Acoustic researches of liquid crystals and prospects of their application in electronic devices of automobile transport

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Abstract. A method for measuring the acoustic parameters of liquid crystals and its anisotropy, parameters characterizing the dynamics of orientation processes in the nematic phase, as well as anisotropic dissipative coefficients and elastic constants with a change in pressure, temperature, and specific volume has been proposed. The dependence of the ultrasound velocity on the temperature, pressure, and parameters of the orienting magnetic field is investigated by a fixed-distance pulse method. In the framework of the hydrodynamics of the nematic phase, the dependence of the ultrasound velocity on the director orientation angle relative to the wave vector is analyzed. A nematic phase elastic modulus and anisotropy of elasticity are calculated. The relaxation character of the dependence of the nematic phase elastic modulus on the physical state thermodynamic parameters is analyzed.

I. Introduction

Improvement of electric equipment of motor transport, the introduction of new electronic technical devices that allow optimizing the operation of on-board devices leads to an increase in the load on the power supply system. This raises the need to develop fundamentally new, less energy-intensive consumers of electrical energy. New possibilities are opened by the use of liquid crystal based information display devices and electronic systems. The principle of operation of liquid crystal devices is based on electric field effects, that is, the control of such devices is carried out by an electric field and is not accompanied by the electric current flow. In such devices, only leakage currents are possible which tend to zero, providing a significant reduction in power consumption. To develop the liquid crystal based devices, information is required on the switching voltage, the duration of the reorientation process under the action of the orienting electric field and other parameters. The high speed operation of the devices, in which nematic liquid crystals (NLC) are used as the working medium, is determined by the time of orientation relaxation, which depends on the elastic and viscous properties of the medium [1]. An effective method for studying the material viscoelastic properties is ultrasonic spectroscopy [2], which makes it possible to obtain extensive and reliable information on the liquid crystals elastic moduli and the viscosity coefficients [3].

2. Materials and methods

The known methods for determining the ultrasound velocity are based on measuring time \( \tau_0 \) of the signal transmittance from the radiating piezoelectric element to the receiving piezoelectric cell [4,5] \( c = \ell / \tau_0 \), where \( \ell \) is the distance between the piezoquartz. The increase in the accuracy of ultrasonic veloc-
ty determination is mainly ensured by a more correct measurement of time τ₀, but the main sources of the errors associated with the need to determine the beginning of the signal weakened due to the absorption of ultrasound in the NLC, as well as due to acoustic and electric noise and a narrow frequency band pass are not eliminated. The methods for determining the ultrasonic velocity from signal decay are more accurate, but random changes in the phase of the decay of the signal lead to an uncertainty in determination of the delay time. To determine the time delay of the signal in the acoustic path of the measuring chamber in a static magnetic field, the authors used the method of pulse self-generation with a repetition frequency \( f = \ell / (\tau₀ + \tau_k) \), where \( \tau_k \) is the delay time of the signal in the electronic part of the measuring device. Thus, the ultrasound velocity is determined using the relation [4,5]:

\[
c = \frac{\ell \cdot f_a}{1 - \tau_k \cdot f_a}
\]

(1)

The measurements were performed in the pressure range \( 10^5 \div 6 \cdot 10^7 \) Pa in the temperature range of the nematic phase existence at the ultrasonic frequency of 2.67 MHz. The relative error in determining the ultrasonic velocity of this frequency is 0.01%. The relative error in determining the velocity anisotropy does not exceed 2%.

The paper presents the results of a study of a liquid crystal LC-440, which is a mixture of two components of p-n-butyl-p-methoxyazoxybenzene (BMOAB) and n-butyl-p-heptanoyloxyazoxybenzene (BHOAB) (2: 1) and a mixture of H-96, which are characterized by a wide temperature interval of the nematic phase. At atmospheric pressure of LC-440, the temperature of the transition from the nematic to the solid phase is \( T_{0f} = 265.7 \) K; the temperature of the phase transition of the NLC tends to isotropic liquid (IL) \( T_{oc} = 345.7 \) K in the LC-440 and \( T_{oc} = 348.0 \) K in H-96. For the investigated substances, an increase in pressure is accompanied by an increase in the temperature of the phase transition:

\[
T_c(P) = T_{oc} + k_c \cdot P,
\]

(2)

where \( k_c \) is the proportionality coefficient equal to 3.28·10⁻⁷ K·Pa⁻¹ for LC-440 and 2.75·10⁻⁷ K·Pa⁻¹ for H-96.

3. The results and discussion

The ultrasound speed and its dependence on the physical state thermodynamic parameters are related to the structure of the liquid and to the specificity of the intermolecular interaction. Therefore, the results of measuring the ultrasound velocity under varying physical conditions can be used to study the molecular structure of matter. The nonlinear character of the ultrasonic waves propagation in a combination with the anisotropy of the elastic constants of anisotropic liquids cause a number of phenomena in LC, the interpretation of which at the microscopic level requires the study of the influence of thermodynamic parameters and external fields on the ultrasound propagation speed.

In the used frequency range, the ultrasonic velocity decreases in investigated substances with increasing temperature with temperature coefficient \( \partial \varepsilon / \partial T \), varying in the range of 4-10 m s⁻¹ K⁻¹ over the entire temperature range of the nematic phase existence, with the exception of the NLC→IL phase transition region, where coefficient \( \partial \varepsilon / \partial T \) increases to 80 m s⁻¹ K⁻¹. The increase in pressure is accompanied by a shift of isobars \( c(T) \) to higher temperatures. The conclusions of model theories of ultrasound velocity in a liquid [6] are consistent with the results obtained. The assumption that each liquid molecule can move within some "free volume" \( (\nu_f) \), within which the potential has the same value sharply increasing at its boundaries, allows one to obtain the expression [7], which can be used to calculate free volume:

\[
\nu_{free} = \frac{\nu_f}{(2 - \nu_f)} \cdot \sqrt{\frac{R \cdot T}{\mu} \cdot \frac{\gamma}{\gamma_f}}
\]

Here \( \nu = V / N \) is the volume occupied by the molecule in the liquid, \( V \) is the specific volume, \( N \) is the number of molecules per unit volume, \( \mu \) is the molar mass, and \( \gamma \) is the ratio of the specific heats in the gas phase. Values of ratio \( \nu_f / \nu \), calculated on the basis of the theory of free volume from the results
of measurements of the ultrasonic velocity with a 2.67 MHz frequency ($\omega \cdot \tau < 1$) and 560 MHz frequency ($\omega \cdot \tau > 1$) [5] coincide within the experimental error (Table 1).

**Table 1.** Dependence of relation $u_\nu/\nu \cdot 10^3$ on the temperature at pressure $10^5$ Pa in LC-440

| $f$, MHz | 2.67 | 315 | 320 | 325 | 330 | 335 | 340 |
|----------|------|-----|-----|-----|-----|-----|-----|
| 2.67     | 0.78 | 0.83 | 0.89 | 0.96 | 1.03 | 1.13 |       |
| 560      | 0.77 | 0.82 | 0.87 | 0.93 | 1.00 | 1.06 |       |

The frequency dependence of the ultrasound velocity (Figure 1) is characterized by dispersion coefficient $\varepsilon = 1 - \left(\frac{c_{2.9}}{c_{560}}\right)^2$, whose value increases as the phase transition NLC - IL temperature approaches.

![Figure 1](image)

**Figure 1.** Dependence of ultrasound velocity in non-oriented H-96 sample on $\Delta T_C$ at ultrasound frequency: 1 - 2.9 MHz; 2-560 MHz.

The classical thermodynamic theories of the nematic phase lead to the conclusion that the ultrasonic velocity propagates isotropically. However, the presence of anisotropy of the ultrasound velocity in the nematic phase has been established experimentally. The velocity of an ultrasonic wave propagating at angle $\theta$ to a magnetic field induction vector strong enough to suppress oscillations of the director in an ultrasonic wave is described by the expression [8]:

$$c(\theta) = \sqrt{k_S} \left(1 + \frac{3 \omega^2 \cdot g^2}{8 \cdot \rho^2 \cdot g_S^2}\right),$$

where $g = (\mu_s + \alpha_s) + (\mu_i + \mu_s + \alpha_s + \alpha_i) \cdot \cos^2 \theta + \alpha_s \cdot \cos^4 \theta$, $\mu$, $\alpha$ - dissipative coefficients of the stress tensor of the Leslie hydrodynamic theory of NLC [9,10], $\omega = 2\pi f$, is the ultrasound frequency, $k_S$ is the ratio of the adiabatic bulk modulus to the density of the NLC.

It has been experimentally established that in the entire temperature range of a nematic phase existence, the inclusion of a magnetic field directed along the wave vector leads to an increase in the ultrasound velocity. The magnetic field, normal to the wave vector, causes a decrease in the ultrasound velocity. Thus, in nematic liquid crystals, velocity anisotropy $\Delta c = c^\perp - c^\parallel$ is positive. The angular dependence of the anisotropy of the ultrasound velocity can be described by the relation:

$$c(\theta) - c^\parallel = c_N \cdot \cos^2 \theta + d_N \cdot \cos^4 \theta$$

where $c_N$ and $d_N$ are coefficients that are functions of the ultrasound frequency, as well as temperature and pressure. Analysis of the ultrasound propagation, carried out within the framework of microscopic theories, [9] leads to the conclusion that the contributions of critical and regular processes in the nematic phase to parameter $d_N$ can be neglected in the low-frequency limit. The coincidence of values $c(\theta)$, calculated according to equation:
\[ c(\theta) - c^* = \Delta c \cdot \cos^2 \theta \]  

(5)

with the results obtained experimentally, confirms the quadratic dependence of the ultrasound velocity on the director orientation angle relative to the wave vector. The increase in pressure leads to a decrease in the anisotropy of the ultrasound velocity. The dependence of \( \Delta c \) on the pressure at temperatures much lower than bleaching temperature \( (\Delta T_c > 10 \text{K}) \) can be described by a linear law:

\[ \Delta c(P) = \Delta c_0 \cdot (1 - k_{\Delta c} \cdot P), \]  

(6)

where \( \Delta c_0 \) is the anisotropy of the ultrasound velocity at atmospheric pressure, coefficient \( k_{\Delta c} \) depends on the type of LC and on the temperature.

In the nematic phase, as the temperature rises as the temperature of the bleaching increases, a sharp increase in the anisotropy of the ultrasound velocity is observed (Figure 2).

**Figure 2** - Dependence of \( \Delta c(T) \) in LC-440 on \( \Delta T_c \) at \( f = 2.67 \text{ MHz} \) and pressure (MPa): 1 - 0.1; 2 - 10; 3 - 20; 4 - 30; 5 - 40; 6 to 50; 7 - 60.

Isobars \( \Delta c/c^* \), represented as a function of \( \Delta T_c = T_c - T \), coincide within the experimental errors.

For the isochors, the anisotropy of ultrasound velocity \( \Delta c \) is characterized by no dependence on temperature and pressure, with the exception of the NLC - IL phase transition region, where a sharp increase in this parameter is observed.

The NLC ultrasound velocity anisotropy is due to the anisotropy of the elasticity of the nematic phase. The free energy density associated with deformation of the orientation of the NLC director can be described by the expression [8]:

\[ F = 0.5 \left[ K_{ii} \cdot (\nabla \cdot \vec{n})^2 + K_{ij} \cdot (\vec{n} \cdot \nabla \times \vec{n})^2 + K_{jj} \cdot (\vec{n} \cdot \nabla \vec{n})^2 \right], \]  

(7)

where \( K_{ii} \) - elasticity constants for a certain type of deformation, proportional to the second power of order parameter \( S \), and inversely proportional to the molar volume to the power of 7/3.

\[ K_{ii} = D_{ii} V_m^{-7/3} S^2. \]  

(8)

Here the coefficient

\[ D_{ii} = \frac{3A}{2} \beta_{ii}^m N_A \]  

(9)

does not depend on temperature, \( A = 1.3 \cdot 10^{-29} \text{ J} \cdot \text{m}^6 \) is a constant in the Mayer-Saupe theory [11], \( \beta_{ii} = \beta_{22} = y/x; \beta_{33} = (y/x)^2 \), \( y \) and \( x \) are the average molecular distances in the direction, respectively parallel and perpendicular to the NLC director, \( m \) is the number of molecules in the cluster. Thus, the determination of the elastic constants for varying \( P, T \)-thermodynamic parameters of the state can give
information on the effect of pressure and temperature on the nature of the intermolecular interaction responsible for the orientation order in the nematic phase. The measurements of the sample density and the angular dependence of the propagation velocity of ultrasound with varying pressure and temperature were first carried out experimentally with the help of the developed original apparatus [4, 5]. They were used to calculate the elastic moduli when the physical state thermodynamic parameters were varied by means of relations connecting elastic modulus $C_{11}$ and $C_{33}$ with density $\rho$ of matter and ultrasound velocity:

$$ C_{ii} = \rho \cdot \left( e^i \right)^2; \quad C_{33} = \rho \cdot \left( e^3 \right)^2. \quad (10) $$

The elastic modulus temperature dependence is described by a quadratic law:

$$ C_{ii}(T) = C_{ii}(T_0) - k_{C_{ii}} T \cdot \Delta T, \quad (11) $$

where $C_{ii}(T_0)$ are the elastic modulus at temperature $T_0$, $k_{C_{ii}}$ and $k_{CC_{ii}}$ are the proportionality coefficients that depend on the pressure.

The increase in pressure is accompanied by an increase in the elastic modulus:

$$ C_{11}(P) = C_{11}^0 (1 + k_{P11} P), \quad (12) $$

$$ C_{33}(P) = C_{33}^0 (1 + k_{P33} P), \quad (13) $$

where $C_{11}^0$ and $C_{33}^0$ are the moduli of elasticity at atmospheric pressure, $k_{P11}$, $k_{PP33}$, $k_{PP33}$ are the coefficients depending on the temperature and the aggregate state of the substance.

The dependence of the elastic modulus on temperature and pressure is due to the effect of the thermodynamic parameters of the state on the molar volume and the order parameter, with the temperature dependence of order parameter $S(T)$ seem to be the main contribution to the temperature dependence of the elastic modulus. The $C_{11}/S$ and $C_{33}/S$ ratio increase with temperature by 20% with an increase in temperature by 50 K at atmospheric pressure in the nematic phase of LC-440 and is practically independent of temperature at high pressures (at $P = 6 \cdot 10^7$ Pa at the same temperature interval, $C_{11}/S$ and $C_{33}/S$ increase by 2%).

The anisotropy of the modulus of elasticity ($C_{33} - C_{11}$) at 20 K $> \Delta T_C > 10$ K does not change with temperature. At $\Delta T_C > 20$ K, the anisotropy of the elastic modulus increases with pressure and decreases at $\Delta T_C < 5$ K.

$$ C_{33}(P) - C_{11}(P) = (C_{33} - C_{11})_0 [1 + k_{33} P], \quad (14) $$

where $(C_{33} - C_{11})_0$ is the anisotropy of the elastic modulus at atmospheric pressure, $k_{33}$ is the proportionality coefficient, which depends on NLC and temperature. The existence of temperature $T_1$ at which coefficient $k_3$ of equation (14) changes sign indicates the relaxation nature of the anisotropy of elasticity.

Thus, the elastic moduli of NLC, characterizing the parameters of liquid crystal devices, are determined by an acoustic method. The nature of their dependence on pressure and temperature is established.

4. Conclusion

Within the framework of the free volume theory, the dependence of the ultrasound velocity and its anisotropy on the state thermodynamic parameters is interpreted. The frequency dependence of the ultrasound velocity is shown in the nematic phase. The dependence of the elastic moduli on the state thermodynamic parameters is due to the effect of pressure and temperature on the order parameter. The quadratic dependence of the NLC elastic moduli on temperature is established. The increase in pressure is accompanied by an increase in the elastic moduli of the nematic phase. The relaxation character of the anisotropy of the elasticity of the NLC is shown. Numerical values of the elastic moduli can be used to calculate the coefficients characterizing the parameters of liquid crystal based electronic devices.

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