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Dielectric and electro-optical properties of solutions of chemically modified fullerene C60 in nematic liquid crystal

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Abstract. Solutions of fullerene molecules C60 with chemically attached molecules of diamine (C60D) in planar oriented nematic liquid crystal (NLC) were obtained by only heating and ultrasonic processing. The C60D concentration changes from 0 up to 3.0 wt.%. Within the ranges of frequencies $10^{-1} - 10^6$ Hz and temperatures 298-343 K, dielectric properties of solutions were investigated. It was shown that, at frequencies higher than 100 Hz, the frequency dispersion of the components of complex dielectric permittivity is absent. A value of conductivity of the solution was determined. It was also shown that the activation energy for the temperature dependence of the conductivity in nematic and isotropic phases does not depend on the concentration of molecules C60D. Obtained and explained were the reasons of the nonmonotonic conductivity dependence of solutions on the concentration of C60D molecules. For frequencies lower than 100 Hz, the dispersion of the components of complex dielectric permittivity is observed. It was shown that the dispersion can be described by the Debye equation. The temperature dependence of a value inverse to the relaxation time correlates with the temperature dependence of conductivity. Presence of C60D molecules in NLC tends to increasing the voltage for the Frederiksz transition. Made was the assumption that this effect may be explained by increase in viscosity of NLC as a consequence of aggregation of fullerene molecules.

Keywords: fullerene molecule, nematic liquid crystal, dielectric and electro-optical properties.

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1. Introduction

The recent decade may be characterized by wide application of liquid crystals (LC) in manufacturing the displays of varied types. At the same time, intense researches in the field of nanotechnology have begun. Therefore, it is reasonable to use nanoparticles to improve certain parameters of LC and to develop materials with new properties that would be inherent neither to nanoparticles, nor to LC [1, 2].

The perspective direction of these researches is modulation of the LC structure by using nanoparticles that, under certain conditions, can create elements of structures with the certain ordering inside it. This

structural ordering can be easily controlled because the structure basic elements are in a liquid anisotropic phase [3].

We showed earlier [4] that presence of 3 wt.% C60D in ferroelectric LC results in disappearance of ferroelectric properties. In this case, all the phases and temperatures of transitions between them were not changed. Made was the assumption that the reason of disappearance of the ferroelectric properties is the substantial growth of rotary viscosity in the solution C60D in LC as a consequence of formation of bonds between the molecules C60D. These bonds can rather easily arise between the C60D molecules due to presence of symmetric diamine molecules.

The purpose of this work was to research the possibilities for manifestation of the structural ordering of C60D molecules in NLC and to define what methods serving as a basis of the changes in NLC properties can be investigated most efficiently [5, 6].

2. Materials and methods

As NLC, we used nematic mixture E25M, while as an impurity we used fullerene C60 with attached molecules of 1,8-octanediamine ($\text{NH}_2\text{-(CH}_2)_8\text{-NH}_2$). They were created in Universidad Nacional Autónoma de México [6]. The C60D concentration was changed within the range 0-3.0 wt.%. Observation by using the polarized microscope has shown that, in the NLC-C60D solution, the temperature of phase transitions within the limits of experimental error 0.5 K was the same as in the pure NLC one.

The studies were carried out with the use of sandwich cells. Transparent layers of In_2O_3 deposited on a glass plate were used as electrodes. Each electrode was separated by measuring and protecting sections via etching. The protecting electrode was grounded during the measurements. To create a planar orientation of the molecules, we used polyamide.

The thickness of a composite layer d varying within the range of 20-23 μm was obtained by introducing a Teflon film between the glass plates over the protecting electrode. Due to a low viscosity of the NLC-C60D composite, filling the cells was achieved via pressurizing this composite between the electrodes. The distance between electrodes was set by two Teflon film strips. The cell was not completely filled with this composite. In that place of the cell where the composite was absent, the distance between the electrodes d was measured by using the interferometric method. The cell assembled was sealed with glue along its perimeter.

Temperature stabilization with an error less than 0.2 K was carried out in a custom-designed thermostat with a low level of electromagnetic noise. The measurements were performed within the temperature range 298-343 K. The sample capacity C and resistance R were measured within the frequency range $10^{-1} - 10^6$ Hz by means of the oscilloscopic method [7]. The measured signal had the triangular shape. The peak voltage value was $U_0 = 0.25$ V. Based on the data obtained, the frequency dependence was analyzed for ϵ' and ϵ'' components of the complex dielectric permittivity.

Electro-optical researches were carried out using the standard technique [8]. The angle between the axes of the polarizer and analyzer was 90° .

3. Experimental results and discussion

3.1. Dielectric properties

Shown in Fig. 1 are the frequency dependences of real ϵ' (curves 1, 3) and imaginary ϵ'' (2, 4) components of the

complex dielectric permittivity for the planar oriented NLC (1, 2) and E25M+3 wt.% C60D (3, 4). All the measurements have been carried out at the temperature 298 K. The obtained spectra can be separated by two parts A and B . In the low-frequency area A ($f < 100$ Hz), observed is an essential (by orders) increase in ϵ' and ϵ'' when the frequency decreases. As it was shown in [9], the presence of this part of the dielectric spectrum is caused by near-electrode phenomena. Properties of this layer will be analyzed after the analysis of bulk properties of the samples under study (part B of the dielectric spectrum).

3.1.1. Bulk region

As it follows from Fig. 1, in the part of the dielectric spectrum where $f > 100$ Hz, the value ϵ' did not depend on frequency, and the value ϵ'' linearly decreased with frequency. The latter is caused by that, for this area of frequencies, the resistance did not depend on frequency. It enabled us to find the conductivity of samples by using alternating current σ_{AC} .

In the part of the linear dependence ϵ'' on frequency (it is marked by lines in Fig. 1), the value σ_{AC} was determined as

$$\sigma_{AC} = \epsilon_0 \epsilon'' \omega, \quad (1)$$

where ϵ_0 is the dielectric permittivity in vacuum, and $\omega = 2\pi f$ is the cyclic frequency.

Fig. 2 shows a temperature dependence of the conductivity for NLC and NLC+C60D with various concentrations of C60D. As it follows from the data obtained, within mesophase limits, a linear dependence of the logarithm of conductivity on inverse temperature (Arrhenius coordinates) is observed

$$\sigma_{AC} = \sigma_0 \exp\left(-\frac{\Delta E_\sigma}{kT}\right), \quad (2)$$

where σ_0 is the direct current conductivity, ΔE_σ is the activation energy of conductivity, k is the Boltzmann constant.

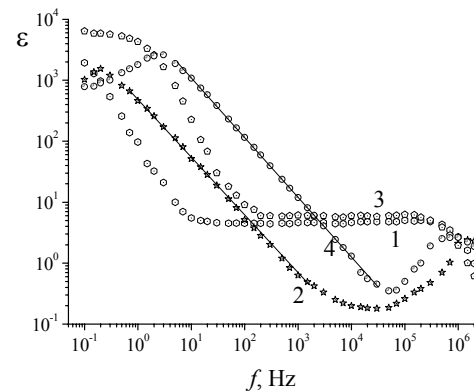


Fig. 1. Frequency dependences of real ϵ' (1, 3) and imaginary ϵ'' (2, 4) components of the complex dielectric permittivity for the planar oriented NLC (1, 2) and E25M+3 wt.% C60D (3, 4).

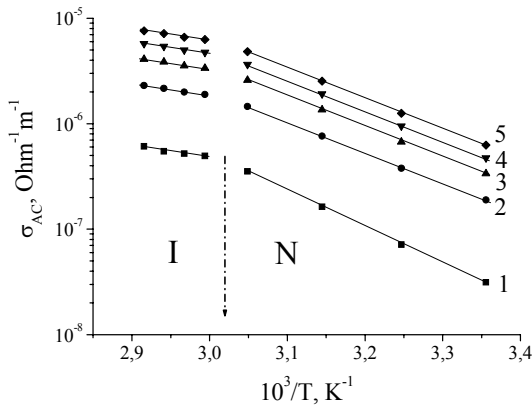


Fig. 2. Temperature dependence of the conductivity for NLC and NLC+C60D with E25M (1), 0.03 wt.% C60D (2), 0.3 wt.% C60D (3), 1 wt.% C60D (4), 3 wt.% C60D (5). I – isotropic phase and N – nematic phase.

As it follows from Fig. 2, the slope of temperature dependences for conductivity in each mesophase of LC (within the limits of experimental errors of measurements) does not depend on presence of C60D and its concentration. It follows from our estimations that in the nematic phase $\Delta E_{\sigma} = 0.55 \pm 0.06$ eV, and in the isotropic phase $\Delta E_{\sigma} = 0.22 \pm 0.06$ eV.

Fig. 3 shows the concentration dependence of conductivity for the solution NLC+C60D at the temperature 298 K for the fullerene concentrations $c \geq 0.03$ wt.%. Being based on the data obtained, it may be inferred that this dependence corresponds to the equation

$$\sigma_{AC} = bc^{1/4}, \quad (3)$$

where b is the factor of proportionality. In accord with [8], for the solution NLC+C60D it is impossible to explain the process of charge carrier formation as based on the simple model of generation-recombination of charge carriers, but it is necessary to take into account participation of complexes with charge carriers in formation of charge carriers.

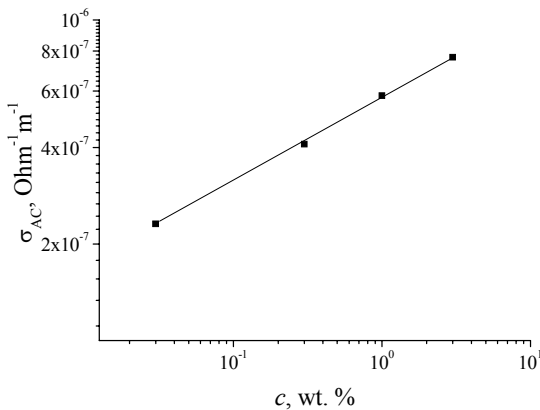


Fig. 3. Concentration dependence of conductivity for the solution NLC+C60D at the temperature 298 K for the fullerene concentrations $c \geq 0.03$ wt.%.

3.1.2. Near-electrode region

As remarked above, the part of a dielectric spectrum A is caused by near-electrode processes. It follows from the work [9] that for planar oriented LC with positive anisotropy of dielectric permittivity (NLC corresponds to these characteristics), characteristic is the relaxation process caused by dipole polarization of the molecules in a near-electrode layer. At low frequencies, almost all the voltage is applied to this layer of the sample, and an alternating current can be caused by oscillations of molecular dipoles within the angles that correspond to fluctuations of the order parameter. Inside the sample bulk, the electric field is much less and the electric current is mainly provided by ion carriers. In this case, the sample can be separated by three parts (two near-electrode layers and bulk) with different mechanisms of charge transfer. When the layers with various electric parameters are in contact, the Maxwell-Wagner polarization may arise [10]. It is this polarization that is responsible for appearance of the relaxation process inside the sample bulk.

Our researches have shown [9] that, for nematic and isotropic phases of LC, the relaxation process caused by dipole polarization in a near-electrode layer is described by the Debye equation:

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

where ε^* is the complex dielectric permittivity, ε_s and ε_{∞} are the dielectric permittivities for frequencies $f=0$ and $f=\infty$, accordingly, τ is the time of dielectric relaxation.

The analysis of the frequency dependences ε' and ε'' obtained experimentally in the part of a dielectric spectrum A has shown that, for all the samples, the dependence $\varepsilon''(\varepsilon')$ (Cole-Cole diagram) is approximated by a semicircle. These dependences between ε' and ε'' , according to theoretical representations, correspond to the Debye relaxation and are described by the equation (4).

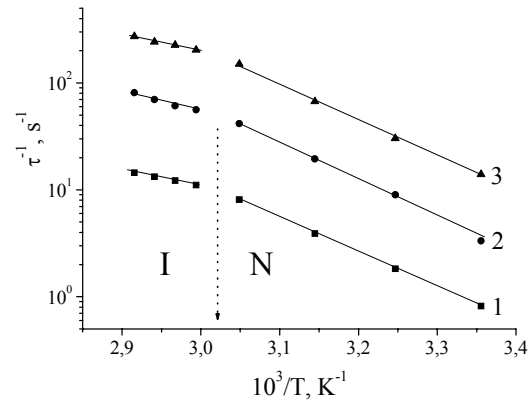


Fig. 4. Temperature dependence τ^{-1} for NLC and NLC+C60D with E25M (1), 1 wt.% C60D (2), 3 wt.% C60D (3). I – isotropic phase and N – nematic phase.

As shown in [9], the time for dipole polarization in the LC near-electrode layer is in inverse proportion to the conductivity of liquid. Therefore, for comparison of the data obtained when analyzing the near-electrode processes with the results summarized in Fig. 2, we have analyzed the temperature dependence of the value inverse to the relaxation time (τ^{-1}).

The temperature dependence τ^{-1} is shown in Fig. 4. It follows from comparison of Figs 2 and 4 that generally confirmed is the conclusion that was made in the work [9] about the relation between the values of relaxation time and conductivity of samples, because well-defined correlation between the temperature dependences τ^{-1} and σ_{AC} is observed in this case.

However, distinction between the data shown in Figs 2 and 4 is also observed. First, for the temperature dependence τ^{-1} , the activation energy is equal to 0.70 ± 0.06 eV for the nematic phase, and 0.37 ± 0.06 eV for isotropic one, which slightly exceeds the corresponding values for the activation energy of conductivity. It can be explained by the fact that the relaxation time depends not only on conductivity, but also on other parameters possessing the same temperature dependence.

3.2. Electro-optic properties

Shown in Fig. 5 is the dependence of the sample transmission normalized by the maximal value on the applied voltage for NLC (1) and NLC+3 wt.% C60D (2). It is clearly seen that introduction of 3 wt.% C60D into LC essentially changes the dependence of conductivity on the voltage. The reason is the non-homogeneous orientation of NLC in the solution NLC+3 wt.% C60D owing to aggregation of fullerene molecules. In this case, the observed ordering of molecules caused by orienting surfaces is imposed by the new ordering caused by aggregation nanoparticles. To determine at what concentration this effect manifests itself most clearly, it is necessary to choose a parameter that characterizes electro-optical properties. This parameter is the voltage of transition from one orientation of molecules to another (in our case, from planar to homeotropic one). This is the voltage of the Frederiksz transition U_F that can be found when analyzing the dependence of transmission on the voltage [8].

The dependence of the value U_F on the concentration is depicted in Fig. 6. It follows from the data obtained that, both for the dependence τ^{-1} on the fullerene concentration and for the dependence $U_F(c)$, the greatest changes are observed when the content of fullerene in a solution varies from 0.1 up to 0.3 wt.%. Just within the limits of these concentrations, observed is intensive formation of bonds between the fullerene molecules. As a consequence, the viscosity of a solution of fullerene in LC sharply increases, which is the main cause for changes in the value U_F . In other words, like to the parameters of near-electrode processes, the parameters of the electro-optical processes are sensitive to ordering of fullerene molecules in LC.

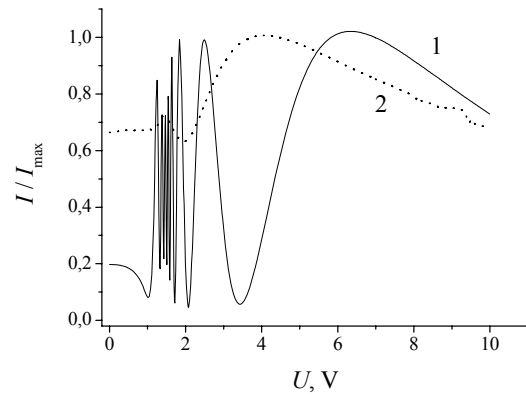


Fig. 5. The dependence of the sample transmission normalized by the maximal value on the applied voltage for NLC (1) and NLC+3 wt.% C60D (2).

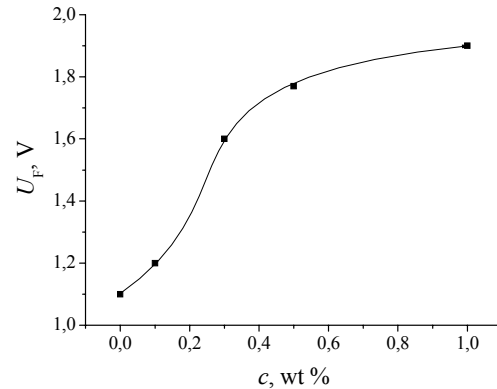


Fig. 6. The dependence of the value U_F on the concentration of C60D.

4. Conclusions

1. The dielectric spectra of the solution E25M+C60D within the ranges of fullerene concentrations (0-3.0 wt.%) and frequencies ($10^{-1} - 10^6$ Hz) can be separated by two parts. For frequencies $f < 100$ Hz, observed is the relaxation process caused by dipole polarization of molecules (the electric field is applied to a near-electrode layer). In the case $f > 100$ Hz, the electric field in a sample is homogeneous, its parameters characterize a bulk part of the structures under study.

2. The conductivity of samples using the alternating current σ_{AC} in each phase linearly changes in the coordinates $\ln \sigma_{AC}(T^{-1})$. The activation energy in each phase of LC does not depend on the fullerene concentration and is equal to 0.55 ± 0.06 eV for the nematic phase, and 0.22 ± 0.06 eV for isotropic one. For fullerene concentrations $c \geq 0.03$ wt.%, $\sigma_{AC} \sim c^{1/4}$. This dependence can be caused by generation of charge carriers through an intermediate state with charge transfer. Using the temperature and concentration dependences σ_{AC} , it is difficult to determine at what concentrations aggregation of molecules can take place.

3. The temperature dependence of the parameter, inverse to the time of dielectric relaxation (τ^{-1}), correlates with temperature dependence σ_{AC} . This fact confirms that the relaxation process in near-electrode layer is caused by molecular dipoles oscillations within the angles that do not exceed fluctuations of the order parameter.

4. The dependence of transmission on the applied voltage essentially varies when introducing fullerene. The voltage of transition from planar to homeotropic orientations of molecules U_F increases with growth of the fullerene concentration. One of the main reasons for presence of this effect is the increase of the solution E25M+C60D viscosity with increasing the fullerene concentration. Therefore, analysis of the U_F value dependence on c enables to determine at what concentration of nanoparticles one can observe fullerene aggregation.

Acknowledgments

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