*Journal of Engineering Physics and Thermophysics, Vol. 83, No. 3, 2010*

# DETERMINATION OF THERMOPHYSICAL PROPERTIES

## STRUCTURIZED SURFACE LAYERS OF NORMAL ALKANES

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UDC 539.2:541.18

*The elevated viscosity of micron interlayers of certain normal alkanes compared to their viscosity in the "volume" is determined experimentally in shear flow using a rotational viscometer. The observed difference is considered to be caused by the manifestation, in such interlayers, of structural inhomogeneity due to the presence of structurized polymolecular surface layers on the substrates bounding them. The structural parameters of such layers, i.e., their equilibrium initial thickness and "hydrodynamic strength," are calculated in the model of a constant-viscosity layer. The measured effective viscosity of the interlayers diminishes with growth in the shear-flow velocity, which is attributed to the "cutting" of the structurized layer. Surfactant doping of the liquids leads to an increase in the effective viscosity of the interlayers, which is produced by the strengthening of the layer structure.*

***Keywords:*** *structurized surface layers, epitropic liquid crystals, viscosity, rheological model, normal alkanes.*

**Introduction.** In investigations of the thermophysical [1] and optical [2–4] properties (birefringence, dichroism of fundamental and impurity absorption bands) of a number of aliphatic and nonmesogenic aromatic liquids in their thin interlayers between dielectric lyophilic substrates (quartz, glass, sapphire), it has been established that polymolecular (~100) epitropic liquid-crystalline (ELC) layers can be formed at the substrate surface [5]. Such structurized layers arise from anisotropic intermolecular interactions in the liquid and from the action of the orienting (directive) field of surface forces of the solid substrate on it. The type of orientation in the layer is determined by the surface microstructure of the substrate, whereas the thickness is determined by its material and molecular length. The presence of such layers has also been demonstrated by the results of rheological investigations of nonmesogenic liquids with anisometric molecules [6, 7], from which it follows that the viscosity of their thin ($D \sim 10$ μm) films differs form the viscosity in the liquid "volume."

It is likely that the organization of such layers is responsible for the fact that in the well-known [8] experiments on studying the dependence of the coefficient of static friction between substrates rubbing in a boundary-lubricant regime and separated by the interlayers of normal alkanes, the interrelationship between their antifrictional activity and the molecular-chain length and material of the rubbing surfaces (steel, glass) has been established.

The practical topicality of rheological investigations of micron interlayers of aliphatic liquids lies in the fact that they form the basis for mineral and synthetic oils that "work" as thin lubricant layers in frictional triads. The solid substrates of the latter are metallic as a rule, and the thickness $d_s$ of the ELC phase on the metal may attain several microns now [9, 10].

Some authors [8] have assumed that in addition to the form of the substrate surface and material determining the character and intensity of interaction on the solid-liquid interface, the phenomenon of structurization of the liquid, i.e., the formation of "boundary" LC layers, is also contributed to by surfactant (usually fatty acids (oleic, stearic)) additives [11] introduced into the oils and improving their service properties.

The presence of such mesomorphic layers in the interlayer is closely related to the wear-prevention characteristics of frictional units operating in mixed-lubrication regimes [9, 12–14]: as the orientation order in the wall layers increases, the wear intensity decreases. It has been established that homeotropic molecular orientation in an ELC im-

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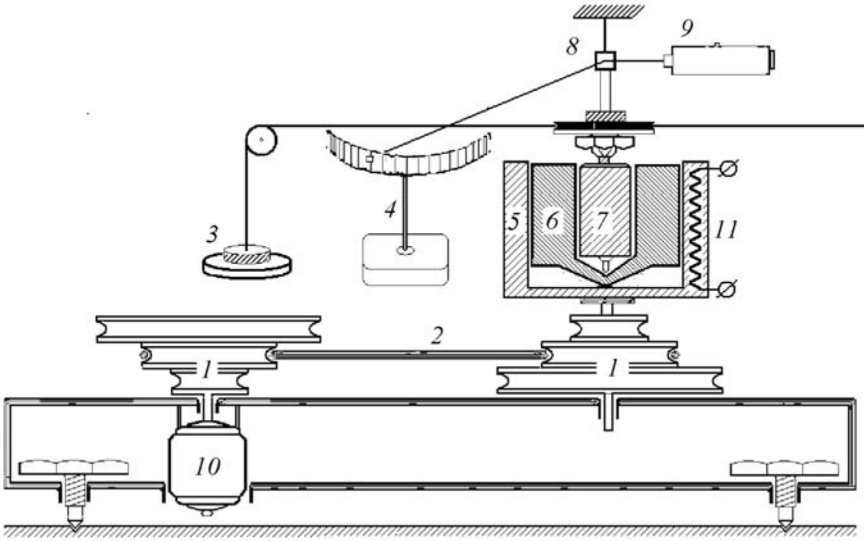

Fig. 1. Diagram of the rotational viscometer: 1) pulleys; 2) belt; 3) weights (counter weights); 4) dial; 5) cup (mounting seat of the external cylinder); 6) external cylinder of the rotational pair; 7) internal cylinder of the rotational pair; 8) mirror; 9) laser; 10) electric motor; 11) electric resistance thermometer.

proves the wear-prevention characteristics of the boundary lubricant layer, increasing its viscosity; planar orientation, conversely, diminishes frictional force but causes the wear of the contacting parts to grow.

**Formulation of the Problem and Objects of Investigation.** With allowance for what has been said above it seems topical to investigate issues of organization of structurized ELC layers on a metal substrate by aliphatic liquids: to determine the influence of both the molecular length of these liquids and their doping with surfactants on the structural properties of surface layers. For solution of these problems we have investigated shear flow of "thin" interlayers of *n*-alkanes ($C_nH_{2n+2}$): $C_{13}H_{28}$, $C_{14}H_{30}$, $C_{16}H_{34}$, and $C_{17}H_{36}$[**], in which the presence of surface structurized layers can have an appreciable effect on their viscous properties. The rheological features of the flow of the presented samples were studied with a rotational viscometer [10] (Fig. 1) designed specially for investigating thin liquid interlayers of thickness $D \sim 1$–$50\ \mu$m. The viscometer operation was based on determination of the torque (moment) of viscous-friction forces $M_{\text{fr}}$ which occurred in the liquid interlayer between coaxial cylinders 6 and 7 in rotation of the external cylinder in cup 5. The drive was from an electric motor 10 via the belt transmission 2 of a system of pulleys 1.

A system of counterweights 3 served as the meter of the torque of viscous-friction forces. The possibility of varying the mass of these counterweights ensured a wide range of measurement of the viscosities of the samples (0.001–0.1 Pa·sec) and the rates of their shear deformations ($\gamma = 10^2$–$10^4$ sec$^{-1}$). The restoring torque $M_{\text{rest}}$ compensating for the torque of viscous-friction forces $M_{\text{fr}}$ was calculated from the deflection (determined by dial 4) angle $\varphi$ of the beam which had been reflected from mirror 8 on exposure to laser 9. The width of the clearance between the cylinders 6 and 7 (thickness of the liquid interlayer) was prescribed by variation of the diameters of the set of changeable internal cylinders.

In the Couette flow of an inhomogeneous (with ELC layers) liquid interlayer, for a certain rate of shear deformation, we established its "effective" viscosity $\eta_{\text{ef}}$. The value of the latter was the viscosity of a homogeneous liquid for which the same deformation rates $\gamma$ correspond to the same shear stresses $\sigma$. The measured "effective" viscosity $\eta_{\text{ef}}$ of micron interlayers of saturated hydrocarbons was compared to their "volume" viscosity $\eta_{\text{v}}$ determined by capillary viscometers of a "large" diameter ($\varnothing$ = 2.62, 1.31, and 0.99 mm) and by the rotational viscometer in interlayers of thickness $D = 30$–$50\ \mu$m; there, the contribution of thin structurized layers exerted no appreciable influence on rheology by virtue of their small relative fraction in such "thick" interlayers. The difference of the viscosity $\eta_{\text{ef}}$ of a micron liquid interlayer from its "volume" value $\eta_{\text{v}}$ ($\eta_{\text{rel}} = \eta_{\text{ef}}/\eta_{\text{v}}$) pointed to the presence of structural ELC layers in it, whereas the dependence of the coefficient of relative viscosity $\eta_{\text{rel}}$ on $\gamma$ demonstrated the character of flow.

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[**] All samples were manufactured at the Novocherkassk Plant of Synthetic Products and were chemically pure.

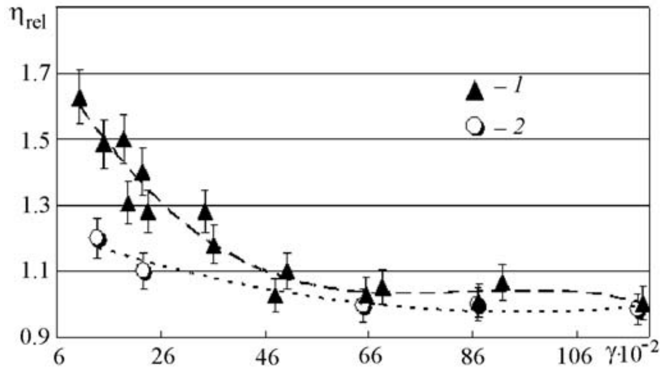

Fig. 2. Viscosity $\eta_{rel}$ of the interlayers of normal alkanes vs. deformation rate $\gamma$: 1) hexa- and heptadecane; 2) tri- and tetradecane ($D \sim 4.5$ μm and $T$ = 295–297 K). $\gamma$, $sec^{-1}$.

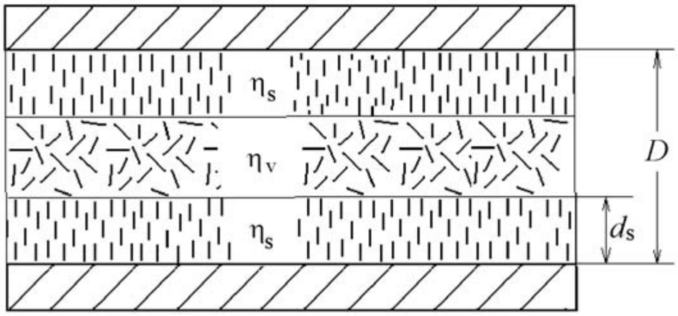

Fig. 3. Model of a "constant-viscosity ELC layer:" in the interlayer of $D$, there are ELC layers ($d_s$-thick each) of constant viscosity $\eta_s$ between the substrates and an interlayer of isotropic liquid with a coefficient of viscosity $\eta_v$ in the central part.

The width of the clearance $D$ between the coaxial cylinders was monitored by calibration viscometric experiments with liquid interlayers of known viscosity, in which surface structurized layers on bounding substrates were not formed. In particular, the viscosity of chromatographically purified vaseline oil, which is known [8, 15, 16] to be incapable of forming surface structurized layers on a metal substrate, was also measured. Possible changes in the clearance in the process of measurement (due to the precession of the internal cylinder) were monitored by the capacitance method. The maximum relative error in determining the clearance (for a clearance of 1.5 μm) was $\delta_D \leq 5\%$. The temperature of the liquid interlayer was measured ($\Delta T = \pm 0.03$ K) with an electric resistance thermometer 11 (see Fig. 1). With the same thermometer we monitored the constancy of the temperature of the interlayer in isothermal experiments on measurement of its viscosity (for different shear-deformation rates $\gamma$). The influence of the slight change in the temperature (no more than ~0.4 K over the period of obtaining the rheological dependence $\eta_{ef}(\gamma)$) of the interlayer on its viscosity was allowed for when the experimental results were calculated. The error in measuring the coefficient of viscosity $\eta_{ef}$ of the interlayer amounted to $\delta_\eta \sim 5\%$ and was mainly due to the error in determining their thickness. The shear-deformation rate $\gamma$ was calculated from the rotational velocity of the cylinder $V$ ($\delta_V < 0.5\%$) and the clearance of the rotational pair ($\gamma = V/D$). Therefore, the same inaccuracy $\delta_D$ of measurement of the interlayer thickness mainly determined the error in measuring the quantity $\gamma$ ($\delta_\gamma \sim 5\%$).

**Results of Rheological Investigations.** Figure 2 gives the rheological dependences of the viscosity $\eta_{rel}$ of interlayers of "pure" investigated liquids of thickness $D \sim 4.5$ μm on the rate of their shear deformation $\gamma$.

As follows from Fig. 2, in thin (of thickness $D \sim 4.5$ μm) interlayers of $C_{13}H_{28}$, $C_{14}H_{30}$, $C_{16}H_{34}$, and $C_{17}H_{36}$ liquids, the effective viscosity $\eta_{ef}$ differs from the viscosity in the "volume" $\eta_v$. For hexa- and heptadecane structurally differing by one $CH_2$ group, we have established no difference between them in the rheological measurements analogously to tri- and tetradecane respectively. However the coefficient of relative viscosity for $\gamma \to 0$ for hepta- and hexade-

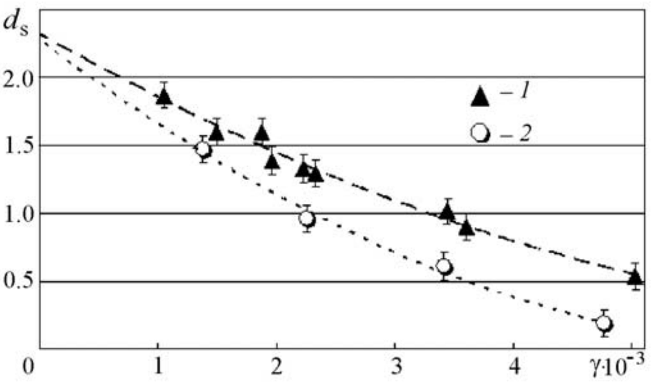

Fig. 4. Calculated dependence of the ELC-layer thickness $d_s$ on the deformation rate $\gamma$ in the model of a "constant-viscosity ELC layer:" 1) $C_{16,17}$; 2) $C_{13,14}$ ($\gamma^*$ ($C_{16,17}$) ~ 3500 $\sec^{-1}$, $\gamma^*$ ($C_{13,14}$) ~ 2400 $\sec^{-1}$, $D \sim 4.5$ μm, and $T$ = 294–297 K). $d_s$, μm; $\gamma$, $\sec^{-1}$.

cane ($\eta_{rel} \approx 1.85$) is much higher than that for tri- and tetradecane ($\eta_{rel} \approx 1.3$). As the deformation rate $\gamma$ increases, the effective viscosity of the liquids decreases; for $\gamma \sim 6000$ $\sec^{-1}$ ($C_{16,17}$) and ~4000 $\sec^{-1}$ ($C_{13,14}$) respectively, it becomes equal to the "volume" viscosity ($\eta_{rel} \approx 1$). Elevated (compared to the "volume" ones) values of the relative viscosity $\eta_{rel}$ of these thin liquid interlayers point to the structurization of their wall layers near the metal substrate. The higher coefficient of relative viscosity and the deformation rate necessary for destroying the structural order of molecules with passage of the liquid into the isotropic phase for the pair of $C_{16,17}$ homologs compared to $C_{13,14}$ demonstrates their better structural organization.

For quantitative evaluation of the structural parameters of the ELC layer in the interlayers of the liquids under study, we have used the rheological model of a "constant-viscosity ELC layer" [10]: the inhomogeneous liquid interlayer contains wall structurized layers of thickness $d_s$:

$$d_s(V) = \frac{D}{2}\,\frac{1-\dfrac{\eta_v}{\eta_{ef}}}{1-\dfrac{\eta_v}{\eta_s}} \tag{1}$$

with a constant coefficient of viscosity $\eta_s$, which is independent of the shear stress $\sigma$, and a layer of isotropic "volume" liquid with a coefficient of viscosity $\eta_v$ in between (Fig. 3).

As the intensity of shear flow in the interlayer grows, the model ELC layers are "cut off": their structure is destroyed on the interface with the isotropic liquid and the layer thickness decreases. From the experimental dependences $\eta_{rel}(\gamma)$, we have calculated, within the framework of the presented model, such structural parameters of the ELC layer as the equilibrium layer thickness $d_{0s}$ ("initial" thickness of this layer in the absence of flow) and the "hydrodynamic strength" $\gamma^*$ showing what deformation rate corresponds to a decrease of $e$ times in the ELC-layer thickness:

$$d_s = d_{0s}\exp\left(-\frac{\gamma}{\gamma^*}\right). \tag{2}$$

Figure 4 gives the dependences of the thickness of the ELC layer $d_s$ on the deformation rate $\gamma$ for the pairs of *n*-alkanes $C_{16,17}$ and $C_{13,14}$, which have been calculated in the model of a "constant-viscosity ELC layer." It is seen in the figure that the initial (for $\gamma \to 0$) equilibrium ELC-layer thickness is $d_{0s} \approx 2$ μm for both alkane pairs. The total thickness of the layers is comparable to the thickness of the interlayers of the investigated liquids $D \sim 4.5$ μm. However, the "hydrodynamic strength" $\gamma^* \sim 2400$ $\sec^{-1}$ for the molecules with a shorter chain length of hydrocarbons ($C_{13,14}$) is lower than that for hexa- and heptadecane, i.e., $\gamma^* \sim 3500$ $\sec^{-1}$ $C_{16,17}$, suggesting the higher "strength" of the $C_{16,17}$ layers compared to $C_{13,14}$, conceivably owing to the better orientation order of molecules in them.

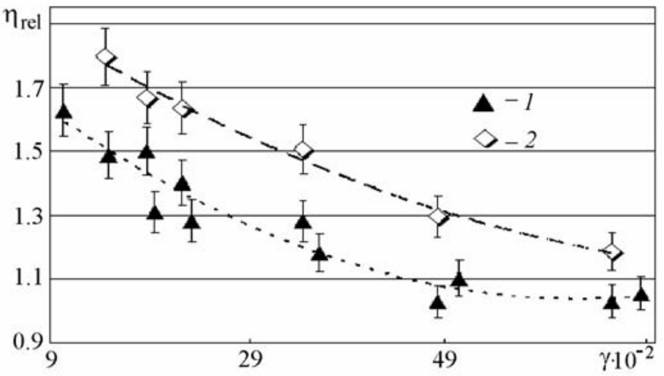

Fig. 5. Viscosity $\eta_{rel}$ vs. deformation rate $\gamma$ for hexadecane: 1) "pure;" 2) doped with ~1% oleic acid ($D \sim 4.5$ μm, and $T = 295–297$ K). $\gamma$, $\text{sec}^{-1}$.

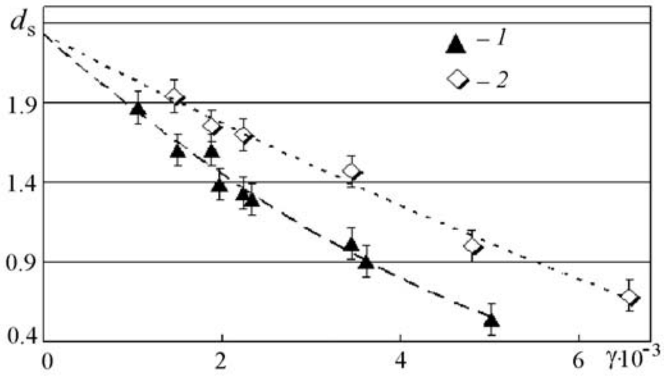

Fig. 6. Calculated dependence of the ELC-layer thickness $d_s$ on the deformation rate $\gamma$ for hexadecane: 1) "pure;" 2) doped with ~1% oleic acid ($\gamma_1^* \sim 3500$ $\text{sec}^{-1}$, $\gamma_2^* \sim 5500$ $\text{sec}^{-1}$, $D \sim 4.5$ μm, and $T = 295–297$ K). $d_s$, μm; $\gamma$, $\text{sec}^{-1}$.

To establish the degree of influence of surfactants on the structural properties of surface layers of *n* alkanes we doped hexadecane with oleic acid[**] ($C_{18}H_{34}O_2$) with a volume concentration of ~1%.

Figure 5 gives rheological dependences $\eta_{rel} = f(\gamma)$ of "pure" hexadecane and a hexadecane solution (with a ~1% volume concentration of oleic acid in it) for their interlayers of thickness $D \sim 4.5$ μm. As follows from the figure, compared to the "pure" hexadecane its doping with oleic acid increases both the relative viscosity ($\eta_{rel} \approx 2.05$ for $\gamma \to 0$) of the thin interlayer of the sample and the deformation rate beginning with which ($\gamma \sim 7000$ $\text{sec}^{-1}$) the viscosity $\eta_{rel}$ is approximately equal to 1.

Figure 6 gives the dependences $d_s = f(\gamma)$ calculated in the model of a "constant-viscosity layer" for the interlayers ($D \sim 4.5$ μm) of "pure" hexadecane and hexadecane doped with oleic acid (~1%). It is seen in the figure that the "hydrodynamic strength" of the hexadecane with a surfactant ($\gamma_2^* \sim 5500$ $\text{sec}^{-1}$) is higher than that of the "pure" hexadecane ($\gamma_1^* \sim 3500$ $\text{sec}^{-1}$), which points to the higher structural order of the wall layers of the heterophase system "hexadecane + 1% oleic acid" due to the formation of the seed single layer of homeotropically oriented surfactant molecules; the double initial equilibrium thickness of the ELC layer ($2d_{0s} \approx D$) is comparable to the thickness of the interlayer of hexadecane with a surfactant ($D \sim 4.5$ μm).

**Conclusions.** Thus, we have experimentally established the difference of the viscosity of micron interlayers of normal alkanes from their viscosity in the "volume." The elevated value of viscosity of the thin interlayers of these liquids compared to the "volume" value of their viscosity points to the structurization of the wall layers of these substances. As the shear-flow velocity grows, the effective viscosity of the interlayers of the above liquids decreases and tends to the "volume" value. The micron surface layers of $C_{13}H_{34}$ and $C_{17}H_{36}$ with a larger molecular longer than that

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[**] Manufactured by Lachema Ltd, pure.

in $C_{13}H_{28}$ and $C_{14}H_{30}$ are more ordered, too. This, in view of the mentioned interrelationship between the antifrictional activity of normal alkanes and their molecular length, confirms the influence of the structurization of surface layers of the liquids on the "static" coefficient of friction between the rubbing surfaces. Doping of the micron hexadecane interlayer with oleic acid (~1%) contributes to the increase in its

effective viscosity due to the formation of the seed single layer of homeotropically oriented surfactant molecules improving the structural strength of the wall layers of this alkane.

## NOTATION

$D$, interlayer thickness, μm; $d_s$, ELC-layer thickness, μm; $d_{0s}$, initial equilibrium layer thickness, μm; $M_{fr}$, torque of viscous-friction forces, N·m; $M_{rest}$, restoring torque, N·m; $T$, liquid-interlayer temperature, K; $V$, linear rotational velocity of the external cylinder, m/sec; $\gamma$, shear-deformation rate, $sec^{-1}$; $\gamma^*$, "hydrodynamic" strength of the layer, $sec^{-1}$; $\delta_D$, relative error of determination of the clearance of the viscometer's rotational pair (interlayer thickness) $D$, %; $\delta_V$, relative error of determination of the linear rotational velocity $V$ of the external cylinder, %; $\delta_\gamma$, relative error of determination of the shear-deformation rate $\gamma$, %; $\delta_\eta$, relative error of determination of the effective viscosity of the interlayer thickness, %; $\eta_{ef}$, coefficient of effective dynamic viscosity of the liquid interlayer, Pa·sec; $\eta_v$, coefficient of dynamic viscosity of the "volume" liquid, Pa·sec; $\eta_{rel}$, coefficient of relative viscosity, $\eta_{rel} = \eta_{ef}/\eta_v$; $\eta_s$, dynamic viscosity of the ELC layer, Pa·sec; $\sigma$, shear stress, $N/m^2$; $\varphi$, deflection angle of the laser beam, rad. Subscripts: 0, initial; 0s, initial structural; rest, restoring; v, volume; rel, relative; fr, friction; ef, effective; s, structural. Superscripts: *, parameter of "hydrodynamic strength."

## REFERENCES

1. Yu. M. Popovskii and B. V. Deryagin, Heat capacity of liquid in disperse systems, *Dokl. Akad. Nauk SSSR*, **159**, No. 4, 807–900 (1964).
2. B. A. Altoiz and Yu. M. Popovskii, *Physics of the Surface Layers of Liquid* [in Russian], Astroprint, Odessa (1996).
3. B. V. Deryagin, G. P. Silenko, and Yu. M. Popovskii, Determination of birefringence and of the equilibrium thickness of the boundary phase of nitrobenzene, *Dokl. Akad. Nauk SSSR*, **239**, No. 41, 828–830 (1978).
4. B. V. Deryagin, B. A. Altoiz, Yu. M. Popovskii, and E. Yu. Shibaeva, Influence of the surface on the formation and properties of boundary mesophases, *Dokl. Akad. Nauk SSSR*, **305**, No. 6, 1392–1395 (1989).
5. B. V. Deryagin, Yu. M. Popovskii, and B. A. Altoiz, *Invention in the USSR "Phenomenon of Formation of the Homogeneous Boundary Liquid-Crystalline Phase of Nonmesogenic Liquid,"* Diploma No. 388, *Otkrytiya Izobreteniya*, No. 12, 1–2 (1991).
6. B. V. Derajguin and V. V. Karasev, Study of boundary viscosity of organic liquids by the blowoff method, *Surf. Colloid Sci.*, **15**, 221–264 (1993).
7. B. V. Deryagin, N. V. Churaev, and V. M. Muller, *Surface Forces* [in Russian], Nauka, Moscow (1985).
8. A. S. Akhmatov, *Molecular Physics of Boundary Friction* [in Russian], Nauka, Moscow (1964).
9. G. I. Fuks, *Viscosity and Plasticity of Petroleum Products* [in Russian], Izd. Komp. Issled., Moscow (2003).
10. B. A. Altoiz, S. K. Aslanov, and A. F. Butenko, Rotational viscometer to investigate micron interlayers, *Physics of Aerodisperse Systems*, No. 42, 53–65 (2005).
11. I. I. Berkovich and D. G. Gromakovskii, *Tribology* [in Russian], Izd. SGTU, Samara (2000).
12. Yu. M. Popovskii, S. V. Sagin, and M. N. Grebenyuk, Influence of orientational order in boundary lubricating layers on the tribotechnical characteristics of friction units, in: *Ship Power Plants: A Volume of Coll. Scientific-Technical Papers*, No. 1, 102–104 (1998).
13. Yu. M. Popovskii, S. A. Khanmamedov, and Yu. V. Zablotskii, Relationship between the orientational order in wall layers and the "lubricating ability," in: *The Problems of the Physics of Shape Formation and Phase Transformations* [in Russian], Izd. KGU, Kalinin (1989), pp. 49–57.
14. I. A. Buyanovskii, V. A. Levchenko, and V. N. Matveenko, Orientational order of boundary layers and lubricating ability of oils, *Inzh.-Fiz. Zh.*, **81**, No. 4, 375–381 (2008).

15. B. A. Altoiz, E. V. Pyzhov, T. V. Naroditskaya, and S. A. Khanmamedov, Tribologic characteristic features of boundary lubricating layers of ship fuels and oils, in: *Ship Machines and Mechanisms*, *A Volume of Scientific-Technical Papers*, No. 8, 45–49 (2003).
16. S. V. Kiriyan and B. A. Altoiz, Epitropic liquid-crystalline layers of synthetic oils and their influence on a shear flow, *Physics of Aerodisperse Systems*, No. 45, 72–77 (2008).