

УДК 539.2:541.18

**Popovskii A.Yu.<sup>1</sup>, Altoiz B.A.<sup>2</sup>, Butenko A.F.<sup>2</sup>**

<sup>1</sup> National University „Odessa Maritime Academy“, e-mail: [alexejpopovskij57@gmail.com](mailto:alexejpopovskij57@gmail.com)

<sup>2</sup> Odessa I.I. Mechnikov National University, e-mail: [altoiz41@gmail.com](mailto:altoiz41@gmail.com)

## **Structural characteristics of the epitropic liquid-crystalline layer of oleic acid**

*The investigations of the structure of thin oleic acid interlayers bounded by quartz and metallized substrates were carried out by the method of admixed adsorption dichroism. It allowed us to determine structural the existence of epitropic liquid crystalline layers of this compound and the peculiarities of structural parameters, which affect on the important lubricant characteristic.*

**Introduction.** The phenomenon of formation of structured wall-adjacent epitropic-liquid crystalline (ELC) layers [1] near the lyophilic substrates [1] has now been established for a number of liquids. These layers (formerly called boundary layers) affect the stability of dispersed systems and character of coagulation processes. For example, the fact of the existence of a ELC layer on aerosol particles significantly reduces the rate of sedimentation and the value of the specific volume of the sedimentation residuum[2]. In recent years, ELC layers formed by unsaturated aliphatic hydrocarbons (alkanes) on conductive substrates attracted the intent attention of researchers [3]. This attention is connected with the fact that alkanes are the basis of modern lubricating mineral oils [4-6], and ELC layers in friction tribounits increase the wear resistance of mechanisms [7-9]. The phenomena of the organization of such structured oil layers at rubbing surfaces usually is due to anti-wear additives (fatty acids).

It was noticed that a surfactant additive of oleic acid (OA) to alkanes and motor oils (at a concentration less than 3-5%) leads increases their “lubricity” [10] and to enlarging of the thickness of their ELC layers [6,11]. It may be connected with the fact that the OA is capable to organize the ELC phase by itself. Then it is possible to expect that the established lyophilicity of metal to OA and peculiarities of the molecular structure of the latest will provide a significant thickness of the ELC layers at the metal surfaces of the friction unit. The study of the properties and features of such OA phase state, in turn, may help to explain the effect of lubricant doping with OA and improve the theoretical model [12] of this phase state.)

The results of this investigation are important and interesting in the applied aspect, as OA is widely used (possible due to the formation of its ELC layers at the interphase boundaries) in various areas of production, such as:

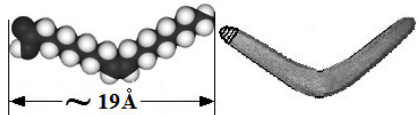
- a plasticizer for paintwork materials production, e.g. it increases the sheeting (the ability of powder flakes to be parallel to the surface during flotation) of aluminum powder in a paint;
- a stabilizer of invert emulsions in oil-based drilling fluids and emulsifiers (adding 0.1 wt.% of OA to bitumens increases their ability to emulsification [13]);
- a solubilizing agent and emulsifier in aerosols;

- components of detergents, linseed oil, varnishes, flotation agents, and components of coolant (due to the high wettability and adhesion to metal surface) while cutting high-alloyed stainless steels and alloys.

Oleic acid ELC layers research is also topical as this compound is the base of modern synthesized lubricating oils (e.g. an OA content in PMO bio-oil is about 91%) and motor fuels from renewable biological resources (rapeseed, seaweed, sunflower products, etc.). The presence of ELC in bio-oils and bio-fuels also affects their technical specification.

**Subjects of research.** The subject of our study was ELC layers of OA, formed at quartz, metal (chromium steel 1X12H2BMΦ) and metallized quartz substrates (nichrome N20C80 coating deposited by thermal evaporation). Oleic (cis-9-octadecenoic) acid is a monounsaturated fatty acid and belongs to the omega-9 class of unsaturated fatty acids [14].

The molecule of this colorless viscous fluid has a small dipole moment; its formula, melting point  $T_m$  and molecular shape (hard “rod” bent in the form of a boomerang) are given in the table. For comparison, a classical Australian Boomerang is shown in the table next to the image of the OA molecule.

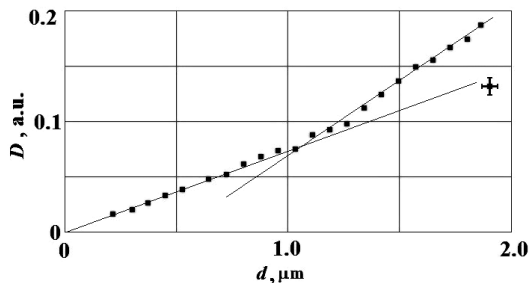
OA formula	$T_m, ^\circ\text{C}$	The shape of the OA molecule
$\begin{array}{ccc} \text{CH}_3-(\text{CH}_2)_7 & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{H} & & (\text{CH}_2)_7-\text{COOH} \end{array}$	16,3	

**Research objectives were:**

- to establish the possibility and conditions for the formation of ELC state in OA interlayers bounded by quartz and conductive substrates;
- to determine the structural characteristics (the equilibrium thickness, the type and degree of molecular ordering) of the OA ELC ;
- to compare the structure of the ELC of the OA layer with the previously studied ELC phase structure of the *n*-hexadecane (its molecular shape is close to OA).

**Research techniques.** The most important structural parameters of an ELC layer are the following – its type of orientation (the location of anisometric molecules relative to the surface), the equilibrium thickness  $d_{0s}$ , and the value of order parameter *S*. These structural parameters in thermotropic LC (the mesomorphicity exists in the bulk [15]) are determined by traditional techniques. But the special optical methods (in particular, based on the analysis of the intrinsic absorption bands dichroism) were developed [16, 17] for measurement of characteristics of ultrathin (micron and sub-micron) ELC interlayers.

However, standard instruments do not allow to measure the parameters of OA electronic absorption. This is due to the fact that its molecules do not contain unsatu-



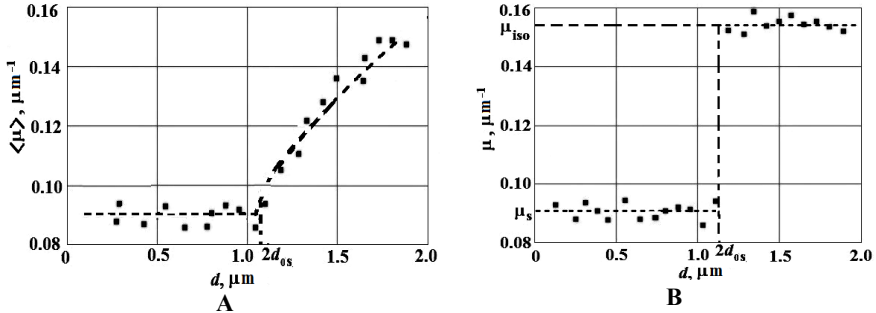
**Fig. 1.** Thickness dependence of the “guest” optical density in oleic interlayer bounded by quartz ( $t = 22.0^\circ\text{C}$ )

rated chemical bonds and therefore its absorption bands are located in the region of the vacuum ultraviolet ( $\nu > 50000 \text{ cm}^{-1}$ ). Therefore, we modified [18] “guest-host” method well-known in LC researches [19]. The structure of the OA-matrix (the “host”) in the interlayer was determined by the analysis of the absorption dichroism (in the region of the atmospheric ultraviolet) of the impurity dye (the “guest”) dissolved in the OA. The information obtained in this way is reliable in case of a sufficient isomorphism degree (the comparability of the molecular shape of the matrix and the impurity).

We used popular organic dyes (“sudan red” and “sudan black”) with high molar extinction and solubility values as “guests” in order to study the structure of ELC phase in alkane liquids. The positions of their absorption bands maxima are  $\lambda_{\text{max}} \sim 0.606 \mu\text{m}$  and  $\lambda_{\text{max}} \sim 0.472 \mu\text{m}$ , respectively. More elongated, in comparison with “sudan red”, molecules of “sudan black” are better comparable in length ( $l_0 \approx 20,5 \text{ \AA}$ ) and in shape with OA molecules, i.e. the degree of isomorphism with the host molecules is higher for them. However, we mainly used the sudan red dye ( $l_0 \approx 10,5 \text{ \AA}$ ) in our experiments. This is due to its higher degree of solubility, greater extinction value, and thus, the possibility of a more qualitative study of the properties of ultrathin ( $d \sim 0.2 \div 10 \mu\text{m}$ ) layers of solutions with a low ( $C \sim 1 \div 2 \text{ weight\%}$ ) concentration [17], in which the presence of a “guest” does not affect the matrix “host” structure.

The dichroism of the “guests” was measured in the wedge-like heterophase (containing ELC layers) interlayers of studied liquids. A special compression of optically polished quartz glasses (the cell windows) formed a gap with a slope of  $\alpha \sim 0.3 \div 0.4 \mu\text{m} / \text{mm}$ . Its topology was determined from an interferogram obtained by scanning an unfilled cell [16]. After the gap had been filled up with the studied liquid, light transmission  $I(d)$  was measured with light probe scanning through the thickness of the wedge-like layer  $d$  at the wavelength of the impurity absorption maximum.

Experimental values of optical density  $D = \ln(I_0/I)$ , (normalized to the maximum light transmission  $I_0$  in the zone of substrates optical contact), for OA interlayers bounded by quartz glasses for various thicknesses  $d$  are presented in fig. 1.



**Fig. 2.** Thickness dependence of the linear absorption coefficient of OA interlayer between dielectric (quartz) substrates (a – average value, b – local value).  $t=22.0^\circ\text{C}$ ,  $\Delta T= 5.7 \text{ K}$

An essential deviation of this dependence from the linear Bouguer law form indicates the fact of heterogeneity - the heterophase nature of the OA layer. The  $D(d)$  dependence was approximated by a broken line (as shown in Fig. 1). The slope of the straight lines correspond to the linear absorption coefficients was chosen from the condition of the total dispersion minimum.

It should be noted that the measurement of dichroism (in the “ray-of-light” geometry) is possible only in the case of transparency of the cell windows (quartz in described experiments). Transparent windows with metallized surfaces were produced by vacuum thermal deposition of a thin ( $h \sim 0.18 \mu\text{m}$ ) semitransparent metallic layer (nichrome N20C80) on a quartz substrate surface. For the strengthening (higher degree of nichrome adhesion to the quartz substrate) of this metal layer, the quartz plates were heated to a temperature of  $\sim 250^\circ\text{C}$  in the vacuum chamber during deposition.

Metal substrate usually provides the ELC layer with a greater value of equilibrium thickness ( $d_s \sim 1,0 \mu\text{m}$ ) [16] as compared with a dielectric substrate ( $d_s \sim 0,3 \mu\text{m}$ ). Therefore another technique was used to form for the formation of a wedge-like gap between metallized substrates — a thin aluminum spacer ( $H \sim 10 \mu\text{m}$ ) was disposed in one of its edges perpendicular to the scanning direction. The further compression of the cell windows formed a linear wedge-like gap with a slope of about  $\alpha \sim 1.2 \mu\text{m}/\text{mm}$ .

A noticeable contrast of the interference pattern obtained during gap scanning resulted from the higher value of light reflectance coefficient in case when metallized substrates were used instead of quartz ones. This result was observed even when gap was filled with fluid. Therefore, essential oscillations appeared on the curve of optical density thickness dependence in the region of the wedge top. They were smoothed by using the moving average method.

**Results of research and analyses.** The dependence  $D(d)$ , which is shown in fig.1, makes it possible to establish the thickness dependencies of the average and local (at the distance  $d$  from the substrate) values of the linear light absorption coefficient of the studied interlayer. These values are determined by equations  $\langle \mu \rangle = D/d$

and  $\mu_l = dD/dl$ . These dependencies for the OA interlayer bounded by quartz substrates are depicted in Fig. 2.

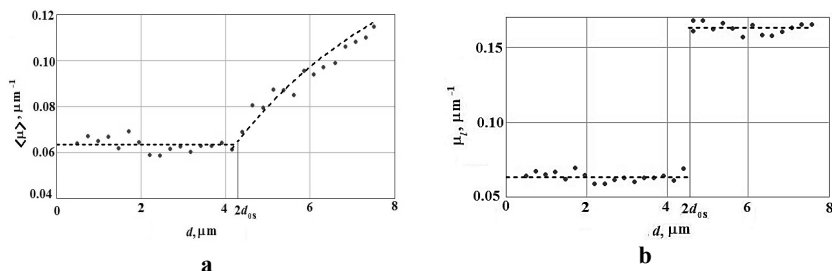
Analysis of the curve behavior from fig.2a shows that the average value  $\langle \mu \rangle$  increases with the interlayer thickness from the lower values up to the bulk one, at that the values of the average and local absorption coefficients practically coincide in the region of small thicknesses. When the interlayer thickness exceeds the critical value  $2d_{0s}$ , average absorption coefficient  $\langle \mu \rangle$  monotonously increases with asymptotically approaching the value for isotropic liquid in bulk. We used the value  $\Delta T = T - T_m$ , as this temperature difference characterizes the ELC phase properties. It is precisely this difference that determines the existence of ELC phase and its main properties (in particular equilibrium thickness  $d_{0s}$ ) according to the developed theoretical model [12].

It is logical to assume that the alteration of the absorption coefficient is due to the change of the interlayer structure. So this interlayer may be represented in a form of the three-component system – two wall-adjacent layers and the isotropic bulk liquid between them. The wall-adjacent layer is characterized by the almost constant value of the absorption coefficient  $\mu_s$  and, accordingly, almost constant degree of ordering  $S$  (both for the dissolved “guest”-molecules and the molecules of the matrix). A centrally disposed layer of isotropic liquid is characterized by zero degree of ordering and a constant value of absorption coefficient  $\mu_{iso} > \mu_s$ . The lower value of the absorption coefficient in the wall-adjacent layer serves as a evidence of homeotropic orientation of molecules there.

Differentiation of the  $D(d)$  dependence reveals the jump-like behavior of the  $\mu_l(d)$  dependence – the value of  $\mu_l$  increases from  $\mu_s$  to  $\mu_{iso}$ . Naturally, the jump corresponds to the salient point of the  $D(d)$  curve. The ratio of the  $\mu_s$  and  $\mu_{iso}$  allows us to calculate the value of the order parameter of the wall-adjacent ELC layer –  $S = 1 - \mu_s/\mu_{iso}$ .

It has been established that OA interlayers bounded by quartz substrates are characterized by the following values of structural parameters –  $S=(0,40\pm 0,03)$  and  $d_{0s}=(0,56\pm 0,04)$   $\mu\text{m}$  at  $\Delta T=5,7$  K. Let us compare these values with the structural parameters of ELC layer of *n*-hexadecane –  $\text{CH}_3\text{--}(\text{CH}_2)_{14}\text{--CH}_3$  [17]. This compound was chosen for a comparison because of its molecular parameters are very close to OA ones – molecule is a nonpolar “straight rod” with molecular size  $l_0 \sim 23,2$  Å and contains 16 carbon atoms. It should be noted here that structural parameters of *n*-hexadecane ELC layer ( $S \sim 0,23$ ,  $d_{0s} \sim 0,23$   $\mu\text{m}$ ) [17] are nearly half the value of OA layer at the same quartz substrates and temperature difference  $\Delta T$ .

The measurements of OA ELC layer parameters formed between metallized substrates were essentially more interesting and important for applications. Fig.3 presents the thickness dependencies of average and local absorption coefficient determined for this type of interlayers at temperature  $20,6^\circ\text{C}$  ( $\Delta T=4,3$  K). The values main structural parameters of such ELC state were –  $S=(0,49\pm 0,03)$  and  $d_{0s}=(2,46\pm 0,05)$   $\mu\text{m}$ . Separately it should be noted that the ELC equilibrium thickness  $d_{0s}$  is nearly 8 times higher compared with the same value measured near the quartz surface.



**Fig. 3.** Thickness dependencies of linear absorption coefficient of OA interlayer bounded by metallized quartz substrats (a–average value, b – local value)

Let us compare these results with the following data obtained for heterophase *n*-hexadecane substrate bounded interlayers. The temperature dependence of ELC layer equilibrium thickness  $d_{0s}$  was measured by different experimental techniques – rotation viscosimetry [21] birefringence measurement in gap light-guide [16] and admixed dichroism [20]. The last method allowed us to establish not only the equilibrium thickness, but the order degree value as well. At the same temperature  $\Delta T$  these values were  $d_{0s} = (1.4 \pm 0.2) \mu\text{m}$  and  $S \sim (0.28 \pm 0.04)$ . It is significant that the values of these parameters are 1.5–3 times less than in the case of oleic acid ELC layers.

**Discussion and conclusion.** The measurements of micron OA interlayers (in gaps between quartz plates and metallized quartz plates) indicate the fact that in such interlayers ELC layers really exist as it was expected. On conductive substrates, the order parameter  $S$  of these layers is higher compared with dielectric surfaces and their equilibrium thickness  $d_{0s}$  is almost half the order of magnitude higher. The equilibrium thicknesses  $d_{0s}$  of the OA and *n*-hexadecane ELC phases formed at the same substrates also essentially differ.

Highly likely, such differences are due to the special structure of OA molecules – their shape, size, polarity, and the presence of active end groups which provide the effect of surface adsorption. The equilibrium thickness of the OA ELC layer near the metal surface is also significantly larger than near quartz one. It maybe related to the higher value of the adsorption energy of OA molecules to the metal substrate. This energy value plays a significant role in the formation mechanism of the ELC phase [12], and it is related to the effect of wettability of the substrate by the liquid. The difference in the lyophilicity of OA to quartz and to metal is confirmed by our measurements of the equilibrium contact angle  $\vartheta$  of “sitting” OA droplets. This liquid wets quartz substrate noticeably worse than metal one: contact angle is  $\vartheta \approx 17^\circ$  in case of quartz and  $\vartheta \approx 13^\circ$  for a metal substrate, for which a steel 1X12H2BMΦ (Johansson gage plates) was used. It means that the steel surface is more lyophilic to OA, which correlates with the literature data [22].

The above-mentioned characteristics of OA molecules and their ability of the ELC phase formation are obviously determine the effect of doping of alkanes and

motor oils with OA additives. It should be noted that the precise understanding of the nature of this action should clarify the nature of OA ELC state. It will also clarify the difference between OA and well studied [16] – nitrobenzene which consists of polar molecules with smaller molecular size value  $l_0 \approx 8,5 \text{ \AA}$ . For the further development of theoretical model [12] of the ELC state, it is certainly necessary to establish the effect of temperature influence on the OA ELC phase properties. Also the future study of OA ELC rheological characteristics is especially important for applications as well.

### References:

1. *Derjaguin B. V., Altoiz B. A., Nikitenko I. I.* Epitropic Liquid Crystal layers of Nonmesogens on Quartz Substrate // Journal of Colloid and Interface Science. 1991. – Vol.145. – №2. – P. 441-446.
2. *Поповский Ю.М.* Влияние граничной фазы на устойчивость и объем осадка суспензии аэросила в нитробензоле – М.: Наука, 1974. С. 242-245.
3. *Веттегрень В. И., Тупицына А. И.* Исследование структуры тонких слоев гексадекана на металлической подложке методом ИК-спектроскопии // Письма в Журнал технической физики. – 1998. – Т. 24. – №. 10. – С.24-27.
4. *Петров А.А.* Углеводороды нефти – М.: Наука, 1974. 264 с.
5. *Сюняев З. И.* Нефтяные дисперсные системы М.: Химия, 1990. -226 с.
6. *Фукс Г. И.* Вязкость и пластичность нефтепродуктов. Москва-Ижевск: Институт компьютерных исследований, 2003. – 328 с.
7. *Мур Д.* Основы и применения трибоники. М.: Мир, 1978. – 488 с.
8. *Кириян С. В., Алтоиз Б. А.* //Трение и износ. 2012. Т.33, Вып.4. С. 367–372.
9. *Гаркунов Д.Н.* Триботехника. М.: МСХА, 2001. – 424 с.
10. *Папок К.К.* Смазочные масла. М.: Воениздат, 1962. –117 с.
11. *Алтоиз Б.А. Кириян С.В.* Структурированные приповерхностные слои нормальных алканов // ИФЖ.- 2010.- Т.83.- №3. – С.608-613.
12. *Алтоиз Б. А., Бондарев В. Н., Шатагина Е. А., Кириян С. В.* Модель организации эпитропной жидкокристаллической фазы // Журнал технической физики. –2014. – №7. – С. 58-61.
13. Физико-химические свойства индивидуальных углеводородов / Под ред. В. М. Татевского. – М.: 1960. – 412 с.
14. Химический энциклопедический словарь под ред., Кнунянц И.Л. – Москва: Советская энциклопедия, 1983. – 407 с.
15. *Жен П. Де.* Физика жидких кристаллов. – Москва: Мир, 1977. – 396 с.
16. *Алтоиз Б. А., Поповский Ю. М.* Физика приповерхностных слоев жидкости. – Одесса: Астропринт, 1996. – 153 с.
17. *Altoiz B.A., Popovskii A.Yu., Butenko A.F.* Equilibrium parameters of a structured n-hexadecane layer// Physics of aerodisperse systems. – 2017. – № 54. – С. 35-44.
18. *Дерягин Б.В., Алтоиз Б.А., Поповский Ю.М.* Ориентационно упорядоченные пристенные слои предельных углеводородов и их производных на поверхности кварца // ДАН СССР. – 1991. – Т.317. – №1. – С. 130-134.

19. *Блинов Л.М.* Электро- и магнитооптика жидких кристаллов. Москва: Наука, 1978. – 384 с.
20. *Алтоиз Б.А., Бутенко А.Ф., Кириян С.В.* Эпитропно-жидкокристаллический слой гексадекана в реологической модели гетерофазной прослойки // Журнал технической физики. – 2018. – Т. 88. – Вып.1. – С. 5-9.
21. *Кириян С. В., Алтоиз Б. А.* Вязкостно-температурные зависимости минерального моторного масла 15W40 в микронных прослойках и структурные характеристики его квазиджидкокристаллических пристеночных слоев // Трение и износ. – 2012. – Т.33. – Вып. 4, – С. 367-372.
22. *Зимон А. Д.* Адгезия жидкостей и смачивание. – Москва: Химия, 1974. – 416 с.

***Поповский А.Ю., Алтоиз Б. А., Бутенко А. Ф.***

### **Структурные характеристики ЭЖК слоя олеиновой кислоты**

АННОТАЦИЯ

Исследования строения тонких прослоек олеиновой кислоты между кварцевыми и металлизированными подложками методом измерения дихроизма молекул «гостей» позволили установить существование эпитропно-жидкокристаллических слоев этой жидкости и отличительные особенности их структурных параметров, определяющих ключевые характеристики смазывающих материалов.

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

### **Структурні характеристики ЕРК шару олеїнової кислоти**

АНОТАЦІЯ

*Дослідження будови тонких прошарків олеїнової кислоти між кварцовими та металізованими підкладками методом вимірювання дихроїзму домішкового поглинання дозволили визначити існування епітропно-рідкокристалічних шарів цієї рідини та відмінні особливості їх структурних параметрів, які визначають ключові характеристики змащуючих матеріалів.*