Influence of pressure and temperature on the attenuation of ultrasound in the nematic phase of the liquid crystal working medium of technical devices in the vicinity of phase transition point

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Abstract. The dependence of the attenuation coefficient of ultrasound in the nematic phase on pressure and temperature, which characterizes the parameters of electronic devices with a liquid-crystal working medium in the vicinity of phase transition point, is studied. Liquid crystals and their mixtures with a wide temperature range of the nematic phase were researched. The analysis is performed taking into account the normal relaxation process associated with conformational transitions of the end chains, and the critical relaxation process due to the nature of this phase transition. The nature of the dependence on the pressure and temperature of the normal, critical and classical components of the attenuation coefficient of ultrasound is established.

I. Introduction

The action of most display systems, of electronic devices, as well as sensors of temperature, pressure, velocity, displacement, rotation angle and other parameters of devices with liquid-crystal working medium used in agricultural machinery are based on the processes of orientation relaxation. The response time of devices with a liquid-crystal working medium depends on the viscoelastic properties of the nematic phase, which are a function of pressure and temperature [1,2]. One of the most effective ways to determine the viscosity and elastic modulus of the nematic liquid crystals (NLC) is an acoustic method that allows us to measure the velocity and absorption of ultrasound associated with the dissipative coefficients and elastic properties of the medium [3,4].

In the vicinity the temperature of phase transition, the sensitivity of acoustic parameters to the thermodynamic parameters of the state, as well as the value of the strength of the orienting electric or magnetic field, increases. The increasing value of the absorption coefficient of ultrasound in the vicinity of phase transitions and the dependence of $\Delta \alpha / f^2$ ($\Delta \alpha$ – is the anisotropy of the attenuation coefficient of ultrasound, $f$ – is the ultrasound frequency) indicates the existence of relaxation mechanisms responsible for the propagation of ultrasound. The problem of propagation of ultrasound in the nematic phase is solved within the framework of generalized hydrodynamics, including frequency dependence of parameters of NLC [5,6]. Thus, in this paper, the dependence of the absorption coefficient of ultrasound in the nematic phase in the vicinity of the phase transition of the NLC – isotropic liquid (IL) and the phase transition of the NLC – smectic "A" liquid crystal (SLC"A") on pressure and temperature is studied.
2. Materials and methods
The most studied substances are MBBA (N-p-methoxybenzylidene-p-butylaniline), EBBA (N-p-ethoxybenzylidene-p-butylaniline), BBBA (N-p-buthoxybenzylidene-p-butylaniline), which allows using reference data for calculations, as well as having a wide temperature range of the nematic phase of the mixture of two nematic components LC-440 and a mixture of four components of nematic N-96 [7,8] and eutectic mixture of MBBA and EBBA LC-404. In the studied pressure range (10^5 – 6·10^7 Pa) the temperature $T_C$ of the NLC – IL phase transition increases linearly with increasing of pressure [6]:

$$T_C(P) = T_C^0 + k_C \cdot P.$$  

The values of the coefficients of proportionality $k_C$ and the temperature of the phase transition of the NLC – IL at atmospheric pressure $T_C^0$ of the studied substances are presented in table 1 [3,6].

| NLC      | MBBA   | EBBA   | BBBA   | LC-440 | LC-404 | N-96  |
|----------|--------|--------|--------|--------|--------|-------|
| $T_C^0$  | 315.4  | 325.5  | 344.9  | 345.7  | 325.2  | 348.0 |
| $k_C \cdot 10^7$ K·Pa | 2.90   | 3.10   | 3.10   | 3.28   | 2.47   | 2.75  |

The studies were performed at an ultrasound frequency of 3.0 MHz. The sample was oriented not by an electric field, but by a magnetic field, in order to exclude the influence of ion movement on the orientation structure of the sample, which occurs in an electric field. The induction of the orienting magnetic field (B≈0.29 T) significantly exceeds the saturation value (=0.1 T), which ensures a uniform orientation of the NLC. The pressure was controlled with an absolute error not exceeding ±0.5 MPa. The relative error of measuring the ratio $\Delta/\alpha$ does not exceed 2% [3,6].

3. The results and discussion
Under the assumption of the existence of two relaxation processes: normal, associated with conformational transitions of end chains, and critical, due to the nature of this phase transition, an expression of the anisotropy of the ultrasound attenuation coefficient is obtained [9,10]:

$$\frac{\Delta\alpha}{f^2} = \left(\frac{\Delta\alpha}{f^2}\right)_n + \left(\frac{\Delta\alpha}{f^2}\right)_k + \left(\frac{\Delta\alpha}{f^2}\right)_0,$$

where the normal $(\Delta\alpha/f^2)_n$, critical $(\Delta\alpha/f^2)_k$ and classic $(\Delta\alpha/f^2)_0$ components are determined by the ratios:

$$\left(\frac{\Delta\alpha}{f^2}\right)_n = \frac{\Delta c_n \cdot \tau_n}{1 + \omega^2 \cdot \tau_n^2},$$

$$\left(\frac{\Delta\alpha}{f^2}\right)_k = \frac{\Delta c_k \cdot \tau_k}{1 + \omega^2 \cdot \tau_k^2},$$

$$\left(\frac{\Delta\alpha}{f^2}\right)_0 = \frac{4 \cdot \pi \cdot \nu_1}{\rho \cdot c^3}.$$

Here:

$$\tau_n = \tau_{on} \cdot \exp \frac{E}{R \cdot T}.$$


\( \tau_n \) and \( \tau_k \) – relaxation time of normal and critical processes, respectively, \( \tau_{on}=3.52 \times 10^{-13} \text{ s} \) for H-96 at \( P=10^5 \) Pa; \( E \) – activation energy, the value of which for H-96 is 21 J/(mole·K); \( \Delta c_0 = \Delta \alpha \cdot S^2 \) – coefficient assumed to be independent on temperature, which is confirmed experimentally for MBBA [11,12]; \( S \) – order parameter, \( T \) – absolute temperature of the experiment, \( R \) – universal gas constant.

The value of the classical contribution is determined from high-frequency measurements of the anisotropy of the ultrasound attenuation coefficient (table 2).

### Table 2. Values of the classical anisotropy component of the ultrasound attenuation coefficient \( \Delta \alpha / f^2 \) in N-96.

| \( \Delta T_C = T_C - T \) | 0 | 2.0 | 5.0 | 10.0 | 15.0 | 25.0 |
|---------------------------|---|-----|-----|------|------|------|
| \( \left( \frac{\Delta \alpha}{f^2} \right)_0 \cdot 10^{14}, m^{-1} \cdot s^2 \) | 0 | 1.5 | 2.0 | 3.1 | 3.4 | 3.9 |

Comparison of the values of the classical component \( (\Delta \alpha / f^2)_0 \) for H-96 (table 2) with the value of the anisotropy of the ultrasound absorption coefficient at a frequency of 3.0 MHz (table 3) shows that the classical component is no more than 4% of the value of \( \Delta \alpha / f^2 \).

### Table 3. Values of \( \Delta \alpha / f^2 \cdot 10^{12}, m^{-1} \cdot s^2 \) in N-96.

| \( T, K \) | 299.9 | 302.7 | 305.9 | 308.8 | 311.5 | 322.5 | 327.7 | 337.2 | 341.5 |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| \( P, MPa \) | | | | | | | | | |
| 0.1 | 2.66 | 2.38 | 2.23 | 2.10 | 2.00 | 1.66 | 1.69 | 1.77 | 1.97 |
| 20 | 3.04 | 3.83 | 2.58 | 2.39 | 2.20 | 1.83 | 1.72 | 1.66 | 1.76 |
| 40 | - | - | 2.88 | 3.73 | 2.62 | 2.02 | 1.86 | 1.64 | 1.67 |

This conclusion is also true for other studied liquid crystals and their mixtures (table 4).

### Table 4. Values of the ratio \( (\Delta \alpha / f^2)_0 / (\Delta \alpha / f^2) \cdot 100\% \) in the studied NLC.

| NLC | MBBA | LC-404 | EBBA | LC-440 |
|-----|------|--------|------|--------|
| \( (\Delta \alpha / f^2)_0 \cdot 100\% \) | 1.1 | 1.4 | 3.8 | 3.2 |

In the vicinity of the NLC – IL phase transition, fluctuations of the order parameter can contribute to the critical term of equation (2). Due to the increase in the relaxation time of a critical process with increasing pressure or with decreasing temperature of the phase transition NLC – IL, the value of \( \tau_k \) more than an order of magnitude the time \( \tau_n \). Therefore, it is the critical contribution that determines the value of the maximum anisotropy of the ultrasound absorption coefficient.

With the help of the ratio of hydrodynamics in a nematic phase [10,11]:

\[
\left( \frac{\Delta \alpha}{f^2} \right)_k = \left( \frac{\Delta c}{c^4 \cdot f^2} \right)_k / c \cdot \tau_k
\]

using the ratio of nematic phase hydrodynamics [10,11], the temperature dependence of the critical contribution to the anisotropy of the ultrasound attenuation coefficient was determined:

\[
\left( \frac{\Delta \alpha}{f^2} \right)_k = \left( \frac{\Delta \alpha}{f^2} \right)_{0k} \cdot \left( \frac{\Delta T_C}{T_C} \right)^\gamma
\]

where the values of \( (\Delta \alpha / f^2)_{0k} \) and \( \gamma \) are functions of pressure (table 5).
Table 5. Values of the parameters of equation (8) for LC–440 in the vicinity of the phase transition NLC – IL point.

| $P$, MPa | 0.1 | 10  | 20  | 30  | 40  | 50  | 60  |
|---------|-----|-----|-----|-----|-----|-----|-----|
| $\left( \frac{\Delta \alpha}{f^2} \right)_{0k}$ $\cdot 10^{12}$, m$^{-1}$ s$^{-2}$ | 0.022 | 0.021 | 0.017 | 0.014 | 0.011 | 0.010 | 0.009 |
| $\gamma$ | 0.90 | 0.94 | 0.96 | 0.99 | 1.03 | 1.08 | 1.12 |

The temperature dependence of the normal anisotropy component of the ultrasound attenuation coefficient is described by the exponential law:

$$\left( \frac{\Delta \alpha}{f^2} \right)_{n} = \left( \frac{\Delta \alpha}{f^2} \right)_{0n} \cdot \exp \left( \frac{E}{R \cdot T} \right)$$  \hspace{1cm} (9)

Here the activation energy $E$ and the multiplier $\left( \frac{\Delta \alpha}{f^2} \right)_{0n}$ depend on the pressure (table 6).

Table 6. The values of activation energy $E$ and the factor $\left( \frac{\Delta \alpha}{f^2} \right)_{0n}$ in LC – 440.

| $P$, MPa | 0.1 | 10 | 20 | 30 | 40 | 50 | 60 |
|---------|-----|----|----|----|----|----|----|
| $\left( \frac{\Delta \alpha}{f^2} \right)_{0n}$ $\cdot 10^{12}$, m$^{-1}$ s$^{-2}$ | 0.078 | 0.042 | 0.034 | 0.014 | 0.009 | 0.005 | 0.003 |
| $E$, kJ/mol | 5.56 | 7.84 | 7.89 | 10.2 | 11.4 | 13.4 | 14.8 |

Dependence of the attenuation coefficient on the frequency of ultrasound, as well as the presence of a maximum value of $\Delta \alpha/f^2$ at $f=3.0$ MHz, in the vicinity of the phase transition of the NLC – smectic "A" liquid crystal (SLC"A") indicates the presence of relaxation processes responsible for the propagation of ultrasound with characteristic times that significantly depend on temperature (Fig.1) [12].
Figure 1. Temperature dependence of $\Delta \alpha / f^2$ in BBBA at $f=3.0$ MHz (lines 1, 2, 3) at a pressure of 1 – 0.1 MPa, 2 – 10 MPa, 3 – 30 MPa, 4 – at $f=15$ MHz and a pressure of 0.1 MPa.

At temperatures close to the temperature of the $T_{NA}$ phase transition NLC – SLC"A", fluctuations of the smectic order parameter $\psi$ [10,13] can contribute to a critical component due to the increase of relaxation time $\tau_\psi$ smectic order parameter and the classical component of the anisotropy of the coefficient of ultrasound attenuation as a result of the divergence of the viscosity $\nu_1$. The temperature dependence of time $\tau_\psi$ is described by the expression:

$$\tau_\psi(T) = \tau_0 \cdot \left(\frac{\Delta T_{NA}}{T}\right)^\beta,$$

(10)

where $\Delta T_{NA} = T - T_{NA}$, $\tau_0$ – temperature-independent parameter, $\beta=1$. Assuming $\tau_k = \tau_\psi$, in the case of $\omega \cdot \tau_k \ll 1$, the critical contribution can be expressed by the equation:

$$\left(\frac{\Delta \alpha}{f^2}\right)_k = \Delta \nu_k \cdot \tau_0 \cdot \left(\frac{\Delta T_{NA}}{T}\right)^\beta.$$

(11)

The classical contribution to the anisotropy of the attenuation coefficient can be expressed by the equation:

$$\left(\frac{\Delta \alpha}{f^2}\right)_0 = \frac{4 \cdot \pi^2 \cdot \nu_1^0}{\rho \cdot c^3} + \frac{4 \cdot \pi^2 \cdot \bar{\nu}_1}{\rho \cdot c^3},$$

(12)

where $\bar{\nu}_1 \sim (\Delta T_{NA}/T)^Y$ is the fluctuation contribution to the viscosity coefficient, $\nu_1^0$ is the value of the viscosity coefficient $\nu_1$ without taking into account fluctuations, $\gamma= -1/3$ according to the similarity theory [10,13] and $\gamma= -1/2$ according to the mean field theory [11,14]. At $1 \text{K} < \Delta T_{NA} < 5 \text{K}$, the value $(\Delta \alpha / f^2)_n$ can be considered independent of temperature due to a weak dependence on the temperature of the parameter of the order $S$ [1,11] and the time $\tau_n$ [6,11].

4. Conclusion

Approximation of the experimental results presented in Fig. 1 using the least squares method shows that in the temperature range $1 \text{K} < \Delta T_{NA} < 5 \text{K}$, the value $\Delta \alpha / f^2$ is described by the first two terms of equation (2). The value of the exponent $\beta$ does not depend on pressure and within the experimental error corresponds to the theoretical value $\beta=1$. An increase in the term $(\Delta \alpha / f^2)_n$ with increasing pressure may be associated with an increase in the normal contribution in equation (2) due to a change in the parameter of the $S$ order. Similar studies performed at atmospheric pressure in the BBBA confirm the existence of two contributions to the anisotropy of the ultrasound attenuation coefficient corresponding to the second and third terms of equation (2). And the contribution due to the divergence of the viscosity coefficient in the vicinity of the phase transition temperature of the NLC-SLC"A" dominates in the temperature range $\Delta T_{NA} < 0.7 \text{K}$.

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