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TRANSITIONS IN A LYOMESOPHASE: A STUDY BY THERMAL ANALYSIS AND ELECTRON MICROSCOPY

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ABSTRACT

The system Na decyl sulfate/water/decanol/Na sulfate, which forms a disc 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^oC, 12^oC and 24^oC. Latent heats show that the first transition must involve other processes besides the fusion of water, while the last one between a coagel CG phase and N_L may be attributed to the order-disorder transition of the hydrocarbon chains (Krafft melting). Freeze-etching replicas have been obtained from samples initially in N_L and CG phases. Results obtained from N_L phase show disc structures of about 2000 Å. Results obtained from CG phase show large lamellar structures and zones of transition to the disc structures.

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I. INTRODUCTION

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

On the other hand these systems appear to behave in many aspects as usual nematics. Recent light scattering results[6] showed that the nematic-isotropic and the nematic-lamellar phase changes in lyotropic liquid crystals are closely similar to analogous transitions in thermotropic liquid crystals. However this result does not exclude the possibility that the basic structural unit of nematic lyomesophases be aggregates of micelles instead of isolated micelles.

The SDS system has a phase transition on cooling from N_L to a coagel CG phase at 22^oC. X-ray diffraction results[7] show that this transition corresponds to the Krafft melting of the hydrocarbon chains. Analysis of diffracted intensities in the CG phase indicate[7] completely anhydrous lamellar aggregates of extended tilted bilayers dispersed in water. Comparison of diffracted peak positions indicate that only three water layers are present between micelles in N_L phase, what gives support to the hypothesis of aggregates of micelles in the nematic phases.

In order to have more information about the state of aggregation of the micelles in the nematic phase, it was found interesting to investigate the system by electron

microscopy (EM) of freeze-etching replicas (FER).

A study of the phase transitions of the system by differential scanning calorimetry (DSC) was also undertaken, since knowledge of the low temperature phases is essential to interpret FER results and may also help to elucidate the characteristics of the N_L phase.

II. CONSIDERATIONS ON THE TECHNIQUES

EM studies of membranes by FER are well stablished[8], although results must be analysed carefully due to the characteristics and limitations of the technique.

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

Lamellar and hexagonal lyomesophases studied by EM of FER showed[12] that the quick cooling of the systems preserve the structure of the phase at the initial temperature. Both lamellar and hexagonal lyomesophases could be characterized by EM and X-ray diffraction in a coherent way. Studies of lamellar phases in ternary and quaternary systems have also been performed[13,14,15]. No attempt of applying this technique to the study of nematic lyomesophases was reported.

When the systems under study present phase transitions on cooling, it is always 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.

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

III. 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 N) has been used. Samples of 13-20 mg have been sealed in aluminium pans; the reference pan was kept empty. The instrumental calibration constant for measuring the latent heat of transition has been obtained from the solid-liquid transition of destilated water.

Replicas have been obtained with a freeze etching device Balzers model BAS 301. For the rapid cooling freon 22 in liquid nitrogen has been used. The cooled sample was fractured in vacuum by a knife at liquid N temperature; etching was obtained by sublimation of ice during 1' with a table temperature of $-90^{\circ}C$. The replicas were obtained by vaporization of C and Pt over the fractured surface and posterior immersion in a solvent. The replicas were analysed in an Electron Transmission Microscope Siemens Elmiskop 1.

IV. RESULTS AND DISCUSSION

A. DSC RESULTS

15 independent DSC runs have been obtained, the majority in heating curves and some in cooling curves, in the temperature interval $-80^{o}C$ to $+60^{o}C$. Figure 1 shows a typical heating curve result. Three endoergic phase transitions appear; the transition temperatures and the latent heats (obtained from peak areas) are shown in Table 1. The quoted errors correspond to fluctuations observed among the several independent heating runs of various samples. The cooling process is difficult to be followed, since then there is no control over the cooling speed, but it has been possible to observe histeresis and super-cooling in the three transitions, with a shift of up to $10^{o}C$ in the transition temperatures.

Admitting that the $CG-N_L$ transition at $24^{o}C$ 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 of anhydrous Na soaps $CH_3-(CH_2)_n-COONa$ indicate[17,18] three phase transitions between the crystalline tridimensional curd phase and the liquid crystalline lamellar neat phase; the two intermediate waxy and subneat phases present 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 inferior to the latent heat of fusion of the corresponding hydrocarbon. This indicates that in soaps the chains keep 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 present also three phases transitions on cooling[17], and seem rather similar to the SDS system under study. The latent heats for the main order-disorder transition 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 the states in crystals and in liquid n-alkanes and that it is higher for hydrated phases than for anhydrous phases. It is accepted that mobility in liquid crystalline phases is much smaller than in liquid paraffins and only a little more than in the gel phase.

There is therefore reasonable agreement between 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 $12^{o}C$ 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 connected to the structure and dynamics of the amphiphile.

In 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 occurs 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, on the contrary, the second transition has a latent heat that is 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 that could be 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 to the fusion of the aqueous portion of the system, but its latent heat cannot be simply explained by the fusion of water. Admitting 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 69 cal/g.

This result is opposed 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 is therefore used to get 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, what 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, part of water with super cooling down to -15°C and part to -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, besides the perfectly bounded water, that does not solidify even at -100°C, there is a more free water that solidifies at -15°C and an intermediate type that solidifes about -50°C.

In SDS system a throughly 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 existence of water bound to the amphiphile. This fact is probably connected to the presence of salt in SDS system. It has been verified with lecithin in presence of salt solutions that the amphiphile and the salt seem to compete to bound the free water and the behavior of the system changes, becoming similar to systems with less water.

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

B. 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 sublimation and four with sublimation to enhance the contrast between the aqueous and the amphiphile portions of the system. Two replicas have been obtained from the sample in the CG phase at 20°C.

These ten replicas have been systematically analysed by transmission EM and over 100 micrographs have been obtained.

Micrographs obtained from the N_L phase show clearly the existence of two types of materials, with structures in the form of platelets with diameter of the order of 2000 Å. Replicas with sublimation show etching of the aqueous portion. Figures 2 and 3 shows typical results with and without sublimation obtained from N_L phase.

It is, however, very difficult to decide from the micrographs whether a water matrix with amphiphilic structures exists or on the contrary whether the matrix is of amphiphilic with aquous globules. But certainly there is not homogeneous distribution of amphiphile and water in the direction of the optical axis, since the depth of lowering is much more than what would be expect for one water layer (< 20 Å) between lamellae.

The structures do not have uniform size, but variations remain within the same order of magnitude. An estimate of the percentual area occupied by the platelets gives the value 0.35 ± 0.05, which is the volume percentage of amphiphile in the system.

In the replicas obtained from the CG phase, there are zones that 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 possible to observe that the circular structures emerge from the extended lamellae and agglomerate in the transition line between the two phases.

The repetition distance of the extended lamellae is difficult to measure, and some micrographs have been obtained with large amplifications, in the resolution limit of the replica technique. A result is shown in figure 6. It is difficult to decide the basic unit of repetition, since frequently the break in the lamellar structure involve more than one lamella. The smaller observable lamellar thickness is compatible with the repetition distance obtained by X-ray[7] in the CG phase (31.4 Å).

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

It is not completely excluded the possibility that the structures seen in the replicas obtained from N_L phase correspond in reality to the CG phase, while the structures seen in the replicas obtained from CG phase could correspond in reality to lower temperature phases. The fact that the observed lamellar structures are very perfect and extense, while X-ray results from CG phase show only three lammelar reflections, could indicate that such shift in phase diagram might have occurred.

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

It is seen that break of the extended lamellae occur in the transition observed by EM. Such a breack 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.

V. CONCLUSIONS

Results obtained by EM from N_L phase are not conclusive, particularly in what regards the radial size of the micelles. The 2000 Å structures observed may correspond to the CG phase and it is not even excluded the possibility that the matrix is made of amphiphile 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 in the CG phase.

Latent heats obtained helped to correlate characteristics of SDS system with those of analogous systems. The transition CG-N_L corresponds essentially to the Krafft melting of the chains. Since CG phase corresponds to anhydrous lamellar aggregates, this results 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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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

TABLE 1 - Results obtained from DSC heating curves: transition temperatures T and latent heat ΔH.

FIGURE CAPTIONS

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

Fig. 2 - Electron micrograph of replica obtained from N_L phase without etching (amplification 20000).

Fig. 3 - Electron micrograph of replica obtained from N_L phase with etching (amplification 20000).

Fig. 4 - Electron micrograph of replica obtained from CG phase with etching (amplification 8000).

Fig. 5 - Electron micrograph of replica obtained from CG phase with etching (amplification 8000).

Fig. 6 - Electron micrograph of replica obtained from CG phase with etching (amplification 80000).

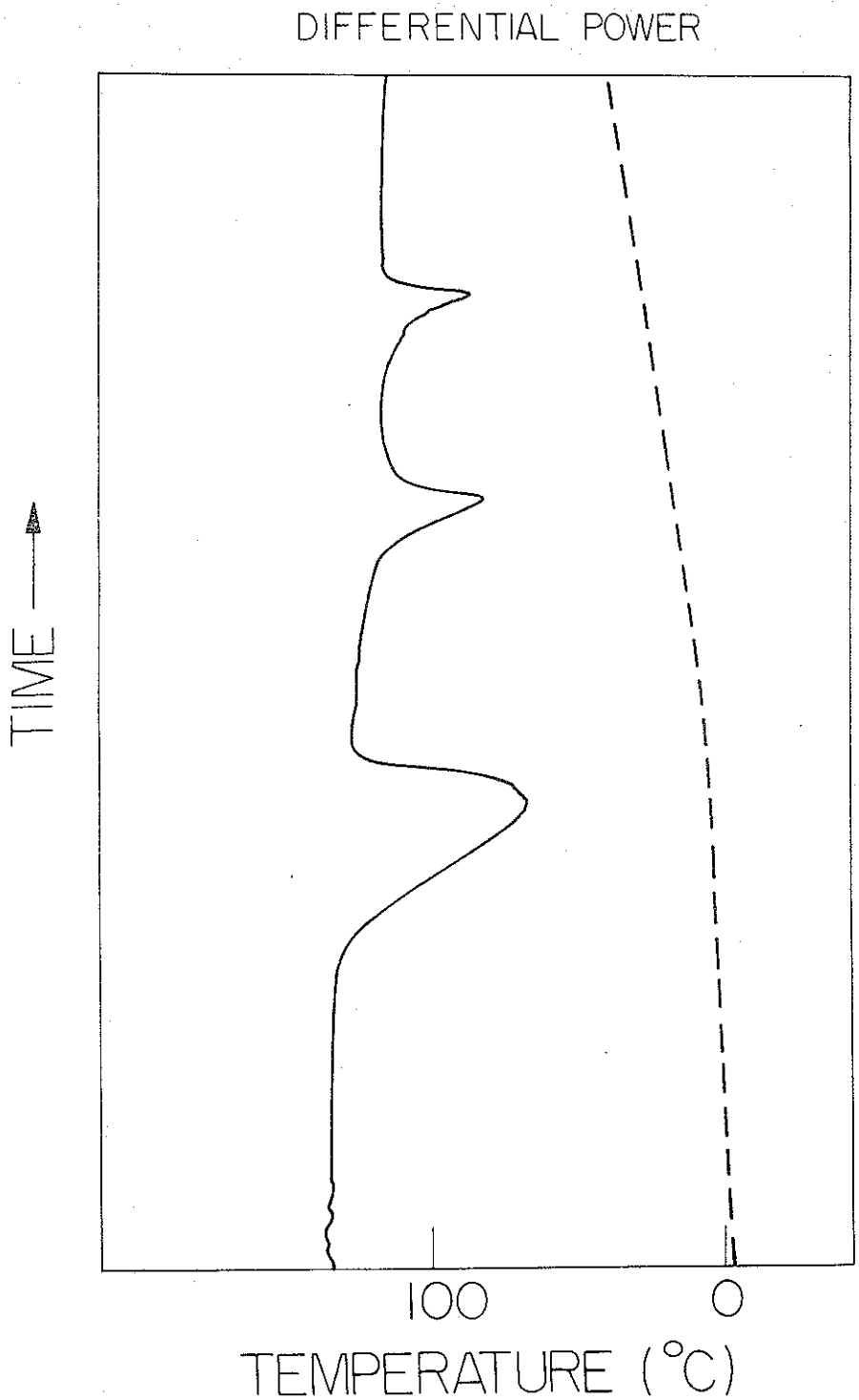

Fig. 1

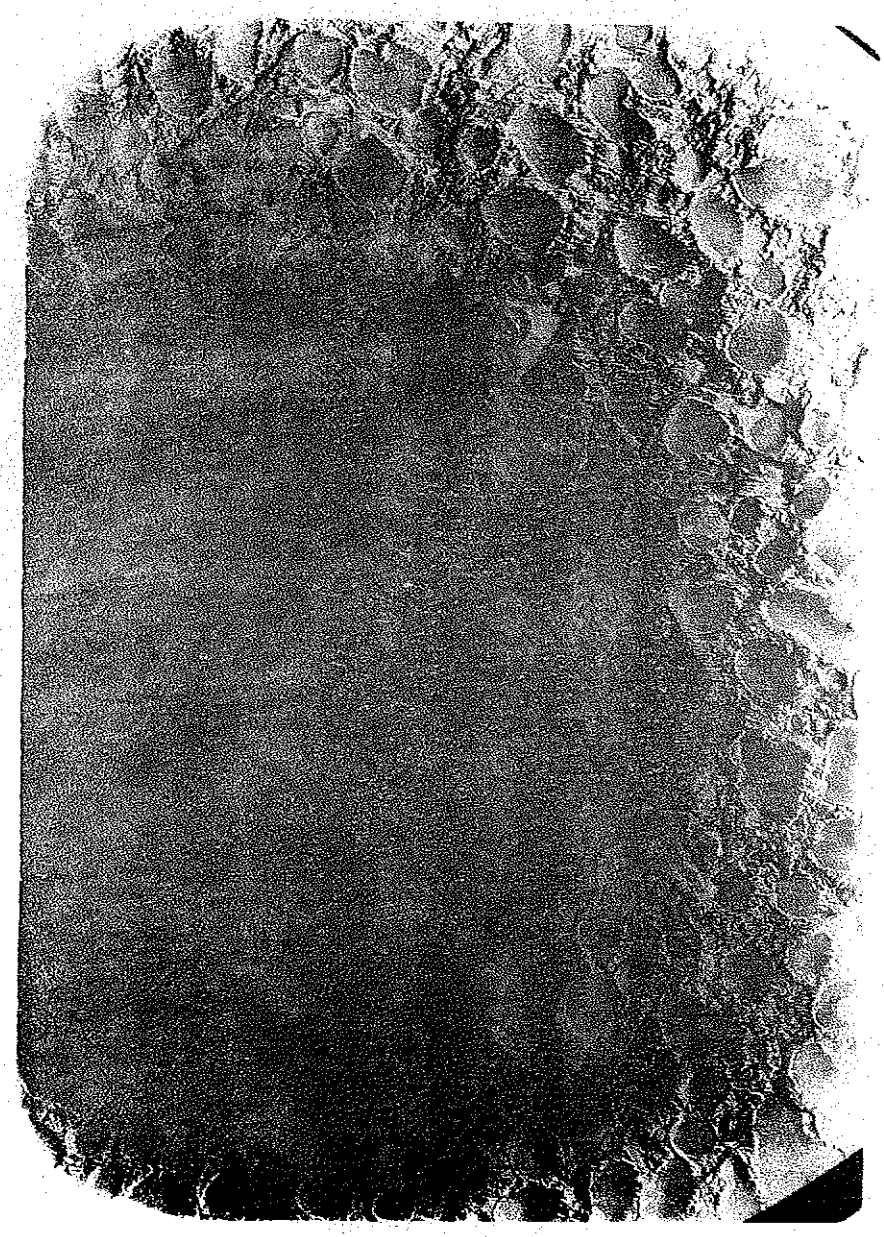

Fig. 2

Fig. 3

Fig. 4

Fig. 5

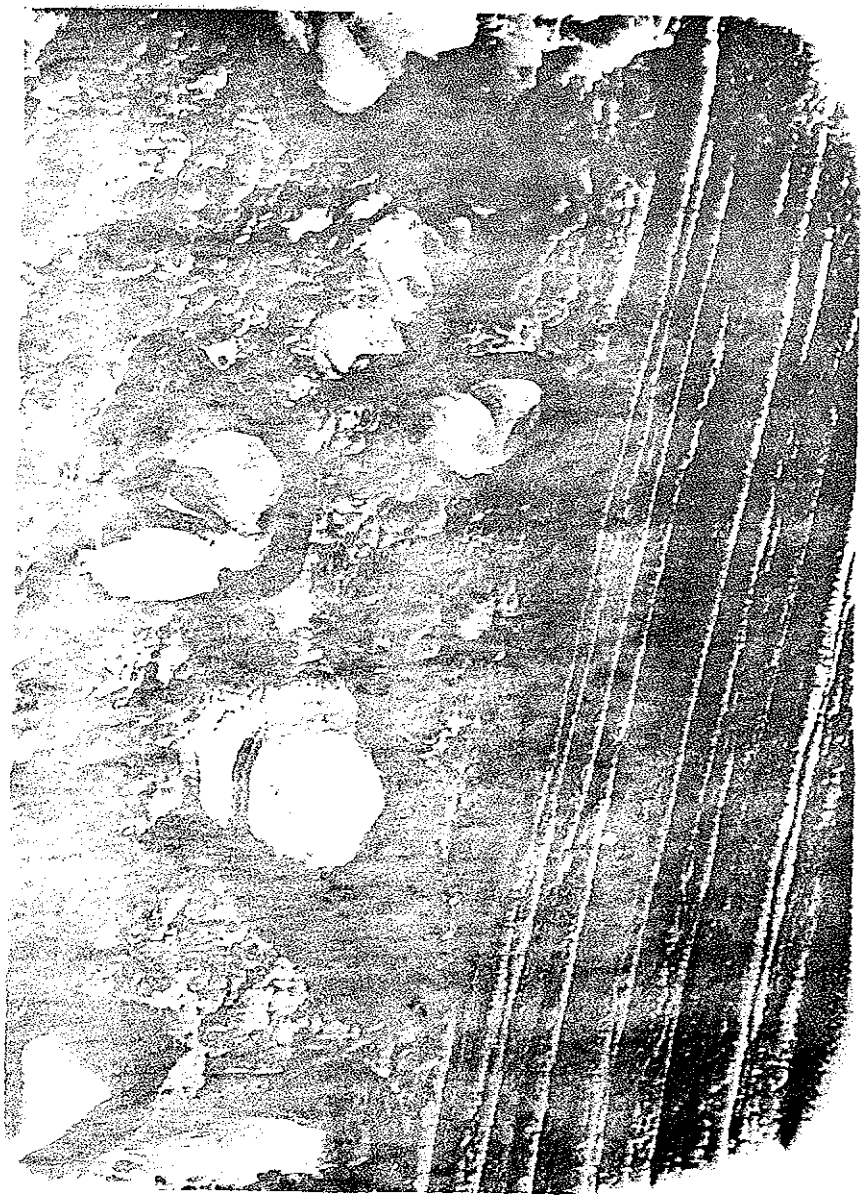

Fig. 6