

## Dielectric and conductivity properties of liquid crystal MBBA doped with single-walled carbon nanotubes

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### Abstract

The effect of single-walled carbon nanotubes (SWCNTs) on the dielectric and conductivity properties of nematic liquid crystal 4-methoxybenzylidene-4'-butylaniline (MBBA) has been studied. It was shown that the additive of SWCNTs with concentration of 0.3% leads to an increase in the order parameter of MBBA. Observation under the polarization microscope has shown that the presence of SWCNTs in MBBA increases the clearing temperature from 46.3°C to 47.4°C. This change can be explained by the improvement of the liquid crystalline orientation order. As a result, the transition to a complete disordering of the molecules (transition to an isotropic state) requires more heat energy, correspondingly, more temperature. The dielectric and conductivity measurements have showed that the longitudinal component of the dielectric permittivity decreases while the transverse component increases as well as dielectric anisotropy. The percolation effect promotes to the dominance of hopping electron conductivity over ionic conductivity, leading to an increase in electric conductivity.

**Keywords:** nematic liquid crystal, carbon nanotubes, order parameter, dielectric permittivity, electric conductivity.

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### 1. Introduction

Single-walled carbon nanotubes (SWCNTs) have a rod-like structure with a diameter comparable to cross-section of molecules of nematic liquid crystal (LC). The presence of SWCNTs enhances the orientation order of nematic LC molecules and improves the display parameters. [1–4] It was shown in [4–7] that the inclusion of SWCNTs in nematic LC with positive dielectric anisotropy increases the clearing temperature and dielectric anisotropy. In this case, the threshold voltage of Fredericisz effect decreases at tiny amount (0.01–0.02 wt. %) of SWCNTs [4–6]. Differential scanning calorimetry and temperature-dependent dielectric studies suggest a decrease in the clearing temperature of nematic liquid crystal 4-pentyl-4'-cyanobiphenyl doped with SWCNT at the concentration of 0.02 and 0.05 wt%. as compared to the pure material [7-8]. In this case, electric conductivity increases by two orders of magnitude. A significant enhancement in the dielectric anisotropy and conductivity of SWCNTs doped nematic liquid crystal 4-ethoxybenzylidene 4'-butylaniline with negative dielectric anisotropy at concentration of 0.01 and 0.02 wt.% was observed in the work. [9] Influence of SWCNTs on the reentrant phenomenon in LCs has been studied in the work. [10] It was shown that the inclusion of SWCNTs into nematic material at concentration of 0.5 wt.% not only induces the layered smectic A mesophase but also leads to the nematic-

smectic-nematic reentrant sequence. It was shown in [11] that the inclusion of SWCNTs significantly affects on the dielectric parameters in the chiral smectic C phase with an inversion of the effect near the transition to the chiral smectic A phase. The enhancement of the electrical conductivity and the change of the dielectric anisotropy in the SWCNT doped ferroelectric LC were observed in [12]. Results are explained by the aligning effect of cholesteric liquid crystal system. Under high electric field, highly concentrated SWCNT doped ferroelectric LC shows enormously large values of dielectric loss [13]. Authors of the work [14] showed that continuous network of SWCNTs is formed in the LC colloid at concentrations between 0.02 and 0.2 wt %, which is characterized by a strong increase of electric conductivity and called the percolation effect.

The aim of present work is investigation of the effect of SWCNTs at concentration corresponding to percolation phenomenon on the dielectric and conductivity properties of nematic liquid crystal 4-methoxybenzylidene-4'-butylaniline.

## 2. Experiments

Nematic liquid crystal 4-methoxybenzylidene-4'-butylaniline (MBBA) from the firm Merck with negative dielectric anisotropy was used as a matrix. The single-walled carbon nanotubes (US, Research Nanomaterials, In.) were added into the liquid crystal with concentration of 0.3 wt. %. Then obtained mixture was shaken in a vortex mixer for 1 hour at temperature 55.0°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 surfactant (polysiloxane) was used for obtaining of homeotropic orientation of LC molecules. The cell thickness was fixed with calibrated 20  $\mu$ m 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. The Carl Zeiss polarization microscope (model 720, Germany) was used for registration of phase transition.

Dielectric and conductivity measurements were carried out by the Precision LCR Meter 1920 (IET Labs. Inc., USA) over the frequency range of 20 Hz–1 MHz and at temperatures between 22.0°C–53.0°C. In such a case, applied voltage was 0.5 V for both LC molecular orientations. Electric capacity  $C$  and dissipation factor (the loss tangent)  $D$  were recorded by means of this device at different frequencies  $f$ . The magnitudes of dielectric permittivity  $\epsilon$  were defined as:

$$\epsilon = \frac{C}{C_0} \quad (1)$$

where  $C_0$  is electric capacity of the empty cell. The real  $\epsilon'$  and image  $\epsilon''$  parts of dielectric permittivity and electric conductance  $\sigma$  were calculated by the expressions:

$$\epsilon' = \frac{\epsilon}{\sqrt{1+D^2}} \quad (2)$$

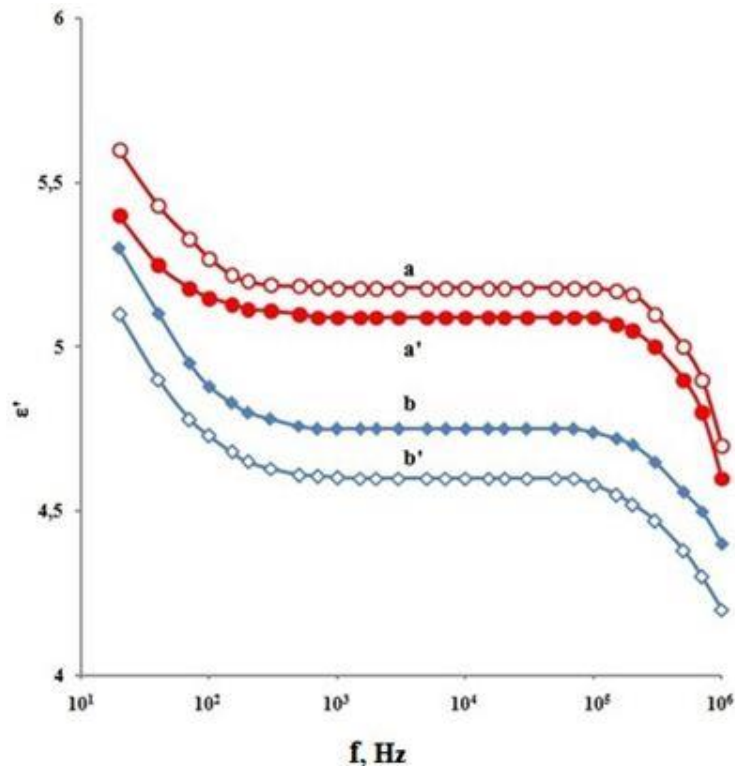
$$\epsilon'' = \epsilon'D \quad (3)$$

$$\sigma = 2\pi f \epsilon_0 \epsilon'' \quad (4)$$

### 3. Results and discussion

Observation under the polarization microscope has shown that the presence of SWCNTs in MBBA increases the clearing temperature from 46.3°C to 47.4°C. This change can be explained by the improvement of the LC orientation order [1]. As a result, the transition to a complete disordering of the molecules (transition to an isotropic state) requires more heat energy, correspondingly, more temperature.

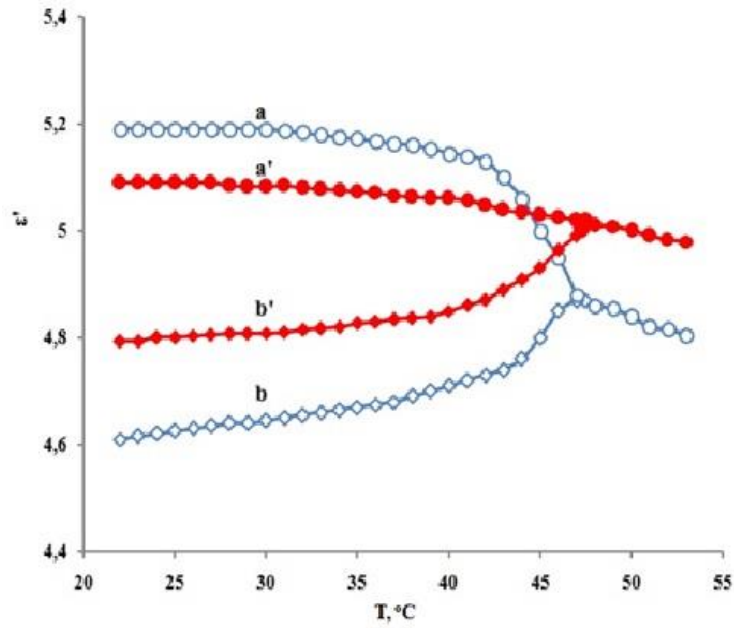
Figure 1 shows the frequency dependences of real  $\epsilon'$  part of dielectric permittivity of both the pure LC and the colloid for homeotropic and planar alignments at temperature of 24.0°C. There are three frequency ranges. At low frequencies, dielectric permittivity is associated with electronic exchange between electrodes and ions [15]. In the middle frequency region, the dielectric permittivity is minimally altered and connected with the bulk properties of the LC. Lastly, relaxation of the samples starts in the high-frequency range. The additive of SWCNTs decreases the longitudinal component of dielectric permittivity from 4.60 to 4.53 while it increases the transverse component from 5.19 to 5.33 at the frequency of 2 kHz. As a result, the dielectric anisotropy changes from 0.59 to 0.80 at temperature 24.0°C.



**Figure 1.** Frequency dependence of components of dielectric permittivity at temperature 24.0°C: (a) the longitudinal component of the pure LC, (a') the longitudinal component of the colloid, (b) the transverse component of the pure LC, (b') the transverse component of the colloid

Figure 2 shows the temperature dependences of dielectric permittivity of the pure LC and the colloid at the frequency of 2 kHz.

As is obvious, the longitudinal component of dielectric permittivity of the colloid is less and the transverse component is more than the corresponding values of the pure LC at all temperatures. The longitudinal and transverse components of the dielectric permittivity of the pure LC are equalized at temperature 46.3°C while they coincide above 47.4°C for the colloid. Therefore, transitions from nematic to isotropic phases in these samples take place at indicated temperatures. These facts are aligned with observations under the polarization microscope. It should be noted that the values of dielectric parameters of the pure MBBA are in good agreement with the literature data [16–17].



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

According to [18] components of dielectric permittivity and dielectric anisotropy can be presented in the form:

$$\varepsilon'_{||} = 1 + \frac{NHF}{\varepsilon_0} \left\{ \gamma_{av} + \frac{2}{3} S \Delta\gamma + F \frac{p_e^2}{3k_B T} \left[ 1 - (1 - 3 \cos^2 \beta) S \right] \right\} \quad (5)$$

$$\varepsilon'_{\perp} = 1 + \frac{NHF}{\varepsilon_0} \left\{ \gamma_{av} - \frac{1}{3} S \Delta\gamma + F \frac{p_e^2}{3k_B T} \left[ 1 + \frac{1}{2} (1 - 3 \cos^2 \beta) S \right] \right\} \quad (6)$$

whence we obtain:

$$\Delta \varepsilon' = \frac{NHF}{\varepsilon_0} \left[ \Delta\gamma - F \frac{p_e^2}{2k_B T} (1 - 3 \cos^2 \beta) \right] S \quad (7)$$

where F is reaction field factor, H is the cavity form factor,  $\gamma_{av} = (\gamma_{||} + 2\gamma_{\perp})/3$  is the average value of polarizability of LC molecules,  $\Delta\gamma = \gamma_{||} - \gamma_{\perp}$  is the anisotropy of polarizability, N is the number of LC molecules per unit volume, S is the order parameter,  $\beta$  is an angle between the point molecular dipole  $\mu$  and the axis of maximum molecular polarizability,  $\varepsilon_0$  is dielectric permittivity of vacuum,  $k_B$  is Boltzmann constant,  $T$  is Kelvin temperature. For liquid crystal with negative dielectric anisotropy, the expressions (5–7) may be transformed as:

$$\varepsilon'_{||} = 1 + \frac{NHF}{\varepsilon_0} \left\{ \gamma_{av} + \frac{2}{3} S \Delta\gamma + F \frac{p_e^2}{3k_B T} \left[ 1 - \frac{1}{4} S \right] \right\} \quad (8)$$

$$\varepsilon'_{\perp} = 1 + \frac{NHF}{\varepsilon_0} \left\{ \gamma_{av} - \frac{1}{3} S \Delta\gamma + F \frac{p_e^2}{3k_B T} \left[ 1 + \frac{1}{8} S \right] \right\} \quad (9)$$

and

$$\Delta \varepsilon' = \frac{NHF}{\varepsilon_0} \left[ \Delta\gamma - F \frac{p_e^2}{8k_B T} \right] S \quad (10)$$

Let us denote by  $\Delta S = S - S_0$ , where  $S_0$  is the order parameter of the pure liquid crystal,  $S$  is the order parameter of the colloid. Elementary transformations lead to the following expressions:

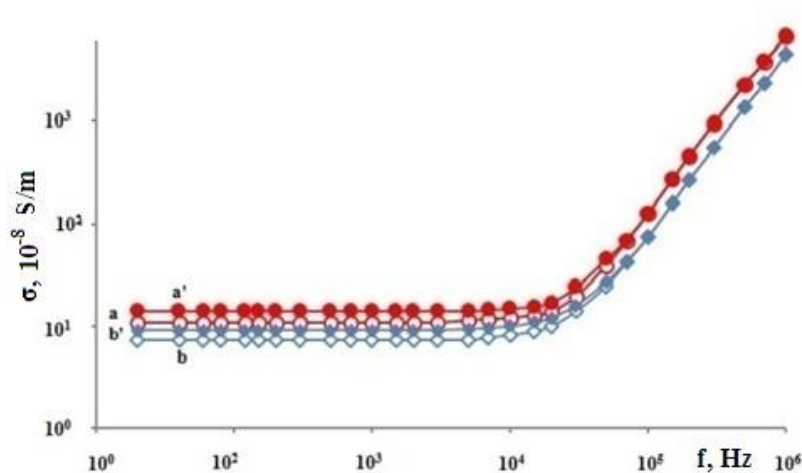
$$\Delta \varepsilon'_{||} = \frac{2NHF}{3\varepsilon_0} \left[ \Delta\gamma - F \frac{p_e^2}{8k_B T} \right] \Delta S \quad (11)$$

$$\Delta \varepsilon'_{\perp} = -\frac{NHF}{3\varepsilon_0} \left[ \Delta\gamma - F \frac{p_e^2}{8k_B T} \right] \Delta S \quad (12)$$

where  $\Delta \varepsilon'_{||}$  is the change of the longitudinal component of the real part of dielectric anisotropy at nanotubes addition,  $\Delta \varepsilon'_{\perp}$  is the change of the transverse component of the real part of dielectric permittivity at nanotubes addition,  $\Delta S$  is the change of the order parameter at addition of nanotubes.

The number of LC molecules per unit volume  $N$  decreases insignificantly because of littleness of the concentration of SWCNTs in LC. As to the order parameter  $S$ , there is strong change in its magnitude. As noted above, SWCNTs in nematic LC cause the effective orientational coupling with LC molecules. The charges transfer from LC molecules to the particles and they are distributed asymmetrically on the SWCNTs inducing a permanent dipole moment on them. [19-20] As a result, SWCNTs are oriented parallel to the LC director enhancing the orientation order  $S$  and, correspondingly,  $\Delta S$  has positive value. Moreover, the expression in parentheses has also a positive value for liquid crystal MBBA. [20] Therefore, according to concerned expressions, the longitudinal component of dielectric permittivity decreases while the transverse component increases as well as the absolute value of dielectric anisotropy. This reasoning is correlated with the experiment.

Frequency dependences of specific conductance for the pure LC and the colloid at temperature 24.0°C are presented in Figure 3.

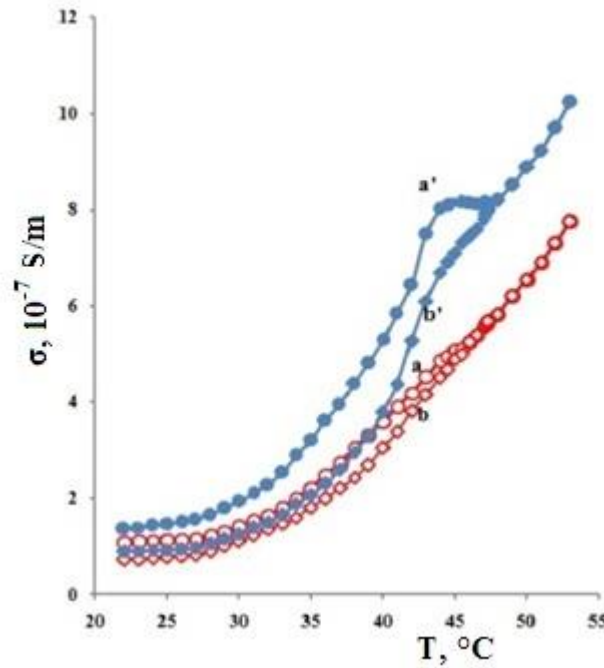


**Figure 3.** Frequency dependence of specific conductance at temperature 24.0°C: (a) the longitudinal component of the pure LC, (a') the longitudinal component of the colloid, (b) the transverse component of the pure LC, (b') the transverse component of the colloid.

As seen from this figure, the longitudinal component is more than the transverse one in the pure LC and the colloid at low and middle frequencies. This is due to that it is easier for

charges to move along the long axes of LC molecules. Wherein, nanotubes enhance the conductivity of both components. Obviously, there is percolation effect in the colloid. In this case, the hopping electronic conductivity dominates over the ionic one. An increase in the conductivity for both the pure LC and the colloid at high frequencies is associated with a noticeable contribution of the bias current. In this case, molecular dipoles follow the electric field with some lag. There is the inhibition of the rotation of these dipoles in an alternating field.

The temperature dependences of specific conductance for the pure LC and the colloids at the frequency of 2 kHz are presented in Figure 4.



**Figure 4.** Temperature dependences of specific conductance at the frequency 2 kHz: (a) the longitudinal component of the pure LC, (a0) the longitudinal component of the colloid, (b) the transverse component of the pure LC, (b0) the transverse component of the colloid.

As can be seen, the conductivity of the colloid is more than that of the pure liquid crystal at all temperatures. The conductivity of both samples increases with increasing temperature, which is associated with a decrease in viscosity. In this case, the equalization of the transverse and longitudinal components of the conductivity of the pure LC occurs at temperature of 46.3°C while it takes place at temperature of 47.4°C for the colloid. These facts agree with the data of observations under polarizing microscope as well as the temperature dependence of the components of the dielectric permittivity.

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  $\sigma_0$  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 the carrier must overcome to move inside a liquid crystalline medium. The larger the  $E$ , the harder the charge carriers move within the LC layer and, accordingly, the lower the conductivity. From the last expression (12), it is possible to find the activation energy of the pure LC and the colloid along the director as well as across the director. The activation energy along the long axis of the molecules of pure MBBA is 32.7 kJ/mol, whereas it is 29.3 kJ/mol for the colloid. The

activation energy perpendicular to the axis of the molecules is 41.4 kJ/mol for pure LC and 37.4 kJ/mol for colloid. The addition of nanotubes to MBBA also lowers the activation energy in the isotropic phase from 20.3 kJ/mol to 19.7 kJ/mol. Apparently, the decrease in activation energy is due to the increase in the conductivity of MBBA upon nanotube addition.

#### 4. Conclusion

The inclusion of silver nanotubes into the liquid crystal 4-methoxybenzylidene-4'-butylaniline leads to the increase of the order parameter at which the temperature of the nematic-isotropic transition increases. As a result, the longitudinal component of the dielectric permittivity decreases while the transverse component and absolute value of dielectric anisotropy increase. Electron hopping conductivity dominates over the ionic conductivity because of the percolation effect. As a result, electric conductivity increases.

#### References

1. D. Singh, U. Bahadur, S.M. Bhushan, R. Dabrowski, R. Dhar, *Materials Letters* **216** (2018) 5.
2. M.D. Lynch, D.L. Patrick, *Nano Letters* **2**(11) (2002) 1197.
3. K.A. Park, S.M. Lee, S.H. Lee, Y.H. Lee, *Journal of Physical Chemistry C* **111**(4) (2007) 1620.
4. D. Singh, U.B. Singh, M.B. Pandey, R. Dabrowski, R. Dhar, *Optical Materials* **84** (2018) 16.
5. L. Dolgov, O. Kovalchuk, N. Lebovka, S. Tomylo, & O. Yaroshchuk, *Carbon Nanotubes* (2010).
6. D. Singh, U.B. Singh, M.B. Pandey, R. Dhar, *Liquid Crystals* **46**(9) (2019) 1389.
7. R. Verma, M. Mishra, R. Dhar, R. Dabrowski, *Liquid Crystals* **44**(3) (2017) 544.
8. R. Verma, M. Mishra, R. Dhar, R. Dabrowski, *Journal of Molecular Liquids* **221** (2016) 190.
9. T. Vimal, S. Pandey, S.K. Gupta, D.P. Singh, R. Manohar, *Journal of Molecular Liquids* **204** (2015) 21.
10. G.V. Varshini, D.S. Shankar Rao, P.K. Mukherjee, S.K. Prasad, *The Journal of Physical Chemistry B* **122**(47) (2018) 10774.
11. N. Sood, S. Khosla, D. Singh, S.S. Bawa, *Liquid Crystals* **39**(10) (2012) 1169.
12. O. Köysal, *Synthetic Metals* **160**(9) (2010) 1097.
13. S.K. Gupta, A. Kumar, A.K. Srivastava, R. Manohar, *Journal of Non-Crystalline Solids* **357**(7) (2011) 1822.
14. V.V. Ponevchinsky, A.I. Goncharuk, V.I. Vasil'ev, N.I. Lebovka, M.S. Soskin, *JETP Letters* **91**(5) (2010) 241.
15. H.-Y. Chen, W. Lee, *Applied Physics Letters* **88**(22) (2006) 222105–222105-3.
16. V.K. Agarwal, A.H. Price, *Journal of Chemical Society, Faraday Transactions 2* **70**(0) (1974) 188.
17. P.K. Tripathi, M. Pande, S. Singh, *Applied Physics A* **122**(9) (2016) 847-1.
18. W. Maier, G. Meier, *Zeitschrift für Naturforschung A* **16**(3) (1961) 262.
19. S.V. Burylov, Y.L. Raikher, *Physical Review E*. **50** (1994) 358.
20. N.R. Jber, A.A. Rashad, M.S. Shihab, *Journal of Molecular Structure* **1043** (2013) 28.