a different scattering material ( $R$  = total radius of the particle).

The scattering amplitude of a single cylinder is (Oster & Riley, 1952; Luzzati, 1968; Husson, Mustacchi & Luzzati, 1960; Husson, 1967):

$$A(H) = 2\pi(K1) \frac{Rc}{H} J_1(HcR) + 2\pi(K2) \frac{R}{H} [J_1(HR) - cJ_1(cHR)], \quad (III)$$

where  $K1$  and  $K2$  are factors concerned with the efficiency of the scattering material which makes up the cylinder and  $J_1$  a Bessel function of the first kind and of first order.

The scattered intensity at the equator produced by a system composed of cylinders which are free to occupy any relative positions with the restriction that the closest distance of approach of the axes is  $d_B$  can be written as (Oster & Riley, 1952)

$$I_B = [A(H)]^2 \left\{ 1 - 2\pi\nu d_B^2 \left[ \frac{J_1(Hd_B)}{Hd_B} \right] \right\}, \quad (IV)$$

where  $\nu$  is the density of particle centers in the plane perpendicular to the  $Z$  axis. The radial distribution function of the cylinder axis is zero for interparticle distances smaller than  $d_B$  and is equal to one for distances bigger than  $d_B$ .

### Model C

This model considers  $N$  cylinders located in fixed positions relative to one another. The scattering

intensity at the equator can be written (Oster & Riley, 1952):

$$I_C = \frac{1}{N^2} [A(H)]^2 \sum_{p=1}^N \sum_{g=1}^N J_0(HS_{pg}), \quad (V)$$

where  $S_{pg}$  is the distance between the  $p$ th and  $g$ th cylinder axes.

The peaks appearing in the function  $I_C$  become sharper and closer to the  $2\theta$  predicted by Bragg's law as the aggregation number ( $N$ ) increases.

### III. Experimental

The mesophase LK was prepared by the NMR laboratory of the Instituto de Quimica da USP, according to conventional procedures (Radley *et al.*, 1976; Fujiwara *et al.*, 1979) with the composition given in Table 1. The volume % was obtained by measuring the partial specific volumes of each component (using a picnometer).

The partial specific volume obtained for potassium laurate was  $(0.92 \pm 0.02) \text{ cm}^3 \text{ g}^{-1}$ .

Samples were sealed in glass capillaries with 0.3 (C1), 0.7 (C2), 1.5 (C3) and 2 mm (C4) diameters, both with and without chemically treated surfaces. Three types of treatments were used:

T1 – with sulfochromic solution. The treatment consists of removing all the organic material present at the glass surface (a cleaning treatment);

T2 – with NaOH. The treatment promotes the substitution of the OH groups at the glass surface by ONa groups;

T3 – with  $(\text{H}_3\text{C})_2\text{SiCl}_2$ . The chemical reaction is very efficient and promotes the location of polar  $\text{CH}_3$  groups at the glass surface, which becomes hydrophobic.

X-ray diffraction patterns were obtained by photographic and also counter methods using a small-angle Rigaku–Denki diffractometer. Both  $\text{Cu } K\alpha$  Ni-filtered and monochromatized (LiF asymmetric crystal) radiation were used.

The capillary was always placed in the vertical direction (transmission geometry), with the axis perpendicular to the X-ray beam. At the sample position, the incident beam had a diameter of 0.3 mm. So, only the capillary C1 was completely immersed in the beam

while for the others the beam passed through their central portions only. The exposure times (for the photographic method) were about 24 h, depending on the sample thickness. All results were obtained at room temperature ( $\sim 295 \text{ K}$ ).

The experimental resolution measured from the width at half height of the incident-beam profile was  $(0.20 \pm 0.02)^\circ$ ; its shape could be reasonably fitted to a Gaussian function.

The usual collimation corrections (Hendricks & Schmidt, 1967, 1973) applied to experimental small-angle scattering curves obtained from a Kratky camera or any geometry employing slits need not be done with pin-hole geometry. Resolution corrections were necessary for the analysis of the full width at half maximum of the diffraction peak. To obtain the intrinsic width of the  $OB$  it was assumed that the experimental intensity was the convolution of the theoretical intensity with the resolution function, all with Gaussian shapes. The measured intensity was corrected by means of the subtraction of the background and the parasitic scattering.

All the samples were also analyzed by optical microscopy, using a Wild microscope with crossed polarizers.

### IV. Experimental results and discussion

In Fig. 1, the diffraction pattern of the mesophase LK in capillary C3 with monochromatic  $\text{Cu } K\alpha$  radiation is presented (line focus, slit-collimation geometry). By

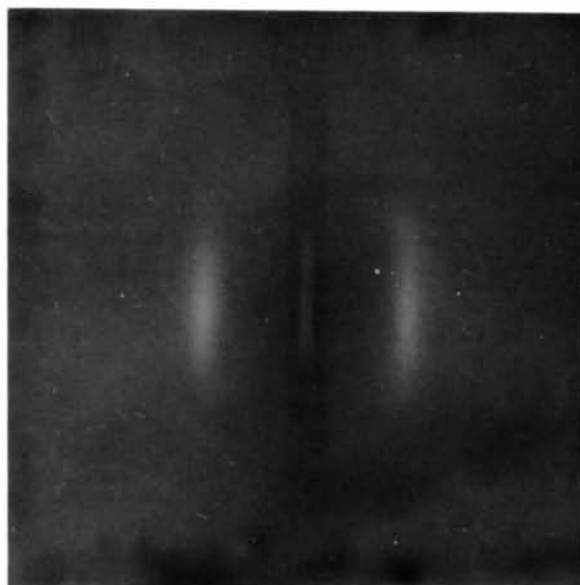


Fig. 1. Small-angle X-ray result with the LK sample in a 1.5 mm thick capillary (monochromatic  $\text{Cu } K\alpha$  radiation line focus). The capillary was set up in the vertical direction in the plane of the figure.

Table 1. Composition in weight % and volume % of the lyomesophase LK

	wt%	vol. %
K laurate	$34.50 \pm 0.06$	$33.2 \pm 0.7$
KCl	$3.00 \pm 0.01$	$1.4 \pm 0.1$
$\text{H}_2\text{O}$	$62.5 \pm 0.1$	$65.5 \pm 1.3$

comparing this pattern, where only one band is observed, with those of paper I the nature of the *IB* is definitively demonstrated; it is made up essentially of white radiation. So, our results agree qualitatively with those obtained by Charvolin *et al.* (1979) for type I mesophases. Collimation corrections not made in this experiment will not modify the main conclusion concerning the *IB*.

At this point, the model of aggregates of micelles proposed in paper I must be reviewed since one of its experimental findings has been shown to be false. Therefore, the question of possible positional ordering in type I lyomesophases will be discussed on the basis of evidence obtained from the position and width of the *OB*. The same procedure was previously adopted for type II lyomesophases (Amaral & Tavares, 1980).

To minimize the exposure times for some experiments Ni-filtered radiation was used, so that the inner bands visible in the figures are due to the white radiation.

Diffraction patterns obtained from the sample of LK in capillaries *C1* (two weeks after preparation) (Fig. 2) are composed of Bragg points in the *OB* region and weak lines with a characteristic distance  $1/\sqrt{3}$  times the characteristic distance of the Bragg points. The hexagonal lattice parameter obtained was  $(46.4 \pm 0.5) \text{ \AA}$ . Thus the surface orientational effects in thin capillaries are very intensified. The existence of the new diffraction indicates the presence of microdomains of a hexagonal micellar order. The preferred equatorial orientation of the Bragg points in the *OB* region indicates that the micellar axes are oriented preferentially parallel to the capillary axis.

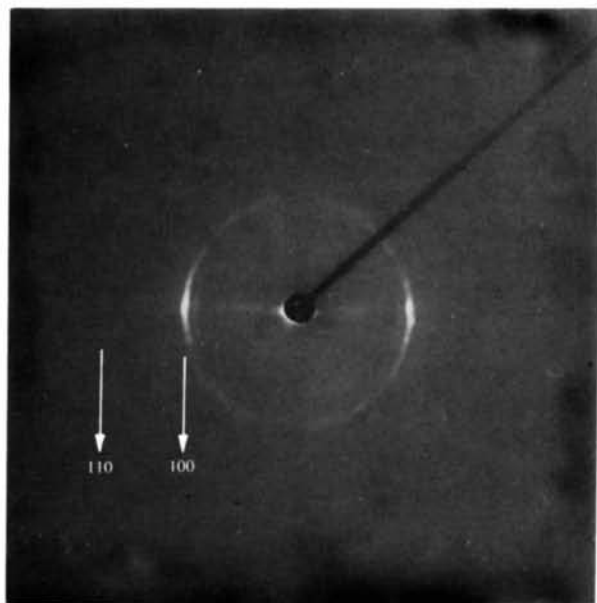


Fig. 2. Small-angle X-ray result with the LK sample in a 0.3 mm thick capillary placed in the vertical direction in the plane of the figure.

Treatment *T1* in capillary *C2* and treatment *T2* in capillaries *C4* do not modify the usual (paper I) diffraction patterns. Thus, no organic deposits (removed with *T1*) could be responsible for the surface effect. Also, the substitution of the hydrogen by sodium at the surface does not modify the wall effect. Treatment *T3* in capillaries *C2*, however, yields Bragg points in the *OB* region and weak points with a characteristic distance  $1/\sqrt{3}$  times the *OB* Bragg point one (Fig. 3). The hexagonal lattice parameter obtained from these diffractions was  $(48.8 \pm 0.6) \text{ \AA}$ . The hydrophobicity of the treated surface favors the formation of microdomains of hexagonal micellar order. This fact can probably be connected to the segregation of the water (not directly bounded to the micelles) from the neighborhood of the walls, increasing the intermicellar interaction.

To verify the nematic characteristics of these mesophases by means of an X-ray diffraction experiment, we obtained for a wall-oriented sample (capillary *C3*) the scattered intensity curve at the equator. Ni-filtered Cu radiation, a point focus with a pin-hole collimation geometry and a linear detector sensitive to the position coupled to a multichannel were used. The remaining white radiation was practically eliminated by using a pulse-height discrimination procedure. Fig. 4 shows the measured intensity already corrected as described in § III (subtraction of the background and the parasitic scattering).

The band is located at the  $2\theta$  position  $(2.04 \pm 0.02)^\circ$ , *i.e.*  $s^{-1} = (43.3 \pm 0.5) \text{ \AA}$ , and the intrinsic full width at half maximum (already corrected for the experimental resolution) is  $\Delta = (0.40 \pm 0.02) \text{ \AA}$ . These

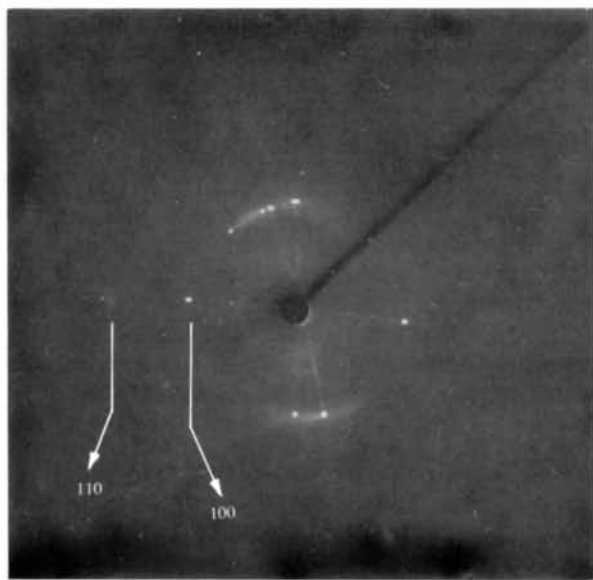


Fig. 3. Small-angle X-ray result with the LK sample in a 0.7 mm thick quartz capillary treated with  $(\text{H}_3\text{C})_2\text{SiCl}_2$ . The capillary was in the vertical direction in the plane of the figure.

parameters agree, within the experimental errors, with the ones obtained in many other experiments using the counter and the photographic detection methods with mesophase LK in our laboratory.

As the scatterers and their reciprocal space have cylindrical symmetry, it is possible to calculate from the experimental scattered intensity the cylindrical Patterson function (Vainshtein, 1966) in the plane perpendicular to the micelle axes. Using this approach, the mean distance between the axes of neighboring parallel micelles was found to be given by  $d_p = (47.0 \pm 0.5) \text{ \AA}$ .

If there is a homogeneous distribution of the micelles in the water, the volume concentration can be written in terms of the radius of the micelle and the mean intermicellar distance ( $d$ ) (Guinier & Fournet, 1955):

$$\varphi_h = \frac{\pi}{2\sqrt{3}} \left[ \frac{2R}{d} \right]^2. \quad (\text{VI})$$

The value of the radius corresponding to  $d_p$  is given by  $R_p = 14.2 \text{ \AA}$  ( $\varphi_h = 0.332$ ).

The length of an extended carbon chain of K laurate (Leibner & Jacobus, 1977) is about  $14.2 \text{ \AA}$  and the polar head has a diameter of about  $3 \text{ \AA}$  (Waddington, 1959), so the extended molecule is  $17 \text{ \AA}$  long.

The values of the lyomesophase micellar radii usually obtained from X-ray data (Luzzati *et al.*, 1960; Husson *et al.*, 1960) are roughly the same as the length of the amphiphilic molecule, even taking into account possible *gauche* conformations.

The value of  $R_p$  is a little smaller than the length of an extended molecule. This may be due to the use of expression (VI) which considers the micelles to be of infinite extent. In the actual system, we can have the same value of  $\varphi_h$  for bigger values of the radius, with the remaining water located among the micelles along their long axes.

Thus, these values of  $d_p$  and  $R_p$  could characterize a nematic structure for mesophase LK. This approach,

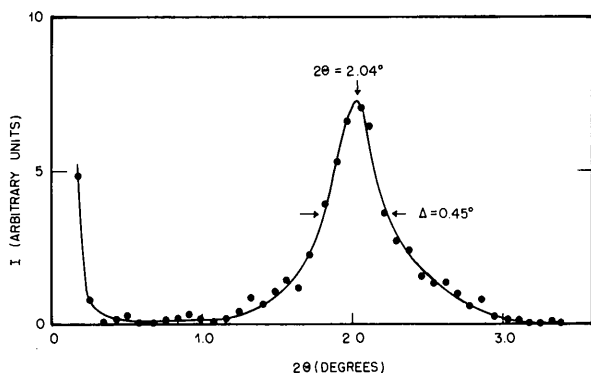


Fig. 4. Experimental diffracted intensity  $I$  after subtraction of the background and the parasitic scattering as a function of the scattering angle  $2\theta$ . The LK sample in a 1.5 mm thick capillary was placed in the vertical direction.

however, does not take the width of the diffraction peak into account.

## V. Discussion of the models

### Model A

In Fig. 5 the scattered intensity  $I_A$  (expression I) is shown as a function of  $2\theta$ . The value of  $d_A$  obtained from expression (II) is  $48.6 \text{ \AA}$  and the radius (expression VI with  $\varphi_h = 0.332$ ) is  $14.7 \text{ \AA}$ . The width at half maximum is about  $0.93^\circ$ .

The value of  $d_p$  is compatible with model A and the resulting value of  $R$  seems reasonable. The width of the band, however, is about twice the experimental value.

### Model B

The calculated values of the electronic densities of the parafinic core ( $\rho_p$ ) and of the water-salt bath ( $\rho_b$ ) are  $(0.275 \pm 0.005) \text{ e \AA}^{-3}$  and  $(0.35 \pm 0.01) \text{ e \AA}^{-3}$  (Husson, 1967; Figueiredo Neto, 1981), respectively.

The value of the electronic density of the polar group ( $\rho_s$ ), calculated from the measured partial specific volume of the K laurate, is  $(0.60 \pm 0.02) \text{ e \AA}^{-3}$ . From geometrical considerations of the polar group, it is possible to show (Figueiredo Neto, 1981) that  $\rho_s$  is in the range  $(1.45 \pm 0.05) \text{ e \AA}^{-3}$  to  $(0.27 \pm 0.01) \text{ e \AA}^{-3}$ .

On setting  $K1$  equal to unity,  $K2$  shows how much bigger the contrast  $|\rho_s - \rho_b|$  is compared with the contrast  $|\rho_b - \rho_p|$ . We set  $K2 = 4$  and it was observed that to within an uncertainty of 40% [*i.e.*  $K2 = (4 \pm 2)$ ] the position and width of the  $OB$  were practically unchanged. Values of  $c$  were chosen between 0.62 and 0.82, which correspond to a polar shell of thickness 3.8 to 1.8  $\text{ \AA}$  for a radius of about 10  $\text{ \AA}$ . It was verified that for values of  $c$  within this range the position and width of the diffraction peak are practically unchanged (within an uncertainty of 2%). For the calculation we set  $c = 0.82$ .

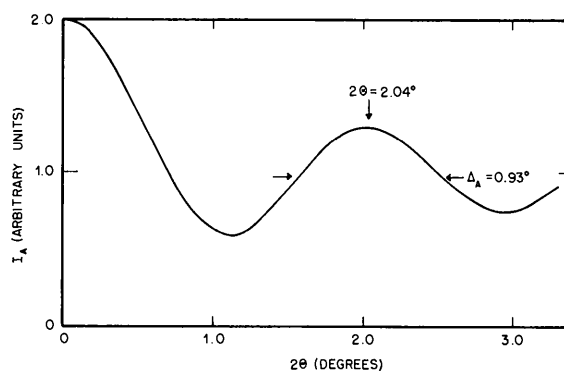


Fig. 5. Theoretical diffracted intensity  $I_A$  as a function of the scattering angle  $2\theta$ : model A.

If we assume a homogeneous distribution of long micelles (of infinite extent) in water, the density of cylinder axes ( $\nu$ ) can be related to the amphiphilic volume concentration ( $\phi_h$ ) and the micellar radius. At this level of approximation,  $\phi_h$  can be interpreted as the ratio of the area occupied by the amphiphile and the total area in the plane perpendicular to the micellar axes, i.e.  $\nu = \phi_h / \pi R^2$ .

The closest distance of approach between the micellar axes ( $d_B$ ) is at least  $2R$  (this value does not take into account a solvation shell of water bound to the micelles).

For  $d_B = 2R$ , the position of the maximum of  $I_B$  agrees (Fig. 6) with the experimental value for  $R = 10.2 \text{ \AA}$ . The width at half maximum of this curve is  $1.62^\circ$ . The mean intermicellar distance obtained from expression (VI) is  $33.8 \text{ \AA}$ , which differs by about  $13 \text{ \AA}$  from that obtained from the Patterson calculation.

The value obtained for the micellar radius, compared with the length of an extended K laurate molecule is very small. It is highly improbable that the carbon chains can be contracted by means of *gauche* conformations to give such a small value for the cylinder radius. For values of  $d_B$  greater than  $2R$ , which take into account a solvation shell of bound water molecules around the micelles, the resulting values for  $R$  are still smaller.

Another difficulty with this model is the width at half maximum of the diffraction peak which comes out to be about four times the experimental value.

### Model C

The model of aggregates of micelles proposed in paper I identifies the *OB* with diffraction from an ordered micellar structure. Since the *OB* is sharp and well defined, and taking into account the diffraction patterns of mesophase LK discussed in § IV (Figs. 2 and 3), it is reasonable to identify (in a first approach) the *OB* with the 100 reflection of a hexagonal array of micelles. From the peak position, the value of  $d_{100} = (43 \pm 1) \text{ \AA}$  is obtained corresponding to a lattice parameter  $a = (50 \pm 1) \text{ \AA}$ .

The number  $N$  of scattering cylinders and the dimension of the aggregate of micelles are related to the

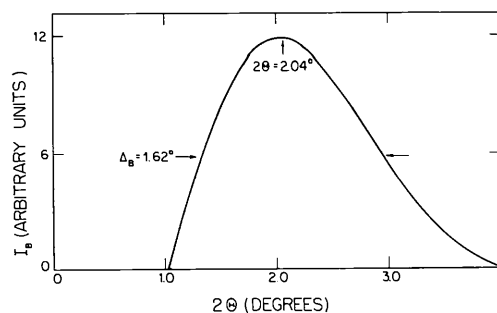


Fig. 6. Theoretical diffracted intensity  $I_B$  as a function of the scattering angle  $2\theta$ : model B.

width at half height of the diffraction peak. Scherrer's expression (Guinier, 1956) can be used to evaluate the dimension of the aggregate in the direction normal to the (100) plane. This approach gives in reality a minimum size for the aggregates. The possibility of defects in the structure, which could also be responsible for a broadening of the peak, is not taken into account.

The corrected width at half height of the *OB* introduced in Scherrer's expression corresponds to about five scattering planes. It is assumed that the aggregates themselves have the form of the unitary cell of the hexagonal lattice. Then, in this picture, five scattering planes correspond to an aggregation number  $N \sim 25$ .

In this model which considers an inhomogeneous distribution of micelles in water, expression (VI) cannot be used. Thus, a value for  $R$  has to be estimated independently. Husson *et al.* (1960), studying the lyomesophase of K laurate/water (middle soap phase) concluded that the radius of the cylinder is practically independent of the amphiphilic concentration. It is expected that the radius of the middle soap phase gives a good approximation to the radius of the micelle in the nematic phase. The value of  $R$  extrapolated to room temperature (Husson *et al.*, 1960) with the evaluated errors is  $(17 \pm 1) \text{ \AA}$ , which is about the length of an extended K laurate molecule. The values of  $K1$ ,  $K2$  and  $c$  are the same as used in model B.

The position and width of the 100 peak depend on the number of micelles in the aggregate. For an aggregate with  $N = 625$  (i.e. dimensions in the plane normal to the micellar axis of about  $1000 \text{ \AA}$ ), the position of the 100 peak is the same as that predicted by Bragg's law. The full width at half maximum of the 100 peak obtained from the curve  $I_C$  for  $N = 25$  is  $0.37^\circ$ .

With the parameters  $N = 25$ ,  $R = 17 \text{ \AA}$ ,  $c = 0.82$ ,  $K1 = 1$  and  $K2 = 4$ , it was possible to proceed by adjusting the lattice parameter until the position of the calculated 100 peak coincided with the experimental value (Fig. 7). A Debye-Waller exponential (with a

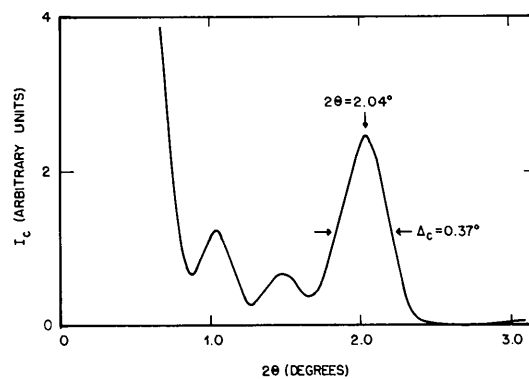


Fig. 7. Theoretical diffracted intensity  $I_C$  as a function of the scattering angle  $2\theta$ : model C.

displacement factor of  $2 \text{ \AA}$ ) was used to take into account the thermal agitation of the scatterers. The adjusted lattice parameter  $a = 47.5 \pm 0.5 \text{ \AA}$  is in very good agreement with the value obtained from the Patterson-function calculation. Inside the aggregates, the lipid volume concentration is  $(0.46 \pm 0.07)$ . The value of  $a$ , obtained by direct application of Bragg's law, differs by about 5% from the adjusted one.

The value of the adjusted parameter lies between that obtained from the diffraction patterns of mesophase LK in chemically treated surface glass capillaries ( $T3$ ) and that found from very thin capillaries.

By comparing the theoretical scattered intensity (Fig. 7) with the experimental results (Fig. 4) we see that the width of the band fits well. There are, however, some obvious discrepancies. There are many peaks for  $2\theta < 2.04^\circ$  in Fig. 7 not present in the experimental pattern and also there is a difference between the calculated and observed widths of the scattering near  $0^\circ$ . It is expected that the profile of the theoretical diffracted intensity will be modified when correlations among different aggregates are introduced. Since the width of the  $OB$  is essentially determined by the interference function of the micelles inside one aggregate, we believe that the interaggregate correlations will not drastically affect the width of the  $OB$ .

The 110 peak of the hexagonal array is not seen in our experiment (Fig. 4). Its intensity, obtained from  $I_C$ , is about  $\frac{1}{2}$  of the 100 intensity. To study the dependence of the relative intensities of the two peaks on the parameters of the model, calculations have been performed varying their values in the intervals  $13 < R < 17 \text{ \AA}$ ,  $0.62 < c < 0.82$  and  $2 < K2 < 6$ .  $I_{100}/I_{110}$  increases for increasing values of  $c$  and decreasing values of  $K2$  and  $R$ . Changes in  $K2$  and  $c$  may lead to  $I_{100}/I_{110} = 3-6$  while  $R = 15 \text{ \AA}$  corresponds to  $I_{100}/I_{110} \simeq 6$ .

Therefore, the non-appearance of the 110 peak does not imply the complete failure of the model. Furthermore, any defect in the structure and larger thermal agitation would act to reduce its intensity preferentially.

#### Comparison between the models

The results obtained with model  $B$  and a radial distribution function typical of a gas show clearly the necessity of introducing some degree of positional correlation between the micelles.

The results obtained with models  $A$  and  $C$  show that a local correlation among first neighbors, typical of a liquid, is not enough to explain the width of the band. Therefore, positional correlations must be extended to intermediate distances. This positional correlation does not directly imply an inhomogeneous distribution of the micelles in water. This point could only be settled by an independent determination of the micellar radius.

Model  $C$ , assuming an inhomogeneous distribution of micelles in water (the formation of aggregates of

micelles) introduces a strong positional correlation at relatively short distances. This model which explains consistently the position and width of the experimental band is however an extreme case of micelle correlation. The intrinsic inhomogeneity of the model is a function of the assumed micellar radius value.

An alternative approach would be to reduce the correlation at short range but to extend it over longer distances. The positional correlation may be introduced in model  $B$  by means of a convenient radial distribution function, different from the one used for obtaining expression (IV). However, to improve the model in this direction, it would be necessary to have more accurate knowledge of both the micellar radius and the micellar scattering factor.

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## Bravais Classes for Incommensurate Crystal Phases

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### Abstract

A full classification is given of the Bravais classes of lattices of symmetry groups of incommensurate crystal phases with an internal (additional) dimensionality  $d$  lower than four. These Bravais classes form the basis for the derivation of superspace groups needed for the symmetry classification of incommensurate crystal phases. By means of examples it is indicated how the information contained in the various tables can be extracted and used, for example, for the derivation of superspace groups.

### I. Introduction

An incommensurate crystal is characterized by the occurrence of at least four periodicities, three of which describe a usual crystal structure, whereas the additional ones are incommensurate with the former ones. Because of the incommensurability there is no three-dimensional lattice translation symmetry. It has been shown, however, that nevertheless the appropriate symmetry group for such a case is a crystallographic space group, not in three but in  $3 + d$  dimensions (de

Wolff, 1974, 1977; Janner & Janssen, 1977), a so-called superspace group. The additional dimension can be interpreted as an internal degree of freedom.

For the simplest case of one additional dimension, the inequivalent  $(3 + 1)$ -dimensional superspace groups have been tabulated together with the corresponding classes of Bravais lattices (de Wolff, Janssen & Janner, 1981). However, there are also examples of crystal phases with an internal dimensionality higher than one. Since it has been shown that in general  $(3 + d)$ -dimensional superspace groups are useful for the classification and for the structure analysis of three-dimensional crystal phases (e.g. Yamamoto, 1982), it is of relevance to investigate these higher-dimensional superspace groups, also. The number of superspace groups, however, increases rapidly with increasing dimension and easily exceeds the number of known incommensurate crystal phases. Therefore, it does not seem to make sense to work out a complete list.

The number of Bravais classes on the other hand is much more restricted. Moreover, they form the basis for the determination of superspace groups and provide a useful framework for their classification. In the present paper we discuss the general theory and give a derivation of a complete list of classes with internal dimension up to three.