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LYOTROPIC "NEMATIC" LIQUID CRYSTALS

by

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MODEL OF AGGREGATES OF MICELLES IN TYPE I LYOTROPIC

"NEMATIC" LIQUID CRYSTALS

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A model of aggregates of cylindrical micelles is quantitatively developed; scattering curves are obtained with counter method and theoretical expressions for the diffracted intensity are adjusted to the experimental results for the ternary system K laurate/KCl/water. The usual hypothesis of homogeneous distribution of micelles in water is abandoned and the inner and outer bands explained as originated from characteristic distances between respectively small aggregates with $N \sim 3-4$ micelles and between micelles in large aggregates with $N \sim 100$ micelles and an hexagonal lattice parameter of $(49.9 \pm 0.5) \text{ \AA}$.

I. INTRODUCTION

Lyotropic liquid crystalline phases are formed by mixtures of two, three or more substances, one of which, at least, with amphiphilic properties. It is convenient to classify these lyomesophases in two groups, regarding their behavior in presence of a magnetic field \vec{H} : the "conventional" lyomesophases, which do not spontaneously orient in the field and the "nematic" lyomesophases which do spontaneously orient in presence of \vec{H} , although with relaxation times much greater

than for thermotropic nematics.

The structures of "conventional" lyomesophases were determined in binary and ternary systems mainly by the work of Luzzati and co-workers (1960,1968) and Ekwall and co-workers (1975). The more common structures are the neat soap, or lamellar structure, with the molecules of amphiphile arranged in extended bilayers intercalated by water layers and the middle soap, with the amphiphilic molecules forming cylindrical micelles hexagonally packed in a water matrix. To determine parameters such as bilayer thickness and cylinder radius, the hypothesis of homogeneous distribution of the micellar units in water is usually made.

Lawson and Flautt (1967) obtained a lyotropic system composed by Na decyl sulfate/decanol/water/Na sulfate which spontaneously orient in presence of \vec{H} . Other lyomesophases with this property have been afterwards developed; NMR studies in this kind of magnetically oriented lyomesophases (Radley et al., 1976; Fujiwara et al., 1979) made it possible to classify them in type I and type II, depending on whether the phase director orients parallel or perpendicular to the field. The two types can be identified by the NMR spectra obtained with sample spinning about on axis perpendicular to \vec{H} , since type I mesophases do not preserve their orientation in this condition while type II do preserve it. The characterization of these mesophases as "nematics" was made by observation of its optical textures in a polarized microscope (Charvolin et al., 1979, Radley & Saupe, 1978 a,b; Charvolin & Hendrikx, 1980 a,b), which resemble nematic ones.

Amaral et al. (1978 a,b, 1979) studied a type II lyomesophase by small angle X-ray scattering, proposing a model

of finite planar micelles, in the form of platelets, surrounded by water. Further results in the same system (Amaral & Tavares, 1980) and in the gel phase (Amaral, 1981) were explained supposing non homogeneous distribution of micelles in water and formation of lamellar aggregates intercalated by the excess water.

The usual hypothesis of homogeneous distribution made in the interpretation of the diffraction patterns of conventional lyotropic mesophases can be misleading for systems with excess water (the "nematic" mesophases have at least 50 wt% of water). In a very interesting experiment, Vincent and co-workers (1966 a,b,c) studied the diluted gel phase of the potassium stearate-water system. The measured repetition distances between amphiphilic bilayers for increasing amounts of water remains approximately constant, showing that the excess water was not distributed homogeneously among the bilayers.

The water in lyotropic mesophases is directly involved in the interaction between polar groups of the amphiphilic molecules and also in the hydration of the salt (when it is present), and the counter-ions; the bound water is called solvation water (Ekwál, 1975). So, the water molecules participate directly in the process of stability of the systems composed by micelles.

In a previous paper (Figueiredo Neto & Amaral, 1981) (hereafter called paper I), we discuss small angle X-ray scattering results and optical microscopy observations done with two type I lyomesophases of potassium laurate and cesium decylsulfate in several experimental conditions: samples in different sample-holders and submitted to electric and magnetic fields. These experimental results with magnetically oriented samples confirm the model of long cylindrical micelles previously

proposed (Fujiwara et al., 1979; Charvolin et al., 1979) (length bigger than 500 \AA) and also indicate the existence of aggregates of micelles separated by the excess water. The analysis of the diffraction patterns is made assuming non homogeneous distribution of micelles in water. A typical photographic result obtained with the mesophase of potassium laurate (LK) in a quartz capillary of 0,7 mm diameter has two bands with characteristic distances of about 40 \AA (outer band - OB), associated to the repetition distances between micelles inside the micellar aggregates and 100 \AA (inner band - IB), associated to the mean distance among aggregate centers. The same mesophase in a capillary of 2 mm diameter presents only IB.

Recent experiments with type I mesophases in chemically treated surface capillaries and samples in the range of temperature of 20°C to 60°C (using photographing technique) (Figueiredo Neto, 1981) confirm the existence of aggregates of micelles. The relations among the characteristic distances obtained from the diffraction patterns indicates that within the aggregates the micelles are hexagonally packed; the aggregates could be thought as microdomains of the middle soap phase order. Depending on the experimental conditions, different sizes of aggregates exist.

As discussed in paper I, surface effects favour the formation of aggregates and in particular, for the mesophase of potassium laurate in a capillary of 0.7 mm diameter, these aggregates of cylindrical micelles are oriented preferentially with the cylindrical axes parallel to the capillary axis.

In paper I the diffraction patterns were obtained by photographing technique. In this paper the model of aggregates of micelles is quantitatively developed; scattering curves are

obtained with a counter method and theoretical expressions for the diffracted intensity are adjusted to the experimental results for the ternary system (K laurate/KCl/water) called LK.

The formation of such aggregates is probably connected to a flocculation process, rather known in colloids. Sparnaay (1959) studied theoretically the interaction between two colloidal particles of cylindrical shape in an ionic bath in terms of the competition of coulombian repulsive and van der Waals attractive forces. This system resemble lyotropic systems of amphiphilic compounds because the surface of the micelles are composed by ionizable groups (responsible for the repulsive interaction) and in their core there are the hydrocarbon chains (responsible for the attractive interaction) (Figueiredo Neto, 1981). The stability of the system is analysed by composing the two forces and for highly screened systems (due to the hydrated counter-ion or the hydrated ions of the salt) there is flocculation, i.e., the attractive interaction is bigger than the coulombian repulsion and aggregates of particles are formed (Sparnaay, 1959).

II. THEORETICAL PART

Scattering amplitude of aggregates of cylinders.

The basis of this formalism was developed by Oster and Riley (1952). They considered a system composed by long particles of cylindrical shape whose dimensions are longer than the wavelenght of the incident radiation. The expressions for the scattered intensity are obtained considering the cylindrical axis perpendicular to the incident and scattered beam. This hypothesis was questioned by de Vries (1972), particularly if

absolute intensity analysis are to be done. However, in the present paper we will follow the conventional procedure, making the analysis in terms of relative intensities.

In a first step the scattering amplitude is obtained and in a second one the interference function is constructed.

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

The scattering amplitude of a single cylinder is obtained by summing the contributions of each part of it, weighted by factors relative to the efficiency of the scattering materials, resulting (Oster & Riley, 1952)

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

where $\vec{H} = 2\pi \vec{s}$, \vec{s} is the scattering vector, $(K1)$ and $(K2)$ are the weights of each scatterer and J_1 the Bessel function of first kind and first order.

Considering now N cylinders packed with their axes normal to the incident beam and located in fixed positions relative to one another, the theoretical scattered intensity ($I_T(H)$) can be written (Oster & Riley, 1952)

$$I_T(H) = \frac{1}{N^2} [A(H)]^2 \sum_p^N \sum_q^N J_0(HS_{pq}) \quad (II)$$

where S_{pq} is the distance between the p th and the q th cylinder axes and J_0 is the Bessel function of first kind of zero order. Expression II is the product of the square of the

structure factor of a simple cylinder $[A(H)]^2$ by a interference function represented by the double summation.

The symmetry of the lattice is introduced in expression II by the term S_{pq} . The peaks appearing on the function $I_T(H)$ became sharper and closer to the 2θ (scattering angle) predicted by the Bragg's law as the aggregation number (N) increases.

Introducing in expression II a Debye-Waller term to take into account some thermal agitation of the system:

$$I_T(H) = \frac{1}{N^2} [A(H)]^2 \sum_p^N \sum_q^N J_0(HS_{pq}) \exp(-\bar{a}^2 H^2) \quad (III)$$

where \bar{a} is the Debye-Waller factor, related to the mean displacement of the scaters.

The approach here used for obtaining $A(H)$ is usually done in the analysis of the X-ray diffraction patterns with conventional lyotropic liquid crystals in the middle soap phase (Luzzati, 1968; Husson, 1960,1967).

In conventional lyomesophases the intensity of the Bragg reflections is obtained directly from $[A(H)]^2$ since the interference function reduces to sharp peaks for large N values.

In this paper $I_T(H)$ is calculated for various values of N because for "nematic" lyomesophases there is not extended long range order.

III. EXPERIMENTAL

The mesophase LK was prepared by the NMR laboratory of the Instituto de Química da USP, according to conventional procedures (Radley et al., 1976; Fujiwara et al., 1979), with

compositions given in Table 1.

The volume % were calculated assuming: 1.0 g/cm³ for the density of the water in the mesophase; complete dissociation of the salt in ions K^+ and Cl^- of radius 1.33 Å and 1.81 Å (Kaye & Laby, 1973) respectively; a volume of 296.4 Å³ (Leibner & Jacobus, 1977) for the parafinic chain of the molecule of potassium laurate and the polar group composed by two spheres of radius 1.33 Å (K^+) (Kaye & Laby, 1973) and 1.58 Å (COO^-) (Waddington, 1959). The effective densities obtained with this approach for the salt and K laurate are 3.6 g/cm³ and 1.2 g/cm³ respectively.

	wt%	vol. %
K laurate	34.49 ± 0.06	31 ± 2
KCl	2.94 ± 0.01	0.91 ± 0.05
H ₂ O	62.6 ± 0.1	68 ± 3

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

Samples were sealed in capillaries of quartz with 0.7 mm diameters (C2 of paper I) and pyrex glass with 2 mm diameter (C4 of paper I). The diffraction patterns obtained by photographing technique (paper I) present bands preferentially oriented in the horizontal equator for both capillaries, thus assuming the applicability of expression III.

X-ray diffraction curves were obtained with a photomultiplier detector using a small angle Rigaku-Denki diffractometer with CuK_{α} radiation (Ni filtered) in a transmission geometry with point focus. The capillaries were vertically placed and the detector moved in the horizontal plane. The incident

beam does not embrace the capillaries, being located in their central part.

The experimental resolution measured from the width at half height of the direct beam profile is $(0.20 \pm 0.02)^\circ$; its shape can be reasonably fitted to a gaussian function.

The sample were also analysed by optical microscopy, using a Wild microscope with crossed polarizers. All results were obtained at room temperature ($\sim 22^\circ\text{C}$).

The measured intensity (I_m) was corrected by through the following expression:

$$I_c(s) = (I_m(s) - I_p(s) \cdot Tr) - BG (1 - Tr) \quad , \quad (IV)$$

where $I_c(s)$ is the corrected intensity, Tr the sample transmission, I_p the parasit scattering and BG the background.

The measured BG was (0.54 ± 0.02) counts/s and the evaluated transmission $Tr = 0.48$.

IV. RESULTS AND DISCUSSION

A) Initial characterization of the aggregates

The model of aggregates of micelles proposed in paper I identifies IB with the distances among aggregates of micelles and OB with the characteristic distances between micelles inside the aggregates. Fig. 1 (a and b) shows the diffraction patterns (I_m) obtained with the mesophase LK in capillaries C2 and C4 respectively; a weak OB for C4 can be detected.

To proceed to a quantitative description of the

model of aggregates of micelles the hypothesis is therefore made that OB and IB can be analysed independently and their intensities can be added. The justification for this procedure is the experimental observation (paper I) that the relative intensities of OB and IB vary with sample thickness and no unique structure model could be found to be responsible for both bands.

Since OB is sharper and well defined it can be identified in a first approach to the 100 reflection of an hexagonal array of micelles; from the peak position at $2\theta = (2.03 \pm 0.02)^\circ$ the value $d_{100} = (44 \pm 1) \text{ \AA}$ is obtained, corresponding to a parameter for the hexagonal lattice $a = (51 \pm 1) \text{ \AA}$.

The number N of scattering cylinders and the dimension of the aggregate of micelles are related to the width at half-height of the diffraction peak. For a first estimate of the aggregation number N , Scherrer's expression (Guinier, 1956) can be used to evaluate the dimension of the aggregate in the direction normal to the 100 plane, admitting that the aggregate is symmetrical in the plane normal to the cylinder axes. This approach gives in reality a minimum size for the aggregates, since the possibility of defects in the structure, which could also be responsible for a broadening of the peak, is not being taken into account.

To obtain the experimental width of OB , the IB contribution under OB was estimated in two limiting curves, that can be seen in Fig. 2, where the corrected intensity I_c has been provided as a function of 2θ .

To obtain the intrinsic width Δ_c of the diffraction peak it was admitted that the measured intensity (I_c) is the

convolution of the theoretical intensity with the resolution function, all with gaussian shapes. This Δ_c value is $(0.17 \pm 0.02)^\circ$, with the error obtained from the two limit curves under OB.

Scherrer's expression (Guinier, 1956) given then an aggregation number $N \sim 100$, corresponding to about 10 scattering planes.

An immediate conclusion is that these aggregates are not the responsible for IB, because the mean distance among them is greater than 500 \AA and cannot be detected in the present experiment. So, two different types of aggregate are related to the two bands.

Since the diffraction patterns obtained in magnetically oriented samples (paper I) reveal that the aggregates (at least the responsible for IB) themselves have cylindrical symmetry, it is assumed that they have the form of the unitary cell of the hexagonal lattice.

The value $N=121$ is chosen for the adjustment of OB, and corresponds to an hexagonal lattice with 11 cylinders in one dimension.

B) Determination of the micelle radius (R) and analysis of the constants (K1) and (K2)

The values of R, K1 and K2 were determined separately in order to keep to a minimum the parameters in the adjustment of I_T .

Husson and co-workers (1960), studying the binary conventional lyotropic system of potassium laurate/water concluded that in the range of concentration of the amphiphilic of 48wt% to 60wt% (constant temperature - middle soap phase), the radius

of the cylinder and the surface per polar group (S) are practically constant. The concentration of lipid in the ternary LK mesophases is about 35 wt%. In terms of the phase diagram of the binary system (Ekwal, 1975), this concentration (for temperatures of about 22°C) is in the coexistence region of the middle soap and the isotropic phase. The addition of the salt to the binary system makes it possible the existence of the "nematic" phase. So, it is expected that the radius (and S) of the middle soap phase give a good approximation to the radius (and S) of the micelle in the "nematic" phase. The value of R extrapolated to room temperature (Husson et al., 1960) with the evaluated error is $(17 \pm 1) \text{ \AA}$. This value is shorter than the extended length of a molecule of potassium laurate, of about 28 \AA , due to contractions induced by gauche conformations. For S we assume the value $(52 \pm 5) \text{ \AA}^2$ (Husson et al., 1960), with an evaluated error.

To determine the constants K1 and K2 it is necessary to know the electronic densities of the paraffinic core (ρ_p), of the water-salt bath (ρ_b) and of the polar shell (ρ_s). The calculated values of ρ_p and ρ_b are $0.28 \text{ e}^-/\text{\AA}^3$ and $0.35 \text{ e}^-/\text{\AA}^3$ (Figueiredo Neto, 1981) respectively. Considering the electronic charge of the polar group (composed by $\text{COO}^- \text{K}^+$) uniformly distributed respectively in: two spheres of radius 1.58 \AA (for the COO^-) (Waddington, 1959) and 1.33 \AA (for the K^+) (Kaye & Laby, 1973); a volume formed by the surface per polar group (S) and 3 \AA of thickness it is concluded that ρ_s is in the range of $1.45 \text{ e}^-/\text{\AA}^3$ to $0.27 \text{ e}^-/\text{\AA}^3$.

Fixing K1 equal to unity, K2 represents how bigger is the contrast ($\rho_s - \rho_b$) in comparison with the contrast ($\rho_b - \rho_p$).

The value $K_2 = 4$ (for $K_1 = 1$) was obtained comparing the ratio of theoretical intensities of the 100 peak and the single particle peak at $2\theta \sim 0.45^\circ$, which is not resolved in the experimental results. The intensity of the single particle peak compared to the 100 one (expression I_m for $N=121$) increases with K_2 and $K_2 = 4$ is an upper limit to the constant. This value is of the same order as obtained by Husson (1960) ($K_2 = 5.8$) for the potassium palmitate (which has the same polar group).

C) Hexagonal lattice parameter adjustment

The position and width of the 100 peak depend on the number of micelles in the aggregate (N) as shown in Fig. 3a and b. The curves were constructed from the I_T given in expression III with different values of N . For an aggregate of $N=625$ (i.e., dimensions in the plane normal to the micellar axis of about 1000 \AA), the position of the 100 peak are the same predicted by Bragg's law. So, this aggregates already simulates an extended bidimensional lattice.

The width at half height of the 100 peak obtained from the curve I_T for $N=121$ is 0.158° (the experimental value is $(0.17 \pm 0.02)^\circ$).

With the parameters $N=121$, $R=17 \text{ \AA}$, $S=52 \text{ \AA}^2$, $c=0.82$, $K_1=1$, $K_2=4$, $\bar{a}=2 \text{ \AA}$, it was possible to proceed to the adjustment of the lattice parameter in terms of the localization of the 100 peak at the angular position $2\theta = 2.03^\circ$. In Fig. 4 this curve is plotted. The adjusted lattice parameter is $(49.9 \pm 0.5) \text{ \AA}$. Inside the aggregates the lipid volume concentration (ϕ_a) is (0.42 ± 0.07) .

Comparing this value with that obtained by direct application of Bragg's law it is seen that within 2.2% that first approach gives a good approximation for the parameter a .

The 110 peak of the hexagonal array was not resolved in our experiment. Its intensity, obtained from I_T , is about 1/2 of the 100 intensity. However, any defect in the structure and larger thermal agitation act to reduce its intensity, being probably the reason for the unobservation of the 110 diffraction. In other experimental conditions, samples at temperatures about 50°C (Figueiredo Neto, 1981) and samples in chemically treated surfaces (Figueiredo Neto, 1981) 100, 110 and 200 reflections are observed.

D) Analysis of IB

As it can be seen in Fig. 4, I_T for aggregates with $N \sim 100$ has no structure that could be identified with IB. The model of aggregates of micelles supposes that this band is build up by the mean distances among aggregates.

It is now assumed that the aggregates responsible for IB and OB have the same parameters, with different values of N .

The procedure adopted was to compare the theoretical diffraction patterns of small aggregates fixed in a unitary cell of a square lattice (lattice parameter ℓ) with the experimental result obtained with the 2 mm thick capillary (Fig. 1b). In this experimental conditions it is expected that there are much more small aggregates (responsible by IB) in comparison to the number of the larger ones, because OB is really weak.

In a first approach the parameter ℓ is obtained from the lipid volume concentration in the bulk (Table 1).

Defining R_{NE} , the effective radius of an aggregate of N micelles, as the mean value of the biggest and the shortest distances in the plane normal to the micellar axes, aggregates of a given N require

$$0.31 = \frac{\pi R_{NE}^2 \phi_a}{\ell^2} \quad (V)$$

Table 2 shows the values of ℓ , R_{NE} and the angular positions of the diffraction peaks corresponding to the distance between the aggregates (A in Fig. 6).

N	$R_{NE}^{\circ} (\text{\AA})$	$\ell^{\circ} (\text{\AA})$	$2\theta_B^{\circ}$
1	17 ± 1	54 ± 7	1.6 ± 0.4
2	29 ± 4	61 ± 7	1.4 ± 0.3
3	39 ± 6	80 ± 9	1.1 ± 0.3
4	51 ± 8	106 ± 13	0.8 ± 0.2
7	64 ± 9	132 ± 16	0.7 ± 0.2

Table 2: Parameters for aggregates with N micelles; see text for parameter's meaning.

To obtain the theoretical diffraction pattern the aggregates were fixed at the points of a square lattice unitary cell and expression III was used with convenient Spq . In Fig. 5 it is shown the cell with aggregates of $N=4$. They are fixed so that no direction of the lattice is privileged.

Fig. 6 shows $I_T(H)$ for $N=4$ and the experimental result with the locations of the $2\theta_B$ of various values of N ($1 \leq N \leq 7$). The deviation between the position of the peak expected from Bragg's law and that calculated from I_T occurs

due to the small number of aggregates considered. This deviation agrees with that expected on basis of the curve in Fig. 3a.

These results indicates that aggregates of about 3-4 micelles each are responsables for IB. This band, in terms of the model, would be composed by the superposition of the patterns of aggregates with $N \sim 3-4$.

The fact that the experimental width of IB is larger than the calculated one evidences that there is not a real structure of aggregates in a lattice and one can only speak of an average distance between them.

V. CONCLUSIONS

The quantitative development of the model of aggregates of micelles identify the aggregation numbers of the structures responsible for the outer and inner bands as $N \sim 100$ and $N \sim 4$ respectively. This analysis evidence that there is a strong correlation among micelles within the aggregates and a weaker one among the aggregates.

The results suggests that external factors (container walls, fields, etc.) favours the formation of the large structures. Aggregates of intermediate size are not observed, probably due to thermal agitation.

The analysis of the process of formation of the aggregates (Figueiredo Neto, 1981), with calculation of attractive and repulsive interactions and conditions of flocculation will be the subject of a forthcoming paper.

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REFERENCES

- Amaral, L.Q., Pimentel, C.A. & Tavares, M.R. (1978a). Acta Cryst. A34(S4) S188.
- Amaral, L.Q., Pimentel, C.A. & Tavares, M.R. (1978b). Collected Abstracts of the IX Hungarian Diffraction Conference, pp.1.
- Amaral, L.Q., Pimentel, C.A., Tavares, M.R. & Vanin, J.A. (1979). J. Chem. Phys. 71, 2940-2945.
- Amaral, L.Q. & Tavares, M.R. (1980). Mol. Cryst. Liq. Cryst. Lett. 56, 203-208.
- Amaral, L.Q. (1981). Acta Cryst. A37 (Suppl.) C-364.
- Charvolin, J., Levelut, A.M. & Samulski, E.T. (1979). J. Physique Lett. 40, L587-L592.
- Charvolin, J. & Hendrikx (1980a). Proc. Conf. Liquid Crystals in One and Two Dimensional Order and their Applications, edited by W. Welfrich & G. Heppke (Springer Series in Chem. Phys.).
- Charvolin, J. & Hendrikx (1980b). J. Physique Lett. 41, L597-L601.
- de Vries, A. (1972). J. Chem. Phys. 56, 4489-4495.
- Ekwal, P. (1975). Advances in Liquid Crystals, edited by G.H. Brown, vol. 1, pp. 1-142. New York: Academic Press.
- Figueiredo Neto, A.M. & Amaral, L.Q. (1981). Mol. Cryst. Liq. Cryst. 74, 109-119.
- Figueiredo Neto, A.M. (1981). Formation of Aggregates of Micelles in Type I Lyotropic Liquid Crystals - Study by X-Ray Diffraction and Other Techniques. Doctoral Thesis, Univ. of São Paulo, São Paulo (Brazil).
- Fujiwara, F., Reeves, L.W., Suzuki, M. & Vanin, J.A. (1979). Solution Chemistry of Surfactants, edited by K.L. Mittal, vol. 1, pp. 63-77. New York: Plenum Press.

- Guinier, A. (1956). Théorie et Technique de la Radiocristallographie. pp. 462-465. Paris: Dunod.
- Husson, F.R., Mustacchi, H. & Luzzati, V. (1960). Acta Cryst. 13, 668-677.
- Husson, F.R. (1967). J. Mol. Biol. 25, 363-382.
- Kaye, G.W.C. & Laby, T.H. (1973). Tables of Physical and Chemical Constants, 14th. ed., pp. 194. London: Longman.
- Lawson, K.D. & Flautt, T.J. (1967). J. Am. Chem. Soc. 89, 5489-5491.
- Leibner, J.E. & Jacobus, J. (1977). J. Phys. Chem. 81, 130-135.
- Luzzati, V., Mustacchi, H., Skoulios, A. & Husson, F.R. (1960). Acta Cryst. 13, 660-667.
- Luzzati, V. (1968). Biological Membranes, edited by D. Chapman, pp. 71-123. London: Academic Press.
- Oster, G. & Riley, D.P. (1952). Acta Cryst. 5, 272-276.
- Radley, K., Reeves, L.W. & Tracey, A.S. (1976). J. Phys. Chem. 80, 174-182.
- Radley, K. & Saupe, A. (1978a). Mol. Crystl. Liq. Cryst. 44, 227-236.
- Radley, K. & Saupe, A. (1978b). Mol. Phys. 35, 1405-1412.
- Sparnaay, M.J. (1959). Rec. Trav. Chim. Pays-Bas Belg. 78, 680-709.
- Vincent, J.M. & Skoulios, A. (1966a,b,c). Acta Cryst. 20, 432-440, 441-447, 447-451.
- Waddington, T.C. (1959). Advances in Inorganic Chemistry and Radio-Chemistry, edited by H.J. Emeléus & A.J. Sharpe, vol. 1, pp. 157-221. New York: Academic Press.

FIGURE CAPTIONS

- FIG. 1 - Experimental diffracted intensity I_m , without corrections, as a function of scattering angle 2θ . Sample K laurate/KCl/water in capillaries of 0.7 mm (a) and 2 mm (b).
- FIG. 2 - Corrected experimental diffracted intensity I_c as a function of scattering angle 2θ . Sample in 0.7 mm capillary. Dashed lines estimate the separation between the two peaks. Δ is the half-width of the outer band.
- FIG. 3 - Peak position, $2\theta_{100}$, (a) and half-width, Δ_T , (b) of the 100 reflection in the calculated diffracted intensity as a function of aggregation number N .
- FIG. 4 - Calculated diffracted intensity I_T in arbitrary units as a function of scattering angle 2θ , for aggregate of $N=121$ cylindrical micelles.
- FIG. 5 - Sketch of the unitary cell of the square lattice with four aggregates of $N=4$ micelles.
 l = parameter of the square lattice
 a = parameter of the hexagonal lattice
 R = radius of the cylinder.
- FIG. 6 - Experimental diffracted intensity, I_m , without corrections, for sample in 2mm capillary and calculated one, I_T , for four aggregates with $N=4$ cylinders each, as a function of scattering angle. The arrows indicate the position expected for peak A in large aggregates, for several N values.





