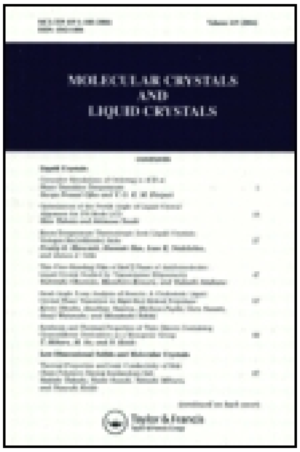

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On the Possible Formation of Macromicelles in a Lyomesophase

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ON THE POSSIBLE FORMATION OF MACROMICELLES IN A LYOMESOPHASE

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ABSTRACT: A model of finite planar micelles (platelets) surrounded by water was previously proposed for a type II lyomesophase. In this paper it is shown that X-ray diffraction results for this lyomesophase are strongly dependent on the container. Results are consistent with the hypothesis that under the influence of orientational forces the platelets aggegate forming macromicelles composed of several amphiphilic bilayers slightly swoolen.

INTRODUCTION: Lyomesophases that orient in presence of magnetic fields $\vec{H}$ and can be used as orientation matrix for NMR studies have been known for more than a decade[1,2]. These magnetically oriented lyomesophases have been classified[3,4,5] as types I and II depending on whether the phase director orients parallel or perpendicular to $\vec{H}$; the two types can be identifyed by the ^{2}H NMR spectra.

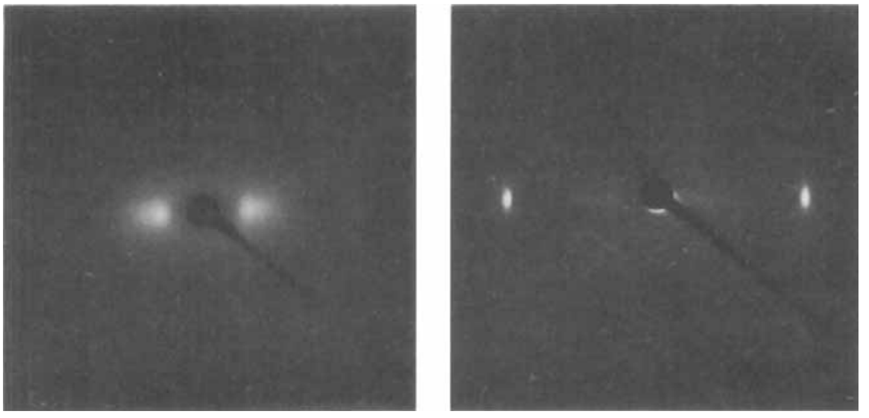
We have reported recently[6,7,8] the study of a type II lyomesophase formed by a quaternary system (Na decyl sulfate/decanol/Na sulfate/water), which has the property of remaining oriented for months after having been exposed to magnetic fields. Small-angle X-ray diffraction patterns have been obtained[8] on unoriented samples (S_o) and on samples previously subjected to the action of magnetic fields, with the X-ray beam parallel ($S_{\parallel}$) and perpendicular ($S_{\perp}$) to $\vec{H}$. Diffraction patterns showed a diffuse inner halo at 80-140 Å and a sharp outer ring at 38 Å, that reduce to spots in the equator for $S_{\parallel}$; no diffraction maxima were produced for $S_{\perp}$.

To explain the observed diffraction patterns a model of finite planar micelles surrounded by water was proposed[8]. These planar micelles consist of an amphiphilic bilayer, in the form of platelets, probably disk-shaped, that align in presence of magnetic fields, with their plane parallel to $\vec{H}$. The observed results[8] evidenced that further orientational restrictions are imposed by the container, and the platelets tend to remain in a plane that contains $\vec{H}$ and the capillary axis. These platelets tend to be parallel and some periodicity appears in the direction of the phase director, perpendicular to the plane of polar heads.

The results previously reported[8] have been obtained with samples conditioned in thin walled glass capillaries of 1.5 - 2.0 mm diameter (GC), which gave a very high attenuation of the X-ray beam. In order to study further the influence of sample container on the orientation of this lyomesophase, the experience was repeated using quartz capillaries of 0.7 mm diameter (QC).

<u>RESULTS AND DISCUSSION</u>: X-ray diffraction patterns were obtained as in the previous study[8] by photographing technique using a small angle Rigaku-Denki diffractometer with CuK_{α} radiation (Ni filtered) in a transmission geometry.

Figure 1 shows $S_{\parallel}$ results with GC and S_{O} results with QC. The scattering of the empty capillaries is negligeable. While there is a marked difference in the results S_{O} , $S_{\parallel}$ and $S_{\perp}$ for samples conditioned in GC[8], no such difference could be observed with QC, which gave $S_{\parallel}$ and $S_{\perp}$ results rather similar to S_{O}. On the other hand results are rather different with GC and QC; the relative intensities of the broad inner halo (B) and of the sharp outer ring (S) changed considerably, as well as the degree of orientation, indicating a much more oriented sample with QC.



(a) (b)

FIGURE 1 - Small angle X-ray diffraction patterns; capillary in vertical direction.
a) sample conditioned in glass capillary (GC) and previously oriented in a magnetic field $\vec{H}$ parallel to the X-ray beam ($S_{\parallel}$); besides the diffuse inner spot (B) the negative shows a weak outer arc (S) centered in the equator.
b) sample conditioned in quartz capillary (QC) and not oriented in magnetic field (S_o).

These results evidence that surface orientation is much stronger with QC, so that no residual magnetic orientation could be obtained in this case. The QC results indicate a monocrystalline structure in one dimension, with planes parallel to the capillary axis.

Some details of the X-ray diffraction analysis performed with GC results[8] must be revised in function of the results obtained with QC here reported.

B had been associated with an average distance between platelets in the direction perpendicular to the plane of polar heads. The distance associated with S corresponds roughly to the calculated[7,8,9] bilayer thickness and therefore to the distance between polar heads in one platelet; however, due to its sharpness, S has been interpreted as a Bragg reflection, appearing only when there is enough periodicity, which happens when the platelets remain parallel and with constant water separation. The analysis[8] in terms of a regular lamellar model, taking into account the volume composition of the sample, showed that one would expect a repetition distance d ~ 100 Å for a bilayered model and d ~ 50 Å for a monolayered model.

With GC, S is much weaker than B and it was suggested[8] that it might correspond to a (300) reflection from a bilayered lamellar structure; from the analysis made[8] this reflection was expected to be four times stronger than the first, second and fourth orders. The first order, besides being weaker, would be hidden under B.

However, the QC results are hardly explained in this basis: S is very strong in this case, while B is weak and yet there is only one sharp peak. This means that if S is a third order reflection, it should be over ten times stronger than the first and second orders, what is not to be expected in a rather imperfect crystalline structure. This indicates that S should better be interpreted as a first order reflection.

If one admits that the platelets of amphiphile are intercalated with water, 38 Å could correspond to a first order reflection only if the platelets consist of a monolayer (stiff interdigitating paraffin chains) of about 20 Å. From the volume composition of the sample[7,8], this division of amphiphile and water along the phase director would imply that, in the plane perpendicular to the director, the platelets would occupy 72% of the surface, what could be reasonable. However there are some arguments against this model.

- the chain order profiles obtained from NMR[10,11] indicate that the degree of order drops for the last carbons, what favours a bilayer model with rotating CH_3 at the middle;

- no sharp lines in the higher angle region have been observed with a Debye-Scherrer camera, and they should be present in the case of stiff interdigitating paraffin chains[12];
- such a model cannot explain the observed broad band at 80-140 Å obtained with GC. One would need to postulate a rather radical modification in the structure in function of the container, with transition from bilayer to monolayer;
- the outer ring is rather sharp and reduces to a point with QC, what means that the platelets in the water would form practically a unidimensional monocrystal; this is hard to believe with so much disordered water between the platelets.

If one admits that the platelets are formed by an amphiphilic bilayer that corresponds roughly to the observed first order reflection, it is necessary to suppose that in some regions the platelets aggregate forming multi-bilayers with little water between them, and these aggregates are intercalated with large water regions. The possibility of irregular distribution of lamellar regions and water regions was left open in the previous study[8].

Such a model could explain all the observed results. With GC the platelets are more or less randomly oriented; under the influence of orientational forces, the platelets tend to be parallel and start to aggregate forming macromicelles composed of several amphiphilic bilayers slightly swoolen. $S_{\parallel}$ with GC shows the coexistence of some macromicelles with many oriented platelets separated by water. With QC the macromicelles dominate; the S width, after correction for geometrical resolution, implies periodicity for at least 1000 Å, and this would be the minimum size of the macromicelles. The fact that only the first order is observed may be connected with a high Debye-Waller factor, what occurs for many thermotropic liquid crystals.

This model of macromicelles can also explain the laser diffraction results on this lyomesophase[13], since it is possible that the macromicelles form hyperstructures with the water.

The rather different diffraction results for GC and QC indicate that the superstructure of this lyomesophase, including the formation of aggregates of platelets, is critically dependent on the orientational forces acting upon it, may them be originated from magnetic fields or from surface orientation. The structure has characteristics between the lamellar and the nematic mesophases.

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