DIELECTRIC, CONDUCTIVITY, AND ELECTRO-OPTIC PROPERTIES OF LIQUID CRYSTAL 5CB DOPED BY SINGLE-WALLED CARBON NANOTUBES

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The effect of single-walled carbon nanotubes (SWCNTs) on the dielectric, conductive, and electro-optic properties of nematic liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) has been studied. It was shown that the additive of SWCNTs with concentration of 0.5% leads to strong interaction between SWCNTs and molecules, which increases the order parameter of 5CB. As a result, the clearing point is raised, the longitudinal component of the dielectric permittivity increases while the transverse component decreases. The incipient percolation effect promotes to the dominance of hopping electron conductivity over ionic conductivity, leading to an increase in specific conductivity. In this case, the elastic splay constant of 5CB is enhanced and, accordingly, the threshold voltage of the S-effect increases. A decrease in the Van-der-Waals interaction between molecules decreases viscosity. As a result, the flip-flop motion of molecules become easier and the switching times are also reduced.

1. INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) are rod-shaped and have a diameter comparable to the transverse size of elongated liquid crystal (LC) molecules. In addition, there is strong interaction of nanotubes with LC molecules, as a result of which they are aligned along the preferred direction (director) of LC molecules [1]. In that respect, liquid crystal with such nanoparticles can significantly change its physical properties.

The aim of this work is to study the effect of SWCNTs on the dielectric, conductivity, and electro-optic properties of nematic liquid crystal 4-cyano-4'-pentylbiphenyl (5CB).

2. EXPERIMENTAL

We used nematic liquid crystal 4-cyano-4'-pentylbiphenyl (firm Merck) with positive dielectric anisotropy as a matrix. The temperature range of the nematic phase of this LC is usually located between 21.3°C and 35.2°C.

The single-walled carbon nanotubes (US, Research Nanomaterials, In.) were added into the liquid crystal with concentration of 0.5 wt. %. Then obtained mixture was shaken in a vortex mixer for 1 hour at temperature 50°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. For obtaining of homeotropic orientation of LC molecules, we used the surfactant (polysiloxane). The cell thickness was fixed with calibrated 20 μm polymer spacers for measurements. Both the colloid and the pure LC were injected into the empty cell by capillary action at the

isotropic state. To increase the dispersion, the cells with the colloid were placed at electric field of 40 V to achieve turbulence and were kept for 2 days. In this case, no aggregation of particles was observed. 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 23°C – 43°C. In this case, applied voltage was 0.5 V for both LC molecular orientations.

A set-up for measurements of electro-optic 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).

Switching times were defined from an electro-optic response by application of unipolar rectangular impulses while 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.

3. RESULTS AND DISCUSSION

According to [2], nanoparticles do not disturb the director field of a LC, if the penetration length ξ is much smaller than their diameter D. The penetration length is defined as ξ =K/W, where K is some average of the Frank elastic constants, W is an anchoring energy of the nematic molecule at the particle surface. The values of the anchoring energy are within $10^{-4} – 10^{-6}$ J/m², elastic constants have the value about $6 \cdot 10^{-12}$ N, and D of single-walled nanotubes is equal to 1 *nm.* Elementary calculations show that the penetration length has an

order between $10^{-8} - 10^{-6}$. It is much more than the SWCNT diameter. Hence, the obtained colloids can be considered as a homogeneous media and they should behave as pure LCs but with the modified parameters.

Observation under polarization microscope has shown that the clearing temperature of the pure LC is located near 35.2° C while the nematic-isotropic transition of the colloid takes place at 37.1° C.

Rod-like particles of single-walled carbon nanotubes in nematic LC cause the effective orientational coupling with LC molecules [3]. The charges transfer from LC molecules to the particles and are distributed asymmetrically on the SWCNTs inducing a permanent dipole moment on them [4]. As a result, SWCNTs are oriented parallel to the LC director enhancing the order parameter S [5]. In this case, the isotropic-nematic transition temperature increases [6].

Fig. 1 and fig. 2 show the frequency dependence of real ε' and imaginary ε'' parts of dielectric permittivity of both the pure LC and the colloid for homeotropic and planar configurations, correspondingly, at temperature of 24°C.

The frequency dependence of ε' can be divided into three ranges. At low frequencies, an increase in dielectric permittivity occurs, which is associated with electronic exchange between electrodes and ions [7]. In this case, the nanotubes increase the double electric layer enhancing the field screening effect. In the middle frequency region, the dielectric permittivity remains almost unchanged and is connected with the bulk properties of the sample. And finally, relaxation of the liquid crystal and the colloid starts in the high-frequency range. As can seen, the additive of carbon nanotubes increases the longitudinal component of real part ε' of dielectric permittivity while it decreases the transverse component in the middle frequency range. In particular, the longitudinal component increases from 19.55 to 20.56 and the transverse component decreases from 6.51 to 5.93 at the frequency of 2 kHz. As a result, the dielectric anisotropy increases from 13.04 to 14.63 at temperature 24^0 C. A presence of SWCNTs also decreases the value ε'' except for low frequencies at homeotropic configuration.

Temperature dependences of the real part of the dielectric permittivity of the colloid and the pure LC for both configurations at the frequency of 2 kHz are presented in fig. 3.

As can be seen, the longitudinal component of dielectric permittivity of the colloid is more and the transverse component is less than the corresponding value of the pure LC at all temperature up to the clearing point. The longitudinal and transverse components of the dielectric permittivity of the pure LC coincide above 35.2° C. It indicates that the isotropic-nematic transition occurs at the indicated temperature in the pure LC. While the components of the dielectric permittivity of the colloid are equalized at temperature of 37.1°C. Therefore, phase transition in the colloid rises to indicated temperature. This fact is consistent with observations under the polarization microscope.
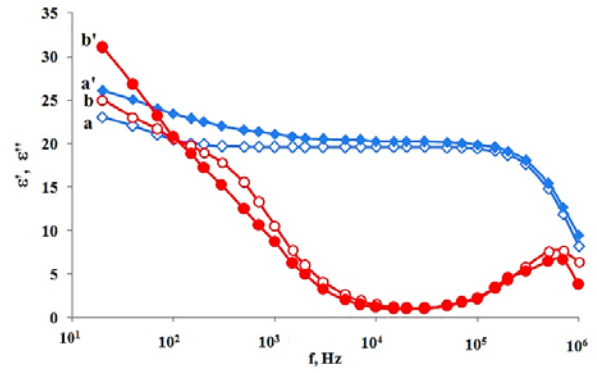

Fig.1. Frequency dependence of real ε' and imaginary ε'' parts of dielectric permittivity at homeotropic configuration (temperature 24^0C): (a) ε' of the pure LC, (a') ε' of the colloid, (b) ε'' of the pure LC, (b') ε'' of the colloid.
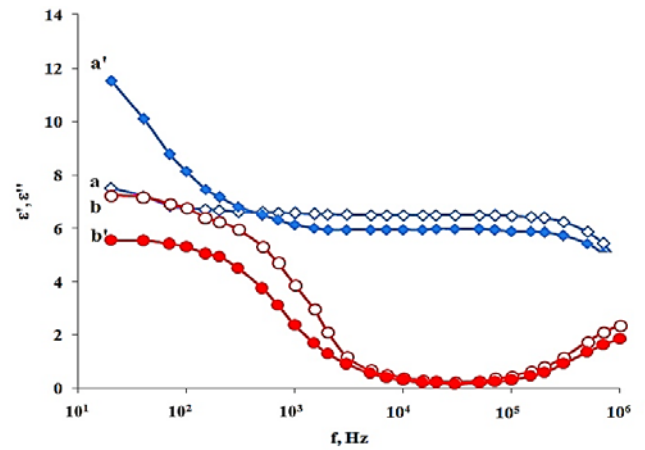

Fig. 2. Frequency dependence of real ε' and imaginary ε'' parts of dielectric permittivity at planar configuration (temperature 24^0C): (a) ε' of the pure LC, (a') ε' of the colloid, (b) ε'' of the pure LC, (b') ε'' of the colloid.
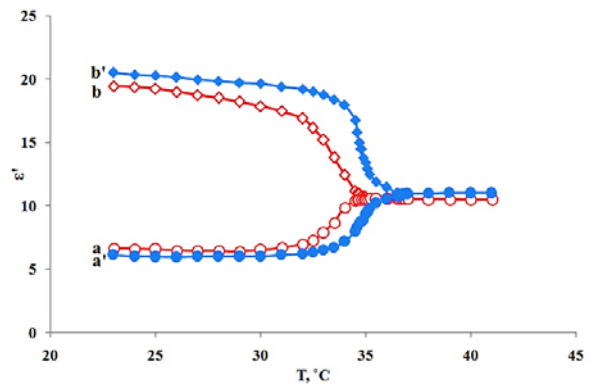

Fig. 3. Temperature dependence of components of dielectric permittivity at the frequency of 2 kHz: (a) the transverse component of the pure LC, (a') the transverse component of the colloid, (b) the longitudinal component of the pure LC, (b') the longitudinal component of the colloid.

The observable changes dielectric permittivity can be explained by the Maier-Meier theory for nematic LC according to which expressions for components of dielectric permittivity are defined as follows [8]:

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

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

Dielectric anisotropy is the difference of these quantities:

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

where F is reaction field factor, H is the cavity form factor, $\gamma_{av} = (\gamma_{II} + 2\gamma_{\perp})/3$ is the average value of polarizability of LC molecules, $\Delta\gamma = \gamma_{II} - \gamma_{\perp}$ is the anisotropy of polarizability, N is the number of LC molecules per unit volume, S is the order parameter, β is an angle between the point molecular dipole p_e and the axis of maximum molecular polarizability, ε_0 is dielectric permittivity of vacuum, k_B is Boltzmann constant, T is Kelvin temperature. These expressions include quantity of molecules N per volume unit and the order parameter S. Since the concentration of the colloid is very small, the number of embedded particles per unit volume is also small. That is, the number of LC molecules per unit volume N decreases insignificantly. As shown above, the additive of nanotubes increases the order parameter S. The second term in the curly brackets of the expressions for components of dielectric permittivity containing the order parameter has different sign. It has the order parameter with a positive coefficient of 2/3 for the longitudinal component, accordingly, this component increases at the additive of nanotubes while the transverse component decreases because of negative coefficient of 1/3 of the same term. These inferences agree with our experimental data.

As can be also seen from figure 3, a maximum of dielectric absorption shifts to the high-frequency region from 640 kHz to 680 kHz. Fig. 4 shows the temperature dependence of the frequency of the dielectric absorption peak for the pure LC and the colloid.

As can be seen, the frequency of the dielectric absorption peak of the colloid is less than for the pure LC at all temperatures. The frequency of the dielectric absorption peak of the pure LC varies from 590 kHz (23°C) to 770 kHz (34°C) while it increases from 645 kHz (23°C) to 780 kHz (34°C) for the colloid.

The relaxation frequencies f_R follow the Arrehenius behavior by equation:

$$f_R = Ae^{-\frac{W}{k_BN_AT}}$$

As may be inferred from this figure, the longitudinal component is more than the transverse one in the pure LC and the colloid at low and middle

where W is the activation energy of the flip-flop motion of the molecules about their short axes., A is some parameter, N_A is the Avogadro number. The slopes of the plots of log f_R versus the inverse of the temperature correspond to the activation energies along the director for the pure and the colloid, which equal to 27 kJ/mol and 23 kJ/mol, correspondingly. The activation energy decreases due to the presence of nanotubes. It indicates to that SWCNTs facilitates the flip-flop motion of the LC molecules.

As is well known, the relaxation time τ of LC molecules is characterized by flip-flop motion of molecules about their short axes. It is determined as follows:

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

where f is the frequency of the applied electric field. The addition of SWCNTs reduces the relaxation time from $2.7 \cdot 10^{-7}$ to $2.1 \cdot 10^{-7}$ s at 23° C and from $2.5 \cdot 10^{-7}$ s to $2.0 \cdot 10^{-7}$ s at 34° C. Obviously, the decrease of the relaxation time for the colloid connects to the decrease in viscosity. Temperature also affects on the relaxation time: an increase in temperature reduces viscosity. As a result, the flip-flop motion of LC molecules becomes easier.
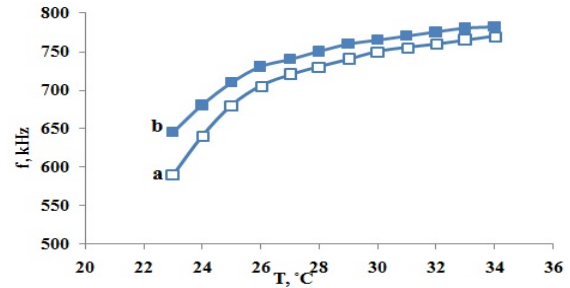

Fig. 4. Temperature dependence of the frequency of a local maximun of ε ": (a) the pure 5 CB, (b) the colloid.

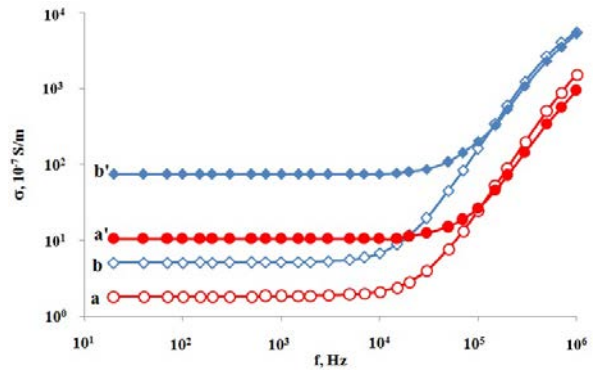*Fig. 5.* Frequency dependence of specific conductance at temperature 24°C: (a) σ_{II} of the pure 5CB, (a') σ_{II} of the colloid, (b) $\sigma_{\perp}$ of the pure 5CB, (b') $\sigma_{\perp}$ of the colloid.

frequencies. This is due to the fact that it is easier for charges to move along the long axes of LC molecules (director). In this case, SWCNTs increase the

conductivity of both components. In such a case, the longitudinal component increases more than the transverse component. In particular, at the frequency of 2 kHz, the longitudinal component of conductivity increases from $5.2 \cdot 10^{-7}$ S/m to $7.4 \cdot 10^{-6}$ S/m while the transverse component increases from $1.9 \cdot 10^{-7}$ S/m to $1.1 \cdot 10^{-6}$ S/m. Starting from 15 kHz, the conductivity increases sharply. At high frequencies, conductivity of the colloid is less than for the pure LC.

The increase in conductivity is connected with the percolation phenomenon and high intrinsic electrical conductivity of carbon nanotubes. Continuous network of SWCNTs is formed in the colloid at a certain concentration called the percolation one. In this case, there is a transition from the ionic conductivity to the dominating charge hopping conductivity.

The conductivity of the LC at high frequencies is determined by the dielectric losses because molecular dipoles follow the electric field with some lag. There is the inhibition of the rotation of these dipoles in an alternating field. It is known that the corresponding conductivity can be represented by the Debye formula:

$$\sigma = 2\pi f \varepsilon_0 \varepsilon'' = \varepsilon_0 \left[\varepsilon(0) - \varepsilon(\infty) \right] (2\pi f)^2 \tau_D$$

where τ_D is the relaxation time for molecular dipoles which is determined as [8]:

$$\tau_D = \frac{\gamma}{2k_B T} ,$$

where γ is the rotational viscosity. The decrease in LC conductivity at high frequencies can be explained by a decrease in rotational viscosity at additive of SWCNTs into the LC.

The temperature dependences of specific conductance for the pure LC and the colloids are presented in fig. 6.
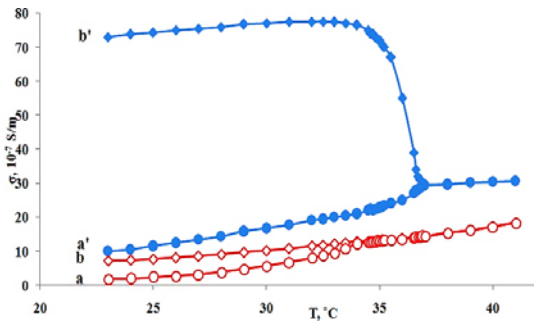

Fig. 6. Temperature dependences of specific conductance at the frequency 2 kHz: (a) σ_{II} of the pure 5 CB, (a') σ_{II} of the colloid, (b) $\sigma_\perp$ of the pure 5CB, (b') $\sigma_\perp$ of the colloid.

With increasing temperature, conductivity increases and the corresponding dependence obeys the Arrhenius law:

$$\sigma = \sigma_0 e^{\frac{E}{k_B N_A T}} ,$$

where σ_o is the pre-exponential factor, E is the activation energy of electrical conductivity. The value of E consists of the activation energy of the motion of the carriers and the energy necessary for the nucleation of new charges. It is an energy barrier which an ion must overcome to move inside a liquid crystalline medium. The larger the E, the harder the ions move within the LC layer and, accordingly, the lower the conductivity.

From the last expression, it is possible to find the activation energy of E_{pII} of the pure LC and E_{cII} of the colloid along the director, $E_{p\perp}$ of the pure LC and $E_{c\perp}$ of the colloid across the director, as well as the activation energy of $E_{p.is}$ of the pure LC and $E_{c.is}$ of the colloid in the isotropic phase. The method is the same as for the the activation energy of flip-flop motion of molecules. The calculated values of the activation energy are given in Table 1.

Table 1
Activation energy (in kJ/mol) of the pure LC and the colloid in the isotropic phase as well as nematic phase along and across director.

	E^{II}			$E_\perp$	$E_{.is}$
Pure LC	39.6			85.4	56.3
Colloid	23.2			78.5	49.1

As one can see from this Table, the presence of SWCNTs decreases the activation energy of charges in nematic phase for both directions. That is, chargesmoves inside the colloid with lesser exertion than in the pure LC.

The measurement of the threshold voltage of the Freedericksz effect by the electro-optical method showed that the addition of nanotubes increases it from 1.2 to 1.6 V.

According to [8], the threshold voltage U_F of the Freedericksz effect is determined by the following equation:

$$U_F = \pi \sqrt{\frac{K_{11}}{\varepsilon_0 \Delta \varepsilon}} ,$$

where K_{11} is splay elastic constant; ε_0 is the permittivity of vacuum; $\Delta \varepsilon$ is the dielectric anisotropy. This expression is true for colloids with a low concentration of particles and their small sizes. Using the numerical values of the threshold voltages and dielectric anisotropy, one can obtain the values of the elastic constants of the pure LC and the colloid. Calculations show that they are equal to $1.685 \cdot 10^{-11}$ N and $3.362 \cdot 10^{-11}$ N, respectively. That is, the additive of SWCNTs into LC increases its elastic constant.

The dependence of the rise time of the Freedericksz effect on the applied voltage for both the pure LC and the colloid is presented in fig. 7.

Apparently, the dependence of the rise time t_{on} on the voltage for both the pure LC and the colloid qualitatively corresponds to the expression [8]:

$$t_{on} = \frac{\gamma_1 d^2}{\varepsilon_0 \Delta\varepsilon (U^2 - U_F{}^2)},$$

where γ_1 is the rotational viscosity, d is the cell thickness, and U is the applied voltage, U_F is the threshold voltage of Freedericksz effect. Moreover, the rise time for the colloid is less than for pure LC at all voltage.

Fig. 8 shows the dependences of the decay time of the pure LC and the colloid on the applied voltage. As can be seen, the decay time of the colloid is less than the pure LC at all voltages. In addition, the decay time starts to increase slightly after the voltage of 6 V.

According to [8], the decay time is determined as follows:

$$t_{off} = \frac{\gamma_1 d^2}{\pi^2 K_{11}}$$

If we assume that this expression is true for a colloid then we can estimate the change in viscosity with the additive of SWCNTs. In particular, using the numerical values of the decay times and elastic constants at the applied voltage of 4 V, one can find the ratio of viscosities which is equal to $\gamma_{1c} = 0.25\,\gamma_{1p}$, where γ_{1c} and γ_{1p} are the viscosities of the colloid and the pure LC, correspondingly. As can be seen, the viscosity decreases with the additive of SWCNTs into the liquid crystal. An increase in the decay time with voltage increasing may be associated with the occurrence of specific turbulence (fig. 9) in the colloid. In this case, the coupling between LC molecules and SWCNTs is violated. As a result, SWCNTs inhibit the relaxation of molecules to their initial state.
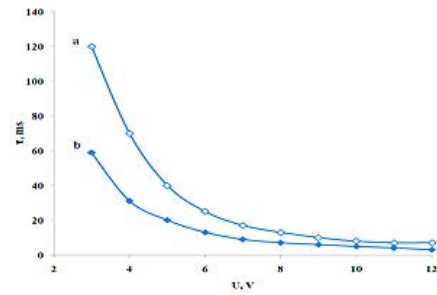

Fig. 7. Voltage dependence of the rise time of the Freedericksz effect: (a) the pure 5CB, (b) the colloid.
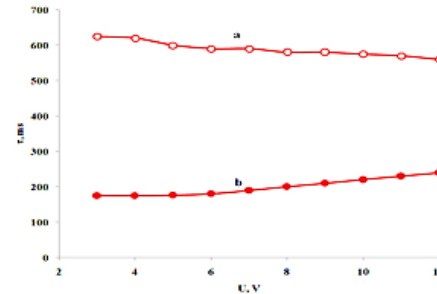

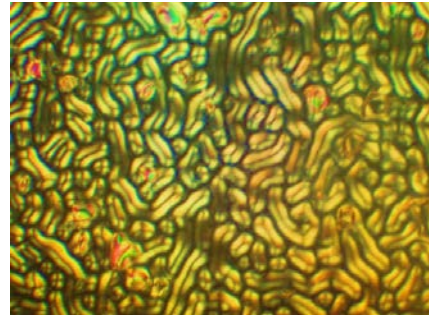*Fig. 8.* Voltage dependence of the decay time of the Freedericksz effect: (a) the pure 5CB, (b) the colloid.

Fig. 9. The image under polarization microscope at the application of voltage of 6 V to the cell with the colloid.

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