Acoustic viscosimetry of nematic liquid crystals at varying pressure and temperature

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It is shown that at constant ΔT the viscosity coefficient α_1 does not depend on pressure. It is established that as T_c is approached the combination of the viscosity coefficients η increases because of the slowing down of the order-parameter relaxation. Analysis shows that the order-parameter relaxation time is a function of ΔT and that at constant ΔT it is independent of pressure. It is revealed that the change of the dissipative parameters that describe the angular dependence of the quantity α/f^2 with changing pressure is determined by a relaxation process connected with conformational transitions in the terminal molecular chains.

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The dynamic properties of nematic liquid crystals (NLC) that are characterized by the presence of an ordered orientational structure, are described by a system of hydrodynamic equations[1] that include as an additional variable the unit vector of the local optical axis (the director **n**). The viscosity properties of NLC are determined by the dissipative part of the stress tensor t_{ij}, which in contrast to the case of an isotropic liquid can be represented in the form

$$t_{ij}=-(\mu_1 d_{kk}+\mu_2 n_k n_p d_{kp})\delta_{ij}-(\mu_3 d_{kk}+\mu_4 n_k n_p d_{kp})n_i n_j$$
$$-\mu_5 N_i n_j-\mu_6 n_i N_j-\mu_7 d_{ij}-\mu_8 d_{ik} n_k n_j-\mu_9 n_i n_k d_{kj}, \tag{1}$$

where μ_{1-9} are dissipative coefficients with the dimensionality of viscosity,

$$d_{ij}={}^1/_2(\partial v_i/\partial x_j+\partial v_j/\partial x_i)$$

is the strain-rate tensor, **v** is the velocity of the liquid, and

$$N_i=(\partial n_i/\partial t+v_\alpha\nabla_\alpha n_i)-{}^1/_2[(\mathrm{rot}\,\mathbf{v})\times\mathbf{n}]_i$$

is the rate of rotation of the director relative to the liquid.

In the case of an incompressible NLC (div $\mathbf{v}=0$) the terms containing μ_1, μ_2, and μ_3 vanish in analogy with the term that contains the coefficient of bulk viscosity of an isotropic liquid; in this case expression (1) takes a form frequently used in hydrodynamic problems, with the notation change $\alpha_i\equiv\mu_{\gamma-3}$, where $3<\gamma\leqslant 9$. The quantities μ_{1-3} have the meaning of the bulk viscosity, and the quantities α_i (the Leslie coefficients), which are connected by the known Onsager relations $\alpha_6-\alpha_5=\alpha_2+\alpha_3$, determine the coefficients of shear viscosity of NLC under various experimental conditions. The determination of certain independent viscosity coefficients α_i from experiments on the influence of shear flow, of a rotating magnetic field, and of many other factors on the orientational structure and on the rheological properties of lilquid crystals entails substantial difficulties. In particular, to calculate α_i it is necessary to measure the shear viscosity in three different experimental geometries of NLC flow in a rectangular capillary,[2] and the results obtained for this parameter are subject to large errors. Therefore, obviously, information on the temperature dependence of the coefficient α_i is as a rule either nonexistent or contradictory (e.g., for MBBA, Refs. 2–4).

The acoustic method of investigation uncovers new possibilities of determining this dissipative parameter. Indeed, the coefficient α of absorption of a longitudinal ultrasound wave propagating at an angle θ to the director is defined by the expression[5]

$$\frac{\alpha}{f^2}(\theta)=\frac{2\pi^2}{\rho c^3}[(\mu_1+\alpha_4)+(\mu_2+\mu_3+\alpha_5+\alpha_6)\cos^2\theta+\alpha_1\cos^4\theta], \tag{2}$$

where f is the ultrasound frequency, ρ is the density, and c is the ultrasound velocity. It follows from the foregoing relations that a study of the angular dependence of the ultrasound absorption coefficient makes possible a direct determination of α_1. In addition, using (2) we can determine the bulk viscosity coefficients μ_i, information on which cannot be obtained by other methods. We note that in accord with the deductions of Ref. 6, expression (2) retains its form at finite ultrasound frequency; in this case the coefficients μ_i must be regarded as frequency-dependent parameters. In particular, in the simplest case of only one relaxation process, the bulk viscosities depend on the frequency in accordance with the relation

$$\mu_i=\mu_i^0(1+\omega^2\tau^2)^{-1},\qquad \omega=2\pi f. \tag{3}$$

Here τ is the relaxation time, and μ_i^0 are the values of the bulk-viscosity coefficients in the limit as $\omega\to 0$.

We note also that acoustic investigations make it possible to establish, besides the temperature dependence of the NLC dissipative coefficients, also their pressure dependence, the determination of which by standard viscosimetry methods entails serious difficulties.

We report here the first results of experimental investigations of the dependences of certain dissipative NLC coefficients on temperature and pressure, obtained by analysis of the anisotropic propagation of ultrasound in *p*-*n*-metoxybenzy-lidene-*p*-butylaniline (MBBA) and *p*-*n*-butoxybenzylidene-*p*-butylaniline (BBBA). The temperature interval of the existence of the nematic phase in these compounds is 293.0–315.4 K and 313.3–344.9 K, respectively. Experiment yielded the angular dependences of the absorption coefficient of ultrasound of frequency $f=3$ MHz propagating in a

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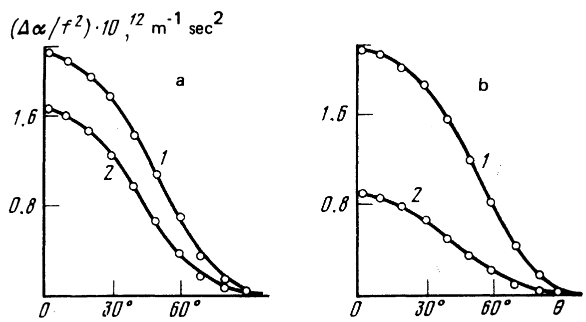

FIG. 1. Angular dependence of $\Delta\alpha/f^2$ at pressures 10^5 (1) and 5×10^7 (2) Pa in MBBA at $T=310.2$ K (a) and BBBA at $T=341$ K (b).

liquid-crystal sample placed in a rotating magnetic field of induction 0.3 T. The measurements were made at low magnetic-field synchronous-rotation velocities by a procedure described in Ref. 7. The pressure in the acoustic chamber ranged from 10^5 to 6×10^7 Pa.

Figure 1 shows typical plots of the angular dependences of the ultrasound absorption coefficient

$$\frac{\Delta\alpha}{f^2}(\theta)=\frac{\alpha}{f^2}(\theta)-\frac{\alpha^\perp}{f^2}$$

at different pressures and temperatures. Here $\alpha^\perp/f^2$ is the value at $\theta=90°$. The curves in Fig. 1 were obtained by a least-squares fit of the experimental data to the relation

$$\frac{\Delta\alpha}{f^2}(\theta)=a\cos^2\theta+b\cos^4\theta. \tag{4}$$

Figure 2 shows plots, typical of both investigated substances, of the coefficients a and b vs pressure and temperature. An interesting feature of these plots is the reversal of the sign of the coefficient b as a function of temperature or pressure. We note that the coefficient a remains in this case positive in the entire range of pressures and temperatures. As can be seen from the foregoing relations, the coefficients a and b vanish at a certain temperature T_c that depends on the pressure. This corresponds, according to (4), to absence of anisotropy of the ultrasound absorption coefficient, i.e., to a transition to the isotropic phase. Thus, acoustic data can be used to determine the pressure dependences of the bleaching temperature, listed in Table I for the two investigated substances. For MBBA the $T_c(P)$ dependence is linear, with a coefficient dT_c/dP amounting to 2.9×10^{-7} K/Pa, in accord with the results by others.[8,9]

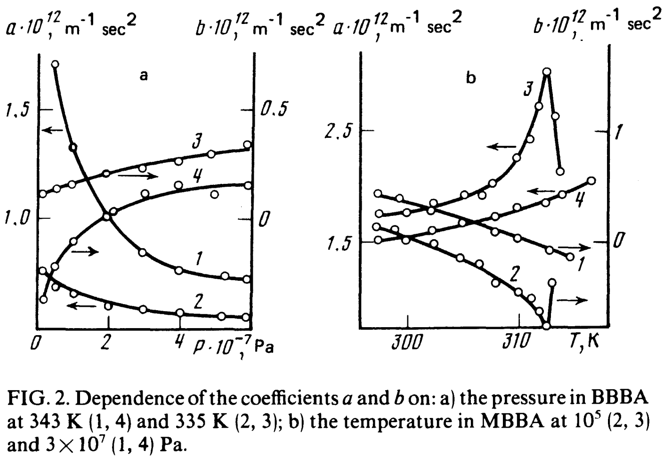

FIG. 2. Dependence of the coefficients a and b on: a) the pressure in BBBA at 343 K (1, 4) and 335 K (2, 3); b) the temperature in MBBA at 10^5 (2, 3) and 3×10^7 (1, 4) Pa.

On the basis of the experimental results we calculated, in accord with (3), the quantities $\mu_2+\mu_3+\alpha_5+\alpha_6$ and α_1 in Eq. (2). In the calculations we took into account the fact that the ultrasound velocity[11] is a function of the parameter $\Delta T=T_c-T$. The values of c and ρ were thus determined from the experimental data at normal pressure[11-14] with allowance for the $T_c(P)$ dependence. We note that the pressure and temperature dependences of $\mu_2+\mu_3+\alpha_5+\alpha_6$ and α_1 obtained in this manner have qualitatively the same form as the corresponding dependences of the coefficients a and b.

In the interpretation of the obtained temperature and pressure dependences of the dissipative coefficients it is necessary to take into account the following circumstances. First, the bulk-viscosity coefficient can be determined by two relaxation processes[15]: the "normal" one connected with the conformational transitions in the terminal molecular chains, and "critical," due to relaxation of the order parameter S. The normal-process relaxation time τ_i, described by an Arrhenius-type relation[16]

$$\tau_i=(A/T)e^{E/kT}, \tag{5}$$

(where A is a constant and E is the activation energy corresponding to the conformational transition) is a function of the absolute temperature and has no anomalies in the vicinity of T_c. In contrast to τ_i, the order-parameter relaxation time τ_c depends on the difference ΔT and increases substantially when T_c is approached.[17] We note that the quantity μ_i^0 in expression (3) is proportional to the product $S\tau_i$ for the normal process and to τ_c for the critical one.[15] Second, the coefficients α_i as shown in Ref. 18, are functions of S and consequently depend on ΔT. Thus, the considered dissipative coefficients of NLC depend substantially on the difference ΔT.

To cast light on the influence of the pressure on these parameters, Figs. 3 and 4 show their dependences on ΔT. A feature of both investigated substances is the independence of the coefficient α_1 of the pressure at identical values of ΔT. In light of the foregoing, this fact is evidence that the pressure dependence of the order parameter reduces to the $S(\Delta T)$ dependence. This conclusion is confirmed by experimental investigations of paraazoxyanisole.[19] The combination of the dissipative coefficients

$$\eta=\mu_2+\mu_3+\alpha_5+\alpha_6$$

in MBBA at fixed values of ΔT increases with increasing pressure. No $\eta(P)$ dependence was observed in BBBA (at constant ΔT) within the limits of measurement error. The published viscosimetric data[3] on MBBA make it possible to estimate the sum $\alpha_5+\alpha_6$ at

$$\alpha_5+\alpha_6=2(\eta_1+\eta_2)-4\eta_3-\gamma_1. \tag{6}$$

Here $\eta_{1,2,3}$ are the shear viscosities in the notation of Ref. 2, and $\gamma_1=\alpha_3-\alpha_2$ is the rotational-viscosity coefficient. Calculation according to Eq. (6) shows that $\alpha_5+\alpha_6$ decreases monotonically as T_c is approached, from 0.3 P at $\Delta T=20$ K

TABLE I. Pressure dependence of bleaching temperature

$P\cdot 10^{-5}$, Pa		1	100	200	300	400	500
T_c, K	MBBA	315.4	318.2	321.4	324.0	327.2	329.8
	BBBA	344.9	348.0	350.8	353.5	356.9	359.8

to 0.04 P at $\Delta T = 1.5$ K. (The values of γ_1 were taken from Ref. 20.) The dependence of the sum $\alpha_5 + \alpha_6$ on the pressure at a fixed value of ΔT was taken into account by approximating the right-hand side of (6) by the Arrhenius law with an activation energy 5 kJ/mol (Ref. 21) The changes of $\alpha_5 + \alpha_6$ at constant ΔT do not exceed 10% in the investigated pressure interval.

The contribution of the intramolecular relaxation process to the bulk viscosities μ_2 and μ_3 can be determined, according to Eqs. (3) and (5), by using the values $A = 6.79\times 10^{-9}$ sec·K and $E = 3.5$ kcal/mol, obtained in an investigation[16] of nematics with the same terminal molecular groups as in MBBA, but with a larger temperature interval of the existence of the mesophase.

It follows from (5) at constant ΔT that the relaxation time of the normal process and consequently that of the normal contribution are functions of pressure and are determined by the $T_c(P)$ dependence. The temperature dependences of the normal contribution to $\mu_v = \mu_2 + \mu_3$, calculated for MBBA with allowance from the data in Table I, are shown in Fig. 5 for three values of the pressure. The constant $\mu_v^0 = \mu_2^0 + \mu_3^0$ (see (3)) was determined in this case from the values of η and $\alpha_5 + \alpha_6$ at $\Delta T = 30$ K and $P = 3\times 10^7$ Pa, while $S(\Delta T)$ was calculated from the data of Ref. 22. According to investigations performed on other nematics,[16] at this value of ΔT the critical contribution to the bulk viscosity can be neglected. At a fixed value of ΔT the normal contribution decreases with increasing pressure and determines almost completely the $\eta(P)$ dependence shown in Fig. 3. We note that the absence from this figure of a pressure dependence of at constant ΔT indicates that the quantity b [Eq. (4)] does not contain bulk-viscosity coefficients. This result agrees with the foregoing conclusions of the hydrodynamic theory.

Figure 5 shows the temperature dependence of the critical contribution $(\mu_v)_c$ and the bulk viscosity coefficients. The value of $(\mu_v)_c$ was determined from the expression

$$(\mu_v)_c = \eta - (\mu_v)_n - (\alpha_5 + \alpha_6).$$

As T_c is approached, $(\mu_v)_c$ increases and is independent of pressure at constant ΔT. We note that in the ΔT interval from 7 to 20 K the exponent of the power-law divergence of the critical contribution is close to unity. The dependence of $(\mu_v)_c$ on ΔT in this region agrees with the theoretical plot, shown dashed in the figure, of the critical contribution[17] for the case $\omega\tau_c \ll 1$ and $\Delta T \gg T_c - T^*$, where T^* is the temperature corresponding to the supercooling limit of the isotropic phase (according to Ref. 23, $T_c - T^* = 1$ K for MBBA). At $\Delta T < 7$ K a decrease of the exponent of the power-law divergence of $(\mu_v)_c$ is observed and is due to violation of the condition $\omega\tau_c \approx 1$. Indeed, according to the data of Ref. 24, the parameter $\omega\tau_c \approx 1$ at $\Delta T = 4$ K and at 3 MHz. Another cause of the noted change of the divergence exponent may be violation of the condition $\Delta T \gg T_c - T^*$. The analysis shows that the order-parameter relaxation time is a function of ΔT and at constant ΔT it is independent of pressure.

The lack of viscosimetric data on BBBA makes a similar analysis for this compound impossible. The absence of an $\eta(P)$ dependence for this compound is possibly due to the smaller, compared with MBBA, relative contribution of the normal process to the bulk viscosity coefficients. As T_c is approached, η increases because of the slowing down of the order-parameter relaxation, and is independent of pressure at a fixed value of ΔT, thus confirming the conclusion drawn above concerning the type of dependence of the critical contribution on the state parameters P and T.

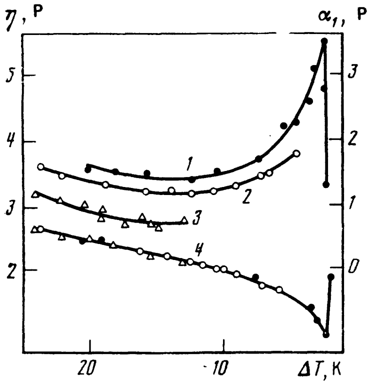

FIG. 3. Dependence of η (1–3) and α_1 (4) on ΔT in MBBA at pressures 10^5 (●), 3×10^7 (○) and 6×10^7 (△) Pa.

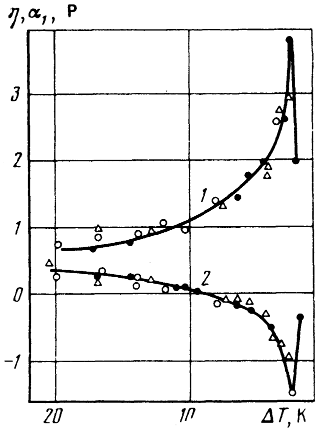

FIG. 4. Temperature dependences of η(1) and α_1(2) in BBBA at pressures 10^5 Pa (●), 3×10^7 Pa (○) and 6×10^7 Pa (△).

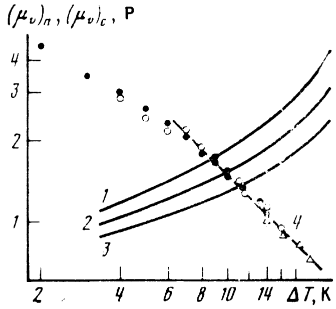

FIG. 5. Dependence of the normal (1–3) and critical (4) contributions to the bulk viscosity coefficient in MBBA at pressures 10^5 Pa (1 and ●), 3×10^7 Pa (2 and ○), and 6×10^7 Pa (3 and △).

Thus, the theoretical premises considered above describe satisfactorily the experimental results on ultrasound propagation in nematic liquid crystals at varying pressure and temperature. The pressure dependence of the dissipative parameters that describe the angular dependence of α/f^2 is determined by a relaxation process connected with conformational transitions in terminal molecular chains.

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