INFLUENCE OF FULLERENES ON DIELECTRIC AND CONDUCTIVITY PROPERTIES OF SMECTIC A LIQUID CRYSTAL WITH NEGATIVE DIELECTRIC ANISOTROPY

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Influence of fullerenes on dielectric and conductivity properties of smectic *A* liquid crystal is investigated. It is shown that the transverse component of the real part of dielectric permittivity increases at the additive of fullerenes while the longitudinal component decreases. At this case, a maximum of dielectric absorption shifts to the high-frequency region. Conductivity increases at low frequencies and decreases at the high ones. Experimental results are explained on the base of the Maier - Meier theory for anisotropic liquids and also participation of fullerenes in ionic conductivity of liquid crystal.

Keywords: Liquid crystal, smectic *A*, fullerenes, dielectric permittivity
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1. INTRODUCTION

Development of nanotechnology has incentivized to the idea to combine the properties of small particles with peculiarities of optic effects in liquid crystals (LC). The small particles embedded into liquid crystals can not only change properties of the matrix but also promote the origin of new optical effects. In particular, injection of conducting and non-conducting submicron particles strongly influences on electrohydrodynamic instability of liquid crystal with negative dielectric anisotropy [1]. Electro-optic parameters of the Clark-Lagerwall effect in the ferroelectric liquid crystal improve at additive of ferroelectric particles [2]. Ferroelectric particles embedded into nematic LCs form local electric fields at application of electric field to their layer which strongly change the dielectric and electro-optic parameters [3-6].

Addition of nanoparticles into LC can lead to more essential changes as they are distributed between LC molecules at low concentration. Fullerenes have the spherical form and the concrete sizes about 1 nm. Currently, there is a small number of works devoted to liquid crystalline colloids based on fullerenes. Particularly, influence of bias voltage on the liquid crystalline colloid based on pure fullerenes is investigated in work [7]. Results of influence of laser radiation on electro-optic properties of similar colloids are presented in the works [8]. Changes of dielectric parameters of nematic LC study in works [9 - 10]. The aim of present work is the study of action of fullerenes on dielectric and conductivity properties of the smectic *A* liquid crystal.

2. EXPERIMENTAL

We used smectic *A* liquid crystal 4-hexyloxyphenyl ether 4'-hexyloxy 3'-nitrobenzoic acid (C2) as a matrix which has structural formula

$C_6H_{13}O$ - ⬡O - COO - ⬡O - OC_6H_{13}

NO_2
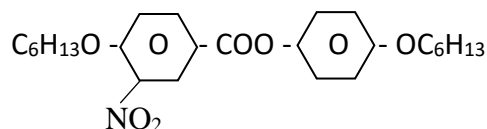
A presence of nitrophenyl dipole group – C- NO_2 of this LC is the reason of the large negative dielectric anisotropy. The fullerenes C_{60} (U.S. Research Nanomaterials, In.) were added into the liquid crystal with 0.5 *wt*. % and were shaken in a vortex mixer for 1 hour at temperature 75°C, followed by sonication with dispergator Ultrasonic Cleaner NATO CD - 4800 (China) for 4 hours.

The cell had a sandwich structure and consisted of two plane-parallel glass plates whose inner surfaces were coated with thin transparent and conductive indium-tin-oxide (ITO) layer. Planar orientation of molecules was attained by coating the inner substrate surfaces with rubbed polyimide layers. The cell thickness was fixed with calibrated 20 μm polymer spacers for measurements. Homeotropic orientation of molecules has been reached by mechanical shift of one substrate concerning another at frequency of 50 Hz for several minutes in the filled cell. Both the colloid and the pure LC were injected into the empty cell by capillary action at the isotropic state. The stuffed cell was kept in the special heater with temperature regulator GL-100 (China). The copper-constantan thermocouple was used for temperature control. An accuracy of temperature determination was 0.1°C.

Dielectric and conductivity measurements were carried out by the Precision LCR Meter 1920 (IET Labs. Inc., USA) in the frequency range of 20 Hz –1 MHz and at temperatures between 30°C –60°C. In this case, applied voltage was 1 V for both LC molecular orientations.

A set-up for measurements of electro-optical parameters was assembled on the base of the Carl Zeiss polarization microscope. The electric impulses of the special form applied to the cell from the functional generator (model G6-28, Russia). A light,

passing through the cell, fell on the photo diode and was registered by digital storage oscilloscope (model 6022BE, Hantek). The threshold voltage was defined using unipolar triangular impulses in quasi -static regime. Besides, a value of the threshold voltage was supervised under the polarization microscope. Frequency dependence of the threshold voltage was registered by application of sinusoidal voltage. The measurements were carried out at temperature 32°C.

3. RESULTS AND DISCUSSION

According to [10], particles do not disturb the director field of a LC if the anchoring parameter $\zeta=WR/K$ is much smaller than 1, where W is the anchoring energy of LC molecules with particle surfaces; 2R is particle size; K is the LC elastic constant. The values of anchoring energy are within 10^{-4} -10^{-6} J/m^2, the elastic constant of LC has an order of 10^{-12} N, and the fullerenes have sizes of 1 nm. Elementary calculations show that the anchoring parameter has an order between 10^{-1}-10^{-3}. It is much less than 1. Thus, the overall disturbance of the director field by fullerenes do not appears still less at similar concentration. Hence, the obtained colloids can be considered as a homogeneous media and they should behave as pure LCs but with the modified parameters. Besides, we may estimate de Broglie wavelength λ of fullerenes as follows:

$$\lambda = \frac{h}{m_0 \upsilon}$$

where h is Planck constant, m_0 is mass of fullerene ($1.2 \cdot 10^{-24}$ kg), υ is the average velocity determined by the following expression:

$$\upsilon = \sqrt{\frac{3k_B T}{m_0}}$$

where k_B is Boltzmann constant, T is Kelvin temperature. Simple validation shows that λ is equal about $3 \cdot 10^{-11}$ m. The sizes of fullerenes (about 1 nm) are more than de Broglie wavelength. Thus, the condition for display of quantum-size effect is not realized and fullerenes behave as classical particles.

Observation under polarization microscope has shown that the clearing temperature decreases from 70.9°C to 69.2°C. Spherical particles of fullerenes infiltrate between LC molecules reducing interaction in between. At this case, there is disordering of LC directions and, accordingly, reduction of order parameter S. As a result, temperature of transition from isotropic to smectic phase decreases according to expression [11]:

$$T_c = (1-f_o) T_p$$

where f_o is volume concentration of particles, T_p and T_c are clearing temperatures of pure LC and the colloid, correspondingly.

The frequency dependences of real ε' and imaginary ε'' parts of dielectric permittivity of both the

pure LC and the corresponding colloid at planar configuration and temperature 32°C are presented in fig. 1. Apparently, ε' slightly decreases from 14,0 at 40 Hz to 13,81 at 20 kHz then it drastically decreases. The value of ε' for the colloid is more than for the pure LC at all frequencies. At this case, it changes from 14,4 at 40 Hz to 14,23 at 30 kHz then its value also drastically decreases. A presence of fullerenes decreases the value ε''. At this case, a maximum of dielectric absorption shifts to the high-frequency region.
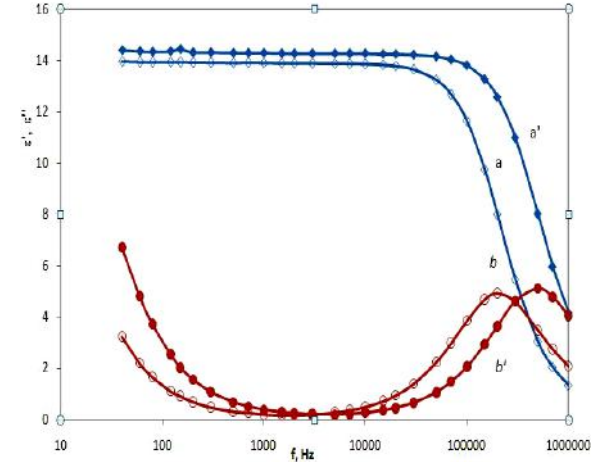

Fig.1. Frequency dependence of real ε' and imaginary ε" components of dielectric permittivity at planar configuration (temperature 32°C): (a) ε' of the pure LC, (a') ε' of the colloid, (b) ε" of the pure LC, (b') ε" of the colloid.

It is known that the relaxation time of LC molecules which is characterized by flipping of molecules from one to an opposite direction and defined as follows:

$$\tau = \frac{1}{2\pi f}$$

where f is the frequency of applied electric field. The additive of fullerenes decreases the relaxation time from $8.0 \cdot 10^{-7}$ c to $3.2 \cdot 10^{-7}$ c at 32° C. Temperature also has an effect on the position of dielectric absorption maximum and, correspondingly, the relaxation time: an increase of temperature reduces viscosity. As a result, the molecule flipping becomes easier (fig. 2).
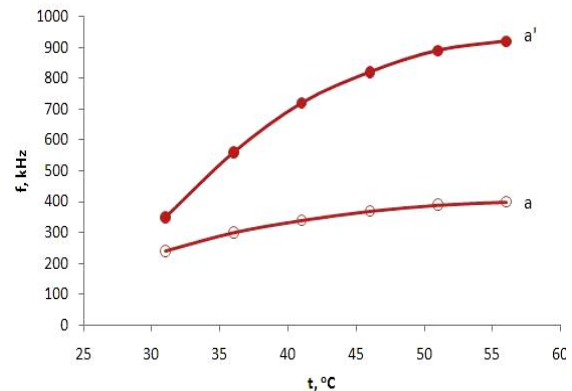

Fig.2. Temperature dependence of a maximum of dielectric absorption: (a) the pure LC, (a') the colloid.

Frequency dependences of real and imaginary components of dielectric permeability of the pure LC and the colloid at homeotropic configuration and temperature 320C are presented in fig. 3. As one can see, ε' of the pure LC equals to 4.25 at 40 Hz then there is dispersion near 500 Hz and its value remains almost invariable and equals 3.91 up to 100 kHz, finally, it sharply decreases. A presence of particles slightly reduces the value ε' to 4.17 at 40 Hz and 3.85 at 100 kHz. Here the dispersion and a maximum of dielectric absorption also observes near 500 Hz.
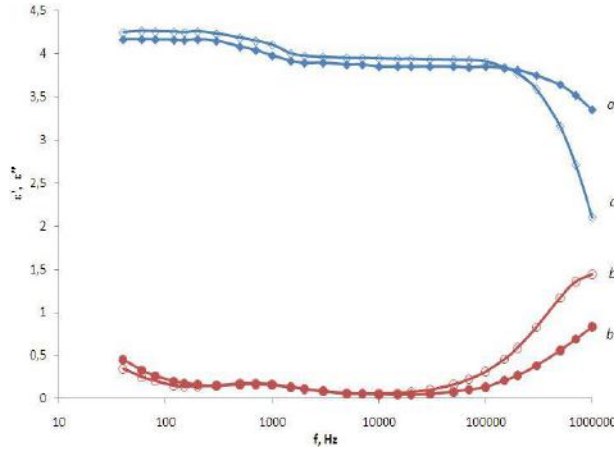

Fig.3. Frequency dependence of real ε' and imaginary ε'' components of dielectric permittivity at homeotropic configuration (temperature 32^0C): (a) ε' of the pure LC, (a') ε' of the colloid, (b) ε'' of the pure LC, (b') ε'' of the colloid.

Obviously, this dispersion connects with the dipole fragment – C-NO$_2$, which non exactly perpendicular to the long molecular axis but has the parallel component along this axis. It should be pointed out the dielectric anisotropy of the pure LC equals to 9.90 at the middle frequencies while this value makes 10.38 for the colloid. In other words, the additive of particles slightly enhances dielectric anisotropy.

The observable experimental facts can be explained by the theory Mayer-Meyer for anisotropic liquids according to which expressions for both components of dielectric permittivity are defined as follows [12]:

$$\varepsilon'_{II} = 1 + \frac{NHF}{\varepsilon_0}\left\{\gamma_{av} + \frac{2}{3}S\Delta\gamma + F\frac{p_e^2}{3k_BT}\left[1 - \frac{1}{2}\left(1 - 3\cos^2\beta\right)S\right]\right\}$$

$$\varepsilon'_{\perp} = 1 + \frac{NHF}{\varepsilon_0}\left\{\gamma_{av} - \frac{1}{3}S\Delta\gamma + F\frac{p_e^2}{3k_BT}\left[1 + \left(1 - 3\cos^2\beta\right)S\right]\right\}$$

here $\gamma_{av} = (\gamma_{II} + 2\gamma_{\perp})/3$ is the average magnitude of polarizability of LC molecules; $\Delta\gamma = \gamma_{II} - \gamma_{\perp}$ is anisotropy of polarizability; N is concentration of LC molecules; S is the order parameter; β is the angle between a dot molecular dipole p_e and an axis of the

maximal polarizability; H is the dimensionless value characterizing the form of the Lorentz cavity; F is the reaction field which changes resultant field in the Lorentz cavity; ε_0 is permittivity of vacuum; k_B is the Boltzmann constant; T is absolute temperature.

Longitudinal component of dielectric permittivity increases while transverse component decreases. These expressions include the order parameter S and quantity of molecules N per volume unit. As concentration of the colloid is very small so the number of the particles per volume unit is also small, namely, with ratio of 0.0029. In other words, N decreases negligible. A different matter the order parameter which is defined as follows [12]:

$$S = \frac{1}{2}(3\cos\theta - 1) \qquad (6)$$

The embedded particles increase an instant angle θ between individual molecules and the preferred direction of molecules (director). In this connection, the order parameter considerably decreases. The last member of the expression for longitudinal and transverse components of dielectric permittivity containing the order parameter has the larger value for transverse component than for the longitudinal one. In this connection, the transverse component increases and the longitudinal component decreases at presence of fullerenes.

Frequency dependences of specific conductance of the pure LC and the colloid are resulted in fig. 4. Apparently, the dispersion connected with the dipole fragment – C-NO$_2$ also is observed on the curves. Here, specific conductance slightly increases before and decreases after this dispersion, correspondingly, at the additive of fullerenes. In particular, the longitudinal component increases from $1.72 \cdot 10^{-5}$ S/m to $1.73 \cdot 10^{-5}$ S/m and the transverse component from $9.92 \cdot 10^{-7}$ S/m to $1.23 \cdot 10^{-6}$ S/m. Put in other words, there is a relation $\sigma_{II}/\sigma_{\perp}$ is equal to 17.3 for the pure LC while it becomes 14.1 at the additive of fullerenes. The longitudinal component decreases from $1.90 \cdot 10^{-1}$ S/m to $8.36 \cdot 10^{-2}$ S/m and the transverse component also decreases from $1.42 \cdot 10^{-2}$ S/m to $6.40 \cdot 10^{-3}$ S/m on the frequency of 300 kHz at the additive of fullerenes. There is a relation $\sigma_{II}/\sigma_{\perp}$ equals to 13.4 for the pure LC and becomes 13.0 at the additive of fullerenes. It is obvious, that similar change of specific conductance is connected by that the fullerenes participate in movement of ions at low frequencies and they are not able to move in time behind them at high frequencies because of time lag.

Ohmic conductivity on alternating current may be presented as:

$$\sigma = 2\pi f \varepsilon_0 \varepsilon''$$

Apparently, the conductivity components ε' strongly increases within the dispersion region. Liquid crystals possess the dielectric anisotropy and, consequently, the relation $\sigma_{II}/\sigma_{\perp} = \varepsilon''_{II}f_{II}/\varepsilon''_{\perp}f_{\perp}$ strongly depends on frequency. In connection with a difference

of frequency ranges of a dispersion ε'_{II} and $\varepsilon'_{\perp}$, maxima ε''_{II} and $\varepsilon''_{\perp}$ are observed at various frequencies and, accordingly, σ_{II} and $\sigma_{\perp}$ start to increase at the same frequencies. The additive of fullerenes shifts dispersion of the real part of dielectric permittivity to the high frequency region. Therefore, the same shift occurs with dispersion of specific conductance.
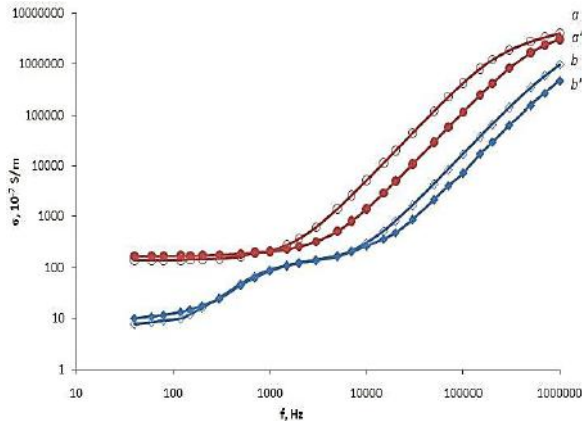

Fig.4. Frequency dependence of specific conductance components at temperature 32°C: (a) σ_{II} *of* the pure LC, (a') σ_{II} of the colloid, (b) $\sigma_{\perp}$ of the pure LC, (*b'*) $\sigma_{\perp}$ of the colloid.

Additionally, the threshold voltage of homeotropic-planar transition decreases from 250V to 185 V at the additive of fullerenes. Threshold voltage of homeotropic - planar transition is defined as follows [13]:

$$U = \sqrt{\frac{Wd}{2\varepsilon_0 |\Delta\varepsilon| \cdot l}}$$

ℓ is length of molecule, W is sum of elastic energy and the energy connected with formation of declinations and dispositions; $\Delta\varepsilon$ is anisotropy of dielectric permittivity, d is the layer thickness. Essential reduction of threshold voltage cannot be connected with an insignificant increase in dielectric anisotropy. Apparently, it is caused by occurrence of defects-germs with which the growth of planar areas begins. Thus, the magnitude of W decreases, that is reflected in value of the threshold voltage.

4. CONCLUSION

It is shown that the additive of fullerenes leads to an increase of the transverse component of real part of dielectric permittivity while the longitudinal component reduces. At this case, there is a shift of a maximum of dielectric absorption to the high-frequency region. Electric conductivity increases at low frequencies and decreases at the high frequencies. Threshold voltage of homeotropic-planar transition decreases from 250 V to 185 V.

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