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Dielectric properties of nematic liquid crystal with impurities of supramolecular Ni-TMTAA-TCNQ complexes

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Abstract. Within the temperature range 288–343 K and frequencies 10^{-1}–10^{6} Hz, the dielectric properties of planar and homeotropic oriented nematic liquid crystal 6CHBT with the impurity of 0–3 wt.% Ni-TMTAA-TCNQ molecules have been investigated. It has been shown that at the lowest frequencies, the dispersion of components of the complex dielectric permittivity in the case of a planar oriented liquid crystal is caused by oscillations of molecular dipoles within the range of angles corresponding to fluctuations of the order parameter under the action of electric field. The values of relaxation times have been estimated, and it has been shown that with the increase in the impurity concentration, the value of the relaxation time decreases. The temperature dependences of the values inverse to the relaxation time have been analyzed. It has been shown that for the middle frequency range the obtained dielectric spectra characterize the bulk properties of the samples, in particular the value of the electrical conductivity. It has been found that with increasing the molecular concentration, the activation energy for the temperature dependence of the electrical conductivity increases. This dependence for the whole range of studied temperatures correlates with the temperature dependence of the values inverse to the relaxation time. It has been shown that at the concentration of the impurity up to 1 wt.%, the conductivity of the samples both in homeotropic and planar orientations of molecules varies according to the power law of the impurity concentration. It has been estimated the value of the exponent for the concentration dependence of conductivity, and it has been shown that it is the same for various molecular orientations.

Keywords: dielectric properties, nematic liquid crystal, planar and homeotropic orientation of molecules, relaxation time, activation energy, molecular complexes Ni-TMTAA-TCNQ.

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1. Introduction

Currently, liquid crystals (LC) are used in most displays manufactured over the whole world. It is certainly one of the triumphal accords of practical application of LC. In further studies of the LC properties, much of the scientific problems are based on the expansion of the LC functional properties due to the introduction of impurities of different types in them [1–7]. From our viewpoint, the capabilities of LC-based devices can be greatly expanded, if the impurities will absorb light in the spectral range visible for human eyes. Nematic liquid crystals (NLC) that are predominantly used up to date in display technologies are transparent in the visible spectral range, because they act as electric field-controlled polarizers. The color picture itself is formed in the LC-based displays by using the optical filters [8, 9]. Therefore, there is only a small part of publications where the task of creating photosensitive NCL was set due to introducing the impurities of different types in them, which would absorb light in the visible region of the optical spectrum.

In the liquid-crystal phase of NLC, due to the influence of orienting surfaces, the long axes of molecules are directed in a certain direction (as extreme cases of this orientation the planar or homeotropic orientations of LC molecules are considered). Therefore, additional task may be to investigate the effects (on NLC) of substances that, beside increasing the photosensitivity, influence on the NLC orientation itself. Therefore, in this work, we have investigated the effect of supramolecular Ni-TMTAA-TCNQ complexes on the properties of the 6CHBT nematic liquid crystal. These molecular complexes, in addition to being photosensitive in the visible range of the spectrum, create ordered spatial structures at certain concentrations. An analysis of our publications has shown that the effect of supramolecular Ni-TMTAA-TCNQ complexes on the properties of NLC has not been previously investigated.

Since our work is a pioneer one, it was important to determine as much as and how the supramolecular complexes of Ni-TMTAA-TCNQ will affect the properties of 6CHBT. In the first phase of the research, it was not possible to cover the full range of research possible in this case. Therefore, the main purpose of the study was to investigate the effect of supramolecular Ni-TMTAA-TCNQ complexes just on the NLC dielectric properties. In doing so, we hoped that it is based on the analysis of dielectric properties that can be estimated as much as significantly the supramolecular Ni-TMTAA-TCNQ complexes could effect on the properties of specifically 6CHBT. Since the properties of both pure liquid crystal and LC with impurities can essentially depend on the orientation of molecules relatively to the electrodes, one of the main tasks of this work was to investigate the influence of Ni-TMTAA-TCNQ impurities on the properties of 6CHBT at various orientation of molecules (planar or homeotropic).

2. Materials and methods

As noted above, we used the nematic liquid crystal 6CHBT for research. This liquid crystal was synthesized and purified from impurities at the Institute of Chemistry, Military Technical University, Warsaw, Poland. For a given LC, the phase transition from the isotropic phase to the nematic one occurs at the temperature T_{IN} = 315.75 K [10]. The Ni-TMTAA-TCNQ supramolecular complexes were synthesized and purified at the Universidad Nacional Automata de Mexico. The test mixture was prepared by directly introducing impurities into LC at room temperature. After that, the resulting mixture was stirred first mechanically by using a magnetic stirrer and then by using УЗДН-2Т (UZDN-2T) ultrasonic disperser at the frequency 22 kHz for 30 min. As the experiment showed, the solubility of molecular complexes in liquid crystal is not high enough. Therefore, the studies were performed for relatively low impurity concentrations within the range 0.03–3 wt.%. It should be noted that even at the highest impurity concentrations (3 wt.%), deposition of the Ni-TMTAA-TCNQ supramolecular complex occurred 3-5 days after the mixture was prepared. For lower impurity concentrations, this process (depending on the amount of impurity concentration) was much slower. Since the measurement of the dielectric properties was carried out for several hours after the mixture was prepared, it can be argued that even at the highest concentrations of Ni-TMTAA-TCNQ, the impurity distribution over the liquid crystal thickness was homogeneous. This conclusion is confirmed by the fact that at the repeated measurements, we obtained the same results as in the previous ones (within the measurement errors).

For investigations of dielectric properties, we used glass sandwich cells with the thickness 25 μm that was set by Teflon substrates placed on the protective electrodes. The orientation of LC molecules in the cells was provided by deposition of an orientation layer. Polyamide was used to create the planar orientation. After deposition (using a centrifuge) of a rather thin (hundreds of nanometers) layer of polyamide, as a result of rubbing in a certain direction an orientation layer was formed, which, as the studies showed, did not affect the LC dielectric properties. To form the homeotropic orientation, we used the 2-wt.% alcohol solution of aquasil. The aquasil layer was also deposited using the centrifuge, and the thickness of the aquasil was close to that of the polyamide.

The orientation of the liquid crystal in the cell was verified using the polarization microscopy. Our studies have shown that even with the highest (3 wt.%) impurity concentration, the orientation of LC molecules in the studied samples was homogeneous. For better control of the cell thickness (the distance between the electrodes), the capacitance of empty cell C_0 was measured before filling with LC. To control the orientation of molecules (planar or homeotropic) and homogeneity of the molecule orientation over the cell area, we used the In_2O_3 electrodes transparent in the visible spectral range. The In_2O_3 electrodes were deposited onto the glass plates.

The measurements of dielectric properties of pure 6CHBT LC as well as LC with Ni-TMTAA-TCNQ mixtures were carried out within the temperature range T = 288–343 K. The temperature stabilizer provided a constant temperature during measurements with the error not exceeding 0.5 K. The frequency dependences of the capacitance C and resistance R were measured using the oscilloscopic method [11]. In order to avoid changes in the orientation of molecules under the action of voltage of the measuring signal (to a greater extent, it concerns the planar orientation of molecules), the variable voltage with the amplitude U_0 = 0.25 V was applied to the sample. The shape of the measuring signal was triangular. Measurements were performed in the frequency range $f = 10^{-1}$–10^6 Hz. According to the obtained values of C and R as well as using the known geometric parameters of measuring cells, we determined the real ε' and imaginary ε'' components of the complex dielectric permittivity.

3. Experimental results

Fig. 1 shows the micrographs of solution comprising the nematic liquid crystal 6CHBT with impurities of 1 wt.% Ni-TMTAA-TCNQ (a) and 3 wt.% Ni-TMTAA-TCNQ (b) for the planar orientation of the liquid crystal molecules at the temperature 298 K by using a microscope. From the analysis of Fig. 1, for the highest of the studied concentration of Ni-TMTAA-TCNQ in 6CHBT, there is a significant difference between the dye clusters in the planar orientation of LC molecules. While at the concentration 1 wt.% they have a disordered structure close to a spherical shape, in the case of 3 wt.% Ni-TMTAA-TCNQ, the clusters of molecules with a cylindrical or plate structure are observed. Moreover, the orientation of the long axes of the clusters occurs mainly in the direction of orientation of the liquid crystal. Obviously, the Ni-TMTAA-TCNQ clusters that have different orientation (as compared to that of molecules) are located near the surface of the electrodes, but near the surface of the electrodes.

A completely different picture regarding the size and structure of clusters is observed in the analysis of microphotographs corresponding to the homeotropic orientation of LC molecules (Fig. 2).

If for the concentration 1 wt.%, morphology of the Ni-TMTAA-TCNQ clusters in planar and homeotropic orientations of molecules (Figs 1a and 2a) are not practically different from each other, then for the concentration 3 wt.% of Ni-TMTAA-TCNQ (Figs 1b, 2b), there is a significant difference. Obviously, even with the homeotropic orientation of LC molecules, the Ni-TMTAA-TCNQ clusters are preferably oriented in the orientation of LC molecules (*i.e.*, perpendicular to the plane of orienting surfaces). But in this case, they have a structure close to cylindrical or plane shape. As will be shown in the next section when analyzing the dielectric properties of 6CHBT, at different concentrations of Ni-TMTAA-TCNQ impurity, the peculiarities of the concentration dependence of conductivity within the range of impurity concentrations 1 up to 3 wt.% can be explained by just formation of cylindrical or plate type clusters.

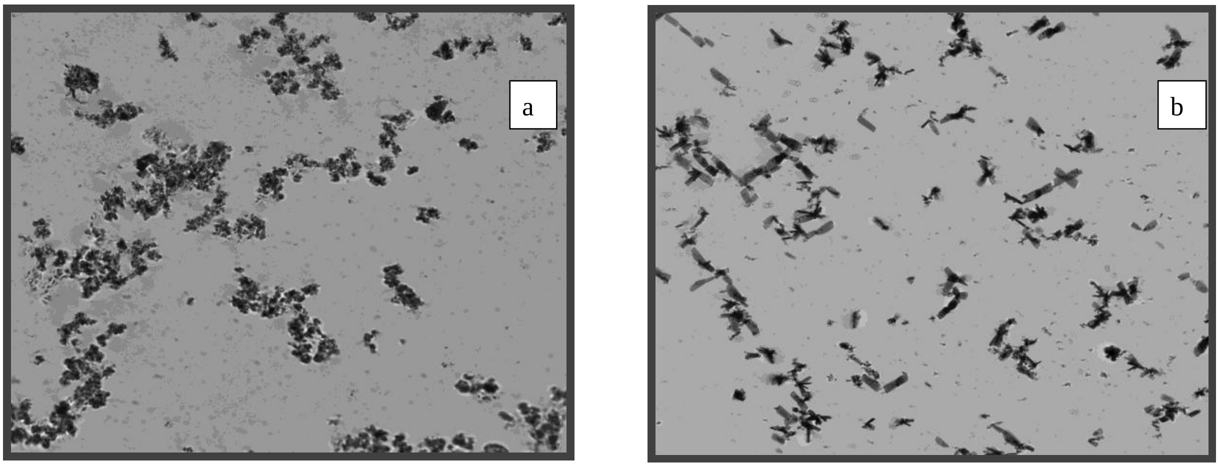

Fig. 1. Micrographs of a solution of nematic liquid crystal 6CHBT with the impurities of 1 wt.% Ni-TMTAA-TCNQ (a) and 3 wt.% Ni-TMTAA-TCNQ (b) for the planar orientation of LC molecules at 298 K.

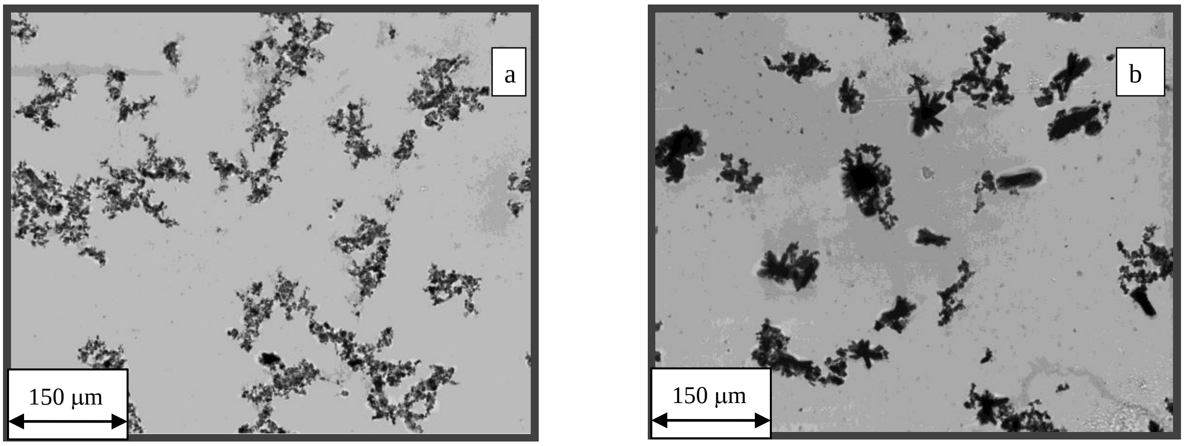

Fig. 2. Micrographs of the 6CHBT nematic liquid crystal solution with impurities of 1 wt.% Ni-TMTAA-TCNQ (a) and 3 wt.% Ni-TMTAA-TCNQ (b) for the homeotropic orientation of liquid crystal molecules at 298 K.

Fig. 3 shows the frequency dependences of the real ε′ component of complex dielectric permittivity for planar (a) and homeotropic (b) orientations of the nematic liquid crystal 6CHBT (*1*) and 6CHBT + 3 wt.% Ni-TMTAA-TCNQ (*2*) at the temperature T = 298 K.

From the analysis of Fig. 3, it follows that for the liquid crystal 6CHBT without impurity the dependences ε′(f) for the planar (Fig. 3a) and homeotropic (Fig. 3b) orientations of the molecules differ markedly. With introduction of 3 wt.% Ni-TMTAA-TCNQ into LC, the difference between dielectric spectra for the planar and homeotropic orientations of the molecules becomes practically insignificant.

It is known [12] that the analysis of dielectric spectra is performed when the frequency spectra of the real and imaginary components of the complex dielectric permittivity are considered together. Therefore, before finding out the reasons of difference in the dielectric spectra of ε′ for planar and homeotropic orientations of 6CHBT molecules for pure LC and LC with the mixture of 3 wt.% Ni-TMTAA-TCNQ, it is logically consider as much as the orientation of LC molecules can affect the frequency dependences of imaginary component ε″ of the dielectric permittivity.

Fig. 4 shows the frequency dependences of the imaginary component ε″ of complex dielectric permittivity for planar (a) and homeotropic (b) orientations of the nematic liquid crystal 6CHBT (*1*) and 6CHBT + 3 wt.% Ni-TMTAA-TCNQ (*2*) at the temperature T = 298 K.

From the analysis of Fig. 4, it follows that, similar to ε′, the values of ε″ of LC 6CHBT without impurities for planar and homeotropic orientations differ significantly more than in the case of 6CHBT + 3 wt.% Ni-TMTAA-TCNQ. This conclusion is typical for the whole frequency range.

As follows from Fig. 3 and Fig. 4, the experimentally obtained dielectric spectra are the result of the manifestation of at least three different processes.

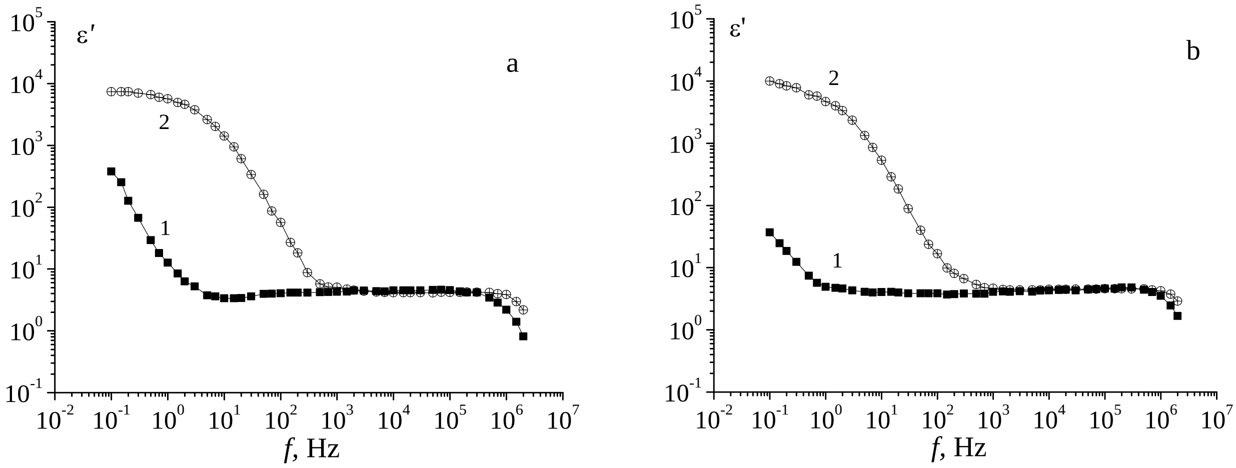

Fig. 3. Frequency dependences of the real component ε′ of the complex dielectric permittivity in the case of planar (a) and homeotropic (b) orientations of molecules for LC 6CHBT without impurities (*1*) and 6CHBT + 3 wt.% Ni-TMTAA-TCNQ (*2*) at the temperature 298 K (nematic phase of liquid crystal).

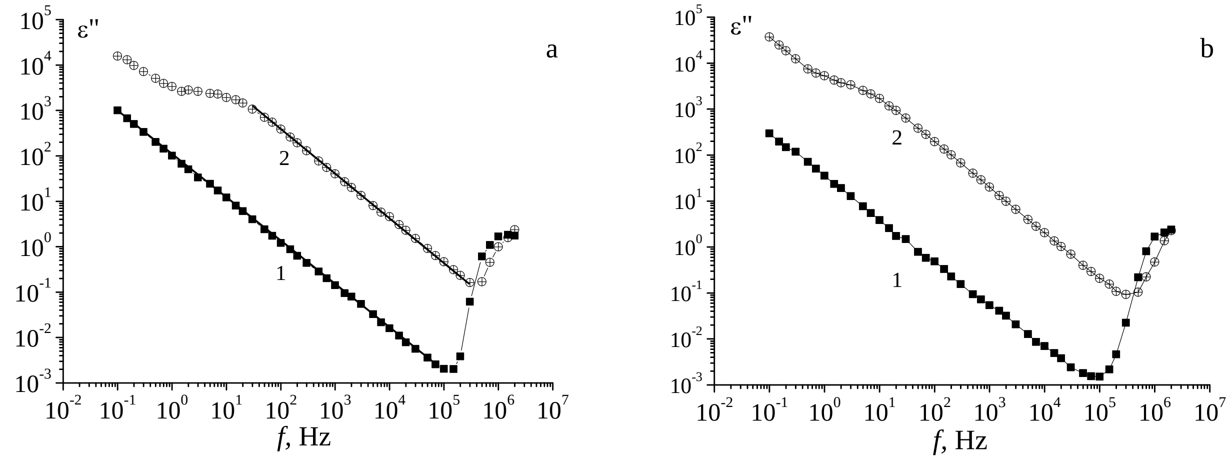

Fig. 4. Frequency dependences of the imaginary component ε″ of complex dielectric permittivity in the case of planar (a) and homeotropic (b) orientations of 6CHBT molecules without impurities (*1*) and 6CHBT + 3 wt.% Ni-TMTAA-TCNQ (*2*) at the temperature 298 K (nematic phase).

Therefore, for a clearer analysis, we separate the whole spectrum into 3 sections (sections of low, medium and highest frequencies). However, we will not clearly determine the frequency ranges at which a particular process manifests itself, since depending on the presence of the impurity and its concentration, these frequency ranges change.

The section of middle frequencies is the most simple to analyze. That is where we will begin to analyze the results. From Figs 3 and 4 it follows that in the section of the dielectric spectrum for the middle frequencies, the ε' value does not depend on the frequency (Fig. 3), and the ε' value linearly decreases with the frequency (the resistance of the sample does not depend on the frequency). According to [18, 19], this section corresponds to the condition when the electric field is homogeneous over the thickness of the liquid crystal and the parameters obtained in this section of the dielectric spectrum characterize the bulk properties of LC. In our case (in accordance with the set task), the parameter that mainly determines the electrical properties was the electrical conductivity.

Being based on the analysis of the dielectric spectra for the middle section of frequencies, we investigated the change in AC conductivity σ_{AC} at different temperatures, different molecule orientations, and different concentrations of Ni-TMTAA-TCNQ impurities. We determined the value of the conductivity by the experimentally found value of ε'' from the relation

$$\sigma_{AC} = \varepsilon_0 \varepsilon'' \omega, \tag{1}$$

where ε_0 is the electric constant and $\omega = 2\pi f$ is the cyclic frequency.

The temperature dependences of σ_{AC} in the homeotropic orientation of molecules for different impurity concentrations are shown in Fig. 5.

The temperature dependences of the σ_{AC} value in the planar orientation of molecules for different impurity concentrations are shown in Fig. 6.

From the data shown in Figs 5 and 6, it follows that the conductivity of 6CHBT without impurities (curves *1*) in the whole temperature range for the planar orientation of molecules (Fig. 6) is less than that for the homeotropic orientation of molecules (Fig. 5). From the viewpoint of theoretical notions about the charge transfer processes in LC, since 6CHBT is a liquid crystal with a positive anisotropy of dielectric permittivity, it means that the σ_{AC} value in homeotropic orientation of molecules (the long axes of molecules are directed along the electric field) should be higher than that in the planar orientation (the long axes of molecules are directed along the normal to the electric field vector). That is, the results obtained for LC without impurities are in good agreement with the charge transfer theory.

The general regularity of the results shown in Figs 5 and 6 is that within the mesophase (nematic or isotropic liquid), they can be described by linear dependences in the coordinates $\lg \sigma_{AC}(T^{-1})$ (Arrhenius coordinates). Analytically, this dependence is approximated by the following relation

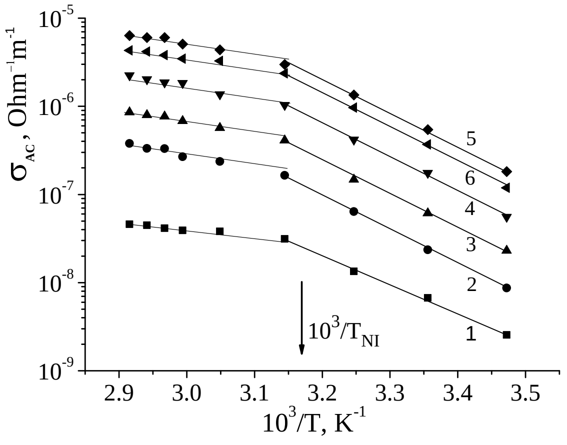

Fig. 5. Temperature dependences of the AC conductivity of the homeotropic oriented nematic liquid crystal 6CHBT on different concentrations of Ni-TMTAA-TCNQ impurity: 0 (*1*), 0.03 (*2*), 0.10 (*3*), 0.30 (*4*), 1.00 (*5*) and 3.00 (*6*) wt.%. The vertical arrow indicates the temperature of transition "nematic-isotropic" (T_{NI}).

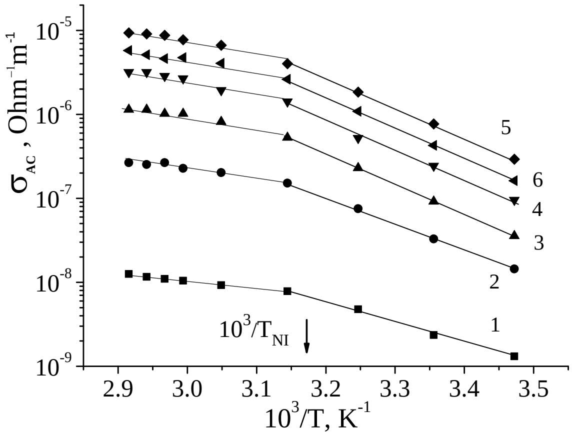

Fig. 6. Temperature dependences of the AC conductivity of a planar oriented nematic liquid crystal 6CHBT for different concentrations of Ni-TMTAA-TCNQ impurity: 0 (*1*), 0.03 (*2*), 0.10 (*3*), 0.30 (*4*), 1.00 (*5*) and 3.00 (*6*) wt.%. The vertical arrow indicates the temperature of transition "nematic-isotropic" (T_{NI}).

$$\sigma_{AC} = \sigma_0 e^{-\frac{E_\sigma}{kT}}, \tag{2}$$

where σ_0 is the electrical conductivity at infinite temperature, E_σ – activation energy of electrical conductivity, and k – Boltzmann constant.

From the analysis given in Figs 5 and 6, it follows that the slope of the curves describing the temperature dependence of conductivity in the isotropic phase for the case of both homeotropic and planar orientations of molecules does not depend on the presence of impurity. Based on relation (2), it indicates that the presence of an impurity does not affect the activation energy of the temperature dependence of conductivity in the isotropic phase.

Table. Dependence of the parameters characterizing the sections of 6CHBT dielectric spectrum for low (E_τ) and medium (σ_{AC}, E_σ) frequencies on the Ni-TMTAA-TCNQ impurity concentration.

Concentration of Ni-TMTAA-TCNQ, wt.%	Homeotrop. σ_{AC}, $\mathrm{Ohm^{-1}m^{-1}}$ (T = 288 K)	Planar σ_{AC}, $\mathrm{Ohm^{-1}m^{-1}}$ (T = 288 K)	Homeotrop. Nematic E_σ, eV	Homeotrop. Isotropic E_σ, eV	Planar Nematic E_σ, eV	Planar Isotropic E_σ, eV	Planar Nematic E_τ, eV	Planar Isotropic E_τ, eV
0	$2.6{\cdot}10^{-9}$	$1.3{\cdot}10^{-9}$	0.47±0.04	0.16±0.04	0.65±0.04	0.18±0.04	0.32±0.04	0.09±0.04
0.03	$1.4{\cdot}10^{-8}$	$8.7{\cdot}10^{-9}$	0.64±0.04	0.21±0.04	0.77±0.04	0.24±0.04	0.44±0.04	0.22±0.04
0.1	$3.6{\cdot}10^{-8}$	$2.3{\cdot}10^{-8}$	0.73±0.04	0.21±0.04	0.77±0.04	0.26±0.04	0.44±0.04	0.22±0.04
0.3	$9.6{\cdot}10^{-8}$	$5.5{\cdot}10^{-8}$	0.73±0.04	0.21±0.04	0.77±0.04	0.26±0.04	0.71±0.04	0.22±0.04
1.0	$2.9{\cdot}10^{-7}$	$1.8{\cdot}10^{-7}$	0.73±0.04	0.21±0.04	0.77±0.04	0.26±0.04	0.71±0.04	0.17±0.04
3.0	$1.6{\cdot}10^{-7}$	$1.2{\cdot}10^{-7}$	0.73±0.04	0.21±0.04	0.77±0.04	0.26±0.04	0.71±0.04	0.17±0.04

According to our calculations, the activation energy of the temperature dependence of conductivity in the isotropic phase of LC in the molecule planar orientation is 0.16 ± 0.04 eV, and in the homeotropic orientation of molecules is 0.18 ± 0.04 eV (Table). When introducing the impurities, the activation energy value of the temperature dependence of conductivity increases slightly (Table), but within the error of the experiment for different orientations of molecules, the values of E_σ remain almost the same. It should take place, because of the molecules in the isotropic phase are not spatially oriented.

If we analyze the dependence of the E_σ-value for the isotropic phase on the impurity concentration, then from the obtained data (Table), we can also conclude that for both planar and homeotropic orientations of molecules, the E_σ-value does not depend on the concentration of Ni-TMTAA-TCNQ within the error of experiments.

In its turn, for the nematic phase of LC, for both planar and homeotropic orientations of molecules, it can be concluded from the analysis of Figs 5 and 6 that the slope of the temperature dependence of conductivity changes with increasing the impurity concentration. The values of activation energies of conductivity estimated on the basis of Eq. (2) for the liquid crystal nematic phase in planar and homeotropic orientations are also listed in Table. The following conclusions can be drawn from this data.

First, there is a difference typical for liquid crystals in the activation energies of electrical conductivity for the planar and homeotropic orientations of molecules in the absence of impurities. Moreover, as it follows from the data summarized in Table, the E_σ-value for planar orientation of molecules is higher than that for homeotropic orientation. In the case of the previously studied by us solutions of modified C60 in the E25M liquid crystal mixture, the activation energy of the temperature dependence of conductivity for the planar orientation of the molecules was almost 1.3 times higher than that for the homeotropic orientation [13]. With regard to the obtained data in this work, this ratio is almost 1.4.

Second, there is no noticeable (within the accuracy of experiments) difference between the E_σ-values in planar and homeotropic orientations in the presence of impurities in LC. From the data adduced in Table, we can conclude that, in the presence of impurities in the liquid crystal, the E_σ-values become almost the same within the experimental errors.

Third, with increasing the Ni-TMTAA-TCNQ impurity concentration, the E_σ-value, in general, increases for both planar and homeotropic orientations of molecules (Table). This is not difficult to explain, since the impurities form additional barriers to charge carrier transfer, creating more deep traps for conduction ions than the LC molecules.

With account of our introducing different concentrations of Ni-TMTAA-TCNQ impurities into 6CHBT, it was also important to analyze the concentration dependence of conductivity in the case of planar and homeotropic orientation of liquid crystal molecules. This dependence for the temperature 288 K (nematic phase) is shown in Fig. 7.

It follows from Fig. 8 that for planar and homeotropic orientations of molecules in a double logarithmic scale up to the concentration 1 wt.%, the linear dependence of conductivity on the concentration of molecules is observed. It means that for the concentration $c \le 1$ wt.%, the conductivity varies according to the power law on the impurity concentration

$$\sigma_{AC} = ac^m , \qquad (3)$$

where a is the coefficient of proportionality and m is the exponent.

This dependence of conductivity on the concentration of impurities is typical not only for liquid crystals but also for liquids in general. For the analysis of the possible conduction mechanisms, for which the relation (3) is satisfied, it is important to estimate the exponent m. Our analysis of the experimental data from Fig. 7 showed that the m-value is the same for the homeotropic and planar orientations of molecules and is equal to 0.86 ± 0.03. In [13], for solutions of modified

C60 in the liquid crystal mixture E25M, we obtained that for planar orientation the *m*-value is 0.46 ± 0.04, and for homeotropic orientation is 0.30 ± 0.04. That is, both in the *m*-value and in the ratio of *m*-values for homeotropic and planar orientations, the data obtained for Ni-TMTAA-TCNQ solutions in 6CHBT liquid crystal differ significantly from the data obtained for solutions of modified C60 in the liquid crystal mixture E25M.

Let us briefly consider what could be the cause of the decrease in conductivity of 6CHBT in the concentration range 1.0–3.0 wt.% Ni-TMTAA-TCNQ. Our analysis of the obtained micrographs showed that at 3.0 wt.% Ni-TMTAA-TCNQ, amount of aggregates of impurities is considerably higher than that at 1.0 wt.% Ni-TMTAA-TCNQ in the case of homeotropic and planar orientations of molecules. These aggregated complexes of molecules, even if they have a charge, but are unlikely to be able to carry it through LC, because their effective mass will be sufficiently high. Besides, these aggregates of Ni-TMTAA-TCNQ molecules, even when they are electrically neutral, can be considered as traps for conduction ions. From our viewpoint, it is these two factors that are the main reason for the decrease in the conductivity of LC 6CHBT from the impurity content in the concentration range 1.0–3.0 wt.%.

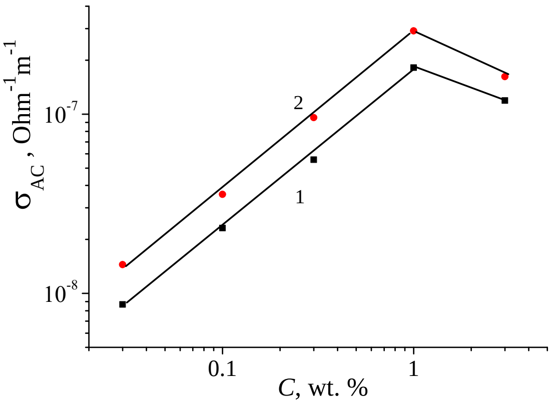

Fig. 7. Dependence of the AC conductivity σ_{AC} of 6CHBT on the concentration of Ni-TMTAA-TCNQ for planar (*1*) and homeotropic (*2*) orientations of the nematic LC at 288 K.

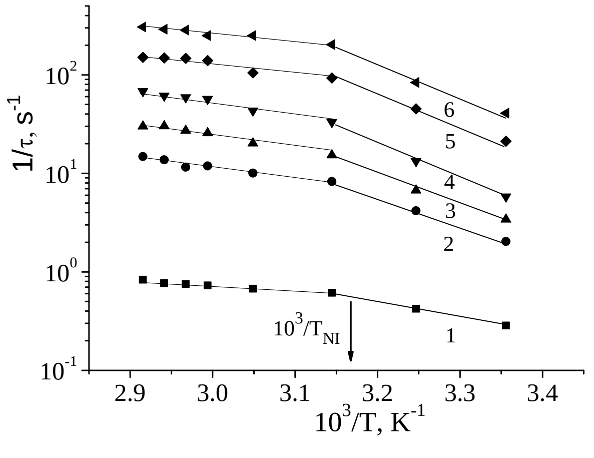

Fig. 8. Temperature dependence of the value of inverse relaxation time τ^{-1} for the planar oriented nematic LC 6CHBT with various concentration of Ni-TMTAA-TCNQ impurity: 0 (*1*), 0.03 (*2*), 0.10 (*3*), 0.30 (*4*), 1.00 (*5*) and 3.00 (*6*) wt.%.

After analyzing the dielectric spectrum in the middle section of the frequency range, it should be done that for the low (within the limits of experimental studies) frequencies. From the data of Figs 5 and 6, it follows that for this frequency range a significant dependence (dispersion) of ε′ and ε″ on the frequency *f* is typical. The very value of ε′ at the lowest frequency (10^{-7} Hz) is 10^3.

As we have shown in [14], the cause of the low-frequency relaxation process in the case of planar orientation of molecules may be rotation of the molecular dipoles (in the range of angles corresponding to the fluctuations of the order parameter) in a thin near-electrode layer with the thickness close to tens of nanometers. Theoretically, this process is described by the Debye relation [14].

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau}, \qquad (4)$$

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

In the case of homeotropic orientation of molecules, rotation of molecules within the angles, corresponding to fluctuations of the order parameter (order of unities of degrees), cannot lead to a significant change in the components of complex dielectric permittivity even in the thin near-electrode layer. In this case of molecule orientation, the low-frequency dispersion may be caused by the near-electrode polarization typical for any liquid [15] due to the charge exchange between the electrode with the electronic conduction type and LC with the ionic conduction type. Dispersion of the components of complex dielectric permittivity for this type of polarization is described by the Cole–Cole relation [15]:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + i\omega\tau)^{1-\alpha}}, \qquad (5)$$

where α is the Cole–Cole parameter, the value which varies from 0 (Debye dispersion) to 1.

The difference between the relaxation processes given by the relations (4) and (5) is that if in the case of the Debye dispersion, the dependence ε″(ε′) (Cole–Cole diagram) can be approximated by a semicircle, then in the case of the Cole–Cole dispersion the dependence ε″(ε′) has the form of an arc.

Of the parameters given in the relations (4) and (5), the most “sensitive” value to various changes is the relaxation time τ. In addition, the value of the relaxation time τ for both the relaxation process described by the relation (4) and the relaxation process described by the relation (5) is inverse proportional to the conductivity of the samples. Therefore, it was logical to check whether this pattern is fulfilled for the samples.

Fig. 8 shows the temperature dependence of the value of inverse relaxation time τ^{-1} for the planar orientation of molecules.

Comparing Figs 6 and 8, we can conclude that in the whole temperature range, in the case of planar orientation of 6CHBT liquid crystal molecules, there is a clear correlation between the value of the AC conductivity and the inverse relaxation time.

Table shows the activation energy values of the temperature dependence of τ^{-1} for planar oriented nematic LC 6CHBT with different concentrations of Ni-TMTAA-TCNQ. Comparing these values, we can conclude that within the experimental errors for each temperature, they are equal to the activation energy for the temperature dependence of conductivity.

As our calculations showed, comparison of the temperature dependences of the τ^{-1} and σ_{AC} values in the case of homeotropic orientation allows to confirm that in this case, the clear correlation between τ^{-1} and σ_{AC} is observed in the whole temperature range as well. Graphically, we do not give the temperature dependence of the τ^{-1} value for homeotropic oriented LC, because we obtained the results similar to the data of Figs 6 and 8, which in principle gives no additional data.

At the beginning of the analysis, we separated all the obtained spectra into 3 sections. Our analysis of the obtained experimental data for the low and middle frequency sections has been given above. It would be logical to compare the experimental results at the high (within the performed studies) frequencies. We will not give this analysis, since the regularities obtained by us in this section of the dielectric spectrum have no differences from those obtained by us for other LC with impurities, in particular, for solutions of modified C60 in the liquid crystal mixture E25M. It has been caused by that the section of the dielectric spectrum for high frequencies corresponds to the dipole polarization of individual molecules, the regularities of which differ very little for liquid crystals related with isotropic liquids.

4. Conclusions

1. Within the temperature range 288–343 K and frequencies 10^{-1}–10^{6} Hz, the dielectric properties of planar and homeotropic oriented nematic liquid crystal 6CHBT with impurities of Ni-TMTAA-TCNQ molecules of the 0–3 wt.% concentration have been investigated. The micrograph analysis shows that aggregation of impurity molecules begins from the concentration 1 wt.%. The molecular aggregates are cylindrical in their shape. In planar orientation, the aggregates of impurity molecules are oriented in the same orientation as that of LC molecules.

2. It has been shown that the whole dielectric spectrum of the samples under study can be separated into 3 sections. For the lowest frequencies, the dispersion of components of the complex dielectric permittivity in the case of a planar oriented liquid crystal is caused by oscillations inherent to molecular dipoles within the angles corresponding to the fluctuations of order parameter under the action of electric field. This type of dispersion is described by the Debye equation. The value of relaxation time has been estimated, and it has been shown that with the increase in the impurity concentration the value of relaxation time decreases. The temperature dependences of the values of inverse relaxation time τ^{-1} have been analyzed. It has been shown that with increasing the concentration of molecules, the activation energy of the temperature dependence of the τ^{-1}-value increases in the nematic phase.

3. It has been shown that for the middle section of frequencies, the obtained dielectric spectra correspond to the bulk properties of samples. The conductivity of samples was chosen as the main parameter characterizing the electrical properties in this frequency section. It has been shown that the activation energy for the temperature dependence of conductivity in the homeotropic orientation of molecules at the temperature 288 K is 1.4 times lower than that in the planar orientation at the same temperature. Being based on the analysis of temperature dependences, it has been estimated that the activation energy for the temperature dependence of conductivity in the isotropic phase is almost 3 times less, on average, than that in the planar orientation. It has been found that as the concentration of molecules increases, the activation energy for the temperature dependence of conductivity increases. This dependence for the whole range of the studied temperatures correlates with the temperature dependence of the τ^{-1}-value.

4. It has been shown that the conductivity of the samples in both homeotropic and planar orientations of molecules changes according to the power law on the concentration of molecules up to the impurity concentration 1 wt.%. The exponent for this dependence is estimated to be 0.86 ± 0.03 and is two times higher than the exponent for the dependence of conductivity of the liquid crystal mixture E25M on the concentration of diamine-modified fullerene C60 [13]. It has been suggested that the decrease in conductivity within the concentration range 1.0–3.0 wt.% is caused by the processes of aggregation of impurity molecules.

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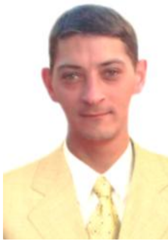

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