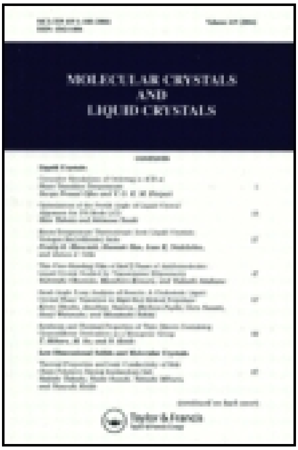

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Freeze-Fracture Electron Microscopy Study of Lamellate Phase in a Sodium Dodecylsulfate-Formamide (SDS-Formamide) System

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We highlighted by freeze-fracture the lamellate phase Lα (1D) in SDS-formamide system. This phase succeeds in increasing concentration into surfactant with the cubic phase Qα (Ia3d). The lamellate phase is observed in electron microscopy and corresponds to high values of the concentrations into amphiphilic going up to 100 %. Of this fact it is easily vitrified by hardening. Our work enabled us to observe in the system SDS-formamide two possible morphologies of the phase Lα: smooth fractures presenting the setbacks in which appears a periodicity, and fractures revealing stacking of plates of decreasing diameter, forming kinds of turrets. In this second case, we give an explanation of the formation of the towers based on germination and growth theory.

I. INTRODUCTION

The lamellate phase was the subject of many studies under taken on surfactant-water systems by techniques such as N.M.R., the differential thermal analysis, x-ray diffraction [1]. In addition large majority of the work by freeze-fracture electron microscopy on the lyotropic phases whose lamellate phase Lα carried on systems comprising water like solvent [2,3,4,5]. Certain authors observed the lamellate phase and studied the defects of them by using several different techniques [2,3]. A new class of lyotropic phases whose phase was recently highlighted by x-ray diffraction in systems comprising others sol-

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vents that water [6,7]. Former work enabled us to detect in non-aqueous systems of other phases such as micellar cubic phase Qα(Pm3n) [8], a two-continue cubic phase Qα(Ia3d) and hexagonal phase Hα (p6m) [9,10]. Our work by freeze-fracture electron microscopy method, that we present here, concerned the lamellate phase Lα in non-aqueous system SDS-formamide. We thus give there after the various aspects observed of the Lα phase and we show that in certain cases this one is formed according to germination and growth process.

II. EXPERIMENTAL TECHNIQUES AND METHODOLOGY

The solutions surfactant-solvent prepared by weighing are locked up in a tight tube so that the composition does not vary during the homogenisation. To obtain mixtures spatially homogeneous several methods were used, the tube containing the mixture is placed in a drying oven with 80°C, sufficient temperature to obtain a good mixture, this during half an hour. In order to accelerate the process of homogenisation on a microscopic scale we used an ultrasound vat by maintaining the tube at the temperature T. The examination of the samples by electron microscopy requires their preparation by the freeze fracture method. Indeed, a film of the solution of a few tens of microns is imprisoned between two fine copper cups 3 mm in diameter. The sandwiches thus formed are placed in a furnace and undergo an isothermal maintenance at the temperature wished during a time given to form the phase Lα then are soaked directly starting from the furnace in a liquid nitrogen bath. This cooling agent proved sufficient to block any crystallization. The vitrified sandwiches are then fractured under ultra-high vacuum (10–7mm Hg). A layer of platinum average thickness of 2 nm, reinforced by a layer of 20 carbon nm is deposited by evaporation on fracture surfaces. After extraction and washing of the counterparts in adapted baths, those are examined under the electron microscope with transmission (JEOL 2000 FX II to 200 Kv).

III. RESULTS

The lamellate phase was detected by x-ray diffraction in our laboratory in the SDS-formamide system. In addition we highlighted by electron microscopy in our system two different morphologies from the Lαa phase:

a- has smooth fractures presenting of the setbacks in which appears a periodicity

b- stacking of decreasing diameter plates, thus forming kinds of turrets

III.1. Smooth fractures of Lα phase

There are then fractures parallel with the plates plan: It is generally noted that the edges of the plates are rounded (Fig.1), which proves it is about a crystal-liquid phase. In a solid lamellate phase, the edges of plates would be right (parallels with the dense lines of molecules) or more or less polygonal (Fig.2). The periodicity observed in the setbacks is obviously related to that of the plates, but it depends on the slope of the cut through the plates, and the slope of this cut compared to the electrons (Fig.3). There is the relation:

$$a'' = \frac{a}{\sin\psi}\cos\varphi$$

Insofar as ψ is unknown, one cannot calculate the periodicity a starting from the periodicity a''. Another process to measure this periodicity would be, for the sufficiently inclined plans of fracture, to measure the width of a "shade" carried by a functioning (Fig.3). One has then: $l' = a(tg\alpha\cos\varphi + \sin\varphi)$ where α is the angle of shade.

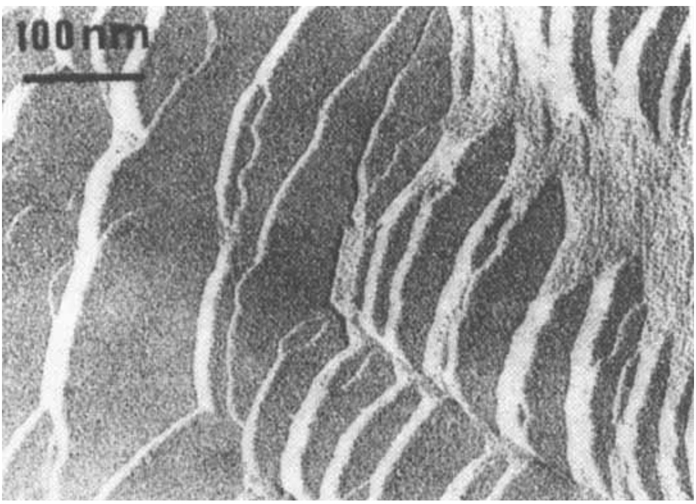

FIGURE 1 Electron micrography of Lα phase smooth fracture

But if one knows the average angle of shade given by the slope of the turntable slide of the apparatus of freeze-fracture compared to the axis of the transmitting electron gun of platinum, one does not know the local angle of shade that depends on the local slope of the fracture compared to the average slope. In addi-

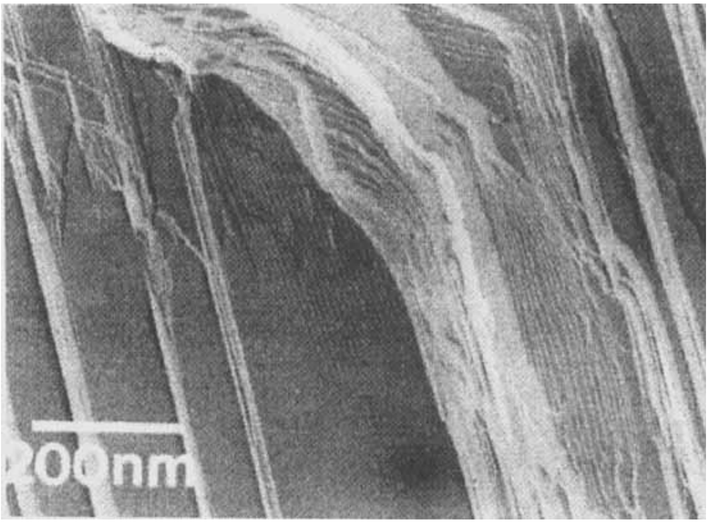

FIGURE 2 Electron micrography of solid phase fracture

tion, one can notice that a same periodicity observed on an image can correspond to different real situations (Fig.4).

III. 2. Turrets fractures of Lα phase

The morphology with turrets observed in our system (Fig.5and Fig.6) is sometimes visible in other systems [5] but did not receive explanation to our knowledge. We propose below a possible interpretation of this structure based on a two-dimensional process germination and growth of the phase there. We will first of all recall some data on this process in the case of a pure crystal phase solidification. Let us consider a liquid phase *L* out of balance, in contact with its presumably solid equilibrium cycle and crystal S, on an interface *L/S* consisted a dense crystallographic π plan. In this case, the evolution towards balance supposes a projection of the π plan in the liquid. But, with balance, an atom isolated from the liquid that would be fixed on the interface would have as much chance to be reemits than to remain fixed on the interface. Out of balance, the growth of the S phase by formation of a new π plan is possible in two cases:

1- a certain number of atoms gathered on surface in order to form a full-course small island of size higher than a certain value critic size *Rc* the small island can then grow laterally by fixing of new atoms on its edge.

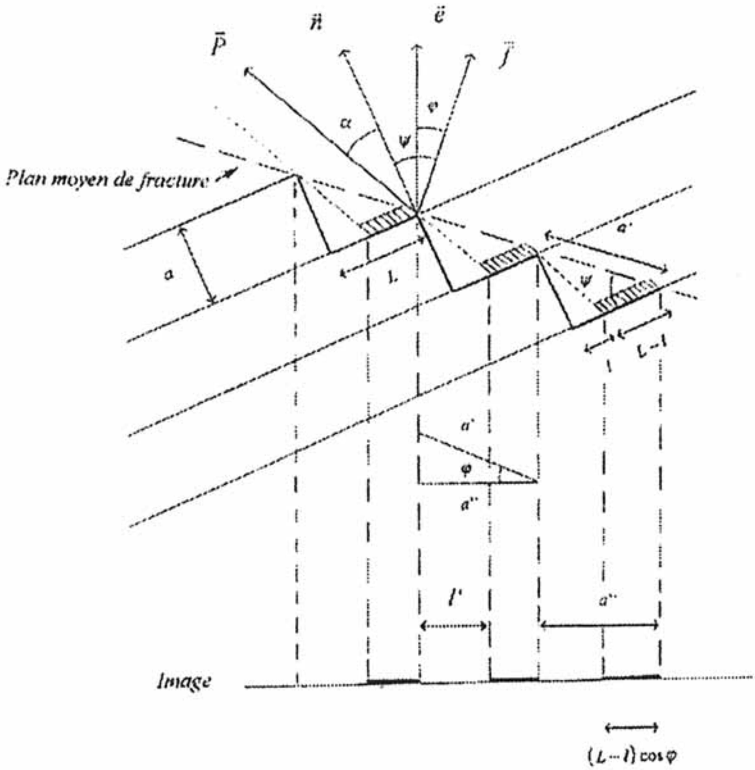

FIGURE 3 Effects of shade in the case of the Lα phase

2- π surface presents defects constituting of the favourable sites of germination (dislocation live for example). The critic size *Rc* of germination is then reduced compared to the preceding case.

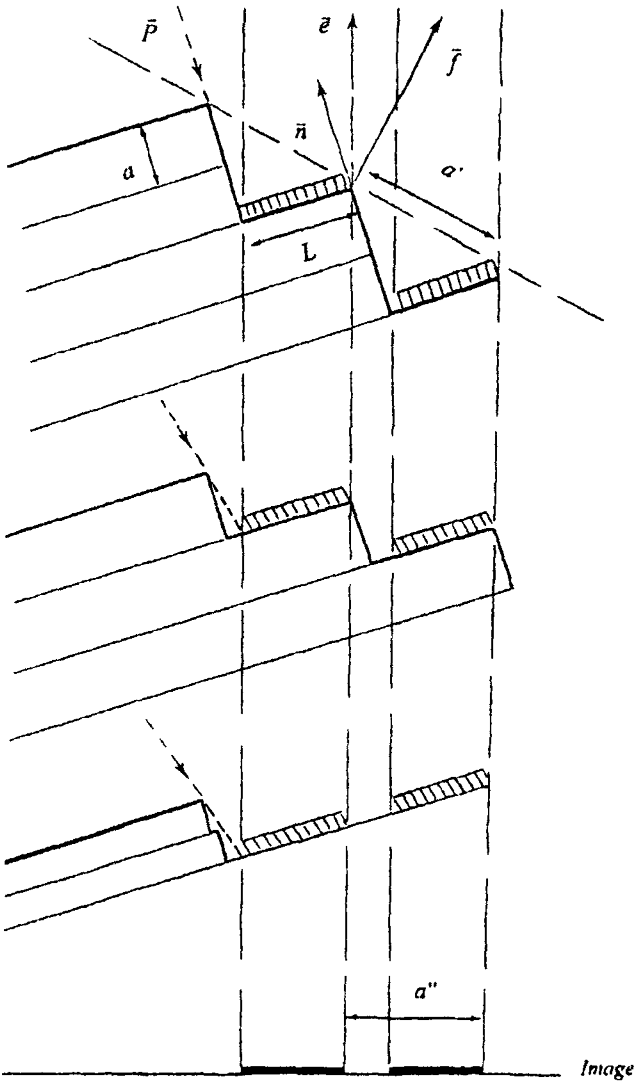

FIGURE 4 A same image can correspond to different fractures from Lα phase

Germination and the growth can occur simultaneously; the structure of the interface resulting will depend then on the relative values the speed of germination *I*s (a number of germs formed per unit of time and surface) and the speed of side growth $Us = dR/dt$. If $Us << Is$, a germ formed at the moment to will occupy all surfaces before another is formed: the interface will be smooth.

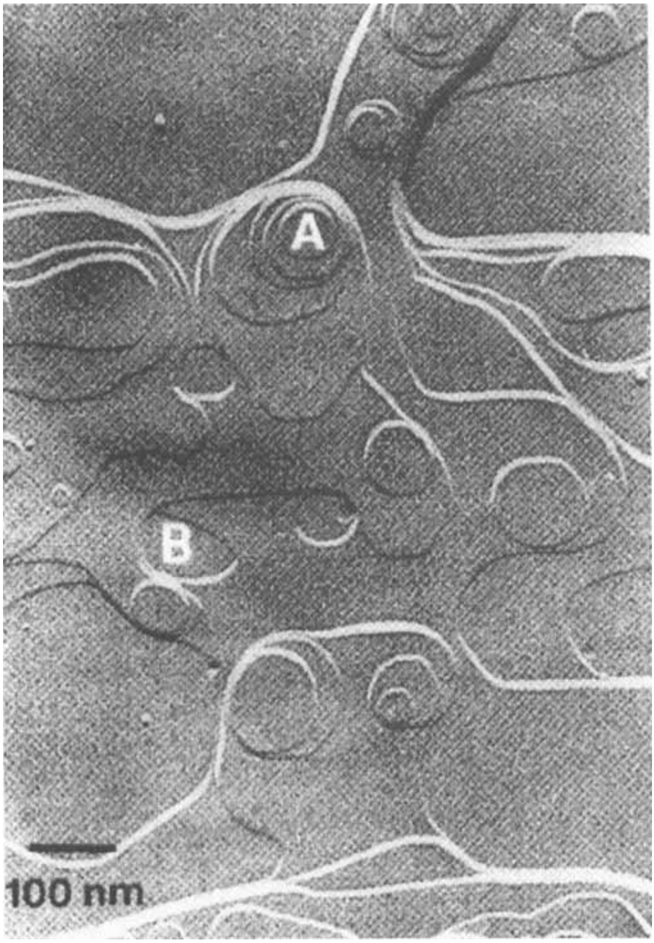

FIGURE 5 Electron micrography of Lα phase turrets fracture (A) and (B) respectively indicate a turret and a basin

If *Us* >> *Is*, The surface will cover germs, at the same time that germs pre-existing will grow, the new germinate being able to superpose to the ancient, form thus beginnings of turrets.

It is therefore very tempted to think that this process applies to our case: structures in turrets would result then from a two-dimensional germination relatively rapid, and a slower growth. This explains the decrease very well in size of slats of a turret given, according to the height. However, a certain number of problems posed:

FIGURE 6 The arrow indicates a turret which one clearly sees the decrease in the face of the plates with the height

a-which stage of the samples preparation this process occurs?

Probably during the thermal treatment the furnace. Before this one, the samples are made up undoubtedly of a very concentrated solid phase and a diluted liquid phase. The formation of $L\alpha$ during the thermal processing would lead to the interface structure with turrets, and the fracture would follow this interface. Another possibility is the existence of internal cracks in the samples. The growth with turrets would occur starting from surfaces of cracks.

b-Which are the sites of initial germination?

The walls of the sandwiches are certainly possible sites, the plates being formed parallel to the wall then, and the fractures being also appreciably parallel with those. However, one observed more or less inclined fractures that suggests other sites of germination are possible.

c-Why turrets have very different heights?

A first explanation could be the existence of heterogeneous germination sites such as dislocations. However, we did not observe such dislocations. Let us notice however that we developed the theory of germination and two-dimensional growth in the case of a pure phase. A significant role is certainly played by the gradients of concentration and the thermal gradients (due to the concerned latent heats) in the vicinity of the interface. This could be the principal cause of the interface structure, by analogy, for example, with the dendritic growths occurring in the solidification of alloys.

d-Why interfaces comprise, not only turrets, but sometimes also basins?

This can occur by coalescence of close turrets. Figure 7 shows the case of 4 turrets coalescence.

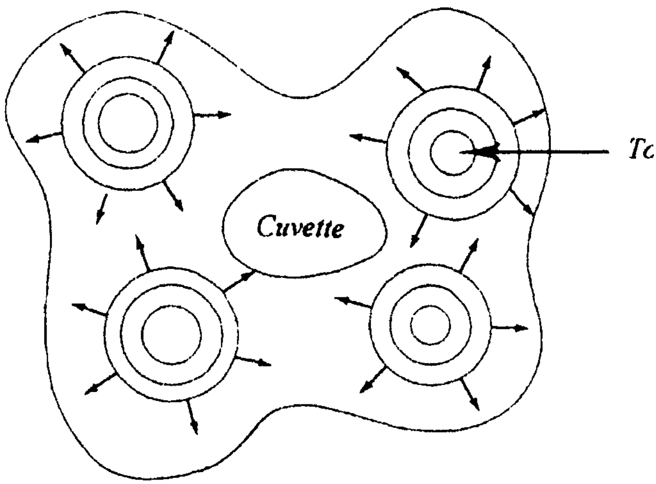

FIGURE 7 Basin formation by coalescence of 4 turrets

IV. DISCUSSION

The fracture occurs almost always parallel to the plan of the plates, and undoubtedly also with the solvent-amphiphilic interface. The resolution of a counterpart is insufficient to observe the provision of amphiphilic in a plate (one would need a resolution quite lower than 1 nm). On the other hand, it underlines the edge of the plates well. This one is curved, which confirms well the liquid nature of molecular arrangement in a plate. We in addition could establish that the configurations out of turrets of these plates would almost certainly result from a two-dimensional process of germination and growth. The support on which perhaps occurs germination is the surface of a solid phase particle. But the most probable support is a face of crack. In the case of micrographies of figures 5 and 6, it would be about an internal crack existing before the fracture. External cracks produce also this structure, but as we could note it, this one then is strongly contaminated.

V. CONCLUSION

Two morphologies of the lamellate Lα phase were clearly observed: a morphology where the plates are smooth and a morphology where those are presented in the form of turrets. We have to our knowledge been the first to explain the formation of these turrets according to process of two-dimensional germination and growth. If our interpretation for the structures out of turrets is correct, one is sure that the fracture individually separates the constitutive turret plates. This allows the measurement of the angle of local shade starting from the knowledge of the lamellate Lα phase period on the one hand, and allows the access to physical data such as speeds of germination and growth on the other hand. Our technique appeared profitable also for the lamellate phase identification. It confirms overall for this phase the result obtained by x-rays, and brings much additional elements on morphologies. It can also describe germination and growth kinetics.

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