

# Structural Phase Transitions in Langmuir Liquid Crystal Films

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**Abstract**—The isotherms of water molecule absorption on hyperfine Langmuir films made based on liquid crystals are investigated. A sharp increase in the adsorption capacity of the films at temperatures of 75°C (for a film with a thickness of ten monolayers) and 102°C (for a film with a thickness of five monolayers) has been revealed. This behavior is explained by structural phase transitions that take place at these temperatures.

**Keywords:** Langmuir–Blodgett films, smectic liquid crystals, adsorption

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## INTRODUCTION

Several papers devoted to the study of Langmuir–Blodgett films that are fabricated based on liquid crystals have been published recently [1–3]. The authors of [4] point to variations in the properties of liquid crystal films with a decrease in their thickness. Thus, changes in the properties of such substances are to be expected when turning from “bulk” layers of liquid crystals to Langmuir films. Such variations may be related, first of all, to a decrease in the mobility of liquid crystal molecules in a Langmuir film. Moreover, there is no certainty that a hyperfine film has a mesomorphic phase.

A para-tetradecyloxybenzyliden-amino-2-methylbutyl-cyanocinnamate (TDO BAM BCC) liquid crystal, whose “bulk” properties have been studied in detail, was chosen as the object of investigation. A method that was proposed in previous papers that consists of measurement of the isotherms of molecule adsorption from a gaseous phase at different temperatures (see, e.g., [5]) was used for recording phase transitions in Langmuir films. A temperature structural phase transition is accompanied by a sharp increase in the number of adsorbed molecules on the film surface. The present study is aimed at revealing phase transitions in Langmuir films of liquid TDO BAM BCC crystals.

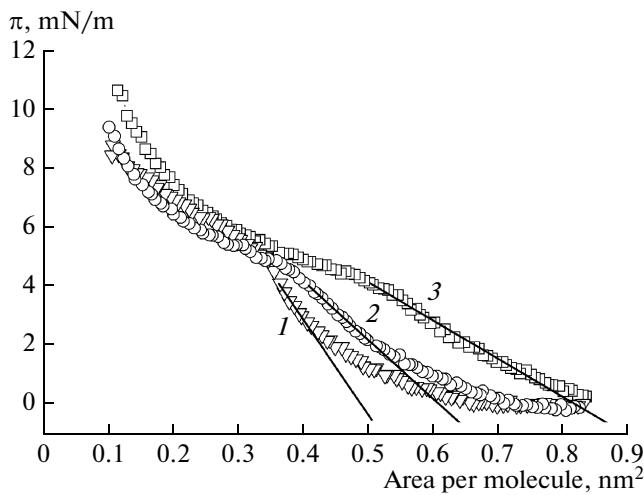
## MEASUREMENT TECHNIQUE

The test objects were films obtained using the Langmuir–Blodgett method based on the Schiff compound of para-tetradecyloxybenzyliden-amino-2-methylbutyl-cyanocinnamate (TDO BAM BCC). This compound is a ferroelectric liquid crystal

(C\* smectic) in the temperature range of 54–70°C [1]. Spontaneous polarization is  $P_s \approx 10^{-9}$  C cm<sup>-2</sup>. The chemical formula of TDO BAM BCC is  $C_{14}H_{29}O-C_6H_{14}-CH=N-C_6H_4-CH=C(CN)-COO-CH_2C^*-H(CH)_3C_2H_5$ . The asterisk marks the carbon atom that provides the chiral structure of the substance. A dipole momentum inclined with respect to the director is created by the CN group. The films were produced using a TDO BAM BCC solution in chloroform with a concentration of  $1-3 \times 10^{-2}$  wt %. The behavior of a monolayer of this substance on an aqueous surface was first studied: the dependence of the surface pressure on the area per one molecule ( $\pi$ -A-isotherm) was measured at temperatures of 21–28.5°C (Fig. 1).

Analysis of the shape of this dependence makes it possible to distinguish three sections of the  $\pi$ -A-isotherm, which correspond to three phase states: a “gaseous” state in the region of the surface pressure not higher than  $1 \text{ mN m}^{-1}$ , a “liquid condensed” state at  $1-5 \text{ mN m}^{-1}$ , and a state at surface pressures higher than  $5 \text{ mN m}^{-1}$ , which is related to molecule aggregation. The shape of the  $\pi$ -A-isotherms changes with a temperature increase. The decrease in the slope of the curve in the region of the transition from the “liquid condensed” state to the state where molecule aggregation takes place corresponds to the increase in the area occupied by one molecule with an increase in the measurement temperature. Corresponding tangents to the curves are shown in Fig. 1. The intersection of the tangents with the X axis shows that with an increase in the measurement temperature from 21°C to 28.5°C the area per one molecule increased from  $0.48 \text{ nm}^2$  to  $0.87 \text{ nm}^2$ , i.e., twofold.

The TDO BAM BCC films were obtained using the Langmuir–Scheffer method (horizontal lifting). This



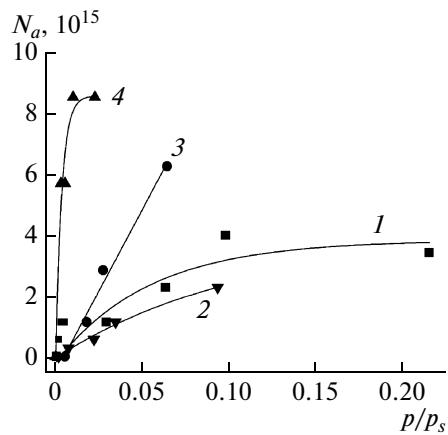
**Fig. 1.** The surface pressure  $\pi$  as a function of the area per one TDO BAM BCC molecule at different temperatures: (1) 21°C, (2) 24.5°C, and (3) 28.5°C.

method makes it possible to obtain films on one side of the substrate. Quartz resonators with a frequency of 5 MHz with five and ten monolayer films were used as the substrates. The number of the adsorbed  $N_a$  molecules was measured using the method of “piezoresonance quartz balance” [6]. The working surface of the geometrical surface of the Langmuir film on the resonator was  $\sim 30 \text{ mm}^2$ . The sensitivity of the method during adsorption was  $\sim 5 \times 10^{12}$  molecules. The error in the measurement of  $N_a$  was determined by the accuracy of recording the pressure of the adsorbed substance ( $p$ ) and did not exceed 5%. The temperature deviation during the experiments did not exceed 0.5 K. In previous papers [5, 7] we showed that adsorption of a number of molecules from a gaseous phase on Langmuir films can lead to their swelling, i.e., the area of adsorbents can vary in the process of adsorption. Thus, in the present study we did not normalize the number of the adsorbed molecules to the area.

## RESULTS AND DISCUSSION

Figure 2 shows the isotherms of water molecule adsorption on TDO BAM BCC films with thicknesses of five monolayers at several temperatures. The adsorbent was introduced at room temperature and, thus, the range of  $p/p_s$  (where  $p_s$  is the pressure of saturated vapors) sharply decreased with an increase in the measurement temperature. As a rule, the time of adsorption equilibrium onset did not exceed 30 min. Analogous times were observed in the process of water adsorption on the surface of PVDF [7] and VDF-TrFE [5] films.

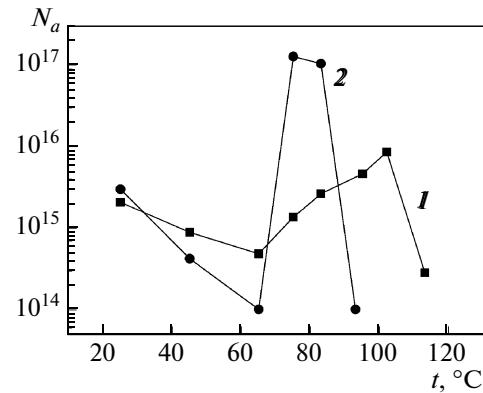
Before the measurements the specimens were kept in a vacuum for 1 day. Then the films were kept in a vacuum at the measurement temperature and only after that the adsorbent was introduced. All adsorption



**Fig. 2.** Isotherms of water molecule adsorption on a TDO BAM BCC film with a thickness of five monolayers. The measurement temperature, °C: (1) 45; (2) 65; (3) 75; and (4) 102.

isotherms were fully reversible. Under a temperature increase, the number of the adsorbed molecules  $N_a$  first decreased (this is usually observed far from the transition temperature) and then sharply increased (at the same value of  $p/p_s$ ) up to the temperature of 102°C (for a five monolayer film) and 75°C (ten monolayers). At temperatures exceeding the  $N_a$  maximum, the number of H<sub>2</sub>O molecules adsorbed on the film rapidly decreased. Figure 3 shows the  $N_a(T)$  dependences obtained from the adsorption isotherms, which clearly illustrate the character of the  $N_a$  variations with temperature on the films with different thicknesses.

Let us analyze the causes of the increased adsorption capacity of TDO BAM BCC films with an increase in temperature. The structure and the character of bonds in Langmuir films based on liquid crystals are not yet clear. However, it can be said with a high degree of reliability that TDO BAM BCC molecules can be bound by weak Van der Waals forces. These



**Fig. 3.** The number of the adsorbed molecules as a function of temperature: (1) a five-monolayer film ( $p/p_s = 0.02$ ); (2) a ten-monolayer film ( $p/p_s = 0.05$ ).

bonds can be destroyed under the effect of adsorbate molecules. A structural phase transition is accompanied by activation of the molecules that the film is made of; this facilitates the diffusion of the adsorbate molecules deep into the film. When the temperature of the phase transition is passed, the film structure becomes less mobile and the number of adsorbed molecules decreases. The small H<sub>2</sub>O molecules can penetrate over the entire film bulk. Such assumptions are confirmed by the data shown in Fig. 3 from which it follows that the adsorption capacity of the film increased with an increase in the film thickness. Thus, in this case we deal with a “bulk” phase transition, as distinct from the “surface” structural transformations, which disappear with an increase in the layer number [7, 8]. A sharp increase in the number of adsorbed molecules with an increase in the film thickness shows that the mobility of TDO BAM BCC molecules sharply decreases with a decrease in the number of the film layers. It is likely that sufficiently thick Langmuir films fabricated based on liquid crystals will be similar in their properties to “bulk” specimens of liquid crystals.

Let us discuss the decrease in the phase transition temperature in the films with an increase in the layer number from five to ten. Such a variation in the phase transition temperature is somewhat surprising. As a rule, a high-temperature phase is characterized by a higher symmetry. A decrease in the number of layers increases the importance of the surface characterized by a lower symmetry as compared to the three-dimensional bulk. Thus, a transition to a low-temperature low-symmetry phase becomes easier with a decrease in the film thickness and the temperature of the phase transition drops. This is likely to be explained as follows. Within the temperature range of 40–110°C, one can observe a number of transformations in the “bulk” TDO BAM BCC films (solid state—C\* smectic—A smectic—isotropic phase) [1]. Thus, different phase transitions can be observed in the films that are five and ten monolayers thick. The limitation of the mobility of the liquid crystal molecules related to a small number of layers can make any transition impossible. In addition, it is not correct to consider various phase transformation temperatures in “bulk” TDO BAM BCC films with the aim of determining the phases

above or below the temperature of the transition in a Langmuir film since the phase transition temperature can shift with a decrease in the number of layers. Summing up the above, we would like to note that additional investigations using other methods are necessary in order to reveal the nature of the observed phase transitions.

## CONCLUSIONS

In this study, structural phase transitions in hyperfine Langmuir films were revealed. The temperature of the phase transition depended on the number of the film layers and increased with a decrease in the film thickness. Thus, structural transformations are observed in hyperfine Langmuir films and the number of the phase transitions and their temperatures do not correspond to the critical temperatures observed in “bulk” specimens of liquid crystals.

## ACKNOWLEDGMENTS

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