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Parameters of LC molecules' movement measured by dielectric spectroscopy in wide temperature range

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ABSTRACT

Dielectric properties of a nematic liquid crystal (NLC) mixture ZhK-1282 were investigated in the frequency range of 10^2–10^6 Hz and a temperature range of −20 to 80 °C. On the basis of the Debye's relaxation polarization model dielectric spectra of temperature dependence of the orientational relaxation time τ and the dielectric strength δe were numerically approximated at the parallel orientation of a molecular director relative to alternating electric field. Influence of ester components in the mixture plays crucial role in relaxation processes at low temperature and external field frequency. The activation energy of the relaxation process of a rotation of molecules around their short axis was measured in a temperature interval of −20 to +15 °C in which the dispersion of a longitudinal component of the dielectric constant takes place. The energy of potential barrier for polar molecules rotation in the mesophase was calculated. The value of the transition entropy from the nematic to isotropic phase was obtained from this calculation. The values of the coefficient of molecular friction and rotational diffusion were obtained by different methods. The experimental data obtained are in a satisfactory agreement with the existing theoretical models.

1. Introduction

Dielectric spectroscopy of nematic liquid crystals (NLC) allows obtaining important dielectric characteristics, i.e. conductivity, typical relaxation times, dielectric constant (constant) and its anisotropy, as well as studying fine features of the NLC molecular dynamics processes [1–4]. In particular, the rotation dynamics of the NLC molecules causes the dispersion of dielectric constant and the change of its anisotropy sign in many nematic mixtures [5–8]. Dielectric spectroscopy is also used as a method of studying of liquid crystals unique phases such as ferroelectric [9–11] and antiferroelectric liquid crystals [12,13], blue phases [14,15] and colloid mixtures based on them.

Studying molecular dynamics processes is an important issue in the LC physics as macroscopic LC performances depend on both molecules' chemical structure and their collective behaviour and agglomeration due to intermolecular interactions.

Therefore, multicomponent NLC mixtures are of both practical and scientific interest as they comprise compounds with both positive and negative anisotropy of the dielectric constant Δe. It results in an ability to change its sign at a specific frequency of an external electric field f_c (crossover frequency). This allows controlling the time of relaxation and response in LC devices using different frequency signals (higher or lower than crossover frequency accordingly) [16–19].

2. Material and methods

This study is devoted to a measurement and analysis of both dielectric spectra and relaxation processes in a nematic LC mixture over a wide temperature range. As a study object we chose the LC mixture ZhK-1282 (NIOPIK, Russia) with the wide nematic mesophase temperature range (253.1 K–335.1 K) which allows conducting researches apart from pre-transitive processes. The ZhK-1282 [20] is composed of alkoxycyanobiphenyl (47% mass), Demus's ester (47%), and Gray's ester (4%). Each component of the mixture (Fig. 1) is a well-researched compound. It gives an opportunity to draw conclusions about each mixture component

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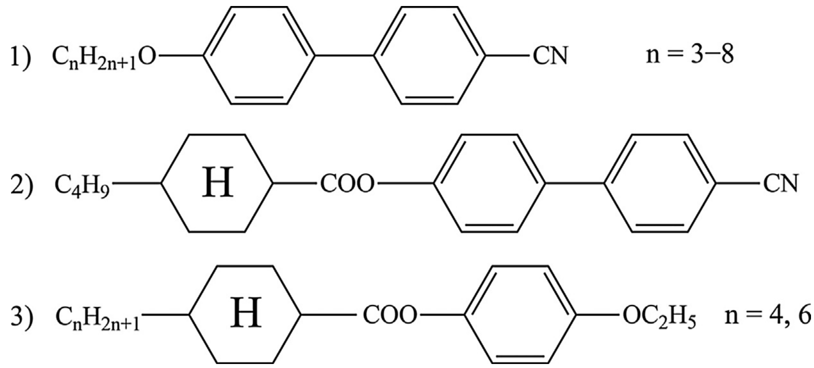

Fig. 1. Structural formulas of components of mixture ZhK-1282 under study: 1) Derivatives of alkoxycyanobiphenyl; 2) Gray's ether; 3) Demus's ether.

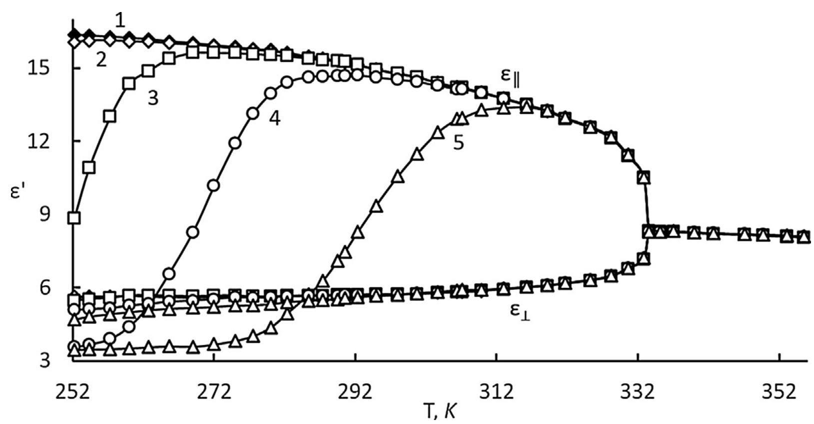

Fig. 2. Temperature dependence of the real part of dielectric constant calculated at different frequencies of the electric field of 1–10^2; 2–10^3; 3–10^4; 4–10^5; 5–10^6 (Hz).

contribution, as well as their collective interaction and behaviour [1,21–24].

Dielectric spectra measurements were taken in a wide frequency f range and temperatures (10^2–10^6 Hz and −20 to 80 °C, accordingly). Calculation of a dielectric constant was done by means of the comparison of an empty capacitor and a capacitor filled with the sample studied. The LC director orientation in the mixture was measured by using a static magnetic field with the induction of 0.52 T in the range of angles of the magnetic field rotation from 0° to 90°with a 10° step. The magnetic field that sets LC mixture orientation is considerably larger than the saturation field and the distance between the capacitor plates is greater that the magnetic coherence length. The dielectric constant values measured by using the static magnetic field and in the NLC cells with both planar and vertical LC alignment are in a good agreement within the ε accuracy of 0.1. Voltage of the applied electric signal was of 1 V. To increase the accuracy of measurements in the calculations, the capacity of connecting wires was taken into account and the stabilization of fluid cryothermostat was set at ±0.5 °C.

3. Results and discussion

Fig. 2 demonstrates temperature dependence of the real part of a dielectric constant measured at different frequencies of the electric field. Longitudinal $\varepsilon'_{||}$ and transverse $\varepsilon'_{\perp}$components correspond respectively to the parallel and perpendicular orientation of long axes of molecules relative to the direction of electric field.

When the temperature reduces, we get in the area of transitive frequencies in nematic mesophase at which the anisotropy of dielectric constant changes its sign (Fig. 2). For example, the crossover frequency for the temperature of 284 K is 10^6 Hz. When the temperature is lowered the crossover frequency decreases according to the Arrhenius law:

$$f_c = f_0 \ \exp\left[-\frac{E}{RT}\right], \tag{1}$$

where E is the activation energy, R is the universal gas constant, and f_0 is the high-temperature ($T \to \infty$) crossover frequency.

The reason for this phenomenon is a dipole-dipole molecular correlation resulting in to their pairing of oppositely directed dipole moments of alkoxycyanobiphenyl and ester molecules within the mixture. Such correlation decreases the positive anisotropy at the increasing of the order parameter. This phenomenon is observed well at the temperature lowering when the dipoles of alkoxycyanobiphenyl stop their rotation along the field; therefore, the main contribution to polarizability is made by the esters with the transverse dipole moment. The dependence observed indicates the influence of molecular interaction mechanisms on the LC mixture anisotropy at the temperature lowering.

There is a discontinuous change of dielectric constant near the transition from the nematic phase to the isotropic phase. The frequency dispersion is not observed in the isotropic phase at the measured range.

Calculation of the imaginary component ε" of dielectric constant was done by using the values of a loss angle tangent and the real part of the dielectric constant on the basis of the following equation [25]:

$$tg\varphi = \frac{\epsilon''}{\epsilon'} + \frac{\sigma}{2\pi f \epsilon_0 \epsilon'}, \tag{2}$$

where σ is the ionic conductivity, ε' is the real component of the dielectric permitivity, and ε_0 is the electric constant.