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INVESTIGATION OF THE TEMPERATURE PHASE TRANSITION IN LANGMUIR-BLODGETT FILMS OF DISCOTICS

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Abstract Small-angle X-ray scattering was used for a definition of a structure of Langmuir-Blodgett films of tetraalkalinooxygidrochinons. The localisation of the molecules in the layer has been proposed. Phase transitions "solid crystal-liquid crystal" in Langmuir-Blodgett films, structural parameters of Langmuir-Blodgett films and the bulk phases were investigated.

Keywords: Langmuir-Blodgett films, discotic phases, diffraction

INTRODUCTION

Substances with both amphyphilic and liquid crystal properties have been synthetized recently. It is interesting to study them from two points of view: as selfassembling of mesogens in liquid crystal phase and as selfassembling at the air-water interphase. Several studies of such molecular behaviour at the water surface were done (1-3). It should be mentioned that a deposition of Langmuir-Blodgett (LB) films of molecules, forming a liquid crystal phase in a given temperature range, may be useful also from a practical point of view. It will make possible to construct devices, which only need very thin liquid crystal films with high ordering.

This work is dedicated to the formation of films of discogens at the air-water interface, to their deposition onto different solid substrates and investigation of structure and thermotropic phase transitions in these films. We have found and investigated by X-ray scattering a phase transition " solid crystal - liquid crystal " in LB films of discogens. A comparison of structural parameters of bulk samples with a molecular organisation in LB films was carried out.

EXPERIMENTAL PART

Materials

The object under investigation was the family of tetraalcalinooxygidrochinons (TAOGCH). Five homologues of this series were investigated: TGOGCH (n=6), TGpOGCH (n=7), TOOGCH (n=8), TNOGCH (n=9) and TDOGCH (n=10). These

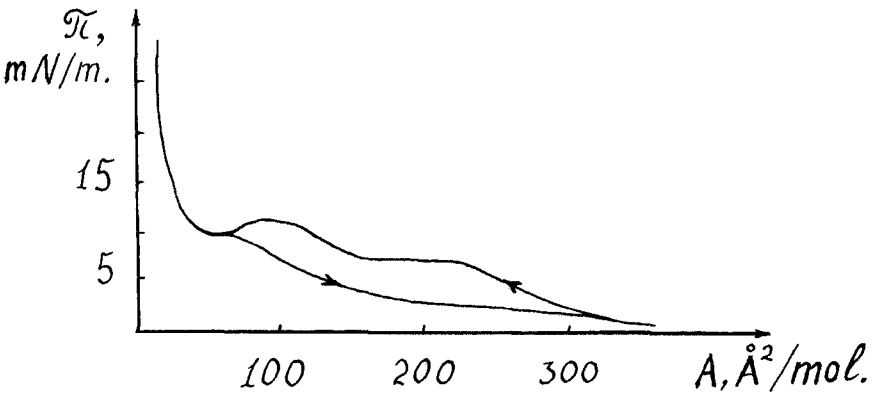

FIGURE 1. π- A isotherm of TGOGCH

substances were synthetized by Akopova O.B. (Ivanovo State University). Three of them (TGpOGCH, TOOGCH and TNOGCH) form a discotic liquid crystal phase in bulk in several temperature ranges (4). Two of them (n=7 and n=8) form enantiotropic and one (n=9) - monotropic liquid crystal phases. The other three compounds (n=6, 8, 10) have two solid crystal phases.

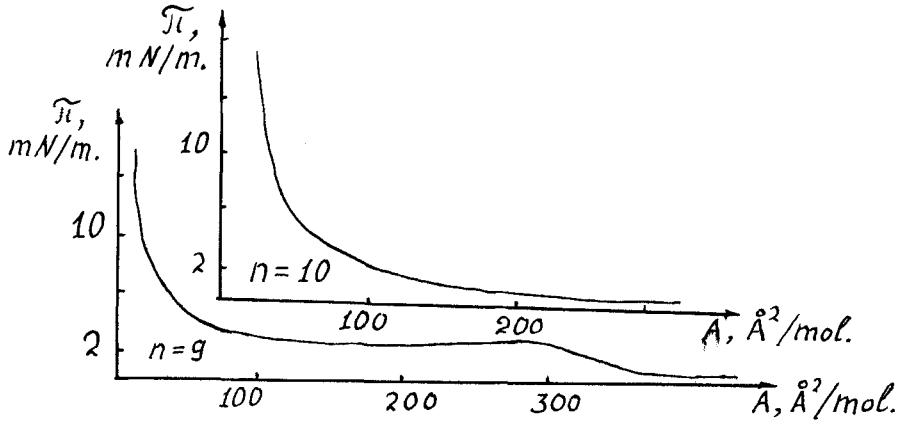

FIGURE 2. πA - Isotherms of TNOGCH and TDOGCH.

DEPOSITION

"Joyce Loebl" Langmuir through was used for monolayer formation and deposition. Films were deposited onto silicon and glass substrates. Surface pressure was about 16 mN/m. The number of layers was waried from 30 to 100.
A small-angle x-ray diffractometer was used for the investigation of LB films structure (5). A linear position-sensitive detector was used for recording X-ray diffraction patterns. Angular resolution of the detector was 0.02°.

RESULTS AND DISCUSSION

π-A isotherm of TGOCH is shown in FIGURE 1. Isotherms of 6,7 and 8 homologues are identical to each other. They have two horizontal plateaus upon compression. The ninth homologue has only one plateau and the tenth homolog isotherm has no plateau at all (see Fig.2). A very small area per one molecule is a characteristic feature of these compounds.

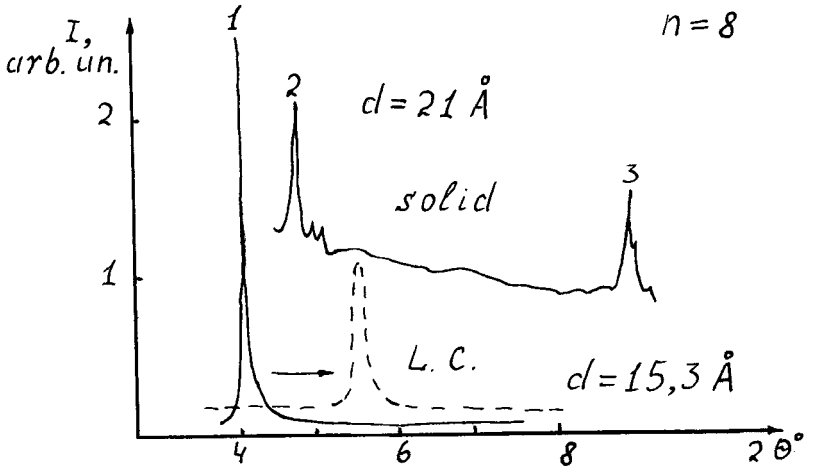

FIGURE 3. X-ray diffraction pattern of TOOGCH (solid line: t=20°C, dotted line: t=76°C).

The X-ray diffraction pattern of TOOGCH (solid line) is shown in fig.3. Usually there are from 3 to 5 reflections in a diffraction pattern. The lamellar structure periods for all compounds under the investigation are presented in table 1. The dash in the table means that there is no liquid crystal phase for the sample when the sample is heated. An additional information about the LB films was obtained by using a photomethod. Two additional reflections were recorded. The angular position of the reflections is at 30

degrees with respect to the positions of layer reflections. The reflections indicate the inclination of some structural fragments with d=4.3 Å.

Two projections of the molecule of the substances under investigation are shown in fig. 4. There are a large center part and 4 short hydrocarbon chains in it. There is no part with a constant electron density in our molecule, so it is very difficult to calculate the electron density profile. In this work we calculated only the Patterson function for our structures. The considerable amount of the molecular

TABLE 1 Structural data of the compounds under investigation in the bulk and LB films

TABLE 1

Homologes number	Isothems	Spacing (Å)			
		LB films		Bulk material	
		Solid	LC	Solid	LC
n = 6	2 plates	16.6	-	17.0	-
n = 7	2 plates	19.4	14.7	19.7	14.9
n = 8	2 plates	21.2	15.3	21.9	15.5
n = 9	1 plate	23.3	-	23.7	-
n = 10	no plates	25.2	-	25.3	-

packing in LB films is shown in fig. 5. The molecules are packed in columns. Discotic molecules are likely to lay horizontally at the water surface at small values of surface pressure. As the film is compressed hydrocarbon chains turn slowly up from the water surface. A first horizontal plateau at A isoterm corresponds to turning of molecules and their discotic part being arranged perpendicular to the water surface. The second plateau corresponds to bilayer and multilayer formation. So, our films were deposited onto solid substrated in a form of multilayers (high pressure). It should be mentioned that the structure is the same independently of the pressure of deposition (we have compared the structure of TOOGCH LB films deposited at surface pressures from 5 mN/m). So, the structure of LB films seems to be realized atthe moment of deposition of molecules onto solid surfaces.

On the other hand we have the opportunity to form micro solid crystal samples on the water surface when the pressure is high. Thus we form very thin (multilayer) crystal films on the water surface and then deposit them onto the solid substrate.

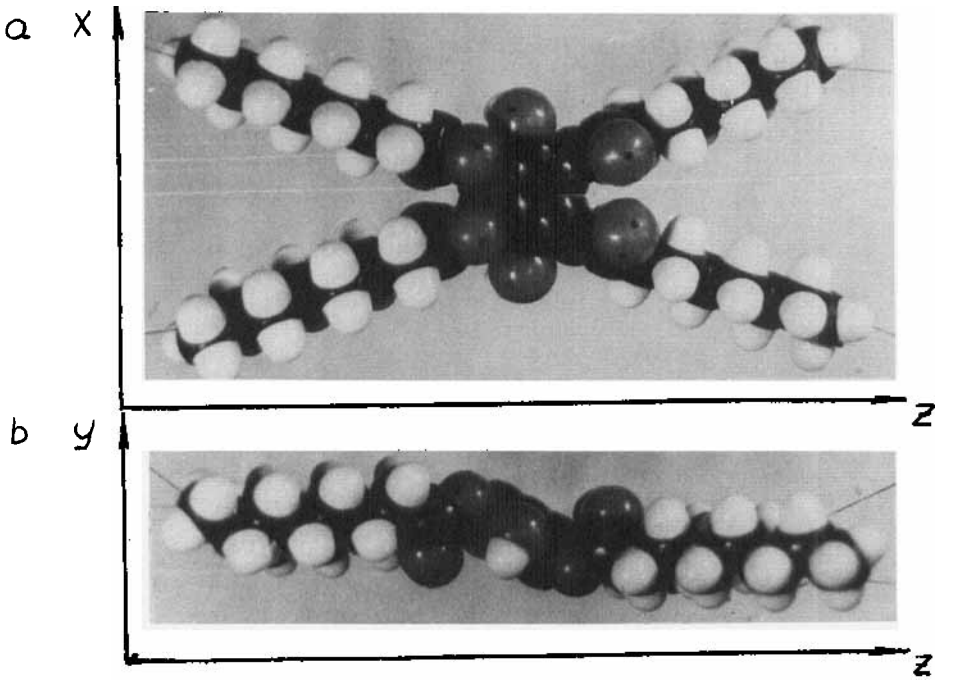

FIGURE 4. Projections of the molecule (a: XZ plane, b: YZ plane).

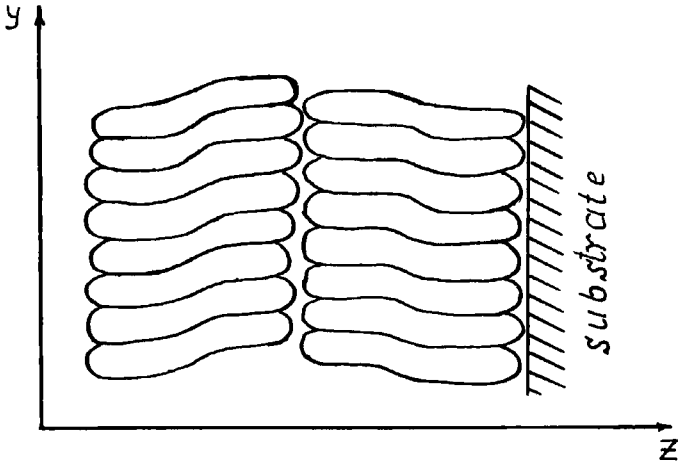

FIGURE 5. Model of the molecular packing in LB films.

Another point of the work was the investigation of the temperature phase transition in LB films of discotics. The

diffractogram of TOOGCH LB film at room temperature is shown in fig. 3 (solid line). The diffractogram of the same sample after heating is also shown in fig. 3 (dotted line, T=76°C). The position of reflections had shifted and the spacing changed from 21.2 Å to 15.3 Å. There is only one reflection in the X-ray pattern of the sample after heating. The correlation length indicates the degree of ordering and is calculated from half width of reflections. It also had changed: from 1000 Å in solid phase to 400 Å in liquid crystal phase.
So, we have seen a phase transition: "solid crystal - liquid crystal" in LB films of discogens. The orientation of the samples after heating remained rather high.

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