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Transitions in a Lyomesophase: A Study by Thermal Analysis and Electron Microscopy†

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The system Na decyl sulfate/water/decanol/Na sulfate, which forms a discotic nematic phase, N_L at room temperature, has been studied by differential scanning calorimetry (DSC) and by electron microscopy (EM). DSC reveals three first order phase transitions at 0°C, 12°C and 24°C. Latent heats show that the first transition must involve other processes in addition to the fusion of water, and that the last transition, between a coagel CG phase and the N_L phase, may be attributed to the order-disorder transition of the hydrocarbon chains (Krafft melting). Freeze-etch replicas have been obtained from samples initially in the N_L and CG phases. Micrographs obtained from the N_L phase show disc structures of about 2000 Å diameter. Micrographs obtained from the CG phase show large lamellar structures and regions of transition to the disc structures.

INTRODUCTION

The system, SDS (Na decyl sulfate/water/decanol/Na sulfate) forms a room temperature nematic N_L lyomesophase composed of disc micelles.[1,2] Evidence has been reported on the existence of positional correlation between micelles both in this system[3] and others which form nematic lyomesophases.[4] The analysis of the interactions between micelles showed[5] that the systems are in conditions suitable for flocculation, but thermal agitation may prevent the occurrence of irreversible flocculation.

On the other hand these systems appear to behave in many aspects as conventional nematics. Recent light scattering results[6] have shown

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that the nematic-isotropic and the nematic-lamellar phase changes in lyotropic liquid crystals are closely similar to the analogous transitions in thermotropic liquid crystals. However this result does not exclude the possibility that the basic structural units of nematic lyomesophases are aggregates of micelles rather than isolated individual micelles.

The SDS system undergoes a phase transition on cooling from N_L to a coagel CG phase at 22°C. X-ray diffraction studies[7] have shown that this transition corresponds to the Krafft point, i.e. the "freezing" of the hydrocarbon chains. Analysis of the diffracted intensities from the CG phase indicate[7] completely anhydrous lamellar aggregates of extended, tilted bilayers dispersed in water. Comparison of diffracted peak positions indicates that only three water layers are present between micelles in the N_L phase, which gives support to the hypothesis that the micelles are aggregated in this phase.

In order to obtain more information about the state of aggregation of the micelles in the nematic phase, the investigation of the system by electron microscopy (EM) of freeze-etched replicas (FER) was undertaken.

The phase transitions of the system were also studied by differential scanning calorimetry (DSC), since knowledge of the low temperature phases is essential for the interpretation of FER results and may also help to elucidate the characteristics of the N_L phase.

CONSIDERATIONS ON THE TECHNIQUES

EM studies of membranes by FER are well established,[8] although results must be viewed critically in light of the limitations of the technique.

Studies of mesophases of anhydrous amphiphiles by EM have been made by conventional replica techniques;[9] studies of thermotropic mesophases by EM have also been carried out.[10] Studies of lyomesophases have been carried out using both chemical fixing[11] and FER.

Lamellar and hexagonal lyomesophases studied by EM of FER showed[12] that a rapid cooling of the systems preserves the structure of the phase at the initial temperature. Both lamellar and hexagonal lyomesophases have been characterized by EM and X-ray diffraction and the results are consistent. Studies of lamellar phases of ternary and quaternary systems have also been made.[13,14,15] No previous attempts to apply these techniques to the study of nematic lyomesophases have been reported.

When the systems under investigation undergo phase transitions on cooling, it is questionable whether the structure of the higher temperature phase is indeed preserved. This is a limitation inherent to the FER technique and therefore it is essential to study the phase transitions of the system by thermal analysis.

The use of differential thermal analysis (DTA) and DSC is quite common in the study[16] of thermotropic liquid crystals. There is an extensive review[17] on thermal analysis of lipids, proteins and biological membranes, but almost nothing can be found on lyotropic liquid crystals in the literature.

EXPERIMENTAL

The samples were prepared in glass tubes of 1.5 cm diameter, by standard procedures, with weight composition Na decyl sulfate 36%, Na sulfate 5%, decanol 5% and water 54%.

A DSC device Shimadzu (model SC-20) with accessories for low temperature (liquid nitrogen) has been used. Samples of 13–20 mg were sealed in aluminum pans; the reference pan was kept empty. The instrumental calibration constant for measuring the latent heat of transition was obtained from the solid-liquid transition of distilled water.

Replicas were obtained with a freeze etching device (Balzers model BAS 301). For the rapid cooling, Freon 22 in liquid nitrogen was used. The cooled sample was fractured under vacuum by a knife at liquid nitrogen temperature; etching was obtained by allowing sublimation to occur from the surface for one minute (with a table temperature of $-90°C$). The replicas were obtained by vaporization of C and Pt onto the fractured surface and subsequent immersion in a solvent. The replicas were analysed in a Transmission Electron Microscope (Siemens Elmiskop 1).

RESULTS AND DISCUSSION

DSC results

Fifteen independent DSC runs were obtained, the majority for heating curves and some for cooling curves, in the temperature interval $-80°C$ to $+60°C$. Figure 1 shows a typical heating curve. Three endothermic phase transitions appear; the transition temperatures

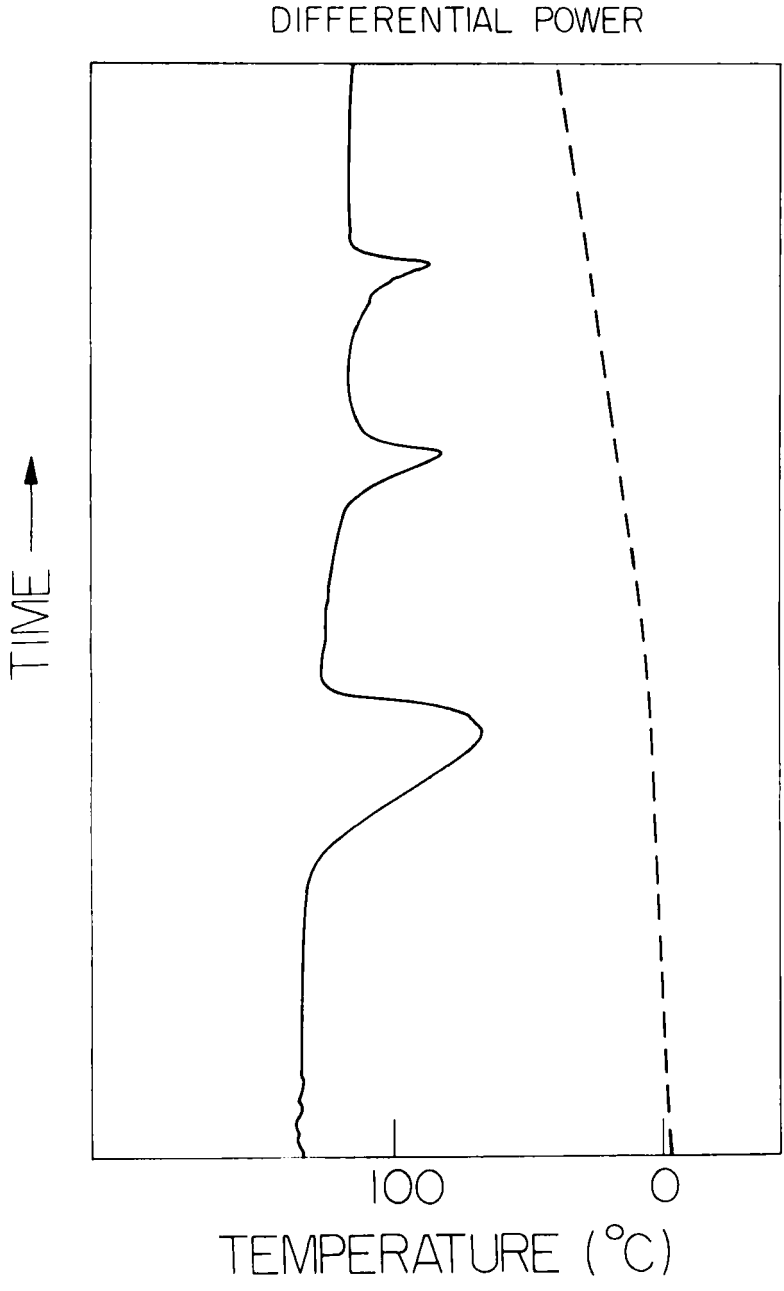

FIGURE 1 DSC heating curve showing differential power (solid line) and sample temperature (broken line).

TABLE I

Results obtained from DSC heating curves: transition temperatures, T and latent heats, ΔH.

T (°C)	ΔH (cal/g)
0.4 ± 0.6	69 ± 2
11.7 ± 0.4	6.6 ± 0.6
23.8 ± 0.7	3.2 ± 0.3

and the latent heats (obtained from peak areas) are shown in Table I. The quoted errors correspond to fluctuations observed among the several independent heating runs of various samples. The cooling process is difficult to follow, since there is no control over the cooling speed, but it was possible to observe hysteresis and super-cooling in the three transitions, with a shift of up to 10 deg. in the transition temperatures.

Assuming that the CG–N_L transition at 24°C is due only to the amphiphilic portion of the system, a value of 2.2 kcal/mol for the latent heat of the Krafft fusion is obtained.

Thermal analysis studies of anhydrous Na soaps CH_3–$(CH_2)_n$–COONa indicate[17,18] three phase transitions between the crystalline curd phase and the liquid crystalline lamellar neat phase; the two intermediate waxy and subneat phases containing bidimensional order of the chains. For n = 10 the latent heats of transition on heating are 2.1; 0.2; 2.0 kcal/mol. The sum of all transition heats between the anhydrous solid and the isotropic liquid is less than that of the latent heat of fusion of the corresponding hydrocarbon. This indicates that in soaps the chains retain a considerable degree of order in the liquid crystalline state and even in the isotropic liquid. The interactions between polar heads are also responsible for the Krafft temperature being much higher in soaps than in hydrocarbons.

Results obtained for the CG–N_L transition are thus in agreement with the latent heat of passage from bidimensional to unidimensional order in the anhydrous soap of same chain length, but with different polar head. On the other hand, the Krafft transition temperature is much lower than for soaps, being of the same order as for phospholipid/water systems.

Membrane/water systems also present three phase transitions on cooling,[17] and appear to be rather similar to the SDS system under study. The latent heats for the main order-disorder transitions in

lecithin membranes with n = 14; 16; 18 are[19] respectively 6.3; 9.7; 10.8 kcal/mol. The analysis of thermodynamic parameters of the Krafft transition in membranes showed[20] that the mobility of carbon chains in the disordered state is intermediate between that in the crystalline state and that of liquid phase of *n*-alkanes and that it is higher for hydrated phases than for anhydrous phases. It is accepted that hydrocarbon chain mobility in liquid crystalline phases is appreciably less than in liquid paraffins and only a little greater than in the gel phase.

There is therefore reasonable agreement between the value for the latent heat of CG–N_L transition and the one that could be expected for chains of same length in lecithins.

The transition at 12°C has not yet been correlated with defined structural changes. X-ray results failed to detect this transition on cooling, probably due to a process of supercooling. A special cooling system, not yet available, would be necessary to study these lower temperature phases by X-ray diffraction.

In phospholipid/water systems with small n values and excess water, a pre-transition at a temperature about 10°C lower than the main transition occurs,[17,21] also dependent on the structure and dynamics of the amphiphile.

In the SDS system the second transition occurs also at a temperature about 12°C lower than the fusion of the chains. However, for lecithin membranes there is a significant difference in broadening between the two transitions and the pre-transition has a latent heat smaller than that of the main transition. For SDS system, in contrast, the second transition has a latent heat more than twice that of the CG–N_L transition. It may be concluded that in SDS the changes occurring in the second transition are much larger than those expected in a process of further ordering of amphiphilic molecules. This transition might involve structural changes between the water and amphiphile portions of the system.

The transition at 0°C must be associated with the fusion of the aqueous portion of the system, but its latent heat cannot be simply explained by the fusion of water. Assuming that all the water is melting, as the sample has 53% water, one would expect a latent heat of only 42.4 cal/g for the sample, a value much lower than the observed value of 69 cal/g.

This situation is opposite to that observed in phospholipid/water systems,[17,21] where the peak at 0°C is, in general, smaller than that expected for fusion of the water, because the bound water does not solidify even when the sample is cooled to −100°C. The latent heat

obtained in this transition may be used therefore to give information about the amount of water bound to the phospholipid. The peak at 0°C appears only for phospholipid/water systems with at least 20% weight in water, which corresponds to the water completely bound (10 molecules of water per phospholipid molecule).

The analysis of the cooling curves for lecithins with excess water shows[17] that solidification of water occurs in two steps, the first (with super cooling) at −15°C and the second at −50°C. In the heating process the fusion peak at 0°C is much larger for samples cooled below −50°C than for samples cooled to −30°C. Therefore, in addition to the completely bound water (which does not solidify even at −100°C) there is unbound water (which solidifies at −15°C) and water in an intermediate category which solidifies at about −50°C.

In SDS system a thorough analysis of the cooling curves was not performed, due to the difficulties in controlling the temperature on cooling. It is possible however to conclude that there is no evidence of the existence of water bound to the amphiphile. This is probably due to the presence of salt in the SDS system. It has been verified, with lecithin in presence of salt solutions, that the amphiphile and the salt seem to compete with each other to bind the free water and the behaviour of the system changes, becoming similar to systems with less water.

The latent heat observed in the SDS system at this 0°C transition indicates that the transition must involve additional processes besides the fusion of water. Perhaps simultaneous processes of breaking of extense lamellar regions occur, with redistribution of amphiphilic and water portions.

EM RESULTS

Ten freeze etching replicas from two independent samples have been obtained. Eight replicas have been obtained from the sample at room temperature in the N_L phase, four of them without etching and four with etching to enhance the contrast between the aqueous and the amphiphile portions of the system. Two replicas were obtained from the sample in the CG phase at 20°C.

These ten replicas were systematically studied by transmission EM and over 100 micrographs were obtained.

Micrographs obtained from the N_L phase (Figures 2 & 3) clearly show the existence of two distinct regions, with structures in the form of platelets with diameters of the order of 2000 Å. Replicas with sublimation show etching of the aqueous portion. For comparison,

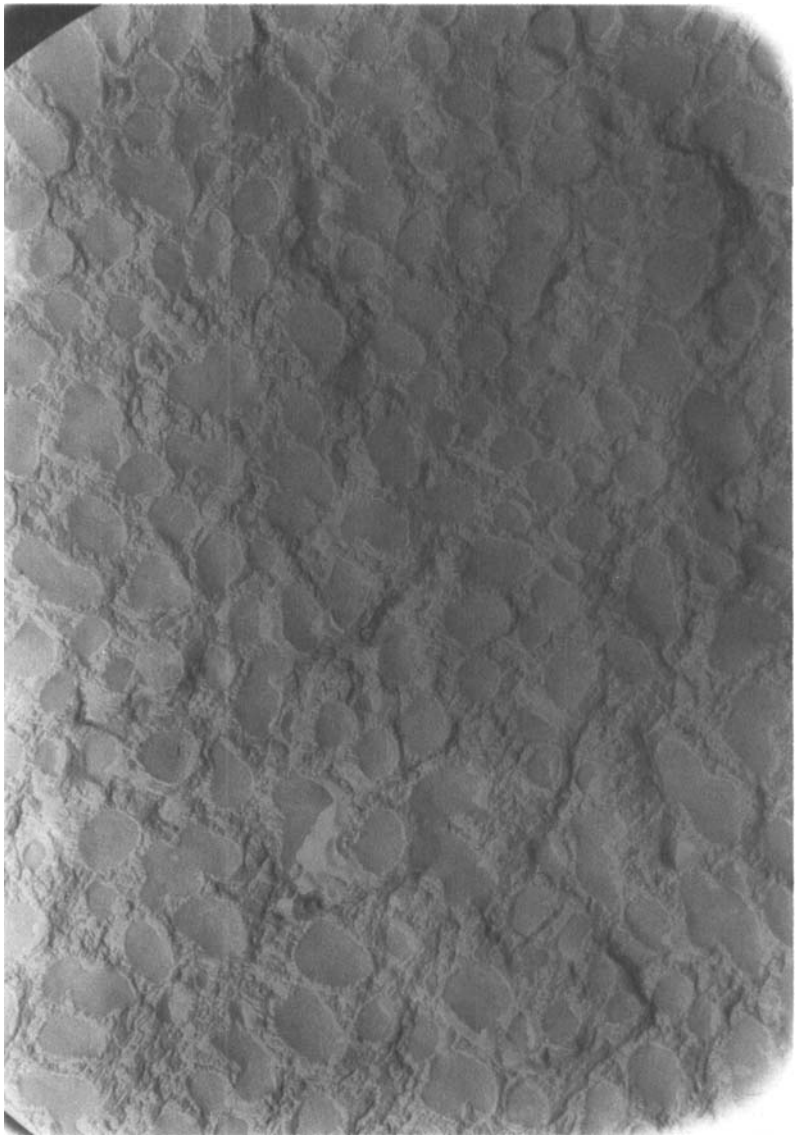

FIGURE 2 Electron micrograph of replica obtained from N_L phase without etching (magnification, ×20,000).

FIGURE 3 Electron micrograph of replica obtained from N_L phase with etching (magnification, ×20,000).

Figures 2 and 3 show typical results with and without sublimation obtained from N_L phase.

It is, however, very difficult to decide from the micrographs whether the continuous phase is aqueous or amphiphilic. But certainly there is not a homogeneous distribution of amphiphile and water in the direction of viewing, since the distance the surface has been lowered is much more than one would expect for one water layer (< 20 Å) between lamellae.

The structures are not of uniform size, but variations remain within an order of magnitude. An estimate of the percentage area occupied by the platelets gives the value 0.35 ± 0.05, which corresponds to the volume percentage of amphiphile in the system.

In the replicas obtained from the CG phase, there are zones which show extended lamellar regions, zones that repeat the results obtained from the N_L phase and also zones that show the process of transition from extended lamellae to the structure with platelets.

Figures 4 and 5 show typical results where the two phases appear. It is apparent that the circular structures emerge from the extended lamellae and agglomerate in the transition line between the two phases.

The repeat distance of the extended lamellae is difficult to measure, and some micrographs have been obtained with large magnifications, at the resolution limit of the replica technique. In figure 6, for example, it is difficult to decide the repeat distance, since frequently the breaks in the lamellar structure involve more than one lamella. The smaller observable lamellar thickness is compatible with the repetition distance obtained by X-rays[7] in the CG phase (31.4 Å).

A doubt that remains is the point whether the observed structures correspond to the N_L and CG phase or if a shift in phase diagram might have occurred during the rapid cooling process to obtain the replicas.

We do not completely exclude the possibility that the structures seen in the replicas obtained from the N_L phase actually correspond to the CG phase, and the structures seen in the replicas obtained from CG phase correspond in reality to lower temperature phases. The fact that the observed lamellar structures are very perfect and extended, while X-ray results from CG phase show only three lamellar reflections, could indicate that such a shift in phase diagram has occurred.

In this case the structures of 2000 Å could correspond to the CG phase, where a separation between anhydrous lamellar aggregates dispersed in water would be expected.[7]

It is seen that breaks of the extended lamellae occur in the transition

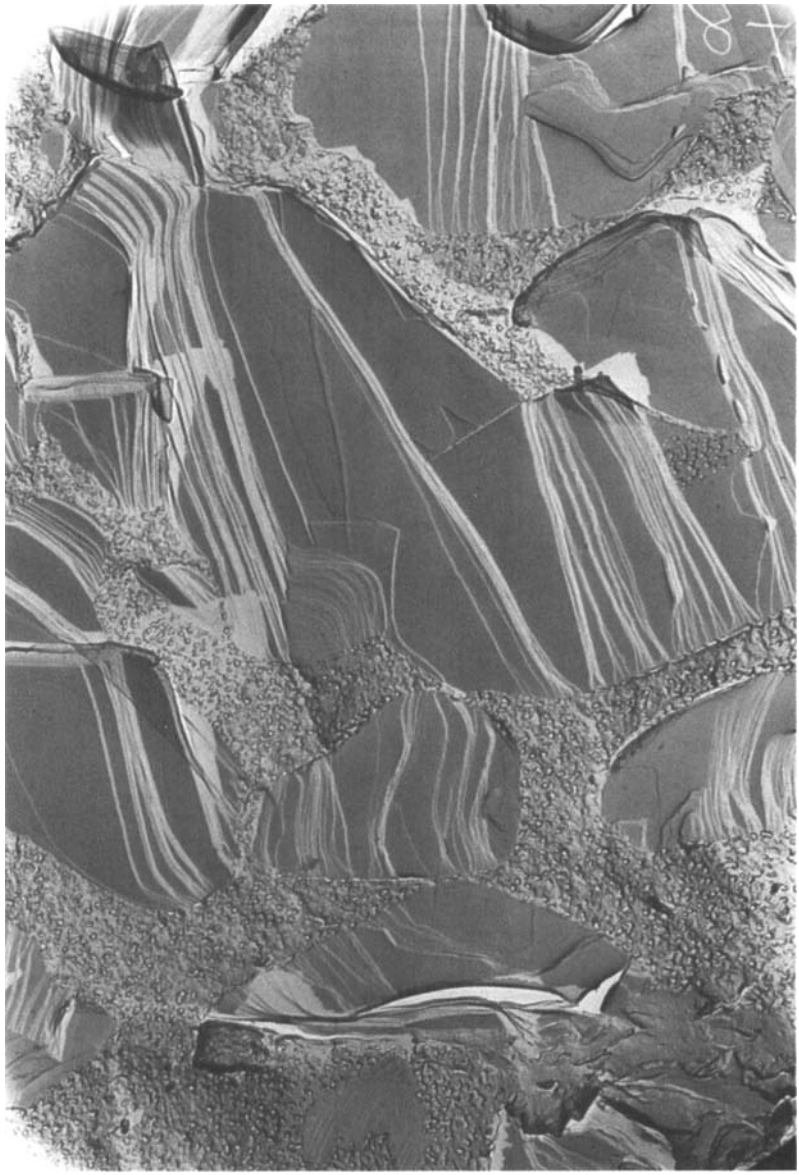

FIGURE 4 Electron micrograph of replica obtained from CG phase with etching (magnification, ×8,000).

FIGURE 5 Electron micrograph of replica obtained from CG phase with etching (magnification, ×8,000).

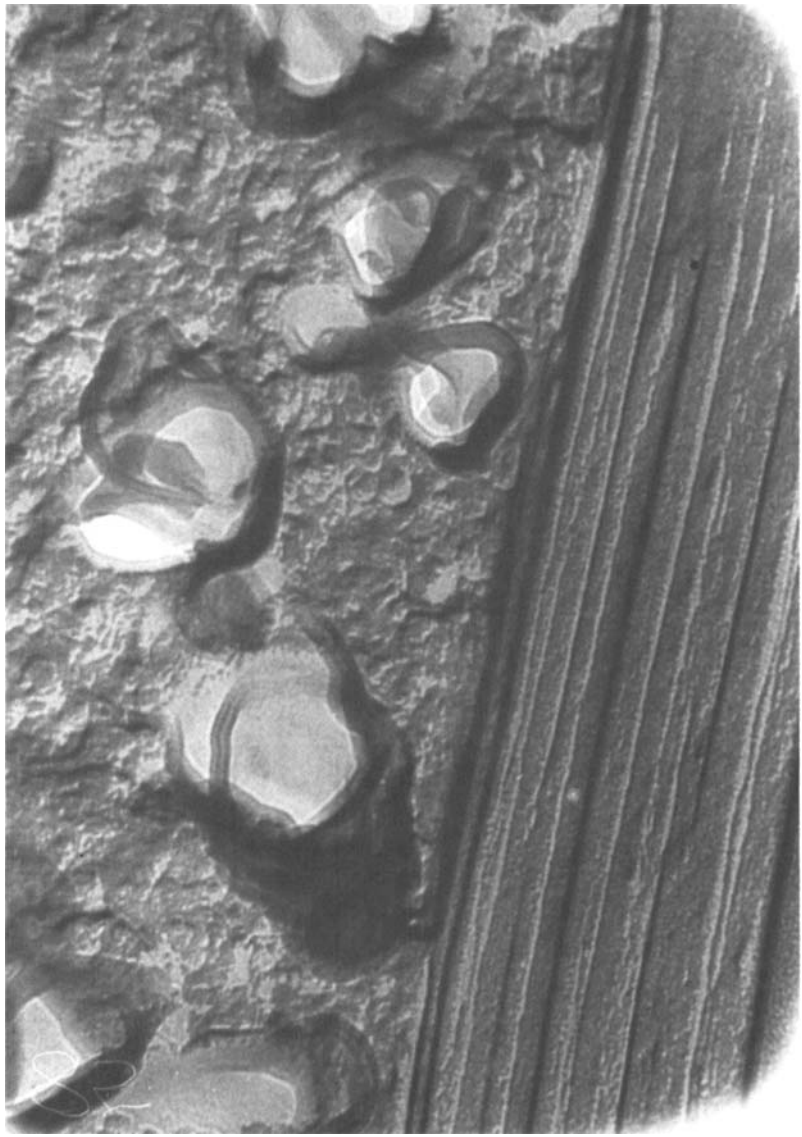

FIGURE 6 Electron micrograph of replica obtained from CG phase with etching (magnification, ×80,000).

observed by EM. Such a break of the lamellae with redistribution of amphiphile and water portions could be the process responsible for the extra latent heat observed in the transition at 12°C.

CONCLUSIONS

Results obtained by EM from N_L phase are not conclusive, particularly with regard to the radial size of the micelles. The 2000 Å structures observed may correspond to the CG phase and we can not rule out the possibility that the matrix is an amphiphile continuum with water globules.

On the other hand it is clear that the break of the extended lamellae of the lower temperature phases implies separation of water and amphiphile portions already present in the CG phase.

Latent heats obtained helped to correlate characteristics of the SDS system with those of analogous systems. The transition CG-N_L corresponds essentially to the Krafft melting of the chains. Since the CG phase corresponds to anhydrous lamellar aggregates, this result gives further support to the hypothesis of aggregates of micelles with only one-two water solvation shells per micelle being the basic structural units of the nematic phase.

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