

STATISTICAL CALCULATION OF THE VISCOUS PROPERTIES OF NEMATIC LIQUID CRYSTALS BY MEANS OF THE KINETIC EQUATION FOR THE TENSOR ORDER PARAMETER

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We carried out statistical calculation of the viscosity coefficients of nematic liquid crystals. As the starting point of calculation, we used the expression for the tensor of viscous stresses obtained within the framework of the relaxational hydrodynamics of investigated media constructed on the basis of Zubarev's method of nonequilibrium statistical ensembles. The relaxational equation for the tensor order parameter was used to calculate the time correlation functions that determine kinetic coefficients. The results of theoretical calculations were compared with experimental data on the temperature dependence for a number of nematogens.

One of the topical problems of the statistical theory of nematic liquid crystals is the description of the viscous properties of these media. The solution of this problem in a general form was accomplished by one of the present authors (V. B. Nemtsov) by Zubarev's method of nonequilibrium statistical ensembles [1, 2]. For this purpose, the equations of generalized relaxation hydrodynamics of nematic liquid crystals were constructed, within the framework of which a general expression was obtained for the viscous stress tensor in the form of the Ericksen–Leslie stress tensor (see, e.g., [3]):

$$\tau_{ij} = \alpha_1 n_i n_j n_k n_l e_{kl} + \alpha_4 e_{ij} + \alpha_5 n_i n_k e_{kj} + \alpha_6 n_j n_k e_{ki} + \alpha_2 n_i N_j + \alpha_3 n_j N_i,$$

which takes into account dissipation losses associated with the symmetric part of the tensor of deformation rates $e_{ij} = \frac{1}{2}(v_{ij} + v_{ji})$ and with the rotations of the director relative to the flow which are characterized by the speed of these rotations $\mathbf{N} = \dot{\mathbf{n}} - \boldsymbol{\omega} \times \mathbf{n}$ ($\boldsymbol{\omega} = \frac{1}{2} \text{rot } \mathbf{v}$).

The Leslie coefficients of viscosity α_r are determined, in contrast to the phenomenological approach, by independent coefficients of material tensors. In turn, the material tensors that form viscous properties are represented in terms of the time correlation functions of the microscopic sources of the densities of dynamic quantities whose means are the state variables of the systems investigated.

In considering isothermal processes in incompressible nematic liquid crystals, as microscopic state parameters we take the densities of the dynamic values of the pulse $\hat{p}_i(\mathbf{x})$, the tensor order parameter $\hat{R}_{ij}(\mathbf{x})$, and the matrix of rotation, which in a linear approximation is replaced by the corresponding vector $\hat{\theta}_i(\mathbf{x})$ of the small angles of rotation of molecules [2]:

$$\begin{Bmatrix} \hat{p}_i(\mathbf{x}) \\ \hat{R}_{ij}(\mathbf{x}) \\ \hat{\theta}_i(\mathbf{x}) \end{Bmatrix} = \sum_{v=1}^N \begin{Bmatrix} p_i^v \\ d_{ij}^v \\ \theta_i^v \end{Bmatrix} \delta(\mathbf{x} - \mathbf{x}^v), \tag{1}$$

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where the tensor order parameter per molecule d_{ij} is associated with the unit vector \mathbf{c} that prescribes its orientation and with the relation $d_{ij} = (3c_i c_j - \delta_{ij})/2$. Then, the set of quantities that form the time correlation functions represent the densities of the microscopic stress tensor $\hat{\tau}_{ij}(\mathbf{x})$, the source of the tensor order parameter

$$\hat{J}_{ij}^R(\mathbf{x}) = \sum_{v=1}^N \omega_n^v (e_{im} d_{mj}^v + e_{jnm} d_{im}^v) \delta(\mathbf{x} - \mathbf{x}^v) \quad (2)$$

and the source of the vector of the small angle of rotation

$$\hat{J}_i^\theta(\mathbf{x}) = \sum_{v=1}^N \omega_i^v \delta(\mathbf{x} - \mathbf{x}^v). \quad (3)$$

Microscopic expressions for the enumerated densities of fluxes and sources can be found in deriving the equations of motion for the state variables [2].

Consequently, within the framework of the foregoing approach, the viscous properties of nematic liquid crystals are described by six tensors of kinetic coefficients which in hydrodynamic approximation (at small wave vectors and frequencies) are defined by the formulas [2]

$$a'_{ijkl} = \frac{\beta}{V} \iint d\mathbf{x} d\mathbf{x}' \int_0^\infty dt \exp[-\varepsilon t] \langle \hat{\tau}_{ij}(\mathbf{x}, t) \hat{\tau}_{kl}(\mathbf{x}', 0) \rangle, \quad (4)$$

$$E'_{ijkl} = \frac{\beta}{V} \iint d\mathbf{x} d\mathbf{x}' \int_0^\infty dt \exp[-\varepsilon t] \langle \hat{J}_{ij}^R(\mathbf{x}, t) \hat{\tau}_{kl}(\mathbf{x}', 0) \rangle, \quad (5)$$

$$\lambda_{ikl} = \frac{\beta}{nV} \iint d\mathbf{x} d\mathbf{x}' \int_0^\infty dt \exp[-\varepsilon t] \langle \hat{J}_i^\theta(\mathbf{x}, t) \hat{\tau}_{kl}(\mathbf{x}', 0) \rangle, \quad (6)$$

$$F_{ijkl} = \frac{1}{V} \iint d\mathbf{x} d\mathbf{x}' \int_0^\infty dt \exp[-\varepsilon t] \langle \hat{J}_{ij}^R(\mathbf{x}, t) \hat{J}_{kl}^R(\mathbf{x}', 0) \rangle, \quad (7)$$

$$A_{ikl} = \frac{1}{nV} \iint d\mathbf{x} d\mathbf{x}' \int_0^\infty dt \exp[-\varepsilon t] \langle \hat{J}_i^\theta(\mathbf{x}, t) \hat{J}_{kl}^R(\mathbf{x}', 0) \rangle, \quad (8)$$

$$b_{ik} = \frac{\beta}{n^2 V} \iint d\mathbf{x} d\mathbf{x}' \int_0^\infty dt \exp[-\varepsilon t] \langle \hat{J}_i^\theta(\mathbf{x}, t) \hat{J}_k^\theta(\mathbf{x}', 0) \rangle, \quad (9)$$

where the space integrals are taken over the volume of the system and the angular brackets denote averaging over an equilibrium ensemble.

The number of independent coefficients of tensors is determined by the material symmetry of the nematic medium, which is described by the group $D_{\infty h}$ [3] and by the properties of the symmetry of the time correlation functions that enter into Eqs. (4)–(9). Here, the tensor a'_{ijkl} (4), which describes standard contributions to the viscosity coefficients, in the case considered has six independent coefficients ($a'_2, a'_3, a'_5, a'_6, a'_7, a'_8$); the tensors E'_{ijkl} (5) and λ_{ijk} (6), which describe the contributions of the interaction of the hydrodynamic flow of the medium with a mean orientation of molecules, have respectively four (E'_2, E'_3, E'_4, E'_5) and two (λ_2, λ_3) independent coefficients; the material tensors F_{ijmn} (7), A_{ijk} (8), and b_{ik} (9), which describe the contributions of orientation processes to the viscosity coefficients of nematic liquid crystals, have three (F_1, F_2, F_3), one (A), and two (b_1, b_2) independent coefficients, respectively. The coefficients indicated determine the viscosity coefficients of nematic liquid crystals in accordance with the formula [2]

$$\alpha_1 = a_8, \quad \alpha_4 = a_2 + a_3, \quad \alpha_2 = \frac{1}{2} \gamma_1 (1 + \lambda), \quad \alpha_3 = \frac{1}{2} \gamma_1 (1 - \lambda),$$

$$\alpha_5 = \frac{1}{2} (a_5 + 2a_6 + a_7 - (\gamma_2^0)^2 (\gamma_1^0)^{-1} + \lambda \gamma_1 (\lambda + 1)), \quad \alpha_6 = \frac{1}{2} (a_5 + 2a_6 + a_7 - (\gamma_2^0)^2 (\gamma_1^0)^{-1} + \lambda \gamma_1 (\lambda - 1)), \quad (10)$$

where

$$\gamma_1^0 = a_7 - 2a_6 + a_5 + 2(a_2 - a_3), \quad \gamma_2^0 = a_7 - a_5;$$

$$a_2 = a'_2 + 2\beta E_2^2 F_1^{-1}, \quad a_3 = a'_3 + 2\beta E_2^2 F_1^{-1}, \quad a_5 = a'_5 + 2\beta (E_2 + E_4)^2 F_3^{-1} - 2\beta E_2^2 F_1^{-1},$$

$$a_6 = a'_6 + 2\beta (E_2 + E_4) (E_2 + E_5) F_3^{-1} - 2\beta E_2^2 F_1^{-1}, \quad a_7 = a'_7 + 2\beta (E_2 + E_5)^2 F_3^{-1} - 2\beta E_2^2 F_1^{-1},$$

$$a_8 = a'_8 + 2\beta (E_2 - E_3)^2 F_2^{-1} - 2\beta (2E_2 + E_4 + E_5)^2 F_3^{-1} + 2\beta E_2^2 F_1^{-1};$$

$$\gamma_1^{-1} = \tilde{b}_1 + (1 + \tilde{\lambda}_3)^2 (\gamma_1^0)^{-1}, \quad \lambda = -\tilde{\lambda}_2 + \gamma_2^0 (1 + \tilde{\lambda}_3) (\gamma_1^0)^{-1},$$

$$\tilde{\lambda}_2 = \lambda_2 + \beta A (2E_2 + E_4 + E_5) F_3^{-1},$$

$$\tilde{\lambda}_3 = \lambda_3 - \beta A (E_5 - E_4) F_3^{-1}, \quad \tilde{b}_1 = b_1 - \beta A^2 (2F_3)^{-1}.$$

Thus, the problem of computation of the viscosity coefficients of nematic liquid crystals is reduced to calculation of the time correlation functions that determine the tensors of material coefficients in accordance with Eqs. (4)–(9).

In solving this problem, we will take as a point of departure the fact that the orientation dynamics plays the determining role in the processes that form the viscous properties of nematic liquid crystals. This conclusion is based on the fact that the tensors of the material coefficients of Eqs. (4)–(9) can be expressed in terms of the time correlation functions of the tensor order parameter and the tensor of the coefficients of rotational diffusion. The latter statement rests on the definition of microscopic sources (2) and (3) and also on the expression for the microscopic stress tensor; this expression was obtained in [4] for the model of the molecules of a nematic liquid crystal in the form of ellipsoids of revolution, which often is used in investigation of the viscous properties of nematics:

$$\tau_{ij}^{\text{KD}} = (2\beta)^{-1} \left\{ 4\chi d_{ij} + bS [(1 - \chi) c_i c_m n_m n_j - (1 + \chi) c_j c_m n_m n_i + 2\chi c_i c_j c_m c_n n_m n_n] \right\},$$

where the parameter of the shape of an ellipsoid of revolution χ is introduced, which is defined in terms of the ratio p of the large half-axis to the small one according to the formula

$$\chi = \frac{p^2 - 1}{p^2 + 1}. \quad (11)$$

Based on the single-particle expression obtained, it is possible to formulate the dynamic value of the stress tensor density, which, with account for the definition of the tensor order parameter (1), is written in the form

$$\begin{aligned} \beta \hat{\tau}_{ij}(\mathbf{x}) = & 2\chi \left(1 + \frac{1}{3} bS \right) \delta \hat{R}_{ij}(\mathbf{x}) + bS (1 - \chi) \delta \hat{R}_{im}(\mathbf{x}) n_m n_j - \\ & - bS (1 + \chi) \delta \hat{R}_{mj}(\mathbf{x}) n_m n_i + \frac{2}{3} \chi bS \delta_{ij} \hat{R}_{mn}(\mathbf{x}) n_m n_n + \frac{4}{3} \chi bS \delta \hat{\tilde{R}}_{ij}(\mathbf{x}), \end{aligned} \quad (12)$$

where the quantity $\hat{\tilde{R}}_{ij}(\mathbf{x}) = \hat{R}_{ijmn}(\mathbf{x}) n_m n_n$ is determined in terms of the tensor order parameter of the fourth rank:

$$\hat{R}_{ijmn}(\mathbf{x}) = \sum_{v=1}^N d_{ij}^v d_{mn}^v \delta(\mathbf{x} - \mathbf{x}^v).$$

Then, as a kinetic equation for calculating the time correlation function, we employ the equation for the tensor order parameter [2, 5]:

$$\frac{d}{dt} \delta R_{ij}(\mathbf{x}, t) = - \sum_{\alpha=1}^3 \tau_{\alpha}^{-1} B_{ijkl}^{(\alpha)} \delta R_{kl}(\mathbf{x}, t), \quad (13)$$

where $\delta R_{ij} = R_{ij} - R_{ij}^0$ is the deviation of the tensor order parameter from its equilibrium value and $B_{ijkl}^{(\alpha)}$ are Stratonovich's matrices [6].

Since the equation of the time evolution of the dynamic quantity coincides in form with the equation of the evolution of the time correlation function of this quantity [7], Eq. (13) allows one to write the corresponding equation for the time correlation function of the tensor order parameter:

$$\frac{d}{dt} g_{ijkl}(t) = - \sum_{\alpha=1}^3 \tau_{\alpha}^{-1} B_{ijmn}^{(\alpha)} g_{mnkl}(t), \quad (14)$$

where the indicated time correlation function is defined by the relation

$$g_{ijkl}(\mathbf{x}, \mathbf{x}', t) = \frac{1}{V} \langle \delta \hat{R}_{ij}(\mathbf{x}, t) \delta \hat{R}_{kl}(\mathbf{x}', 0) \rangle. \quad (15)$$

Since, according to (1), the tensor order parameter is a symmetric traceless tensor of the second rank, its time correlation function (15) has three independent coefficients, and its material structure is prescribed by the formula

$$g_{ijkl} = \sum_{\alpha=1}^3 g_{\alpha} B_{ijmn}^{(\alpha)}.$$

Consequently, the solution of Eq. (15) has the form

$$g_\alpha(t) = g_\alpha(0) \exp(-t/\tau_\alpha), \quad \tau_\alpha = \frac{g_\alpha(0)}{F_\alpha}, \quad (16)$$

where F_α are the independent coefficients of the tensor F_{ijmn} (7) and $g_\alpha(0)$ are the independent coefficients of the static correlation function of the tensor order parameter, which in the single-particle approximation are determined by the molecular parameters of a nematic medium and the scalar order parameter S in accordance with the formulas [2]

$$g_1 = \frac{3n}{8} (1 - S - b^{-1}), \quad g_2 = \frac{3n}{4} (1 + S - 2S^2 - 3b^{-1}), \quad g_3 = \frac{3n}{2b}. \quad (17)$$

Thus, to calculate the tensors (4)–(9) that describe the material properties of nematic liquid crystals, they are to be expressed with the aid of microscopic sources (2), (3) and microscopic stress tensor (12) in terms of the time integrals of the time correlation function of the tensor order parameter (15), which are calculated with the aid of formulas (16) and (17), and in terms of the tensor of the coefficients of rotational diffusion:

$$D_{ik} = \frac{n}{V} \int d\mathbf{x} \int d\mathbf{x}' \int_0^\infty dt \exp(-\varepsilon t) \langle \hat{\omega}_i(\mathbf{x}, t) \hat{\omega}_k(\mathbf{x}', 0) \rangle,$$

where the dynamic value of the angular-velocity density is defined by the expression

$$\hat{\omega}_i(\mathbf{x}, t) = \frac{1}{n} \sum_{v=1}^N \omega_i^v(t) \delta(\mathbf{x} - \mathbf{x}^v),$$

moreover the introduced tensor of rotational diffusion in the case of a single-axis medium, such as a nematic liquid crystal, has two independent coefficients (of transverse D_\perp and longitudinal D_\parallel diffusion):

$$D_{mn} = D_\perp (\delta_{mn} - n_m n_n) + D_\parallel n_m n_n.$$

For the kinetic tensors a'_{ijkl} , b_{ik} , A_{ijk} , and F_{ijmn} , the above-described program of computations is implemented by direct substitution of the equations for the microscopic stress tensor (12) and microscopic sources of the tensor order parameter (2) and small angles of rotation (3) into the corresponding formulas (4) and (7)–(9). Then, the independent coefficients of the indicated material tensors are written in the form

$$\begin{aligned} a'_2 = a'_3 &= \frac{2}{9\beta} (b\chi)^2 \left\{ \left(\frac{3}{b} + S \right)^2 G_1 + 4S \left(\frac{3}{b} + S \right) G'_1 + 4S^2 G''_1 \right\}, \\ a'_5 &= \frac{2}{9\beta} (b\chi)^2 \left\{ - \left(\frac{3}{b} + S \right)^2 G_1 + \frac{1}{4} \left(\frac{6}{b} - S + \frac{3}{\chi} S \right)^2 G_3 - \right. \\ &\quad \left. - 4S \left(\frac{3}{b} + S \right) G'_1 + 2S \left(\frac{6}{b} - S + \frac{3}{\chi} S \right) G'_3 - 4S^2 (G''_1 - G''_3) \right\}, \\ a'_6 &= \frac{2}{9\beta} (b\chi)^2 \left\{ - \left(\frac{3}{b} + S \right)^2 G_1 + \frac{1}{4} \left[\left(\frac{6}{b} - S \right)^2 - \left(\frac{3}{\chi} S \right)^2 \right] G_3 - \right. \end{aligned}$$

$$\begin{aligned}
& -4S\left(\frac{3}{b}+S\right)G'_1+2S\left(\frac{6}{b}-S\right)G'_3-4S^2(G''_1-G''_3)\}, \\
& a'_7=\frac{2}{9\beta}(b\chi)^2\left\{-\left(\frac{3}{b}+S\right)^2G_1+\frac{1}{4}\left(\frac{6}{b}-S-\frac{3}{\chi}S\right)^2G_3-\right. \\
& \left.-4S\left(\frac{3}{b}+S\right)G'_1+2S\left(\frac{6}{b}-S-\frac{3}{\chi}S\right)G'_3-4S^2(G''_1-G''_3)\right\}, \\
& a'_8=\frac{2}{9\beta}(b\chi)^2\left\{\left(\frac{3}{b}+S\right)^2G_1+3\left(\frac{3}{b}-S\right)^2G_2-\left(\frac{6}{b}-S\right)^2G_3+4S\left(\frac{3}{b}+S\right)G'_1+\right. \\
& \left.+12S\left(\frac{3}{b}-S\right)G'_2-8S\left(\frac{6}{b}-S\right)G'_3-4S^2(G''_1-3G''_3-4G''_3)\right\};
\end{aligned} \tag{18}$$

$$b_1=\frac{\beta}{3n}[(2+S)D_{\perp}+(1-S)D_{\parallel}], \quad \beta_2=\frac{\beta S}{n}(D_{\parallel}-D_{\perp}); \tag{19}$$

$$A=3SD_{\perp}; \tag{20}$$

$$F_1=\frac{3}{2}nD_{\perp}(1-S+b^{-1}), \quad F_2=9nD_{\perp}b^{-1}, \quad F_3=\frac{3}{2}nD_{\perp}(2+S-4b^{-1}), \tag{21}$$

where $G_{\alpha} = g_{\alpha}\tau_{\alpha}$, $G'_{\alpha} = g'_{\alpha}\tau_{\alpha}$, and $G''_{\alpha} = g''_{\alpha}\tau_{\alpha}$, with the subscript α running from 1 to 3; g'_{α} and g''_{α} are independent coefficients of static correlation functions determined by the tensor order parameter of fourth rank; they are expressed in terms of the scalar order parameter S by the formulas

$$g'_1=-\frac{g_1}{2}-\frac{3n}{16bS}(1-S-5b^{-1}), \quad g'_2=\frac{g_2}{2}-\frac{9n}{8bS}(1+S-5b^{-1}-2S^2),$$

$$g'_3=g_3+\frac{3n}{4bS}(1-S-5b^{-1});$$

$$g''_1=-\frac{g_1}{2}-2g'_1+\frac{3n}{16(bS)^2}(5S+7-35b^{-1}),$$

$$g''_2=-\frac{g_2}{2}+2g'_2+\frac{9n}{8(bS)^2}(5S+7-35b^{-1}-6S^2),$$

$$g''_3=g_3+g'_3-\frac{3n}{4(bS)^2}(5S+7-35b^{-1}).$$

It should be noted that in deriving relations (20) and (21) for the independent coefficients of material tensors A_{ijk} and F_{ijmn} we used the condition of decoupling of correlations [8, 1], which is frequently applied in the kinetic theory and which is based on the fact that the time of relaxation of the angular velocity of molecules in nematic liquid crystals is much smaller than the time of relaxation of the tensor order parameter [2].

In contrast to the case considered above, direct calculation of the tensors \dot{E}'_{ijkl} (5) and λ_{ijk} (6) encounters difficulties because the time correlation functions that determine these tensors are odd functions of time

reversal. Therefore, in [9, 10] a method of alternative computation of these tensors was suggested, which, in the approximation of small frequencies and wave vectors, leads to the following relations for the tensors considered:

$$E'_{ijkl} = \sum_{\alpha=1}^3 \tau_{\alpha}^{-1} B_{ijmn}^{(\alpha)} B_{mnkl}, \quad (22)$$

$$\begin{aligned} \lambda_{ijk} = (3n)^{-1} A_{psk} \sum_{\alpha=1}^3 \tau_{\alpha} [2\chi (3 + bS) B_{ijps}^{\alpha} + 3bS (1 - \chi) B_{imps}^{\alpha} n_m n_j - \\ - 3bS (1 + \chi) B_{mjps}^{\alpha} n_m n_i + 2\chi bS \delta_{ij} B_{mnps}^{\alpha} n_m n_n], \end{aligned} \quad (23)$$

where the following notation is introduced:

$$B_{ijkl} = \frac{1}{V} \int d\mathbf{x} \int d\mathbf{x}' \int_0^{\infty} dt \exp(-\varepsilon t) \langle \delta \hat{R}_{ij}(\mathbf{x}, t) \hat{\tau}_{kl}(\mathbf{x}', 0) \rangle.$$

The formulas obtained make it possible to avoid the above difficulties in calculation of material tensors that describe the interaction of a hydrodynamic flow and orientations of a medium. On substituting the definitions of microscopic sources (2) and (3) and microscopic stress tensor (12) into Eqs. (22) and (23), we obtain the following expressions for their independent coefficients:

$$\begin{aligned} E'_1 &= (9\beta)^{-1} \chi [(3 - bS) g_2 - 3(3 + bS) g_1 + bS (g'_2 - 3g'_1)], \\ E'_2 &= (3\beta)^{-1} \chi [(3 + bS) g_1 + 2bS g'_1], \\ E'_3 &= (3\beta)^{-1} \chi [(3 + bS) g_1 - (3 - bS) g_2 + 2bS (g'_1 - g'_2)], \end{aligned} \quad (24)$$

$$E'_{4,5} = (6\beta)^{-1} \chi [(6 - bS) g_3 - 2(3 + bS) g_1 + 6bS (g'_3 - g'_1)] \pm (6\beta)^{-1} bS g_3;$$

$$\lambda_2 = -\chi S \frac{6b^{-1} - S(1 - 4S)}{2 + S - 4b^{-1}}, \quad \lambda_3 = -\frac{3S^2}{2 + S - 4b^{-1}}. \quad (25)$$

Thus, the coefficients of viscosity of nematic liquid crystals (10) with account for the performed calculations, whose results are represented by formulas (18)–(21), (24), and (25), are expressed in terms of the coefficient of rotational self-diffusion D_{\perp} , number density of particles n , scalar order parameter S , and molecular parameters of the system, namely, the parameter of the shape of a molecule χ and the parameter of intermolecular interaction b .

The temperature dependence of the scalar order parameter S will be modeled by a function of the form [11]

$$S = \left[1 - C_1 \left(1 - \frac{\Delta T}{T_{NI}} \right) \right]^{C_2}, \quad (26)$$

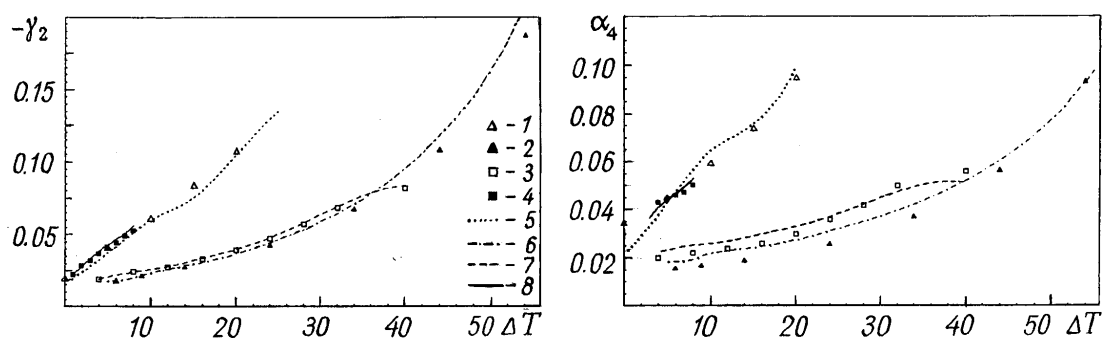


Fig. 1. Dependence of the coefficients of rotational γ_2 and shear α_4 viscosity on the temperature difference ΔT . Experimental data: 1) MBBA [16]; 2) mixture No. 5 [18]; 3) mixture No. 4 [17]; 4) DIBAB [17]. Theoretical calculations: 5) MBBA; 6) mixture No. 4; 7) mixture No. 5; 8) DIBAB. $-\gamma_2, \alpha_4$, Pa·sec; ΔT , K.

where $\Delta T = T_{\text{NI}} - T$ is the deviation of the temperature of the medium from the temperature of the phase change "nematic–isotropic liquid" T_{NI} (since $T < T_{\text{NI}}$, $\Delta T > 0$). With the constants equal to $C_1 = 0.98$ and $C_2 = 0.22$, relation (26) represents in analytical form the dependence of S on temperature in the Maier–Saupe approximation over the range of existence of a nematic phase with an accuracy of up to 1%.

We take the parameter of intermolecular interaction b equal to 4.5415 [12, 2]; we also avail ourselves of the fact that the density n practically does not change over the narrow temperature range of the existence of a mesophase; therefore, we will assume its value to be equal to the mean value over this range.

Statistical calculation of the coefficient of rotational diffusion D_{\perp} is a separate problem not solved completely up to now. Therefore, we make use of the available solution that relates the coefficient of self-diffusion to the coefficient of rotational viscosity γ_1 from the experimental values of which the coefficient of rotational self-diffusion is determined [2].

The definition of the parameter χ (11) in terms of the ratio of the semiaxes of the ellipsoid that models the shape of a molecule provides an obvious way of finding χ for a known molecular structure of the substance under study. However, there are a number of factors that make the determination of the considered parameter ambiguous. First, the molecules of a nematogen can be assumed to be rigid only in a certain approximation, making the value of the parameter χ "float" around a certain value. Moreover, there is a widespread opinion that as a structural unit of nematogens one should use not a molecule but a certain molecular cluster [13], and this may also lead to a change in the effective parameter χ . Nevertheless, in what follows, χ will be calculated precisely on the basis of its definition (11) for each nematogen studied.

Thus, the calculation performed makes it possible to compare theoretical predictions with experimental data, i.e., the results of measurement of the viscosity coefficients of such nematogens as MBBA (4-methoxybenzylidene-4'-*n*-butylanilin, the range of existence of nematic liquid crystals: 22–47°C) [14], DIBAB (*p*, *p*'-dibutylazoxybenzene, 20–31°C), mixture No. 4 (*p*-methoxy-*p*-butylazoxybenzene, 26–74°C) [15], and mixture No. 5 (a mixture of azoxybenzenes, –5–74°C) [16].

Figure 1 presents the dependences of the coefficients of rotational γ_2 and shear α_4 viscosities of the indicated nematogens on the departure of temperature ΔT from the point of phase change "isotropic liquid–nematic."

Figure 2 contains the graphs of the temperature dependence of the Mesovich viscosity coefficients η_b and η_c (see, e.g., [2, 11]), which are often used in experimental works dealing with the investigation of the viscous properties of nematic crystals and which are defined by the expressions

$$\eta_a = \alpha_4/2, \quad \eta_b = \eta_a + (\gamma_1 + \gamma_3 + 2\gamma_2)/4, \quad \eta_c = \eta_a + (\gamma_1 + \gamma_3 - 2\gamma_2)/4,$$

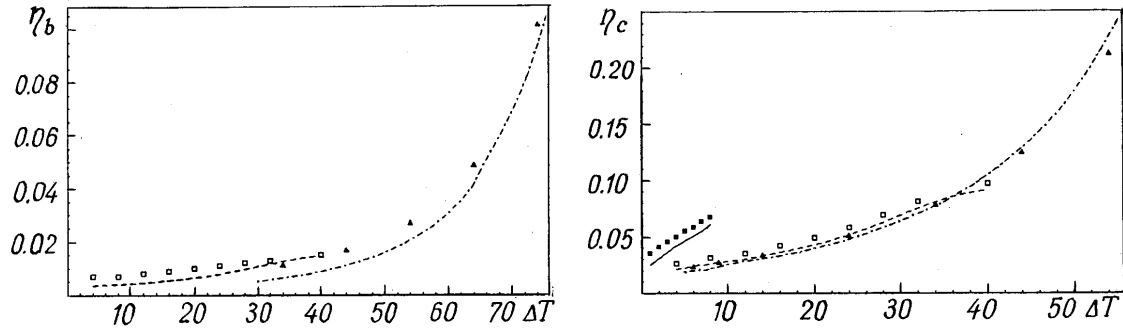


Fig. 2. Dependence of the viscosity coefficients η_b and η_c on the temperature ΔT (notation is the same as in Fig. 1). η_b and η_c , Pa·sec.

with η_a characterizing the viscosity of a nematic medium when the director is perpendicular to the velocity of a hydrodynamic flow and its gradient, η_b , when the director is parallel to the direction of the flow, and η_c , when the director is parallel to the flow velocity gradient. Sometimes, these coefficients are denoted otherwise [11]: $\eta_1 = \eta_c$, $\eta_2 = \eta_b$, $\eta_3 = \eta_a$.

The graphs demonstrate a good agreement of theoretical calculations with experimental data. This distinguishes the theory developed in the present work from the currently popular theories of the viscosity of nematic liquid crystals of the type of Kuzuu–Doi [17, 18], which are incapable of describing shear viscosity of nematic liquid crystals [19].

NOTATION

\mathbf{v} , velocity of hydrodynamic flow of a medium; \mathbf{n} , unit vector that determines the symmetry axis of the medium (director); $\dot{\mathbf{n}}$, time derivative of the director; \mathbf{N} , speed of rotations of the director relative to the flow; $\boldsymbol{\tau}_{ij}$, tensor of viscous stresses; e_{ij} , deformation rate tensor; α_r , Leslie viscosity coefficients ($r = 1, 2, 3, 4, 5, 6$); δ_{ij} , Kronecker's symbol; \mathbf{x} , radius-vector of the point in space; \mathbf{x}^v , radius-vector of the v -th molecule; $\delta(\mathbf{x} - \mathbf{x}^v)$, Dirac delta-function; \mathbf{c} , unit vector prescribing the orientation of the molecule of the medium; $\boldsymbol{\omega}^v$, vector of angular speed of rotation of the v -th molecule; $\hat{\boldsymbol{\omega}}(\mathbf{x})$, density of the dynamic value of the angular velocity; ϵ_{ijk} , Levi–Civita tensor; $\hat{p}_i(\mathbf{x})$, density of the dynamic value of the pulse; $\hat{R}_{ij}(\mathbf{x})$, density of the dynamic value of the tensor order parameter; $\hat{R}_{ijmn}(\mathbf{x})$, density of the dynamic value of the tensor order parameter of 4th rank; R_{ij}^0 , equilibrium value of the tensor order parameter; $\boldsymbol{\theta}_i(\mathbf{x})$, density of the dynamic value of small angles of the rotation of molecules; d_{ij} , tensor parameter of the order per molecule; \mathbf{p}^v , vector of the pulse of the v -th molecule; $\boldsymbol{\theta}^v$, vector of the angle of rotation of the χ -th molecule; $\hat{\boldsymbol{\tau}}_{ij}(\mathbf{x})$, density of the microscopic stress tensor; $\boldsymbol{\tau}_{ij}^{\text{KD}}$, microscopic stress tensor of Kuzuu–Doi; $\hat{J}_{ij}^R(\mathbf{x})$, density of the source of the tensor order parameter; $\hat{J}_i^\theta(\mathbf{x})$, density of the source of the vector of the small angle of rotation; N , number of particles in the system; b , parameter of the intermolecular interaction; a'_{ijkl} , b_{ik} , A_{ijk} , F_{ijmn} , E'_{ijkl} , and λ_{ijk} , tensors of kinetic coefficients; D_{ij} , tensor of the coefficients of rotational diffusion; D_\perp , coefficient of the transverse rotational diffusion; D_\parallel , coefficient of longitudinal rotational diffusion; τ_α , times of relaxation of the tensor order parameter; n , equilibrium density of the number of particles; S , scalar order parameter; T , absolute temperature; T_{NI} , phase-change temperature of the nematic–isotropic liquid; β , reciprocal thermodynamic temperature; γ_1 , γ_2 , and γ_3 , coefficients of rotational viscosity.

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