Relaxation processes in nematic liquid crystals in the nonstationary regime of a rotation of magnetic field

Alexey N. Larionov[1][*], *Nikolai A.* Us[2], *Valentin N.* Mashin[2], *Vadim P.* Zakusilov[2], and *Angelika V.* Mashina[2]

[1] Voronezh State Agrarian University after Emperor Peter the Great, 1, Michurin st., Voronezh, 394087, Russia

[2] Military educational scientific center air force "Air force Academy named after Professor N E Zhykovsky and Y A Gagarin", 54-a, Staryh Bolshevikov st., Voronezh, 394064, Russia

Abstract. The prospects of using the nonstationary regime of motion of the director for studying the relaxation properties of liquid crystals in the low-temperature interval of the nematic phase are shown. In the nonstationary regime, the phase shift between the direction and the wave vector is 45 and does not depend on the angular velocity of rotation of the magnetic field. A eutectic mixture of nematic liquid crystals with a wider temperature range of the nematic phase compared to individual components has been studied. A decrease in the anisotropy of the absorption coefficient in the nonstationary regime is associated with a partial violation of the homogeneous orientation of the sample. The nature of the dependence of the low-frequency component of the phase characteristic on the thermodynamic parameters of the state is established. Within the framework of the hydrodynamics of the nematic phase, relations were obtained that allow calculating the dissipative coefficients responsible for the performance of liquid crystal technical devices.

1 Introduction

The replacement of pure components with mixtures of nematic liquid crystals as an element of modern technical devices provides an extension of the temperature range of their application. However, in the low-temperature range of the nematic phase, a delayed reaction of electronic devices with liquid crystal components to the influence of an external control signal is observed. An informative method for studying the relaxation properties of nematic liquid crystals and their mixtures is the study of their behavior in rotating magnetic fields. In this case, two modes of motion of the long axes of molecules are realized – stationary, in which the long axes of the molecules rotate synchronously with the magnetic field with a phase delay relative to the magnetic field induction vector, and nonstationary regime. In the nonstationary regime, which prevails in the low-temperature range of the nematic phase, the movement of the long axes of molecules has a complex character, the study of which

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[*] Corresponding author: larionovan@yandex.ru

provides extensive information about the relaxation properties of the nematic phase. The analysis of the experimental results obtained within the framework of the hydrodynamics of the nematic phase provides the information necessary for calculating the parameters of electronic devices with a liquid crystal working fluid. Acoustic spectroscopy is a convenient way to study the orientation structure of matter.

2 Materials and methods

A eutectic mixture (LC-404) of p-n-methoxybenzylidene-p-butylaniline (MBBA) and p-n-ethoxybenzylidene-p-butylaniline (EBBA) with a wider temperature range of the nematic phase compared with the components of the mixture was studied [1,2]. The studies were performed in the nematic phase of LC-404 in the pressure range from 10^5 Pa to 6×10^7 Pa. The mixture was oriented by the magnetic field of a permanent magnet with an induction of B=0.15 T, exceeding the saturation value, which ensured a uniform orientation of the sample in a static magnetic field [3]. The rotation of the magnetic field was provided by the rotary stand UPG-56 [3,4]. The angular velocity of rotation of the permanent magnet varied in the range from 0.1 rad/s to 1.5 rad/s. The hydrostatic pressure was created by the MP-600 cargo piston pressure gauge [4]. The use of a two-circuit temperature control system of the sample ensured temperature stability of at least 0.05 K under conditions of exposure to air flow caused by the rotation of a permanent magnet. Measurement of the anisotropy of the ultrasound absorption coefficient ($\Delta\alpha=\alpha_1-\alpha_2$, where α_1 and α_2 are the absorption coefficient of ultrasound, respectively, with parallel and normal orientation of the wave vector and the magnetic field induction vector) was performed by a fixed–distance pulse method at an ultrasound frequency of f=2.8 MHz and f=8.28 MHz. The relative error in determining the anisotropy of the absorption coefficient does not exceed 1.5%.

3 Results and discussion

The rotation of a permanent magnet with an angular velocity whose value ω_H is less than the critical ω_K is accompanied by a periodic change in the absorption coefficient of ultrasound with a period π/ω_H. At low angular velocities of rotation of the magnetic field, the absorption coefficient of ultrasound varies in phase with the field. An increase in ω_H leads to a phase delay in the change in the ultrasound absorption coefficient relative to the magnetic field induction vector, but the value of $\Delta\alpha(\omega_H t)/f^2$ does not change [4]. When the angular velocity of rotation of the magnetic field reaches a critical value of ω_K, a distortion of the dependence $\Delta\alpha(\omega_H t)/f^2$ occurs, manifested in a decrease in the anisotropy of the ultrasound absorption coefficient (figure 1.a). The phase delay φ of the dependence $\Delta\alpha(\omega_H t)/f^2$ at $\omega_H=\omega_K$ reaches 45˚. An increase in the angular velocity of rotation of the magnetic field in the range of values $\omega_H>\omega_K$ leads to the appearance of a low-frequency component on the phase characteristic $\Delta\alpha(\omega_H t)/f^2$ with the frequency Ω (figure 1.b), that is, the spectrum of the phase characteristic becomes more complicated.
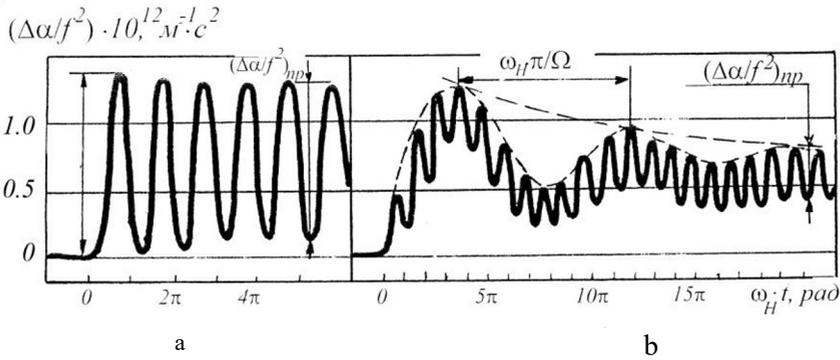
Fig. 1. Phase characteristic $\Delta\alpha(\omega_H t)/f^2$ in LC-404 at f=2.8 MHz, T=298.5 K, P=20 MPa, angular velocity of rotation of the magnetic field a) ω_H=0.16 rad/s, b) ω_H=0.48 rad/s

The low-frequency component fades over time, which has not been explained within the framework of the hydrodynamics of the nematic phase. It is possible that the attenuation of the low-frequency component is associated with the process of partial destruction of the homogeneous orientation of the sample at $\omega_H>\omega_K$ [5]. The duration of the attenuation process of the low-frequency component significantly exceeds the duration of the process of decreasing the value of $\Delta\alpha/f^2$ at $\omega_H=\omega_K$. The characteristic attenuation time of the low-frequency component τ_Ω depends on the temperature, pressure and angular velocity of rotation of the magnetic field, but does not depend on the frequency of ultrasound in the studied frequency range. Upon completion of the transient process in the nonstationary regime, the phase characteristic of the anisotropy of the ultrasound absorption coefficient turns out to be similar to the dependence of $\Delta\alpha(\omega_H t)/f^2$ in the stationary regime, but the value of $\Delta\alpha/f^2$ has a lower value equal to $(\Delta\alpha/f^2)_{pr}$ (figure 1). An increase in pressure at a fixed temperature is accompanied by a decrease in the angular velocity, at which the director regime of motion changes both at an ultrasound frequency of f=2.8 MHz and at f=8.28 MHz. An increase of temperature at constant pressure leads to a decrease of the value of the angular velocity, at which the director regime of motion changes both at the frequency of ultrasound f=2.8 MHz and at f=8.28 MHz [6]. The frequency of ultrasound in the studied range of ultrasound frequencies has no effect on both the angular velocity ω_K, at which the director movement regime changes, and the nature of the dependence of the parameter ω_K on pressure and temperature (table 1,2).

Table 1. Dependence of ω_K on pressure and temperature in the LC 404 at *f*=2.8 MHz

P, МПа T, К	0.1	10	20	30	40
289.7	0.240	0.188	0.144	0.118	0.092
295.7	0.260	0.200	0.157	0.144	0.118
300.6	0.288	0.240	0.211	0.182	0.132
305.6	0.317	0.266	0.238	0.187	0.144
310.5	0.365	0.288	0.242	0.192	0.151
315.4	0.393	0.324	0.249	0.276	0.198
320.3	0.550	0.429	0.347	0.276	0.232
322.5	0.686	0.610	0.428	0.393	0.276
323.6	0.740	0.666	0.652	0.505	0.393

Table 2. Dependence of ω_K on pressure and temperature in the LC 404 at f=8.28 МГц

P, МПа T, К	0.1	10	20	30	40
290.0	0.240	0.188	0.144	0.118	0.092
293.5	0.252	0.198	0.155	0.138	0.114
299.5	0.275	0.232	0.166	0.153	0.130
305.6	0.312	0.258	0.199	0.169	0.154
308.8	0.356	0.288	0.230	0.192	0.165
312.1	0.393	0.310	0.250	0.208	0.176
317.1	0.500	0.389	0.300	0.240	0.202
323.1	0.707	0.628	0.550	0.393	0.288

The value of the frequency Ω is a function of the angular velocity of rotation of the magnetic field and P, T are the thermodynamic parameters of the state. An increase of temperature at a fixed pressure is accompanied by an increase of frequencies Ω [1,7]. As it approaches the phase transition region, the nematic liquid crystal – isotropic liquid fluctuates at temperatures and pressure by the value of Ω and is restored [3,8]. An increase of the angular velocity of rotation of the magnetic field leads to a change of the graphs of the dependence of $\Omega(T)$ in the region of higher temperatures and lower frequencies of Ω. The value of Ω does not depend on the frequency of ultrasound, which makes it possible to use the resolution of acoustic studies to calculate the parameters of liquid crystal technical devices. The dependence of Ω on pressure is exponential

$$\Omega(P) = \Omega_0 \cdot \exp(-k_\Omega \cdot P), \tag{1}$$

where k_Ω=(0.33±0.08)×10^{-7} Pa^{-1} in the temperature range (289÷323) K and does not depend on the angular velocity ω_H in the studied range ω_H, Ω_0 is the frequency of the low–frequency component at atmospheric pressure (table 3). At higher temperatures, the value of k_Ω decreases with increasing temperature.

Table 3. Dependence of Ω_0 (rad/s) on temperature and angular velocity of rotation of the magnetic field

T, К $\omega_{H,}$ rad/s	290.0	293.5	296.8	299.5
0.262	0.157	0.279	0.698	-
0.314	0.112	0.175	0.345	0.465
0.628	0.050	0.070	0.145	0.165

The increase of pressure is accompanied by a shift in the dependence of $\Delta\alpha(P)/f^2$ to the region of higher temperatures. For the ultrasound frequency f=8.28 MHz, a decrease ($\Delta\alpha/f^2$) is observed with an increase of the angular velocity of rotation of the magnetic field. An increase of pressure leads to a decrease in the ratio $(\Delta\alpha/f^2)_{pr}$. The value $(\Delta\alpha/f^2)_{pr}$ does not depend on the pressure at the inversion temperature. In the stationary regime, the dependence $\Delta\alpha(T)/f^2$ has a characteristic maximum in the region of the nematic liquid crystal - isotropic liquid phase transition and a minimum at the inversion temperature (figure 2). In the nonstationary regime, an increase of the angular velocity ω_H leads to a decrease of the maximum and disappearance of the minimum of the parameter $\Delta\alpha/f^2$ at the clearance temperature and a shift of the maximum to the region of higher temperatures (figure 2).
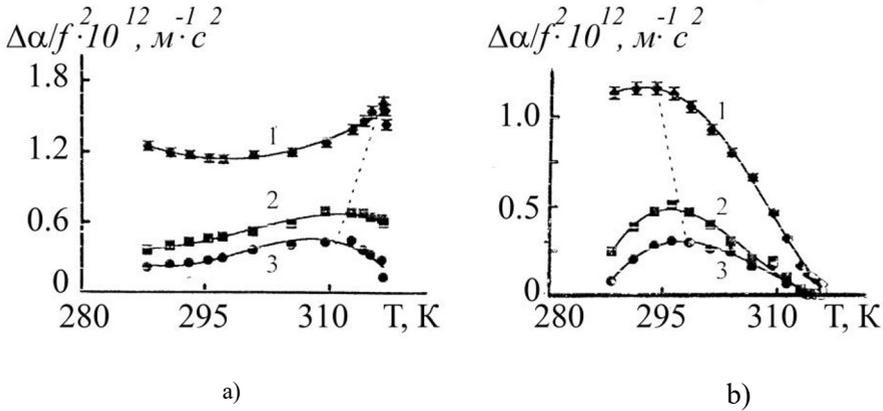
Fig. 2. Temperature dependence $\Delta\alpha/f^2$ at a pressure of 10^5 Pa, angular velocities of rotation of the magnetic field: 1 – 0.052 rad/s; 2 - $\omega_H = \omega_K$; 3 – 0.628 rad/s at ultrasound frequencies: a) – 2.8 MHz; b) – 8.28 MHz

At an ultrasound frequency of 8.28 MHz (figure 2.b) in stationary regime, with an increase in temperature, a gradual decrease in the value of $\Delta\alpha(T)/f^2$ is observed. An increase of the angular velocity of rotation of the magnetic field leads to a shift of the maximum ratio $\Delta\alpha(T)/f^2$ to the region of higher temperatures. The dependence of the anisotropy of the ultrasound absorption coefficient at a frequency of 2.8 MHz is exponential, and in the nonstationary regime, the dependence of $\Delta\alpha(P)/f^2$ has a more complex form, while for a frequency of 8.28 MHz, the dependence of $\Delta\alpha/f^2$ on pressure is characterized by an exponential decrease. After the completion of the transient attenuation process of the low-frequency component, the phase characteristic tends to a stationary value $(\Delta\alpha/f^2)_{pr}$, the dependence of which on pressure is described by the law

$$(\Delta\alpha(P)/f^2)_{np} = (\Delta\alpha/f^2)_{np\,0} \cdot exp(-k_{\Delta\alpha} \cdot P), \tag{2}$$

where $(\Delta\alpha/f^2)_{np0}$ is the anisotropy value of the ultrasound absorption coefficient at atmospheric pressure, $k_{\Delta\alpha}$ is a coefficient that is a function of temperature and does not depend on the angular velocity of rotation of the magnetic field (table 4). Expression (2) is performed over the entire temperature range of the nematic phase, and with increasing temperature, the ratio $\Delta\alpha/f^2$ increases smoothly at an ultrasound frequency of 2.8 MHz, and at an ultrasound frequency of 8.28 MHz it gradually decreases.

Table 4. Values of the coefficient $k_{\Delta\alpha} \times 10^7$, Pa^{-1}

T, K \ f, MHz	293.0	298.5	305.0
2.8	0.035	0.059	0.087
8.28	0.025	0.021	0.09

The application of the hydrodynamics of the nematic phase to the description of ultrasound propagation made it possible to obtain an expression of the dependence of the ultrasound absorption coefficient on the angle θ between the director and the wave vector [4,8]

$$\frac{\Delta\alpha}{f^2} = a \cdot cos^2\theta + b \cdot cos^4\theta, \tag{3}$$

where the parameters a and b are functions of the shear and volume viscosity coefficients [1,6]. In nonstationary regime, the coefficient a* increases monotonously with increasing

temperature at a frequency of 2.8 MHz and changes in a more complex way at f =8.28 MHz. At ultrasound frequencies of 2.8 MHz and 8.28 MHz, the a* coefficient is positive throughout the temperature range of the nematic phase. The coefficient b* changes sign at a frequency of 8.28 MHz over the entire temperature range, while at a frequency of 2.8 MHz, the coefficient b* is negative over the entire temperature range of the nematic phase at pressures from 10^5 Pa to $3 \cdot 10^7$ Pa, and at higher pressures in the low-temperature region, the coefficient b* takes positive values. At a temperature of T_b at a frequency of 2.8 MHz, the dependence of the b* coefficient on pressure was found, and the temperature of T_b does not depend on the frequency of ultrasound [6,8].

The influence of pressure on the parameters a* and b* increases with an increase in the frequency of ultrasound. The dependence of the coefficients a* and b* on pressure for the studied frequencies is described by a linear law

$$\begin{cases} a^*(P) = (a^*)_0 + k_a \cdot P, \\ b^*(P) = (b^*)_0 + k_b \cdot P, \end{cases} \tag{4}$$

where the parameters a* (P) and b* (P) are the values of the coefficients at pressure P, $(a^*)_0$ and $(b^*)_0$ are the coefficients at atmospheric pressure (table 5,6).

Table 5. The values of the coefficient $k_a \times 10^4$, Pa^{-1}

f, MHz \ T, K	293.0	300.6	305.0	310.5
2.8	8.08	10.10	11.10	13.22
8.28	-7.20	-8.16	-8.94	-10.50

Table 6. Values of the coefficient $k_b \cdot 10^4$, Pa^{-1}

f, MHz \ T, K	293.0	300.6	305.0	310.5
2.8	-12.10	-14.60	-18.30	-20.20
8.28	0.34	1.72	0.44	1.47

At a pressure of 1.9×10^7 Pa at ultrasound frequencies of 2.8 MHz and 8.28 MHz, parameter b* does not depend on pressure.

4 Conclusion

The nonstationary regime is characterized by a phase shift φ= 45° between the induction vector and the extreme value of the ultrasound absorption coefficient. An increase of pressure, angular velocity, or a decrease of temperature is accompanied by a decrease of the absorption coefficient of ultrasound in a nonstationary regime. The absence of dependence of the frequency of the low-frequency component of the phase characteristic of the ultrasound absorption coefficient makes it possible to use the results of acoustic studies to calculate the parameters of liquid crystal technical devices. Within the framework of the hydrodynamics of the nematic phase, relations are obtained that establish a relationship between the acoustic parameters and the dissipative coefficients of the substance. This makes it possible to determine the nature of the dependence of the coefficients of volume and shear viscosity on pressure and temperature, as well as to calculate the coefficient of rotational viscosity characterizing the performance of liquid crystal.

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