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The structure of overlapped epitropic LC

The proposed model of the structure of the wall-adjacent epitropic liquid crystalline layer considers it as an oligomeric system of thread-like associates in a non-associated liquid. The results of ELC studies of layers of aliphatic hydrocarbon - n-hexadecane are analyzed. The study of the ELC phase in n-alkanes is important both for the modification of the quantitative physical theory of this phenomenon, and in a practical sense, as it allows to solve practical problems related to the control of boundary friction in mechanisms and parts of machines. Previously, the results of rheological and structural-optical studies of the properties of these systems were considered separately, and the results obtained in the molecular-statistical model were not correlated in detail with the results of rheological measurements for the case of overlapped near-surface layers. To interpret the results of studies (by rheological and optical methods) of such a layer in interlayers of n-hexadecane, symmetrically limited by conductive substrates, it is proposed to take into account the increase in the concentration of the ordered component ("pile") under the condition that the wall layers of epitropic liquid crystals in the interlayer overlap. It will also allow to take into account the results obtained in the molecular statistical model in the processing of rheological data.

Key words: epitropic liquid crystalline layer, associate, alkane, viscosity.

Introduction. The effect of a solid substrate action on near-surface non-mesogenic liquid layers, which induces there an orientationally ordered supramolecular structure such as the epitropic LC phase [1], has been known for quite a long period of time [1, 2], but its study still allows us to obtain a new information about the nature of interaction of liquids and solid bodies in the region of their interphase boundary. The studying of ELC properties is continued to this day both by experimental [5 - 10] and theoretical [3, 4, 11, 12] methods. The investigation of ELC phase in n-alkanes is important both for modifying the quantitative physical theory of this phenomenon [11 - 14] and in a practical sense [15], since it allows us to solve practical problems related to the control of boundary friction in mechanisms and machine parts.

Characteristics of ELC layer structural component. In a series of works [19-20] modification of the classical methods for studying the structure of bulk liquids [21], makes it possible to establish that for large thicknesses (larger than twice the equilibrium thickness of the ELC layer $D > 2d_{s0}$) the liquid layers are heterophase - between the structured ELC layers adjacent to the substrate, there is exists a “bulk” isotropic liquid. Thinner ($D < 2d_{s0}$) interlayers are homophase and contain only an orientationally ordered ELC layer. Concepts developed for analyzing the results of the rheological investigations of interlayers [24 - 27] allow one to interpret the main

flow characteristics using a structural-rheological model, which operates [26, 27] with the values of the viscosity μ_0 and thickness of ELC layers d_s . In the absence of a shear flow of liquid, the ELC layers near each of the substrates have an equilibrium thickness d_{0s} , and the thickness isotropic “bulk” liquid of the interlayer (viscosity η_{vol}) is equal to $D - 2d_{0s}$.

On the other side, in accordance with the statistical model [11, 14], the ELC layer is treated as a homogeneous mixture of “pile” (with a fraction q) of “thread-like” molecular associates of medium length d_{0s} (consisting mainly of liquid dimers) between which there is an unassociated “isotropic” liquid (with a fraction $1 - q$). Adjoined to the adsorption centers of the substrate surface, such a quasi-polymer “pile” exists above the melting point T_m in the overheated temperature range $\Delta T = (T - T_m) \sim 30 - 40K$.

The characteristics of the “pile” (configuration and concentration of associates) depend on the properties of liquid molecules, the degree of overheating ΔT , the intensity of shear flow and the ratio between the average size of associates d_{0s} and the thickness of the interlayer D (under the condition $D < d_{0s}$). With increasing overheating ΔT , the peripheral molecules break away from associates and move into the “bulk” liquid, and the associates themselves desorb and change their conformational flexibility. In the process of such “orientational” melting [28] of the ELC layer, both its thickness and the proportion of “pile” q in it decrease, and the latent heat of this melting corresponds in order of magnitude to the phase transition of the ELC - isotropic liquid [17, 19]. From the idea that on each of the substrates bounding the symmetrical heterogeneous interlayer there is a “pile” of an ELC layer of finite thickness d_{0s} , it follows the possible type of structure of such an interlayer at different ratios D and d_{0s} .

An increase in the intensity of the shear flow leads to a change in the configuration of associates and to a decrease in their concentration (they are partially “cut off”) with a corresponding decrease both in the viscosity ($\mu(\gamma) < \mu_0$) and in the thickness of the ELC layer (the layer is “cut off” [24]), so it is obvious that the function $d_s(\gamma, \Delta T)$ is monotonically decreasing in both parameters. This effect is also reflected in the value of the interlayer effective viscosity η_{eff} . When the thickness of the heterophase symmetrical interlayer decreases to a value $D = 2d_s$, the value η_{eff} increases, because of the decreasing of the less viscous central interlayer (“bulk” isotropic liquid) relative proportion. With a further decrease in the interlayer thickness, the viscosity also increases due to the appearance of an “overlapped” region between two ELC layers, since with the interpenetration of a “pile”, the viscosity of the central part of the interlayer increases to a value $\mu^* > \mu$. The value of the isothermal effective viscosity of such interlayers, as well as the marginal (in the absence of flow, at $\gamma \rightarrow 0$) effective viscosity may be calculated by solving of the Navier-Stokes equation for the selected rheomodel [30]. The value of inverse effective viscosity in dimensionless form depends linearly on the inverse thickness of the interlayer [26]:

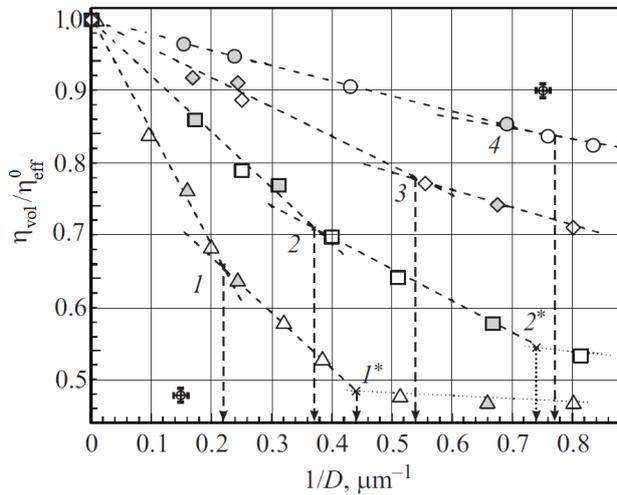


Fig. 1. Dependences of the “marginal” relative viscosity of *n*-hexadecane on the reverse interlayer thickness $1/D$ [25] for different overheating temperatures ΔT , K: Δ – 1.5, \square – 6.5, \diamond – 12, o – 18 [26]. The numbers 1 – 4 indicate the kinking points of the dependence at $D = 2d_{0s}$, and the numbers 1* - 2* indicate the kinking points at $D = d_{0s}$.

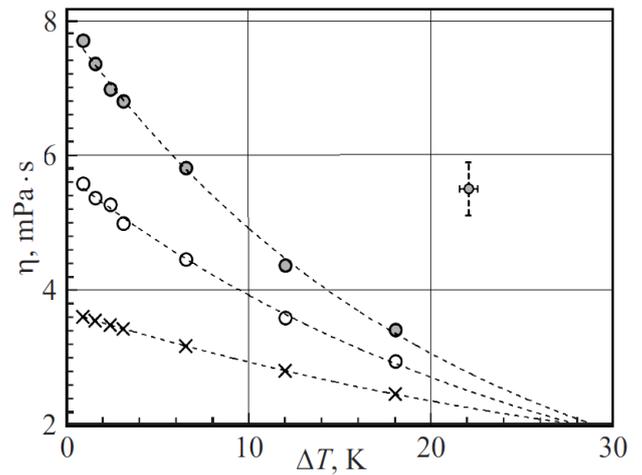


Fig. 2. Dependences of the “marginal” viscosity coefficients of *n*-hexadecane on steel on the overheating temperature above the melting point ΔT , K: o – for an “not overlapped” ELC layer, \bullet – for a completely “overlapped” ELC layer. x – for isotropic “bulk” liquid [26].

$$\frac{\eta_{vol}}{\eta_{eff}^0} = \begin{cases} 1 - \left(1 - \frac{\eta_{vol}}{\mu_0}\right) \cdot \frac{2d_{0s}}{D}, & D > 2d_{0s} \\ \eta_{vol} \left(\frac{2}{\mu_0} - \frac{1}{\mu_{0}^*}\right) - \eta_{vol} \left(\frac{1}{\mu_0} - \frac{1}{\mu_{0}^*}\right) \cdot \frac{2d_{0s}}{D}, & d_{0s} < D < 2d_{0s} \end{cases}, \quad (1)$$

here the parameters indexed by zero correspond to equilibrium values.

It gives a possibility to simplify the analysis of the results of viscosity interlayers measurement in order to establish the changes in their structure in accordance with the proposed model.

Fig. 1 shows graphs of four experimental dependencies for different temperatures of *n*-hexadecane interlayers [25]. The abscissas of the first break points correspond to the inverse double equilibrium thicknesses of the layers $1/(2d_{0s})$, and of the seconds - to their inverse values $1/d_{0s}$, while their ordinates determine the values of the coefficients of the “marginal” viscosities of a homogenous ELC layer – in “not overlapped” and “overlapped” cases. Hence it is possible to establish the temperature dependences of these “marginal” coefficients (Fig. 2). As it can be seen from Fig. 3, the viscosity of the ELC layer is higher than the proper bulk value, and the viscosity of the overlapped ELC layer is even higher, but with increasing temperature both these values and their difference decrease, and at $\Delta T \approx 30$ K all three viscosity coefficients become almost the same.

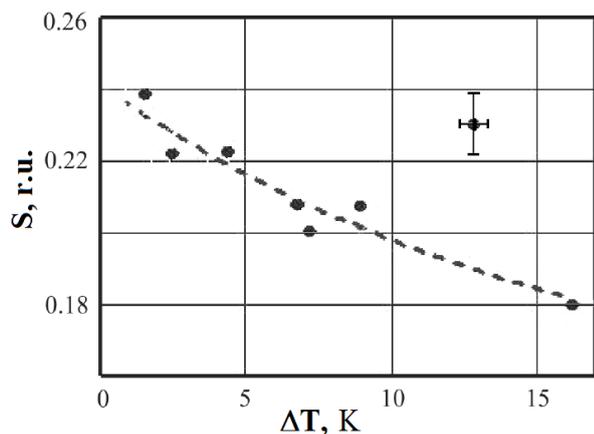


Fig.3. Temperature dependence of the equilibrium value of the orientational order parameter S for an ELC layer of n -hexadecane on a metallized quartz substrate, found by the admixed absorption dichroism method [29].

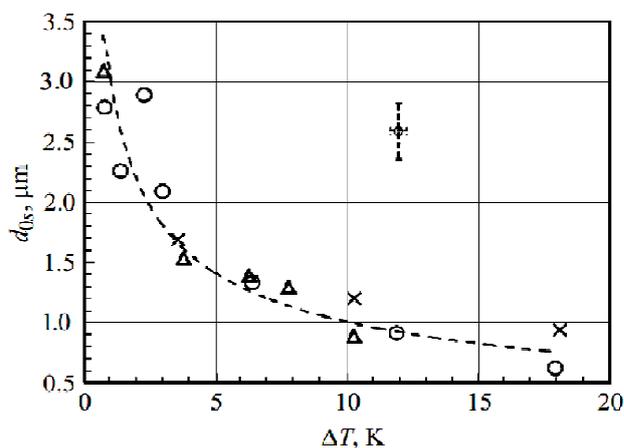


Fig. 4. Temperature dependence of the equilibrium thickness of the ELC layer of n -hexadecane on a metal according to measurement data: X – impurity dichroism, O – anisotropy of the induced birefringence, Δ – viscosimetry [24, 27, 29]. The dotted line is the approximating trend.

Properties of the ELC layer structural component. The dependencies presented in Fig. 1, make it possible to get an additional information about the structural properties of an ensemble of oligomeric associates adsorbed on the active centers of the substrate, which can be considered as a quasi-polymer solution.

We will assume that the viscosity of the structural component of such a solution is equal to η_s , and its relative concentration in the layer is q . Similar values for the isotropic component of such a solution are equal to η_{vol} and $(1 - q)$. For a completely overlapped layer, these values are respectively equal - η_s^* and q^* for a structured component (“pile”), and for an isotropic liquid – η_{vol} and $(1 - q^*)$, respectively. It is obvious that the degree of orientational ordering is connected with the concentration of pile “threads” oriented normal to the substrate and with their flexibility (directly proportional to a first approximation).

Therefore, it is necessary to determine the parameters of orientational ordering in a homogeneous ELC layer for the cases of a completely non overlapped ELC layer ($D = 2d_{0s}$) – S and of a completely overlapped ELC layer ($D = d_{s0}$) – S^* . Previously, in optical experiments of determination of ELC order parameter S by admixed dichroism measurements, the slope of the graph of optical density thickness dependence $D_{opt} = f(D)$ (under the first assumption of ELC structure homogeneity) was averaged, i.e. this dependence for small interlayer thicknesses was assumed to be linear [29]. Relevant temperature dependencies for the equilibrium thickness of the wall-adjacent ELC layer and its order parameter were obtained (fig.3 and fig.4).

In order to take into account possible changes of S in the overlapped part of the interlayer, an expression for the thickness dependence of the optical density should be written in the form:

$$D_{opt}(D, k) = \int_0^D [1 - S(t, k)] \cdot \mu_{iso} \cdot dt, \quad (2)$$

where μ_{iso} – is the linear absorption coefficient of an isotropic bulk liquid (of admixed molecules), and k – is a set of varied parameters within the framework of the selected model dependence.

Minimization of the objective function $F(k) = \sum_i [D_{opt}(D_i, k) - D_{opt_i}^{exp}]^2$ gives the possibility to establish the type of dependencies $S(\Delta T)$ and $S^*(\Delta T)$.

In order to calculate the viscosity and concentration of a structurally ordered oligomeric component of a mixture from known viscosity values of the isotropic component and the total viscosity of the entire mixture, various model relationships may be used, which, generally speaking, lead to similar results. So, using e.g. the Kendall–Monroe cube roots relation [30], we can write the system of equations:

$$\begin{cases} \sqrt[3]{\mu_0} - q \cdot \sqrt[3]{\eta_s} - (1 - q) \cdot \sqrt[3]{\eta_{vol}} = 0 \\ \sqrt[3]{\mu_0^*} - q^* \cdot \sqrt[3]{\eta_s^*} - (1 - q^*) \cdot \sqrt[3]{\eta_{vol}} = 0 \end{cases}, \quad (3)$$

which, allow us to get a numerical solution with considering additional restrictions on the concentration and viscosity of the “pile” components:

$$S < q < q^*; S^* < q^* < 1; \mu_0^* < \eta_s < \eta_s^* \quad (4)$$

for each value of the overheating temperature ΔT .

Conclusion. There was developed a concept of ELC layer as a two-component mixture, which similar to a concentrated quasi-polymer solution. This concept has been proposed for the analysis and processing of experimental results of optical and rheological measurements, which makes it possible to find the quantitative characteristics of the system oligomeric component and to compare it with the results obtained within the framework of a statistical model.

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Поповський О.Ю., Алтоїз Б.А., Бутенко О.Ф.
Структура перекритих епітропних РК

АНОТАЦІЯ

Запропоновано модель будови пристінного епітропного рідкокристалічного шару як олігомерної системи ниткоподібних асоціатів у неасоційованій рідині. Аналізуються результати досліджень ЕРК шарів аліфатичного вуглеводня – *n*-гексадекану. Дослідження ЕРК-фази в *n*-алканах є важливим як для модифікації кількісної фізичної теорії цього явища, так і в практичному сенсі, оскільки дозволяє вирішувати практичні задачі, пов'язані з контролем граничного тертя в механізмах і деталях машин. Раніше результати реологічних та структурно-оптичних досліджень властивостей цих систем розглядалися окремо і результати отримані в молекулярно-статистичній моделі ніяк не корелювалися із результатами віскозіметричних вимірів. Для інтерпретації результатів досліджень (реологічними та оптичними методами) такого шару в прошарках *n*-гексадекану, симетрично обмежених провідними підкладками, запропоновано враховувати збільшення концентрації впорядкованої компоненти (“ворсу”) за умови перекриття пристінних шарів епітропних рідких кристалів у прошарку. Це дозволить також врахувати в обробці реологічних даних результати отримані в молекулярно-статистичній моделі.

Ключові слова: епітропний рідкокристалічний шар, асоціат, алкани, в'язкість.