Influence of pressure and temperature on the parameters of liquid-crystalline working fluids of technical devices

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Abstract. The promising use of liquid crystals for the development of technical devices is substantiated. The acoustic method is used to study the dependence of parameters of liquid crystals on the pressure and temperature, which characterize the operating speed of electronic devices with a liquid-crystalline working fluid. We studied the relaxation properties of mixtures of nematic liquid crystals LC-440 and N-96. Within the framework of the molecular statistical theories of the nematic phase, the dependence of the coefficient of rotational viscosity on temperature and pressure is analyzed. The influence of the structure of molecules and molecular complexes of nematic liquid crystals on the dependence of the coefficient of rotational viscosity on external conditions is established. The results of original studies of the dependence of the coefficient of rotational viscosity on pressure and temperature at a constant volume are presented.

I. Introduction

Liquid crystals are widely used in the manufacture of electro-optical arrays of information display devices [1]. The high mobility of molecules of nematic liquid crystals (NLC), which coincides in order of magnitude with the mobility of the molecules of associated liquids, combined with the anisotropy of the physical properties inherent in solids, leads to the appearance of specific properties of liquid crystals. This makes it possible to use liquid crystals as a working medium for information storage systems, optical modulators, smoothly adjustable delay lines, various measuring transducers and other technical devices. One of the significant advantages of liquid crystal devices is due to the fact that their action is based on field effects. This eliminates the loss of energy in the operation due to the Joule resistive loss. In the practical usage, the study of the time scale of the processes inherent for the mesophase defines a specific area of frequency-time characteristics, the study of which is necessary for designing liquid-crystalline devices. Anisometry of the molecular structure and the peculiarity of the interaction of molecules of liquid crystals lead to a high sensitivity of their structure and viscoelastic parameters to the temperature and pressure impacts. Experimental methods for studying the effect of pressure and temperature on the parameters of liquid crystals provide information mainly on the properties of thin NLC layers [2], the molecular structure and kinetic processes in which depend significantly on the boundary conditions. In this regard, it seems promising to use the acoustic method of research, since along with the possibility of studying the relaxation properties of large volumes of NLC, this method allows to obtain information on the molecular-kinetic parameters characterizing the orientation relaxation in the mesophase, which are a function of temperature and pressure [3,4].
2. Materials and methods

Ultrasound absorption coefficient ($\alpha$) was measured by the method of a fixed distance at a frequency of 3.0 MHz in a magnetic field rotating at an angular velocity in the range of 0.01–1.5 rad/s. The magnetic field induction varied in the range of 0.12–0.29 T, which exceeds the saturation value (0.1 T) and ensures a uniform orientation of the sample [5, 6]. The dual-circuit temperature stabilization system allows you to set and maintain the temperature with an accuracy of ±0.01 K. The pressure varied in the range $10^3$–6 $10^4$ Pa. The relative error in determining the parameter $\Delta \alpha/\alpha^2$ ($\Delta \alpha = \alpha^2 - \alpha^2$, where $\alpha^2$ and $\alpha^2$ are the absorption coefficients of ultrasound in a NLC in a magnetic field, respectively, parallel and perpendicular to the wave vector, and $f$ is ultrasound frequency) does not exceed 2%. The relative error in determining the rotational viscosity coefficient $\gamma_1$ and the orientation relaxation time $\tau$ is 2%.

The expansion of the temperature range of mixtures of nematic liquid crystals relative to the components of the mixture led to the choice of the mixture of LC-440 and a mixture of four components (HN-96) containing p-n-butyl-p-hexyloxyazobenzene (p-n-butyl-p-gexyloxyazobenzene), p-n-butyl-p-methoxyazobenzene (LC-434) (p-n-butyl-p-metoxyazobenzene), n-butyl p- (n-hexyloxphenoxycarbonyl) -phenylcarbonate (H-22), n-butyl p- (n-ethoxyphenoxycarbonyl) -phenyl carbonate (N-23). An increase in pressure is accompanied by an increase in the temperature of phase transitions NLC – isotropic liquid ($T_C$) and NLC - solid phase ($T_s$). In the investigated pressure range, the dependences $T_C(P)$ and $T_s(P)$ are linear:

$$T_C(P) = T_{C0} - k_C P, \quad T_s(P) = T_{s0} - k_s P,$$

where $T_{C0}$ and $T_{s0}$ are phase transition temperatures at atmospheric pressure, in N-96 $T_{C0} = 348.0$ K, $T_{s0} = 345.7$ K in the LC-440 and $T_{C0} = 348.0$ K in N-96; $k_C$ and $k_s$ are the proportionality coefficients; and $k_C > k_s$, therefore, an increase in pressure leads to an expansion of the temperature range of the nematic phase. This makes it possible to carry out studies at high pressures far from the temperatures $T_{C0}$ and $T_{s0}$, that is, under the conditions of the absence of the influence of pre-transition effects on the measurement results.

3. The results and discussion

A finite response time of orientation equilibration of NLCs exposed to a magnetic field leads to the characteristic features of the propagation of ultrasound in rotational magnetic fields. The analysis of the time dependence of the ultrasound absorption coefficient in an NLC in a rotating magnetic field was performed within the framework of the hydrodynamics of the nematic phase under the assumption that the ultrasound propagation depends on the mutual orientation of the director and the wave vector. Let us substitute the solution of the equation of motion of the director [7] into the equation of the angular dependence of the ultrasound absorption coefficient [8,9]:

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

where $\theta$ is the angle between the magnetic induction vector and the wave vector, $a$ and $b$ are combinations of the shear and bulk viscosity coefficients of the NLC, which makes it possible to obtain the explicit form of the phase dependence $\Delta \alpha (\omega H t)/f^2$ [10]. Analysis of the phase characteristics of the ultrasound absorption coefficient in a magnetic field rotating with an angular velocity $\omega H$ smaller than the critical value $\omega H_0$ allows to obtain the expression of the phase shift [6] between the director and the magnetic induction vector, which is a function of the thermodynamic state parameters.

Analysis of the phase characteristics of the absorption coefficient in a rotating magnetic field, carried out within the framework of the hydrodynamics of the nematic phase, makes it possible to calculate the ratio $\gamma_1/\Delta \chi$ of the coefficient of rotational viscosity to the anisotropy of the magnetic susceptibility ($\Delta \chi = \chi_\parallel - \chi_\perp$, where $\chi_\parallel$ and $\chi_\perp$ are magnetic susceptibilities of NLC in a magnetic field of parallel and normal orientation, respectively) in a wide range of temperatures and pressures. Comparison of these values calculated on the basis of the data obtained in the stationary and non-stationary modes of the director's motion indicates their coincidence within the experimental error [11]. Rotational viscosity is not associated with a macroscopic shear but is a specific property of a liquid crystal and should reflect the
degree of orientation of the molecules; that is, the coefficient $\gamma_1$ is a function of not only the temperature, but also the order parameter:

$$\gamma_1(T) = \alpha_1 \cdot S \exp \left( \frac{E_1}{R \cdot T} \right) + \alpha_2 \cdot S^2 \exp \left( \frac{E_2}{R \cdot T} \right),$$

where $\alpha_1$ and $\alpha_2$ are the proportionality coefficients; $E_1$ and $E_2$ are the activation energies; $R$ is the universal gas constant. Checking the parameters of the model corresponding to the equation (3) showed that $\alpha_1 << \alpha_2$ for liquid crystals with high saturation. In this case, the major contribution in the $\gamma_1$ ($S$) dependence is the second term containing $S^2$, and the contribution of the first term of equation (3) is insignificant. With an increase in the length of the molecular conjugation system, the role of the term containing the $\alpha_1 S$ factor increases, and the role of the second term decreases. For NLCs with long conjugation systems, the term containing the $\alpha_2 S^2$ factor disappears completely. Thus, two limiting cases are possible: $\alpha_1 = 0$ for NLC with a saturated bond, and $\alpha_2 = 0$ for molecules with long conjugation systems.

To determine the dependence of the coefficient of rotational viscosity on the thermodynamic parameters of the state, it should be taken into account that the rotation of the molecules around the short axis requires the presence of free space in the vicinity of the molecule and the energy necessary to make a rotational jump [8,12]. Based on the assumption that the intermolecular interaction is described by the Mayer-Zaupe potential [13], the temperature dependence of the coefficient of rotational viscosity can be described by the equation [14]:

$$\gamma_1(T) = S^2 \cdot \exp \left( \frac{e \cdot S + Q \cdot S^2}{k \cdot T - T_0} \right),$$

that is, it is determined by two exponential factors, the first of which takes into account the probability that the molecule or molecular complex has the energy needed to overcome a potential barrier of height $e \cdot S$, and the second takes into account the probability of having enough space to rotate the molecule or molecular complex around the short axis. Here $e, Q, T_0$ are fitting parameters, $S$ is the order parameter, which is a function of temperature and pressure. Since an increase in pressure leads to a shift of the plot of the dependence of $\gamma_1(T)$ along the temperature axis (Figure 1) by $\Delta T_C = T_C(P) - T$, where $T$ is the temperature at which the experiment was conducted to determine the dependence of the coefficient of rotational viscosity on pressure, it is advisable to enter the temperature $T_1 = T_C - \Delta T_C = T - k_c P$, therefore $T = T_1 + k_c P$. Substitution of temperature $T_1$ into expression (3), which contains only the first term on the right-hand side, allows to derive the dependence of the coefficient of rotational viscosity on pressure and temperature [12]:

$$\gamma_1(P,T) = S \cdot \alpha_1 \exp \left( \frac{E_v}{R \cdot T_1} \right),$$

where $\alpha_1$ does not depend on temperature and pressure, $E_v = E + V_0 P$, where $E$ is the activation energy at atmospheric pressure equal to 32 kJ/mol in LCD 440, $V_0$ has a meaning of free volume and equals $2.7 \cdot 10^{-8}$ J-Pa/mol in LCD 440 and increases with increasing temperature or decreasing pressure.

In the vicinity of the phase transition temperatures, a deviation of the experimental dependence $\gamma_1(P, T)$ from that described by equation (5) is observed. Considering the divergence temperature $T_0$ and the temperature $T^*$, at which the order parameter and the coefficient of rotational viscosity vanish at a pressure $P$, depending on pressure [14]:

$$T^*(P) = T_0 \cdot \left( \frac{P}{\alpha} + 1 \right)^C.$$

The dependence of the coefficient of rotational viscosity on pressure and temperature can be represented as [12,14]:

$$\gamma_1(P,T) = \alpha_1 \left( 1 - \frac{T}{T^*} \right)^{2\beta} \cdot \exp \left( \frac{B}{T - T_0} \right).$$

Here, the first factor takes into account the temperature dependence of the order parameter, $T_0$ is the divergence temperature of the parameter $\gamma_1$. 
This equation describes well the experimental results [5, 6], represented by dots in Figures 1, 2. Solid lines are drawn on the basis of equations (6) and (7). Here, the parameters of equations (6) and (7) for N-96 have the following meanings: $B = 266.5$ K; $\beta = 5.48$; $T_0^* = 345.3$ K; $\alpha = 2.70 \cdot 10^8$ Pa; $c = 0.6$; $\alpha_1 = 1.52$ Pa ∙ s; $T_0 = 281.9$ K. To calculate the coefficient of rotational viscosity under pressure, the values of anisotropy of magnetic susceptibility are used, which are obtained under the assumption that the order parameter depends on the temperature difference between the $T_C$ clearing temperature and the temperature $T$ of the experiment with $\Delta \chi \sim S$.

To study the dependence of the coefficient of rotational viscosity on the specific volume, a two-channel chamber was developed and made [5]. This development also made it possible to study the dependence of the coefficient of rotational viscosity on pressure and temperature at a constant specific volume and to calculate the activation energy of rotational viscosity at a constant volume:

$$E_V = R \left[ \frac{\partial (\ln \gamma_1)}{\partial (\frac{1}{T})} \right]_V,$$

This characterizes exclusively the temperature dependence of the coefficient of rotational viscosity without taking into account the effect of density. The activation energy $E_V$ does not depend on the specific volume and is 23 kJ/mol in the temperature range $\Delta T_C = 0 \div 35$ K in LCD-440. Away from the temperature of the clearing ($\Delta T_C = 35 \div 55$ K), the activation energy $E_V$ increases by approximately 20%. This may be due to a decrease in the activation energy at constant pressure $E_P$ with increasing pressure (Table 1).

| $P$, 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 dependence of the activation energy $E_P$ on the pressure can be explained using the thermodynamic relation [7]:

$$E_V = E_P - R \cdot T^2 \cdot \left( \frac{\partial P}{\partial T} \right)_V \cdot \alpha_V^*,$$

(9)

where $\alpha_V^*$ is the tangent of the inclination angle of the isotherms $\ln \gamma$ (Figure 2). Since the value of $E_P$ is proportional to the total energy required to overcome the potential barrier and the formation of a hole (free volume), and $E_V$ is the formation energy, the inequality $E_P/E_V > 1$ must be satisfied. This ratio decreases with increasing pressure (Table 2).

| $P$, MPa | 0.1 | 10 | 20 | 30 | 40 | 50 | 60 |
|----------|-----|----|----|----|----|----|----|
| $E_P/E_V$ | 1.38 | 1.37 | 1.32 | 1.231 | 1.16 | 1.07 | 1.01 |

4. Conclusion

The informativeness of the acoustic method of studying of pressure and temperature influence on the parameters of liquid crystals is shown. In the framework of the nematic phase hydrodynamics, a method is developed for determining the coefficient of rotational viscosity, which can be used to calculate the orientation relaxation time characterizing the time response of liquid-crystalline technical devices. The influence of the structure of molecules and molecular complexes of liquid crystals on the pressure and temperature dependences of the coefficient of rotational viscosity is established. The equation is presented for the dependence of the rotational viscosity coefficient on pressure and temperature, which takes into account critical phenomena in the vicinity of phase transitions. The usage of the two-channel chamber made it possible to establish the dependence of the molecular rotation activation energy at constant pressure and constant specific volume. An increase in temperature leads to an increase in the activation energy at a constant volume.

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