Changes in Adsorption and Optical Properties of Liquid Crystal Langmuir Films at Structural Phase Transition

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Abstract—The adsorption isotherms of water molecules, absorption spectra, and spectra of diffuse scattering and polarization of reflected light are studied for ultrathin Langmuir films prepared based on liquid crystals. A structural phase transition near 70°C is detected. Some specific features of the reflection spectra at the phase transition temperature are found. Suggestions are made regarding the nature of the phase transition.

INTRODUCTION

Recently, several papers devoted to Langmuir–Blodgett (LB) films prepared based on liquid crystals (LCs) [1–3] were published. In [4], it was pointed out that some properties of LC films vary as the film thickness decreases. Because of this, a change in the properties of these substances should be expected when passing from the bulk LC layers to LB films. This change may be related primarily to the decrease in the LC molecule mobility in an LB film. Moreover, we cannot say with certainty that an ultrathin film has a mesomorphic phase.

As an object of study, we chose *para*-tetradecyloxy-benzylideneamino-2-methylbutylcyanocinnamate (TDOBAMBCC) LC, the bulk properties of which were studied quite explicitly. To detect the phase transitions (PTs) in LB films, we used a method that consists of measuring the isotherms of molecule adsorption from the gas phase at different temperatures [5]. Passage through the structural PT temperature was accompanied by a sharp increase in the number of molecules adsorbed on the film surface. One of the objectives of this study was to determine PTs in LB films of TDOBAMBCC LCs. Valuable information on the nature of these transitions can be obtained from a study of the optical properties of films at different temperatures in a range that includes the PT temperature. For this reason, we studied the temperature dependences of the absorption and diffuse-scattering spectra of LB films of TDOBAMBCC, which can exist in the form of LC in the bulk phase.

EXPERIMENTAL

The studied samples were films prepared by the LB method based on the Schiff compound TDOBAM-BCC. This compound is a ferroelectric LC (smectic *C*) in the temperature range of 54–70°C. The spontaneous polarization is $P_s \approx 10^{-9}$ C cm^{-2}. The chemical formula of TDOBAMBCC is $C_{14}H_{29}O-C_6H_4-CH= N-C_6H_4-CH=C(CN)-COO- CH_2C^*H(CH)_3C_2H_5$. The asterisk indicates that the carbon atom is responsible for the chiral structure of the substance. A dipole moment directed at an angle to the director is produced by the CN group.

To obtain the films, we used a TDOBAMBCC solution in chloroform. The solution concentration was $(1-3) \times 10^{-2}$ wt %. In the measurements of the adsorption isotherms, the substrates were the 5-MHz quartz resonators, on which films 5 or 10 layers thick were deposited. The number of adsorbed molecules N_a was measured by the method of piezoresonance quartz balance [6]. The working area of the geometric surface of LB film on the resonator was about 30 mm^2. The method sensitivity at adsorption was about 5×10^{12} molecules. The error in measuring N_a was specified by the accuracy of the adsorbate vapor pressure (p) and did not exceed 5%. The temperature deviation during experiments was no more than 0.5 K. It was shown in [5, 7] that the adsorption of some molecules from the gas phase on LB films may lead to their swelling, i.e., the adsorbent area can change. For this reason, the number of adsorbed molecules was not normalized to the area.

Optical measurements were performed on 30-monolayer films. The latter were transferred from water surface to silica glass substrates by the Langmuir–Schaefer method (horizontal lift). The film thickness on the substrate was 20 nm. The absorption spectra were measured with a UV-3600 Shimadzu double-beam spectrophotometer with an operating range of
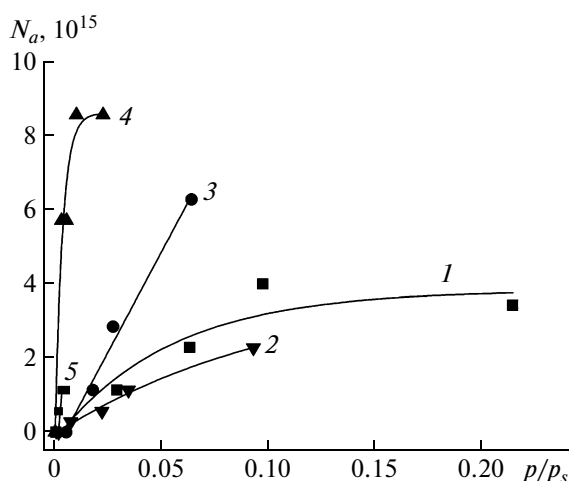
Fig. 1. Adsorption isotherms of water molecules on a 5-monolayer TDOBAMBCC film at temperatures $T = ($ *1*$)$ 45, (2) 65, (3) 75, (4) 102, and (5) 113°C.
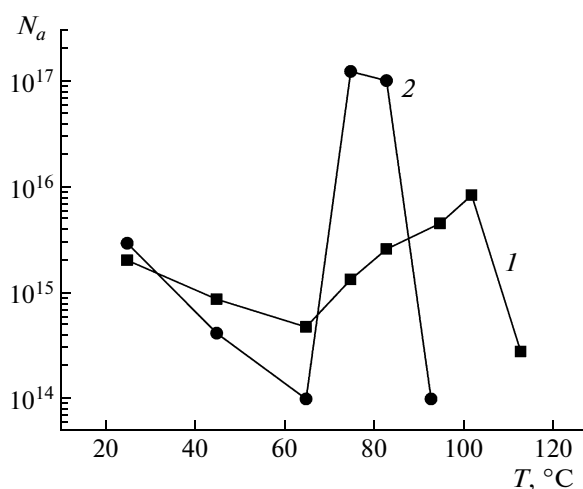

Fig. 2. Temperature dependences of number of adsorbed molecules: (*1*) 5-monolayer film ($p/p_s = 0.02$) and (2) 10-monolayer film ($p/p_s = 0.05$).

185−3300 nm and an error in setting the wavelength of ±0.2 nm in the UV and visible regions.

The spectra of diffuse scattering and polarization of reflected light were measured with a Perkin-Elmer LS-55 spectrometer, which operated in the spectral range of 200−900 nm with a slit spectral width of 2.5−20 nm. The polarized light spectra could be measured using the built-in polarizing filter wheels in the paths of the incident and recorded light beams.

To study the structural transformations in the LB film, spectral measurements were carried out at different temperatures in the range of 17−110°C. A special hot stage was developed for this purpose. The heating element had a transparent window to transmit light. A thermal sensor (thermocouple) was situated against the window on the opposite side from the heater, symmetrically with respect to the LB film. The error in setting temperature in the experiment was ±1°C.

RESULTS AND DISCUSSION

First of all, we studied the behavior of the TDOBAMBCC monolayer on the water surface. The dependence of the surface pressure on the area per molecule (π-A isotherm) was measured at temperatures of 21−28.5°C. The estimation of the average monolayer thickness (based on the area per molecule calculated from the compression curves) yields values of 2.97−2.74 nm for temperatures that change from 21 to 28.5°C. After transferring the film to the silica glass substrate, the thickness of one monolayer was 0.6−0.7 nm (according to capacitance measurements). This value suggests that the molecules in the LB film transferred to the substrate make a small angle with the substrate plane (11−15°). This molecular arrangement is similar to that in smectic C layers. According to the data of [1], the film is in the polar phase in the

temperature range of 20−110°C. No phase transitions were found by electrophysical methods.

Figure 1 shows adsorption isotherms for water molecules on 5-monolayer TDOBAMBCC films at several temperatures. The adsorbate was fed at room temperature, which is why the range of p/p_s (p_s is the saturated vapor pressure) sharply decreases with temperature. As a rule, the adsorption equilibrium was established in no more than 30 min. Similar times were observed for the adsorption of water on the surface of PVDF [7] and VDF-TrFE [5] films.

Before measurements, samples were evacuated for 24 h, after which the films were kept in a vacuum at the measurement temperature; only after this procedure, was the adsorbate introduced. All adsorption isotherms were completely reversible. As the temperature increased, the number of adsorbed molecules N_a first decreased (which is usually observed far from the transition temperature) and then sharply increased (at the same ratio p/p_s) up to 102°C (film 5 monolayers thick) and 75°C (10 monolayers). At temperatures above the point that corresponds to the maximum N_a value, a rapid decrease in the number of H_2O molecules adsorbed on the film was observed. Figure 2 shows the dependences $N_a(T)$ obtained from the adsorption isotherms. These dependences clearly illustrate the character of variation in N_a with temperature for films of different thicknesses. Let us consider the reasons for the increase in the adsorption capacity of TDOBAMBCC films with temperature. At present, the structure and character of bonds in LC-based LB films are unclear. At the same time, one can say with sufficient confidence that TDOBAMBCC molecules may be bound by weak van der Waals forces. These bonds can be broken when affected by adsorbate molecules. The structural PT is accompanied by the acti-
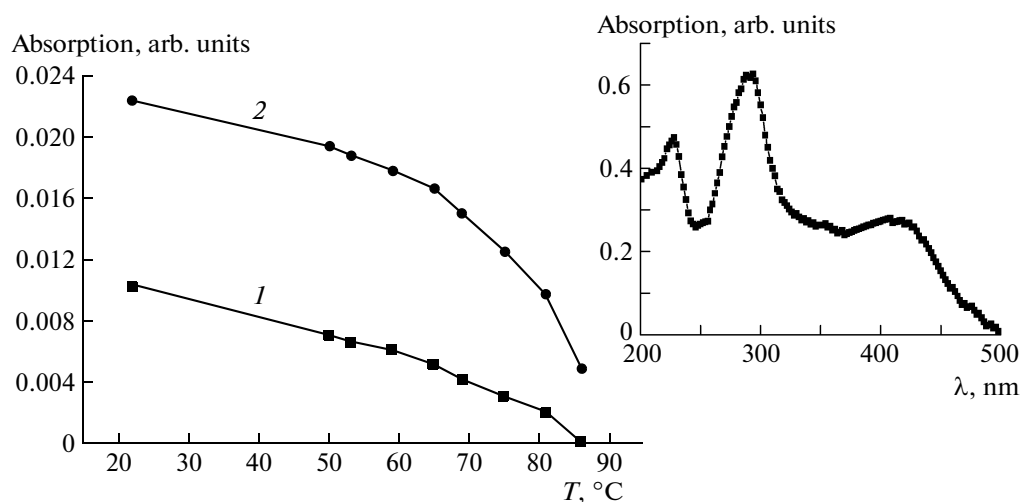
Fig. 3. Temperature dependences of intensity of absorption bands of TDOBAMBCC, peaking at (*1*) 227 and (*2*) 291 nm. Inset shows TDOBAMBCC absorption spectrum.

vation of molecules that enter the film composition, which facilitates the diffusion of adsorbate molecules in the film bulk. When passing through the PT point, the film structure becomes less mobile and the number of adsorbed molecules decreases. The H_2O molecules, which are small in size, may penetrate throughout the entire film volume. These suggestions are confirmed by the data presented in Fig. 2. As follows from the figure, the adsorption capacity of the film increases with its thickness. Thus, in this case, we are dealing with the bulk PT, as opposed to the surface structural transformations, which disappear with an increase in the number of layers [7, 8]. The rapid increase in the number of adsorbed molecules with increasing film thickness indicates that the mobility of TDOBAMBCC molecules sharply drops as the number of the film layers decreases. Apparently, one would expect the properties of fairly thick LB films based on LC to approach those of bulk LC samples.

Let us discuss the increase in the PT temperature with a decrease in the number of layers from ten to five. A number of transformations are observed in bulk TDOBAMBCC films (solid state–smectic *C**–smectic *A*–isotropic phase) in the temperature range of 40–110°C [1]. Therefore, different PTs can be observed in 5- and 10-monolayer films. The restriction of the LC molecule mobility related to the small number of layers may forbid some transitions. Moreover, when identifying the phases below and above the transition temperature in an LB film, it is hardly correct to rely on particular temperatures of the phase transformations in the bulk TDOBAMBCC films because the PT point may shift with a decrease in the number of layers. To sum up the aforesaid, we should note that the elucidation of the nature of the PT found requires additional studies involving other techniques.

The absorption spectrum of the films transferred to the substrate in the UV and visible regions contains three characteristic bands that peak near 227, 291, and 422 nm (Fig. 3, inset). As the temperature increases from 20 to 100°C, the 422-nm band does not change significantly, while the intensities of the bands at 227 and 291 nm gradually decrease (Fig. 3). There are no specific features at the temperatures of possible PTs in the film. The energy of the light photons in the observed absorption bands corresponds to the electronic excitations of TDOBAMBCC molecules. Since these molecules are bound by weak forces of the van der Waals type and the PTs are structural, the latter do not affect the energy of electronic transitions.

Then, we obtained the spectra of diffuse light scattering from the surfaces of the films under study at different temperatures. The diffuse scattering was chosen to minimize the effect of the radiation reflected from the polished surface of silica substrate. We separately measured the spectra of the vertically polarized (perpendicularly to the plane of incidence) and horizontally polarized (in the plane of incidence) components of the diffusely reflected radiation in the case of exposing the sample to natural light. The general view of smoothed reflection spectra is shown in Fig. 4, the maximum of diffuse scattering corresponds to a wavelength near 400–420 nm.

As the next step, we studied the temperature dependences of the spectra of polarized components and total intensity of diffusely reflected light. Figure 5 shows the temperature dependences of the total intensity of the vertically and horizontally polarized components of reflected light at 420 and 580 nm.

It can be seen in Fig. 5 that the temperature dependences of the intensity of diffusely reflected light at different wavelengths behave similarly. A sharp decrease (with a minimum near 70°C) is observed in
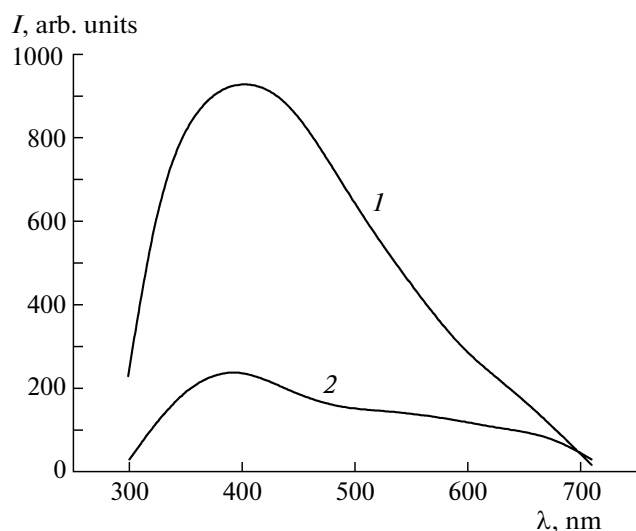
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Fig. 4. Spectra of (*1*) vertically and (*2*) horizontally polarized components of diffusely reflected light at 24°C.

affect the polarization characteristics of scattered light.

Since, as follows from Fig. 4, the light reflected from the film proved to be partially polarized (basically perpendicularly to the plane of incidence), we studied the degree of polarization of reflected light. The degree of polarization of diffusely scattered light was calculated from the spectral data for vertically and horizontally polarized components. Figure 6 shows the temperature dependence of the degree of polarization of light diffusely reflected from the film at a wavelength of 580 nm (the formula for calculating the degree of polarization is given in the figure caption). It should be noted that the initial degree of polarization of diffusely scattered light at room temperature was specified by the geometry of the experiment (as the partial polarization at reflection from a dielectric film).

It can be seen in the figure that the degree of polarization of the light reflected from the LC-based LB film sharply changes in the range of 60−90°C and approaches a maximum near 70°C, the point at which the structural phase transition was detected.

In [1], an LB film was found to be in the polar state in a wide temperature range of 50−105°C; the polarization of the film somewhat increased with temperature. The latter may be due to several reasons. First, the state of the LB film immediately after its deposition on the substrate at room temperature may differ from the most thermodynamically favorable one. Both upon heating and with an increase in the internal energy of the film with respect to its binding energy with the substrate, one or several successive transformations of the film structure can be observed, which

the intensity of the light reflected in a chosen direction in a wide wavelength range at temperatures of 60−90°C. This can be explained by the fact that the spatial distribution of the diffusely scattered radiation flux, its intensity, and other properties are determined by the illumination conditions, the properties of the reflecting medium, the presence of inhomogeneities in it, and the structure of these inhomogeneities. Therefore, significant changes in the film structure may lead, e.g., to variations in the angular distribution of scattered light and violation of Lambert's law. In addition, a change in the angular distribution of the dipole moments of molecules in the film may significantly
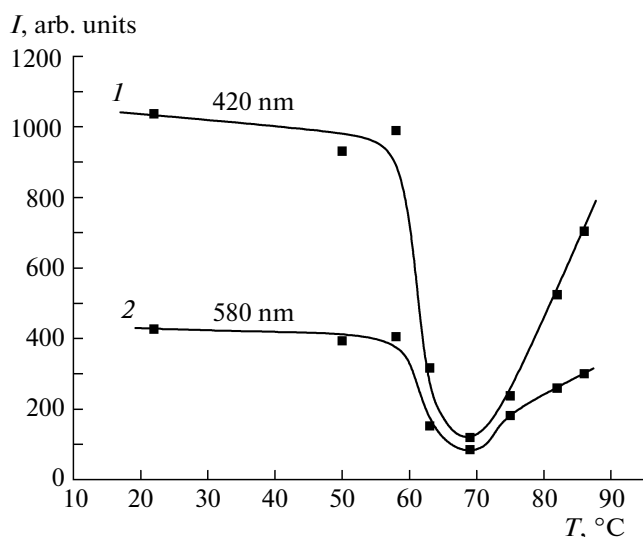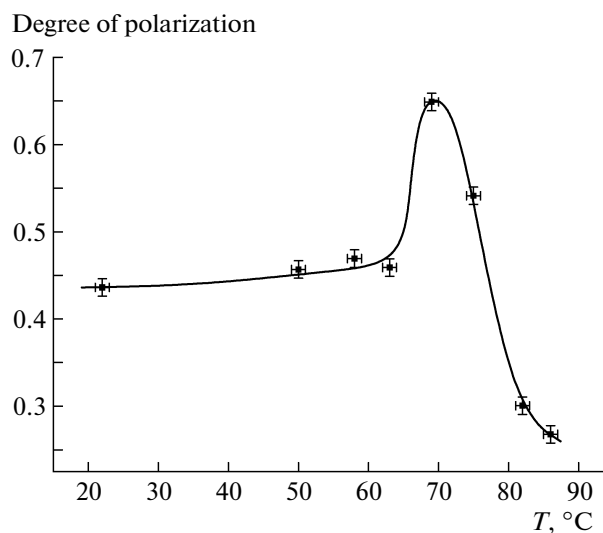
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Fig. 5. Temperature dependences of intensity of diffusely scattered light at (*1*) 420 and (*2*) 580 nm.

Degree of polarization

Fig. 6. Temperature dependence of degree of polarization $\left(P = \dfrac{I_{max} - I_{min}}{I_{max} + I_{min}} \right)$ of reflected light at a wavelength of 580 nm.

transfer the film to a more thermodynamically stable state. In this case, the additional ordering of the dipole moments of molecules and, correspondingly, polarization enhancement may occur. Second, it cannot be excluded that the polarization growth is due to the enhanced dissociation of the molecules that enter the film composition and the motion of the ions produced in the external field. Thus, it is possible that, in the case of TDOBAMBCC, we are dealing with a PT of one of the two (order–disorder or displacive) types or with PTs of both types simultaneously.

The polar phase, which has dipole moments in each unit cell, should reflect light of different polarizations differently. The observed effects of changing the intensity and degree of polarization of reflected light can be explained by the existence of structural PTs in films in the temperature range of 50–100°C.

Since the orientational ordering is the main structural characteristic of LCs, it is natural that all of their properties are determined in a particular way by the degree of orientational order. During structural transformations related to phase transitions, the anisotropic properties of the film change [4], which is likely to affect the spatial distribution of the signal reflected from the film and to sharply change its degree of polarization.

It is interesting to note that films similar to those studied by us were investigated in [1], where no phase transitions were found in the temperature range of 20–100°C using electrophysical and electro-optical methods. In this study, using adsorption and optical methods, we found signs of structural transformation in the films under consideration near 70°C. Since the nature of the detected PT is still unclear, it is no surprise that some characteristics of the films do not change during phase transformation.

CONCLUSIONS

The spectra of optical absorption and diffuse reflection of light from TDOBAMBCC films at wavelengths of 200–800 nm in the temperature range of 20–100°C were recorded. The structural phase transition in the film at 70°C and a sharp decrease in the diffuse reflection coefficient near this temperature were found. The reflected light was found to be partially polarized. The temperature dependence of the degree of polarization of reflected light was studied. Near the phase transition point, a sharp increase in the degree of polarization of the light diffusely reflected from the films was observed, followed by a drop.

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