Dynamic of orientation processes in liquid crystal systems of technical devices

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Abstract. The relaxation properties of nematic liquid crystals by the pulsed method of a fixed distance in a rotating magnetic field are investigated. The adequacy of the solution of the equation of motion of the nematic director in the conditions of asynchronous motion of the director and the magnetic field induction vector was experimentally confirmed. The values of the rotational viscosity coefficient and the orientation relaxation time that characterize the parameters of devices with a liquid-crystal working medium in a wide range of pressures and temperatures are calculated. In the framework of the free volume theory, the dependence of the rotational viscosity coefficient on temperature and pressure is analyzed.

I. Introduction
The widespread use of liquid crystals (LC) as a working medium in information display devices, optical modulators, information storage systems and various types of sensors in agricultural machinery leads to increased interest in experimental and theoretical studies of the properties of liquid crystals exposed to rapidly changing external magnetic and electric fields [1]. The high mobility of nematic phase molecules alongside with the anisotropy of their properties provide an high sensitivity of nematic liquid crystals (NLC) to the action of orienting fields. In this regard, it is relevant to study the influence of macroscopic relaxation processes, which can be caused by the rotation of individual molecules or molecular complexes, on the integral dynamic behavior of the NLC in periodically changing magnetic fields [2]. The existence of adequate solutions of the equation of motion of the director in rotating magnetic fields obtained within the framework of NLC hydrodynamics determines the effectiveness of experimental study of the influence of the rotational magnetic field on the dynamics of orientation processes in the nematic phase, which allows obtaining the parameters necessary for calculating technical devices with a liquid-crystal working medium [3,4]. Acoustic spectroscopy is an effective method for studying the kinetics of orientation processes in the mesophase, since alongside with the possibility of studying large volumes of matter in the absence of the influence of boundary effects on the measurement results, acoustic studies allow us to calculate dissipative coefficients and elastic constants, which are functions of P, T – thermodynamic state parameters. In the interval of low temperatures of nematic phase in a rotational
magnetic field, the asynchronous movement of the magnetic field and the director of the NLC is realized, so this work is devoted to the study of the relaxation properties of the nematic phase under the influence of fast rotating magnetic fields at varying pressure and temperature [5,6].

2. Materials and methods

Investigation have been made by the pulsed method of a fixed distance at an ultrasound frequency of \( f = 2.9 \) MHz in a rotating magnetic field, the induction of which (\( B = 0.15 \div 0.29 \) T) exceed critical value, that provides homogeneous orientation of the sample. Range of angular velocity of rotation of the magnetic field (\( \omega_H = 0.01 \div 1.85 \) radn/s) gives the possibility to realize synchronous (with the magnetic field) regime of NLC director movement as well as asynchronous one [7,8]. The relative error in measuring the anisotropy of the ultrasound absorption coefficient \( \Delta\alpha = \alpha^\parallel - \alpha^\perp \) and \( \alpha^\parallel \) and \( \alpha^\perp \) – the absorption coefficient, respectively, for parallel and perpendicular orientation of the director to the wave vector) does not exceed 2% [7,8]. The absolute pressure measurement error is 0.05 MPa. The relative error in determining the rotational viscosity coefficient (\( \gamma_1 \)) and the orientation relaxation time (\( \tau_0 \)) is equal to 3%. Taking into account the problems solved in this work, we have studied compounds which are in the nematic phase in a wide range of temperatures close to room temperature: MBBA (N-p-methoxybenzylidene-p-butylaniline), BBBA (N-p-buthoxybenzylidene-p-butylaniline) as well as a mixture of two nematic components LC-440 and a mixture of four components of nematic N-96 [3,9]. The temperature \( T_C \) of the NLC–isotropic liquid phase transition at atmospheric pressure is equal to 315.4 K in MBBA, 344.9 K in BBBA, 345.7 K in LC-440, and 348.0 K in N-96.

3. The results and discussion

Assuming that there are no macroscopic flows, and neglecting the influence of the chamber surfaces on the orientation in the volume of the NLC, since the linear dimensions of the sample significantly exceed the magnetic coherence length, equation of the motion of the director in a rotational magnetic field (\( B_x = B \cdot \cos(\omega_H t), B_y = B \cdot \sin(\omega_H t), B_z = 0 \)) can be converted to a differential equation of the form \( h' + gh = q \), which has four solutions [7,10]. Here \( h = t g(\omega_H t - \psi) \), \( g = -\omega_H \), \( q = \omega_H \left[ 1 - \frac{1}{4} \cdot (\Delta\chi \cdot H^2 / \gamma_1 \omega_H^2) \right] \), where \( \Delta\chi = \chi^\parallel - \chi^\perp \) – is the anisotropy of the magnetic susceptibility, \( \chi^\parallel \) and \( \chi^\perp \) – are the magnetic susceptibility, respectively, in the direction of the director and perpendicular to the director, \( \psi \) – is the initial phase. For \( p \cdot q < 0 \), which is equivalent to the requirement \( \omega_H > \omega_0 \) [7], where \( \omega_0 \) is the angular velocity of rotation of the magnetic field, at which there is a change in the mode of movement of the director, the change in the phase angle between the magnetic induction vector and the director over time is complex and is determined by the ratio [1]

\[
tg(\omega_H t - \psi) = \frac{t g[\omega_H \cdot \sqrt{1 - \varepsilon^2} \cdot t]}{\sqrt{1 - \varepsilon^2} + \varepsilon \cdot t g[\omega_H \cdot \sqrt{1 - \varepsilon^2} \cdot t]}. \tag{1}
\]

Using the expression of the dependence of the ultrasound attenuation coefficient on the angle between the director and the wave vector [3], an explicit form of the time dependence of the ultrasound attenuation coefficient has been obtained

\[
\frac{\Delta\alpha(\omega_H t)}{f^2} = a \cdot \sin^2(\omega_H t - \xi) + b \cdot \sin^4(\omega_H t - \xi), \tag{2}
\]

\[
\xi = \arctg \frac{t g[\omega_H \cdot \sqrt{1 - \varepsilon^2} \cdot t]}{\sqrt{1 - \varepsilon^2} + \varepsilon \cdot t g[\omega_H \cdot \sqrt{1 - \varepsilon^2} \cdot t]}. \tag{3}
\]

Comparison of graphs of the time dependence of the attenuation coefficient of ultrasound (Figure 1), constructed using the expression (2) and obtained experimentally, indicates their qualitative similarity (if to take into account the presence of a low-frequency component with the frequency \( \Omega \)) [7]. However,
the nature of attenuation the low-frequency component of the ultrasound attenuation coefficient does
not correspond to the conclusions of hydrodynamics about the stability of the parameter $\Delta \alpha/f^2$ in time.
The frequency $\Omega$ is a function of temperature, pressure, angular velocity, and magnetic field induction.
An increase of temperature is accompanied by a decrease of the period $T_\Omega=\pi/\Omega$ of the low-frequency
component of the phase characteristic of the ultrasound attenuation coefficient with the temperature.
Coefficient $dT_\Omega/dT$ decreases as the temperature increases. The decrease in the angular velocity of ro-
tation of the magnetic field is accompanied by an increase of the value of $\Omega$. The values of $\Omega_1$ and $\Omega_2$,
measured at the angular velocity of rotation of the magnetic field, respectively, $\omega_{H1}$ and $\omega_{H2}$, are related
to the values of $\omega_{H}$ by the ratio

$$\frac{\Omega_1}{\Omega_2} = \frac{\omega_{H2}}{\omega_{H1}}, \quad (4)$$

which is performed in the entire studied range of angular velocities $\omega_{H}$ and magnetic field inductions,
pressures and temperatures (Table 1,2).

![Figure 1](image_url)

**Figure 1.** The time dependence of $\Delta \alpha/f^2$ in MBBA at $f=2.9$ MHz, $\omega_{H}=1.53$ radn/s, $T=315.4$ K and a
pressure of $2\cdot10^5$ Pa: a) constructed theoretically, b) obtained experimentally.

| Table 1. Dependence of the ratio $\Omega_1/\Omega_2$ on temperature in a Lc N-96 in a magnetic field by induction
of 0.15 T at angular rotational velocity of $\omega_{H1}=0.21$ radn/s and $\omega_{H2}=0.47$ radn/s. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| T, K            | 299.9           | 302.7           | 305.9           | 314.4           | 316.7           | 322.5           |
| $\Omega_1/\Omega_2$ | 2.31            | 2.15            | 2.18            | 2.21            | 2.26            | 2.31            |

| Table 2. Dependence of the ratio $\Omega_1/\Omega_2$ on temperature in a Lc N-96 in a magnetic field by induction
of 0.15 T at angular rotational velocity of $\omega_{H1}=0.26$ radn/s and $\omega_{H2}=0.31$ radn/s. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| T, K            | 302.7           | 305.9           | 308.8           | 314.4           | 318.9           | 325.3           |
| $\Omega_1/\Omega_2$ | 1.20            | 1.18            | 1.18            | 1.18            | 1.20            | 1.21            |

According to equation (4), the product of $\omega_{H}\times\Omega$ does not depend on the angular velocity of rotation of
the magnetic field (Table 3,4). An increase of temperature or a decrease of pressure is accompanied by
an increase in the product of $\omega_{H}\times\Omega$.

Comparison of the values $(\omega_{H}\times\Omega_1)$ and $(\omega_{H}\times\Omega_2)$, calculated in a magnetic field by induction, respec-
tively $B_1=0.29$ T and $B_2=0.15$ T, shows that the ratio $(\omega_{H}\times\Omega_1)/(\omega_{H}\times\Omega_2)$ does not depend on the temperature
and the value of $\omega_{H}$, and for example, for N-96, it is equal to $23.8\pm0.8$.

The increase of pressure is accompanied by an exponential decrease of the frequency $\Omega$. 

\[ \Omega(P) = \Omega_0 \cdot \exp(-k_\Omega \cdot P), \]  

where \( \Omega_0 \) is the value of \( \Omega \) at atmospheric pressure, the parameter \( k_\Omega \) does not depend on the angular velocity of rotation of the magnetic field and temperature (except for the region of phase transitions) and is equal to 0.29x10\(^{-7}\) Pa\(^{-1}\) in MBBA and in BBBA, 0.36x10\(^{-7}\) Pa\(^{-1}\) in LC-440 and 0.33x10\(^{-7}\) Pa\(^{-1}\) in N-96. In the region of the phase transition of the NLC – smectic “A” liquid crystal, the pressure increase is accompanied by a sharp decrease of the frequency \( \Omega \).

**Table 3.** Dependence of the product \( \omega_H \cdot \Omega \cdot 10^2 \) (radn/s\(^2\)) on temperature and the angular velocity of rotation of magnetic field by induction of B=0.29 T in N-96 at a pressure P=10\(^5\) Pa.

| T, K   | \( \omega_H \), radn/s |
|--------|------------------------|
| 290.8  | 0.6                    |
| 302.7  | 2.5                    |
| 311.5  | -                      |
| 317.1  | -                      |

**Table 4.** Dependence of the product \( \omega_H \cdot \Omega \cdot 10^2 \) (radn/s\(^2\)) on temperature and the angular velocity of rotation of magnetic field by induction of B=0.29 T in N-96 at a pressure P=10\(^5\) Pa.

| P, MPa | T, K   | 301.0 | 315.0 | 329.5 | 340.5 |
|--------|--------|-------|-------|-------|-------|
| 10     | 0.24   | 0.26  | 0.28  | 0.29  |
| 30     | 0.20   | 0.25  | 0.26  | 0.27  |
| 60     | 0.18   | 0.23  | 0.24  | 0.25  |

The frequency spectrum of the time dependence (1) contains a frequency \( \omega_0^a = 2\pi/\tau_0^a \) and a low-frequency component of the frequency \( \omega_- \) [1,7]. In asynchronous mode the director oscillates near the current position with frequency \( \omega_H \) and simultaneously rotates in the direction of rotation of the field with an average angular velocity

\[ \omega_- = \omega_H - \sqrt{\omega_H^2 - \omega_0^a}, \]

Comparison of the values \( \omega_- \) calculated theoretically according to equation (6) and the frequencies \( \Omega \) obtained experimentally indicates that they coincide in order of magnitude (Table 5). This allows us to apply the expression (6) to define the parameter \( \omega_0^a \), received in asynchronous mode. By entering a notation \( \omega_H = n \cdot \omega_- \), the expression (6) can be converted to the form [7]

\[ \omega_0^a = \frac{\omega_H \cdot \sqrt{2n - 1}}{n}. \]

The values \( \omega_0^a \) calculated according to equation (7), within the experimental error, coincide with similar values determined experimentally. Thus, the frequency values \( \omega_0^a \) can be used to calculate the orientation relaxation time \( \tau_0^a = 2\pi/\omega_0^a \).

One of the features of asynchronous mode is the attenuating nature of the low-frequency component of the time dependence of the coefficient of ultrasound absorption, which may be associated with the occurrence of transient processes when the orientation of the NLC decreases in asynchronous mode. In a sample that is initially uniformly oriented and then placed in a magnetic field rotating at the angular velocity of \( \omega_H > \omega_0 \), the amplitude of the low-frequency component decreases exponentially.
\[ \frac{\Delta \alpha}{f^2} = \left( \frac{\Delta \alpha_0}{f_0^2} \right) \cdot \exp \left( -\frac{t}{\tau_\Omega} \right), \]  

where \( \Delta \alpha_0 \) is the anisotropy of the coefficient of the ultrasound attenuation in a static magnetic field, \( \tau_\Omega \) is the characteristic attenuation time of the low-frequency component. After the transition process is completed, the duration of the a non-uniform distribution of the director is established

\[ \tau_\Omega = \frac{c_H \cdot \omega_H}{\omega_0 \cdot \Omega}. \]  

Table 5. The dependence of the theoretically calculated (\( \omega_0 \)) and experimentally determined (\( \Omega \)) values of the frequency of the low-frequency component on temperature in an MBBA at atmospheric pressure

| \( \omega_0, \text{radn/s} \) | \( T, \text{K} \) | 297.4 | 302.2 | 302.2 | 308.2 | 312.2 |
|-------------------------------|----------------|--------|--------|--------|--------|--------|
| 1.137 \( \Omega, \text{radn/s} \) | 0.14 | 0.23 | 0.30 | - | - |
| 1.137 \( \omega, \text{radn/s} \) | 0.09 | 0.17 | 0.26 | - | - |
| 1.527 \( \Omega, \text{radn/s} \) | 0.10 | 0.16 | 0.22 | 0.27 | 0.44 |
| 1.527 \( \omega, \text{radn/s} \) | 0.07 | 0.13 | 0.18 | 0.26 | 0.40 |
| 1.850 \( \Omega, \text{radn/s} \) | 0.08 | 0.12 | 0.17 | 0.23 | 0.38 |
| 1.850 \( \omega, \text{radn/s} \) | 0.05 | 0.11 | 0.16 | 0.21 | 0.36 |

In the studied liquid crystals, the parameter \( \Omega \) does not depend on the angular velocity of rotation of the magnetic field and P, T – thermodynamic state parameters, but it depends on the substance and is equal to 1.6 for MBBA and 3.1 for BBBA. The absence of dependence of the production \( c_H \cdot \omega_H \) on the thermodynamic state parameters indicates that the influence of temperature and pressure on the attenuation character of the low-frequency component in asynchronous mode is due to the influence of these parameters on the orientation relaxation in the NLC. The values of \( \tau_0 \) has been calculated using the equation (9) are consistent with similar values obtained experimentally.

The characteristic attenuation time of the low-frequency component is a function of the pressure, temperature, induction, and angular velocity of rotation of the magnetic field [11]. The temperature dependence of the parameter \( \tau_\Omega \) is described by an exponential Arrhenius law. The pressure has a greater influence on the value \( \tau_\Omega \) than on the time \( \tau_0 \) of orientation relaxation

\[ \tau_\Omega(P) = \tau_\Omega^0 \cdot (1 + k_H \cdot P^{2.5}), \]  

where \( \tau_\Omega^0 \) and \( \tau_\Omega(P) \) are the values, respectively, at atmospheric pressure and pressure \( P \). The coefficient \( k_H \) increases with a decrease of temperature or an increase of the value of \( \omega_H \).

After completion of the attenuation process of the low-frequency component, the equation of the time dependence of the attenuation coefficient in asynchronous mode (1.5.2) is converted to the form

\[ \frac{\Delta \alpha(\omega_H t)}{f^2} = a + \frac{\omega_0}{\omega_+} \cdot \sin 2(\omega_H t - \phi_0) - \frac{b}{2} \cdot \frac{\omega_0}{\omega_+} \cdot \cos 4(\omega_H t - \phi_0), \]  

where \( \omega_+ = \omega_H + \omega_1 \), \( \omega_1 = \sqrt{\omega_H^2 + \omega_0^2} \). Comparison of the values of the anisotropy of the ultrasound attenuation coefficient after the completion of transients (\( \Delta \alpha/f^2 \)), calculated according to equation (11) and obtained experimentally confirms the agreement of the results of theoretical analysis with experimental data. Analysis of dependence of (\( \Delta \alpha/f^2 \)) on \( \omega_H \) showed that for the studied substances in the pressure range of \( 10^5 \text{...6} \times 10^7 \text{ Pa} \), the ratio is performed

\[ \frac{\Delta \alpha(\omega_H > \omega_0)}{\Delta \alpha(\omega_H < \omega_0)} = \left( \frac{\omega_0}{\omega_H} \right)^{x_1}. \]
Here the exponent of the degree $x_1$ does not depend on temperature and pressure and in the studied substances takes values equal to 1.0±0.2.

The value $\omega_0$ were used to determine the rotational viscosity coefficient $\gamma_1$ and the orientation relaxation time. The experimentally established dependence of the orientation relaxation time on the P, T – thermodynamic state parameters is described by the exponential law and is satisfactorily interpreted in the framework of the free volume theory [3]

$$\tau(P, T) = \tau_{1} \cdot \exp \left( \frac{E_p + V \cdot P}{R \cdot T_0} \right),$$

where $\tau_1$, $T_0 = T - k \cdot P$, $T$ – experiment temperature, $k = \partial T / \partial P$, $S$ – nematic order parameter, $E_p$ – activation energy at constant pressure, parameter $V = k \cdot E / T_0$ has the meaning of free volume, which, as shown by calculations [2,3] increases from $3.2 \cdot 10^{-5}$ m$^3$/(mol·Pa) at $\Delta T_g = T_g(P) - T=57,0$ K to $3.8 \cdot 10^{-5}$ m$^3$/(mol·Pa) $\Delta T_g=3,0$ K in N-96. The activation energy $E_p$ depends on the pressure (Table 6).

**Table 6.** The dependence of the activation energy ($E_P$) on the pressure in the 440LC-440.

| P, MPa | 0.1 | 10  | 20  | 30  | 40  | 50  | 60  |
|--------|-----|-----|-----|-----|-----|-----|-----|
| $E_P$ kJ/mol | 31.7 | 31.4 | 30.3 | 27.8 | 26.7 | 24.6 | 23.3 |

The $E_P$ value is the total activation energy required to overcome the potential barrier and form a free volume. Therefore, a decrease in $E_P$ with increasing pressure can be explained by the fact that with increasing pressure the temperature of the experiment for a fixed volume produced in the region of higher temperatures $T = T_g(P) - \Delta T_g$, where the activation energy at constant volume, the decrease in $E_P$ with increasing pressure, due to the fact that with increasing pressure the measurement of the orientation relaxation for a fixed volume produced at higher temperatures $T = T_g(P) - \Delta T_g$ decreases the activation energy $E_V$ at constant volume, associated with the $E_P$ by the ratio [3]

$$E_p = E_V + R \cdot T^2 \cdot \left( \frac{\partial P}{\partial T} \right)_V \cdot \alpha_T,$$

where $R$ is the universal gas constant, $\alpha_T$ is the tangent of the angle of inclination of the isotherm $\ln\tau(P)$, the values of $(\partial P / \partial T)_V$ has been determined graphically.

4. Conclusion

Acoustic spectroscopy of nematic liquid crystals in a fast rotational magnetic field is an effective method for studying the viscoelastic properties of NLC. In the low-temperature range of the nematic phase in a rotating magnetic field, the nematic director moves asynchronously relative to the field. Experimentally confirmed the adequacy of the solution of the equations of motion of the director obtained in the framework of hydrodynamics of NLC, which allowed to calculate the coefficient of rotational viscosity and orientation relaxation time, which characterizes the technical performance of devices with liquid-crystal working medium. The nature of the dependence of the orientation relaxation time of the NLC on the thermodynamic parameters of the state has been interpreted in framework of free volume theory.

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