Influence of Li-TCNQ impurities on dielectric properties of planar-oriented nematic liquid crystal

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Abstract. The dielectric properties of planar-oriented nematic liquid crystal E25M with Li-TCNQ impurities have been investigated within the frequency range $10^{-1}...10^6$ Hz and temperatures 298...343 K. The concentration of impurities varied between 0 and 0.1 wt.%. It has been shown that the presence of a small impurity of Li-TCNQ in liquid crystal increases electrical conductivity, influences on the value of the conductivity activation energy in the nematic phase and practically does not change the activation energy in the isotropic phase. The times of dielectric relaxation τ for the low-frequency part of the spectrum of complex dielectric constant components have been estimated. It has been shown that, within the frame of existence of the liquid crystal phase, the temperature dependence of τ^{-1} linearly depends on the inverse value of the temperature in the Arrhenius coordinates and is well agreed with the temperature dependence of conductivity.

Keywords: dielectric spectroscopy, nematic liquid crystal, Li-TCNQ impurity, activation energy.

1. Introduction

As it is known, currently liquid crystals are widely used in display technology. In more than 80% of the displays made in the whole world, the active element is liquid crystals. Many publications imply that liquid crystals can also be used in devices other than device displays. To do this, one need to somehow change their properties.

Conductivity is one of the important parameters of liquid crystals. Since the main effect of the display operation is change in orientation of molecules under the influence of electric field, in the display technology developers try to use liquid crystals with low electrical conductivity. However, an increase in the conductivity of liquid crystals can significantly to expand opportunities of practical application of these substances. Therefore, the search for impurities, with the help of which one can effectively change conductivity, as well as other electrical parameters of liquid crystal, is an important scientific and applied task.

The purpose of this work was to study the possibility of increasing the conductivity of the liquid crystal mixture E25M by introducing Li-TCNQ impurities [1-5]. Earlier [6], we showed that introduction of the modified C60 impurity into E25M liquid crystal leads to an increase in the conductivity of liquid crystal. Since Li-TCNQ impurity, in contrast to the C60 one, absorbs light better in the visible spectral region, then, in addition to changing the electrical properties, when this impurity is introduced into the liquid crystal, the optical properties of liquid crystal must also change.

2. Materials and methods

For research purposes, we used the nematic liquid crystal E25M prepared in BDH Chemicals Ltd. For this liquid crystal, the phase transition from the isotropic phase to the nematic one is observed at the temperature $T_{IN} = 331$ K. The studied mixture of liquid crystal with Li-TCNQ was prepared using direct introduction into
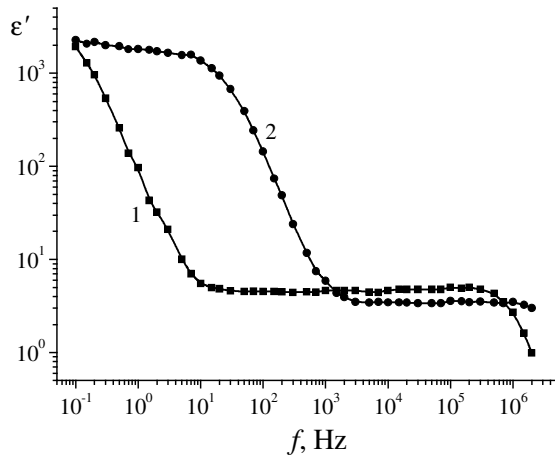
Fig. 1. Frequency dependences of the real component of the complex dielectric permittivity ε' for E25M (1) and E25M + 0.1 wt.% Li-TCNQ (2) at the temperature 298 K (nematic phase of liquid crystal).

liquid crystal at room temperature $T = 293$ K. Then the mixture was stirred mechanically with a magnetic stirrer, and then it was placed into the ultrasonic disperser UZDN-2T at the frequency of 22 kHz for 30 min. As the experiment showed, the solubility of Li-TCNQ in the liquid crystal is not sufficiently high, therefore, studies were performed for low concentrations of impurities within the range 0.003 to 0.1 wt.%.

To investigate dielectric properties, we used sandwich type glass cells with the thickness 25 μm that were set by the Teflon substrates. The orientation of the molecules of liquid crystal in the cells was provided by depositing the polyamide orienting layer and further rubbing. The orientation of liquid crystal in the cell was controlled using the crossed polarizers. The studies have shown that in all the samples planar orientation of molecules was provided technologically clearly (long axes of elliptical molecules were oriented in one direction parallel to the substrate plane).

For better control of the cell thickness (as well as the distance between the electrodes), before filling with liquid crystal, the capacitance of the empty cell C_0 was measured. To avoid edge effects, the cell electrodes were separated into two parts: the internal (measuring) and outer ones. During the measurement, the outer electrode was grounded. The role of the electrode was played by In_2O_3 deposited on the glass. The separation of the electrode into two parts was carried out by etching.

All measurements were performed within the temperature range 293 to 343 K. The temperature stabilization error during measurements did not exceed 0.5 K. The frequency dependences of C and R were measured using the oscilloscopic method [7]. The alternating voltage of the triangular shape with the amplitude $U_0 = 0.25$ V within the frequency range $f = 10^{-1}...10^6$ Hz was applied to the sample.

3. Experimental results and discussion

As already noted, Li-TCNQ has a low solubility in the liquid crystal E25M. In order to avoid the processes of precipitation of Li-TCNQ molecules on the electrode surface, we filled up the prepared E25M + Li-TCNQ mixture into the cell to be examined already before the measurement itself. In this case, the mixture was heated to the temperature 343 K (to increase the solubility) and then, being based on the capillary effect, was filled into the heated cell. During filling the cell, the liquid crystal remained in the isotropic phase. Measurements for various temperatures were performed when the samples were cooled.

Fig. 1 shows the frequency dependences of the real component of the complex permittivity ε' for the planar-oriented nematic liquid crystal E25M (1) and for E25M + 0.1 wt.% Li-TCNQ mixture (2) at the temperature $T = 298$ K.

As it follows from the analysis of the data shown in Fig. 1, the entire spectrum of ε' can be separated into three sections. First, we analyze the spectrum for pure liquid crystal (curve *1*). For the frequencies $f < 10$ Hz, a sharp increase of the ε' value with decreasing the frequency is observed. This low-frequency dispersion is caused by a change in orientation of molecules in the near-electrode sections of the liquid crystal under action of an electric field within the angles corresponding to fluctuations of the order parameter of the liquid crystal (several degrees). In order to this process to be effective, almost all the electric field is applied to a thin (about ten nanometers) of the near-electrode layer. Since this process is due to redistribution of the electric field in the sample, its parameters depend on the conductivity of the bulk part of the sample.

As shown in Fig. 1, embedding the Li-TCNQ impurity most significantly affects the parameters of the low-frequency region of the spectrum for the real component of complex permittivity. As it will be shown further, this occurs precisely by increasing the conductivity of the liquid crystal when introducing the Li-TCNQ impurity.

From Fig. 1 (curve *1*) it follows that, within the frequency range 10 to 10^5 Hz, the ε' value does not depend on the frequency. This section of the spectrum corresponds to the frequencies, at which the electric field is applied to the bulk part of the sample. In this case, the ε' value corresponds to the passport data of the liquid crystal. It is important to note that introduction of Li-TCNQ impurity leads to a slight decrease in the ε' value, as follows from the analysis of Fig. 1. Since the liquid crystal mixture E25M studied by us has a positive value of anisotropy of the dielectric permittivity (the dielectric permittivity at the homeotropic orientation is greater than that at the planar orientation), this effect can be explained by the additional to the orienting surfaces action ordering of the molecules under the action of the impurity. Such an effect may be both bulk (due to interaction of impurity molecules
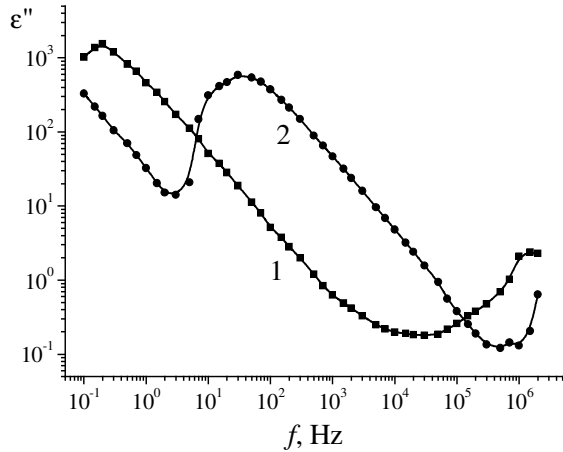
Fig. 2. Frequency dependences of the imaginary component of the complex dielectric permittivity ε'' for E25M (1) and E25M + 0.1 wt.% Li-TCNQ (2) at a temperature of 298 K (the nematic phase of liquid crystal).

Fig. 3. Temperature dependence of the conductivity of nematic liquid crystal E25M with various concentrations of the Li-TCNQ impurity: 0 (*1*), 0.003 (*2*), 0.01 (*3*), 0.1 (*4*) wt.%.

with the liquid crystal ones) and the surface one due to improvement of orienting action of the electrodes because of adsorption of the impurity molecules on their surface. We believe that improving the orienting ability of electrodes in consequence of adsorption of Li-TCNQ impurity molecules at the electrodes is the main mechanism for reducing the ε' value.

The third section of the ε' dispersion begins from the frequencies $f > 10^5$ Hz. For this section, a decrease in the ε' value is typical. As it is known from the theoretical notions about polarization of liquids, the ε' dispersion for these frequencies is due to the fact that the molecules do not have time equal to the change in the voltage of the measuring signal from zero to the amplitude value to turn to a certain angle. Since this type of dipole polarization is characteristic for all liquids, we will not separately consider its analysis and influence of impurities on the parameters of this process.

Fig. 2 shows the frequency dependence for the imaginary component of the complex dielectric permittivity ε'' for E25M (curve *1*) and E25M + 0.1 wt.% Li-TCNQ (curve *2*). From the analysis of these data, it follows that, like to the case of ε', the dielectric spectrum can be separated into three sections. First, let's analyze the second (if the increase in the frequency is taken as the basis of separation) section of the dielectric spectrum. In contrast to the spectral dependence of ε' (in the second section of the dielectric spectrum, the ε' value did not depend on the frequency) for the second section of the spectral dependence of ε'', as it is evident from Fig. 2, the inverse proportional dependence of ε'' on f is typical. This dependence of ε'' on f corresponds to the condition that the sample resistance does not depend on the frequency. In this case, when knowing the resistance determined in the second section of the frequency dependence of ε'', we can determine the sample conductivity on the alternating current σ_{AC}. To calculate the conductivity, we used the following relation:
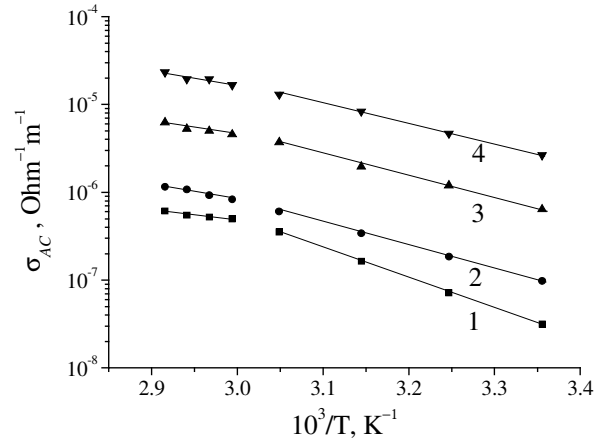
$$\sigma_{AC} = \varepsilon_v \varepsilon'' \omega , \qquad (1)$$

where ε_v is the dielectric constant, and $\omega = 2\pi f$ is the cyclic frequency.

After determing the magnitude of conductivity, it was important to analyze its dependence on temperature. The temperature dependences of conductivity for E25M with various concentrations of Li-TCNQ impurity are plotted in Fig. 3.

As it follows from Fig. 3, within the temperature interval of the existence of a mesophase of liquid crystal, the conductivity linearly depends on the inverse temperature in the Arrhenius coordinates. That is, the temperature dependence of the conductivity can be described by the relation:

$$\sigma_{AC} = \sigma_0 e^{-\frac{\Delta E_\sigma}{kT}} , \qquad (2)$$

where σ_0 is the conductivity at infinitely high temperature, ΔE_σ – activation energy for the temperature dependence of conductivity, and k – Boltzmann's constant.

As it follows from the analysis of Fig. 3, the slope of curve for the temperature dependence of conductivity in the isotropic phase does not depend on the presence of an impurity. According to the equation (2), it indicates that the presence of an impurity in the isotropic phase does not effect on the activation energy of the conductivity ΔE_σ. According to our estimations, the ΔE_σ value for an isotropic phase of liquid crystal is (0.22 ± 0.06) eV, regardless of the impurity concentration. This value coincides with our data obtained for the E25M mixture with modified fullerene in the work [6].

Also, as it follows from the analysis of Fig. 3, for the nematic phase the slope of curves in the temperature dependence for the conductivity changes somewhat depending on the content of Li-TCNQ in liquid crystal.

According to our estimations, for E25M the ΔE_σ value in the nematic phase is (0.55 ± 0.06) eV, and for E25M + 0.1 wt.% Li-TCNQ $\Delta E_\sigma = (0.3 \pm 0.06)$ eV. In our previous studies, for the E25M mixture with modified fullerene [6], we did not observe the effect of the impurity on the activation energy of conductivity in the nematic phase at planar orientation of molecules. In the work [6], the effect of impurity on the activation energy of conductivity was observed at the homotropic orientation of molecules. We can assume that this difference between the results is caused by different interaction of the modified fullerene and Li-TCNQ with the molecules of liquid crystal.

After analyzing the second section of the dielectric spectrum, we will consider the first section in more detail. As it was noted above, the relaxation process in the first section of the spectrum of components of the complex dielectric constant is caused by fluctuation of dipolar molecules in the near-electrode region within the angles equal to fluctuations of the order parameter. Our analysis shows that this relaxation process corresponds to the Debye dispersion and is described by the relation

$$\varepsilon^* = \varepsilon_\infty \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega t}, \qquad (3)$$

where ε^* is the dielectric permittivity, ε_0 and ε_∞ are dielectric permittivity for the frequencies $f = 0$ and $f = \infty$, respectively, and τ is the relaxation time.

The performed by us analysis of the relaxation process caused by rotation of the dipolar molecules in the near-electrode area of the sample shows that the relaxation time should be inversely proportional to the conductivity of the sample. Therefore, to confirm the assumption about the nature of relaxation process in the first section of the dielectric spectrum shown in Figs. 1 and 2, we have analyzed the temperature dependence of inverse relaxation time $1/\tau$. The temperature dependence of $1/\tau$ of liquid crystal E25M with various concentrations of Li-TCNQ impurity is shown in Fig. 4.
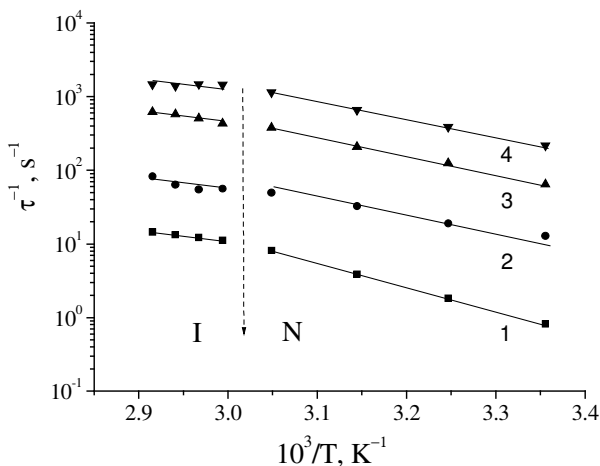
Fig. 4. Temperature dependences of inverse relaxation time τ^{-1} for nematic liquid crystal E25M with various concentrations of Li-TCNQ impurity: 0 (*1*), 0.003 (*2*), 0.01 (*3*), 0.1 (*4*) wt.%.

If we compare the temperature dependences of the conductivity σ_{AC} and inverse relaxation time τ^{-1} (Figs. 3 and 4), one can note rather good correlation between these dependences. This reaffirms our assumption that the relaxation process in the first section of the dielectric spectrum is caused by the change in orientation of the molecular dipoles in the near-electrode region of the spectrum due to oscillations within the angles corresponding to fluctuations of the order parameter.

Let's briefly analyze the third section of the dielectric spectrum for $f > 10^5$ Hz. Our analysis shows that the third section can also be described by the relation (3). It is known from the theory that this relaxation process is due to the fact that the molecular dipoles do not have time to turn to a certain angle during the change in the voltage of the measuring signal. Since, as noted above, this process is inherent to any liquids and has been studied in detail, we did not analyze it.

4. Conclusions

1. Dielectric spectra of components of complex dielectric permittivity for the mixtures of planar-oriented nematic liquid crystal E25M with a low concentration of Li-TCNQ impurities at the temperatures 298 to 343 K and within the frequency range $10^{-1}...10^6$ Hz have been investigated. It has been shown that the whole dielectric spectrum can be separated into three sections. For low frequencies (in the case of E25M without impurities it is for $f < 10$ Hz), the essential dependence of the dielectric permittivity on the frequency is caused by redistribution of the electric field to provide current in the near-electrode sections of the sample as a result of oscillation of the molecular dipoles within the angles equal to fluctuations of the order parameter. At the medium frequencies, the electric field is applied to the whole volume. It allows us to find the conductivity and dielectric permittivity of the sample. The third section of the dielectric spectrum begins at the frequencies $f > 10^5$ Hz. The third section, like to the first one, of the dielectric spectra is described by the Debye equation and is caused by the fact that during the time of change in voltage of the measuring signal the molecule dipoles do not have time to turn to a certain angle.

2. The conductivity σ_{AC} of both pure liquid crystal E25M and that with Li-TCNQ impurities is linearly dependent on the inverse temperature value in the Arrhenius coordinates ($\ln \sigma_{AC}(T^{-1})$). It has been shown that the activation energy of conductivity in the isotropic phase of liquid crystal does not depend on the concentration of the impurity and is equal to $\Delta E_\sigma = (0.22 \pm 0.06)$ eV. In the case of the nematic phase, the activation energy of the conductivity decreases with increasing the concentration of the impurity from $\Delta E_\sigma = (0.55 \pm 0.06)$ eV for pure E25M to $\Delta E_\sigma = (0.3 \pm 0.06)$ eV for E25M + 0.1 wt.% Li-TCNQ.

3. The times of dielectric relaxation τ for the relaxation process caused by rotation of the molecular dipoles in the near-electrode regions of the samples within the angles corresponding to fluctuations of the

order parameter have been estimated. It has been shown that the temperature dependence of inverse relaxation time τ^{-1} has a linear form in the Arrhenius coordinates and is well agreed with the temperature dependence of the conductivity σ_{AC}. This fact confirms the proposed mechanism of the low-frequency relaxation process.

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