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Equilibrium parameters of a structured *n*-hexadecane layer

The temperature dependences of the structural characteristics of the quasi-liquid-crystalline n-hexadecane layers − their equilibrium thickness and the degree of orientational order were determined by such optical methods as measurements of admixture dichroism and the anisotropy of heterophase interlayers. The values of these epitropic liquid-crystalline layer parameters were compared with those established earlier in rheological experiments.

Introduction. It is well known that the solid surface is able to alter significantly wetting layer properties and may induce the spatially restricted state in some organic liquid in close vicinity of the substrate. This state is characterized by some peculiarities of physical-chemical characteristics which are sufficiently different from the bulk liquid ones. These peculiarities are caused by the fact of orientational ordering in the wall adjacent layer, which is much similar to classical mesophase. That is why this state was referred to as a special boundary phase of liquid or epitropic liquid crystalline (*ELC*) state [1]. The investigation of this quasi liquid crystalline phase structure is important and actual not only in fundamental aspect, but also is of undoubted interest from the application point of view. It is due to correlation between *ELC* properties of some alkanes (the main component of modern engine oils) and tribological characteristics of liquid interlayers in mechanisms, which in turn determine the conditions of accident-free operation and the minimum wear of friction mechanisms. In particular, it refers to the investigation of *n*-hexadecane, which is a homologue of alkane hydrocarbons row. Experimental studies and molecular dynamics simulations of *n*-hexadecane thin interlayers proved the presence of special properties of these objects [2-5].

Rheological investigations [6, 7] of thin symmetrical heterophase liquid interlayers (including *ELC* layers) (between metal substrates) made it possible to study the peculiarities of their transport phenomena and to establish the effect of shear flow on the temperature dependences of viscosity and stationary thickness of such *ECL* layers.

The obtained results were interpreted within the framework of the structural-rheological model [7, 8], according to which in a heterophase interlayer each of the substrates induces an *ELC* layer with the thickness d_s. This layer should be considered as a two-component mixture of a high-viscosity component and a low viscosity component of an isotropic liquid (the corresponding values of their viscosities and relative parts are η_s, s and η_{vol}, $1–s$). These values determined the magnitude of experimentally measured *ELC* layer viscosity η. From the other side this value may be calculated as the viscosity of the two liquids mixture.. This calculation may be based on different model relationships [9 −11] (e.g. cubic root equation of Kendall- Monroe, double logarithmic equation of Valter - Refutas, the formulae connected with additivity of fluidities and etc.). In the first approximation the value of the layer viscosity η is determined by the linear superposition of viscosities of mixture components:

$$\eta = \eta_s \cdot s + \eta_{\text{vol}} \cdot (1-s) = (\eta_s - \eta_{\text{vol}}) \cdot s + \eta_{\text{vol}} . \qquad (1)$$

Heating leads to the process of orientational melting of the [12] layer that is why the thickness of the layer d_s and the relative part s of the ordered phase in it decrease (as, indeed, the values of η_s and η_{vol}). Therefore, the stationary (in steady-state flow) thickness of the structured layer $d_s(\gamma)$ decreases with increasing of the shear deformation rate γ (c^{-1}), taking the maximum equilibrium value $d_{0s} = d_s(\gamma \to 0)$ in the absence of the flow ($\gamma = 0$). Also, the shear flow, deforming the *ELC* layer, shifts the direction of the orientation of the vector of the director.

To explain the nature and mechanism of the formation of the *ELC* layer, its statistical model was proposed [13]. In this work, the highly viscous structured component of the layer is regarded as the "pile" of molecular associates which is adsorbed at the substrate. Within the framework of such a model, a theoretical calculation was made of the temperature dependence of the equilibrium thickness of the *ELC* layer $d_{0s}(\Delta T = T - T_m)$, where T_m is the melting point of its crystal.

A comparatively good agreement between the experimental results and the theoretical prediction for such polar aromatic hydrocarbon liquid as nitrobenzene achieved in the framework of the model showed the perspective of using such a model.

The model allows further development in order to describe the *ELC* state of non-mesogenic liquids of a different nature, consisting of non-polar but anisometric molecules. Experimental data that are necessary for comparison with the theoretical dependence $d_{0s}(\Delta T)$ may be obtained both in rheological and in optical experiments. It should be noted that this dependence is the most important tribological characteristic of the lubricant interlayer.

In rheological experiments carried out at isothermal conditions (with interlayers of different thicknesses), the value of the *ELC* layer "equilibrium" thickness d_{0s} was determined from the measured dependence $d_s(\gamma)$ by extrapolation to its value in the absence of the flow ($\gamma \to 0$). However, the extrapolation procedure always gives a considerable error, since measurements at extremely low values of the shear rate are rather difficult.

Therefore, one important **research task** of our investigation was to measure the temperature dependence of the equilibrium thickness by independent optical methods, in order to establish the reliability of the same functional dependence obtained by processing rheological experiments. Correlation of these dependences allows one to form a holistic view about the nature of the *ELC* state. Besides it is principally impossible to determine the value of the structural parameter s in rheological experiments. It, in turn, makes impossible the estimation of isotropic and high-viscosity

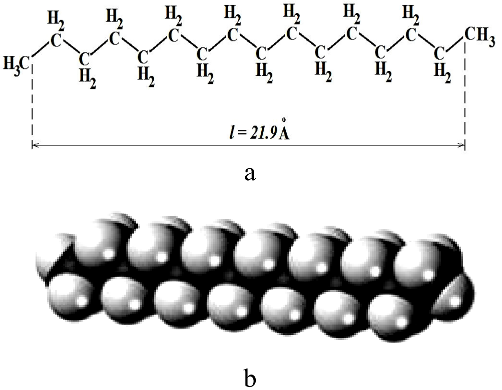

Fig 1. Structural formulae of *n*-hexadecane (a) and its Stuart-Briegleb model, which takes into account Van der Waals radii of atoms (b)

components contributions to the total viscosity of the layer (1) and its temperature dependence. However, since the parameter *s* is an analogue of the orientational order parameter *q*[1] of liquid crystals [14], the measurement (by optical methods) of the degree of ordering $q(\Delta T)$ makes it possible to make a reliable estimation of temperature dependence of these contributions.

The **subject of our study** was the *ELC* wall-adjacent *n*-hexadecane layers[2] contained in interlayers symmetrically bounded by metallic substrates in the absence of their flow, i.e. in the so called "static" friction triads. The elongated molecular form is a peculiarity of alkane structural characteristics. In the normal trans-isomeric state of aliphatic hydrocarbons the atoms in molecules are linked by single bonds, molecules have a filamentary (nematic) shape, and their hydrocarbon chains have the same polyethylene structure CH_3-$(CH_2)_n$-CH_3 [15]. *n*-Hexadecane molecules ($n = 16$, melting temperature $T_m = 291.2$ K) look like "rods"(Fig. 1) with the length $l \approx 21.9$ Å [15].

A character feature of the **methods of investigation** was using the classical techniques developed for analysis of the structure of thermotropic *LC* [14], but specially modified for the case of *ELC* layer. Dichroism and optical anisotropy-birefringence (*BR*) [16] in heterophase interlayers were measured. Such methods, non-destructive for the *ELC* layer, allow us to establish exactly the values of its equilibrium thickness and order degree parameter in the absence of the flow. Earlier [16], the procedure of determination of the structural characteristics of the *ELC* layers of organic compounds by dichroism measurements was carried out in their interlayers, bounded by transparent dielectric substrates (quartz, sapphire, glass). To compare the results of measurements of the structural parameters of the *n*-hexadecane *ELC* layer obtained by the dichroism method with the results obtained in the described rheologi-

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[1] This parameter also varies within the range from $q = 1$ (maximally structured layer) to $q = 0$ (disordered isotropic liquid).

[2] NZSP production, chemically pure qualification.

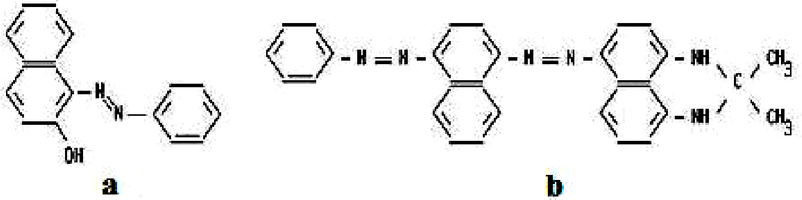

Fig.2. Structural formulae of dyes – “red sudan” (a) and “black sudan” (b)

cal experiments in a metallic rotational pair, it was necessary that the physical characteristics of the substrates (which bounded the liquid interlayer) were similar, i.e. the substrates in optical experiments should be also metallic.

On the other hand, in the method of measuring dichroism, the ray-of-light geometry of the experiment [17] assumes the transparency of the substrates. This contradiction was eliminated by vacuum thermal deposition of a thin semitransparent metallic layer (nichrome) on a substrate surface (optically polished quartz glasses[3]). As the serial equipment of spectral analysis did not allow us to study the absorption bands of the investigated aliphatic hydrocarbons located in the vacuum ultraviolet region ($\nu > 50000 \, \mathrm{sm}^{-1}$), we used the admixtured absorption method of the guest-host type.

The reliability of the information obtained by this method is determined by the degree of isomorphism of the matrix and impurity molecules, so that the structural characteristics of the impurity molecules should be comparable with the corresponding parameters of the solvent matrix. At the same time, the dyes used must have a high extinction in the region of atmospheric ultraviolet and good solubility in the studied liquids also. The latter requirement led to the use of popular dyes – “sudan red” (maximum absorption band λ_{max} ~ 0.472 mcm) and “sudan black” (maximum absorption band λ_{max} ~ 0.606 mcm).

Fig. 2 shows the structural formulae of these compounds. From this figure one can see that the “black sudan” molecules are more extended in comparison with the “red sudan” ones (quantum chemical evaluations of their lengths give $l \approx 2.05$ nm and $l \approx 1.05$ nm). Hence the “black sudan” molecules have the higher degree of isomorphism i.e. they are better compared in length and form with the "rods" of *n*-hexadecane. Nevertheless we usually used “red sudan” as guest impurity. This is due to its higher solubility and greater light extinction value which makes it possible to provide the reliable results of structure parameter investigation of thin interlayers (d~ 0.2÷5 mcm) of solutions of such a low concentration (1÷3 weight %) in which the presence of an impurity practically has no influence on the structure of the studied hydrocarbon liquid matrix.

Beforehand, a wedge-like gap was formed by controlled (by interference colors) compression of the metallized quartz windows of the cell. Its profile was determined by the analysis of an interferogram, which was obtained by scanning this gap with a narrow monochromatic light probe [16]. Then the gap was filled in with the studied

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[3] Sizes $(\varnothing = 15 \text{ mm}, \, \boldsymbol{h} = 3 \text{ mm})$, average value of asperities ~ 20 nm.

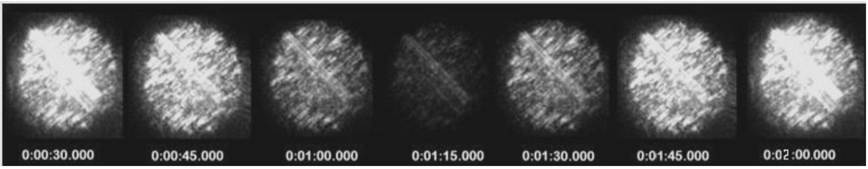

Fig. 3. The sequence of frames "captured" by the program for finding the minimum intensity (interval 15 s)

liquid, and the thickness dependence of the interlayer optical density $D = f(d)$ was measured.

The deviation of this dependence from the linear Booger form indicates the heterophase state of the interlayer. For the homeotropic orientation of molecules in the wall-adjacent *ELC* layers this dependence looks like a concave broken line, which may be approximated by such two linear dependences that minimize the total variance of experimental results. One of them in the region of small values of d corresponds to the absorption of the *ELC* layer, the other one – to the bulk isotropic *n*-hexadecane state.

The value of *ELC* layer BR was measured with the help of a special micropolarimeter setup, with a laser (λ = 0.65 mcm) used as a light source. The investigated sample was a liquid interlayer bounded by steel substrates (gaging rods[4]), oriented in such a direction that the light beam was parallel to the surface of the bounding substrates (the geometry of the experiment called "the sample in the gap" [17]). The sample was placed between crossed Nicol prizms, and the magnitude of the phase shift was determined with the help of the Senarmon compensator (a plate of $1/4\,\lambda$), which was set to a position corresponding to the minimum of the transmitted light intensity[5].

In order to automate the experimental procedure and to increase the reliability of the data obtained, the second eyepiece of the binocular microscope was interfaced with a web camera that allowed us to digitize the variation of the field of view illumination with the rotation (by step motor) of the compensator in a real-time mode. The camera recorded a frame-by-frame video file of the sequence of alterations in transmitted (through the interlayer of a known thickness d) light intensity for each step of an angle of rotation (~ 0.01 rad).

Fig.3 illustrates the photographs of the video recorded frames of the light-guide output gap. One can see the alterations in the intensity of light transmitted through the interlayer of the sample (d = 50 mcm, T = 300 K), under the compensator rotation. At each photo the program displays the corresponding time from the beginning of the scanning procedure. From the video file, a frame with a minimum intensity was found programmatically and, accordingly, the azimuth of the extinguishing angle associated with the phase difference δ between the components $\boldsymbol{E}_p$ and $\boldsymbol{E}_s$ of elliptically

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[4] Steel Ioganson tablets (4 × 10 mm) with a high degree of metal surfaces smoothness (12 grade of finish, average deviation of the profile R_a = 0,02 – 0,04 mcm).

[5] The experimental procedure with an analysis of the method errors was described in detail in [15].

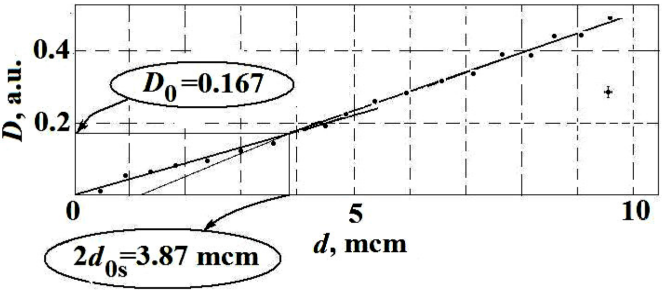

Fig.4. The thickness dependence of the optical density ***D*** of admixture absorption of the *n*-hexadecane interlayer $\Delta T = 2.5$ K)

polarized light was determined. A thickness dependence $\delta(d)$ of a structurally inhomogeneous interlayer allows one [17] to establish the equilibrium thickness d_{0s} of the *ELC* layer and the value of its optical anisotropy.

Results and discussion. Measurement of the admixture dichroism of the dye as a “guest” in the wedge-like interlayers of *n*-hexadecane at various temperatures ΔT allowed us to determine the optical density $D(d, \Delta T)$ dependences on their thickness. From the analysis of each series of such experiments, the temperature dependences of the structural parameters $d_{0s}(\Delta T)$ and $q(\Delta T)$ of the *n*-hexadecane *ELC* layer on the metallized substrate were established. One of these dependences, measured at the temperature $\Delta T = 293.7\text{-}291.2 = 2.5$ K, is shown in Fig. 4.

The abscissa of the intersection point of these lines corresponds to the twice thickness of the wall-adjacent layer, and the values of their slope coefficients (μ_s and μ_{iso}) allowed us to calculate the value of the order parameter of the impurity molecules ($q = 1 - \mu_s / \mu_{iso}$). To eliminate the effect of interference oscillations (significant due to the increasing of the light reflection coefficient from a semi-transparent metalized surface), the experimental curve was preliminary smoothed by a moving average method (on the basis of 5 points). Experimental graph in fig.4 demonstrates that at a temperature of 2.5 K above the *n*-hexadecane melting point the equilibrium thickness of its ELC layer is $d_{0s} = 3.87/2 \sim 1.9$ mcm, the linear absorption coefficients of the admixture absorption of the *ELC* layer and of the isotropic "bulk" liquid are, respectively, $\mu_s \sim 4.3 \cdot 10^{-2}$ mcm^{-1} and $\mu_{\text{iso}} \sim 5.5 \cdot 10^{-2}$ mcm^{-1}. These values, in turn, determine the value of the order parameter q of the impurity molecules in the *ELC* layer $q(2.5) \sim 0.22$. The same temperature dependence of the equilibrium thickness $d_{0\text{s}}(\Delta T)$ of the *n*-hexadecane *ELC* layer was also determined in measurements of the optical anisotropy of its liquid interlayers.

The results of the determination of the temperature dependence of the *n*-hexadecane *ELC* layer equilibrium thickness $d_{0\text{s}}(\Delta T)$ by these two independent optical methods are shown in Fig. 5.

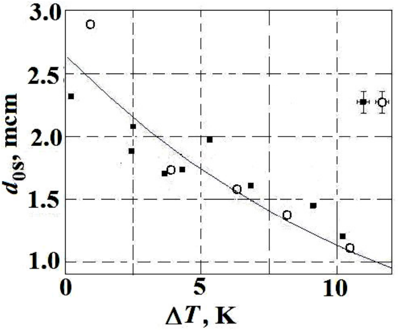

Fig. 5. Temperature dependence of the equilibrium thickness of the *n*-hexadecane ELC layer from the data of optical measurements. ▪ − obtained by measuring of the admixture dichroism, **o** − obtained by BR measurements, solid line − approximation of rheological measurements [18].

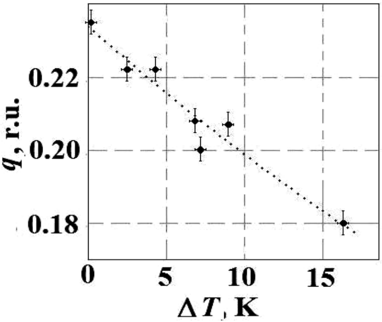

Fig. 6. Temperature dependence of the equilibrium value of the orientational order parameter *q* of the *n*-hexadecane *ELC* layer obtained by measurements of admixture dichroism

In addition, for comparison the line of the exponential trend $d_{0s}(\Delta T)$ is plotted on Fig.5. The equation of the trend was obtained by approximating the results of rheological measurements of the effective viscosity in the shear flow of the same heterophase interlayers of *n*-hexadecane. A sufficiently high degree of correlation of optical and rheological experimental results indicates their reliability and adequacy of the suggested structural-rheological model of the heterophase interlayers.

Fig. 6 illustrates the experimental results of $q(\Delta T)$ found by the dichroism method and shows the line of the approximating exponential dependence. The value found for the orientation order parameter of the guest molecules makes it possible to estimate the order parameter of the ordered *n*-hexadecane *ELC* matrix in which the molecules of the "red sudan" impurity are dissolved (solution concentration $C \sim 2.37$ weight percent). Obviously, the order degree of the matrix molecules will not be lower than that of the impurity ones, which correlates with the values of the orientational order parameter of aromatic ELC found earlier (by the intrinsic absorption dichroism method) [16].

By using the approximation found for the parameter $q(\Delta T)$ and its analogy with the parameter $s(\Delta T)$, the temperature dependences of the viscosity of the *ELC* of the *n*-hexadecane interlayer and its components were calculated, basing on equation (1). These contributions were calculated taking into account the rheological measurements of the effective viscosity and the values of the equilibrium structural parameters found in optical measurements. The results of calculated temperature dependences are presented in Fig. 7.

In the same figure, the temperature dependence of the sample "bulk" viscosity is shown for comparison. As can be seen from the figure, while heating, the graphs of the isotropic and bulk viscosity components approach, due to an increase in the con-

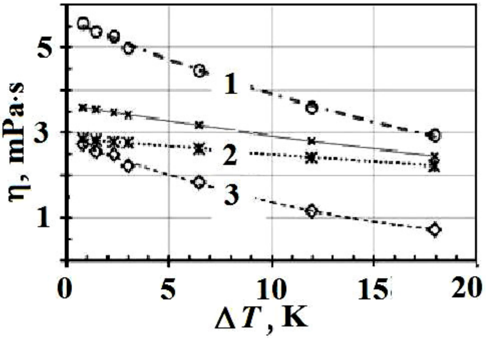

Fig.7. Temperature dependences of viscosity coefficients:
1 − *ELC* layer, 2 − "isotropic" component of the layer $\eta_{\text{vol}} \cdot (1 - s) = f_1(\Delta T)$, 3 − "high-viscosity" layer component $\eta_s \cdot s = f_2(\Delta T)$, (✕) − viscosity of *n*-hexadecane in the bulk $\eta_{\text{vol}}(\Delta T)$

tribution from the isotropic component (a decrease of the order parameter in the ELC layer).

Conclusions. Optical measurements of the dichroism and birefringence of heterophase *n*-hexadecane interlayers symmetrically bounded by metallic substrates made it possible to establish the nature of the temperature dependence of the equilibrium thickness of the *ELC* layer. This dependence satisfactorily correlates with the "limiting" (in the absence of flow) dependence $d_{0s}(\Delta T)$ obtained in rheological experiments. This fact indicates the reliability of obtained results, the adequacy of the integrated approach in the *ELC* state research, and gives a possibility of using the obtained results for subsequent comparison with theoretical values calculated from the molecular-statistical model of the *ELC* layer.

We have to note that experimental data on the temperature dependence of the orientational order parameter of the *n*-hexadecane molecules in its *ELC* layer obtained from dichroism measurements are also significant, so the obtained form of the dependence $q(\Delta T)$ makes it possible to estimate the temperature dependences of the viscosity of the structured and isotropic components of the *ELC* layer.

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Равновесные параметры структурированного пристенного слоя *н*-гексадекана

АННОТАЦИЯ

Оптическими методами (измерениями примесного дихроизма и анизотропии гетерофазных прослоек) определены температурные зависимости структурных характеристик пристенных квазижидкокристаллических слоев н-гексадекана − их равновесной толщины и степени упорядоченности. Проведено сравнение значений этих параметров эпитропного жидкокристаллического слоя с установленными ранее в реологических экспериментах.

Алтоїз Б. А., Поповський О. Ю., Бутенко О. Ф.

Рівноважні параметри структурованого пристінного шару *н*-гексадекану

АНОТАЦІЯ

Оптичними методами (вимірюваннями домішкового дихроїзму та анізотропії гетерофазних прошарків) визначено температурні залежності структурних параметрів пристінних квазірідкокристалічних шарів н-гексадекану – їх рівноважної товщини та ступені впорядкованості. Наведено порівняння значень цих параметрів з тими,що були встановлені раніше у реологічних експериментах.