DIELECTRIC RELAXATION IN THE COLLOID FULLERENES - LIQUID CRYSTAL 5CB

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Influence of fullerenes C_{60} on dielectric properties of liquid crystal 5CB is investigated. It is shown that at additive of fullerenes the components of the dielectric permittivity decrease, and the longitudinal component decreases by greater extent than its transverse component. The dielectric anisotropy also decreases. The dielectric absorption is shifted to low frequencies. The experimental results are explained by the Maier- Meier theory for anisotropic liquids.

1. INTRODUCTION

The progress of nanotechnology has leaded to the idea to combine the properties of nanoparticles with peculiarities of optic effects in liquid crystals (LC). Additive of nanoparticles into LC can essentially change its properties as they are distributed between LC molecules at low concentration. Fullerenes have a spherical shape and definitive dimension about 1nm. The injection of fullerenes into LC leads to the structurization and self-organization of the system [1].

Currently, there is a small number of works devoted to liquid crystalline colloids based on pristine fullerenes. Particularly, influence of bias voltage on the liquid crystalline colloid based on pure fullerenes is investigated in work [2]. Results of influence of laser radiation on electro-optic properties of similar colloids are presented in the work [3]. Determination of phase transition from nematic to isotropic state in fullerenes-doped nematic liquid crystal E7 from temperature dependence of conductivity and dielectric parameters was carried out in work [4].

The aim of present work is the study of influence of fullerenes C_{60} on dielectric properties of the nematic liquid crystal 4-cyano-4'-pentylbiphenyl.

2. EXPERIMENTAL

We used nematic liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) with positive dielectric anisotropy as a matrix. 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 45°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. 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 measurements were carried out by the Precision LCR Meter 1920 (IET Labs. Inc., USA) in the frequency range of 100 Hz –1 MHz and at temperatures between 22°C–60°C. In this case, applied voltage was 0.2 V for planar LC molecular orientation while we carried out the measurements for homeotropic LC orientation using the applied voltage 1 V.

3. RESULTS AND DISCUSSION

According to [5], particles do not disturb the director field of a LC if the anchoring parameter ζ =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/m², 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 does not appear 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.

Observation under polarisation microscope has shown that the clearing temperature decreases from 35.2°C to 34.1°C. Spherical particles of fullerenes infiltrate between LC molecules reducing interaction in between. At this case, there is disordering of LC directions. As a result, temperature of transition from isotropic to nematic phase decreases according to expression [6]:

$$T_c = (1\text{-}f_o) \, T_p$$

where f_o is volume concentration of particles, T_p and T_c are clearing temperatures of the 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 homeotropic and planar configurations and temperature 23^0C are presented in fig. 1 and fig. 2.

As one can see, both components of dielectric permittivity decreases at the additive of fullerenes.

Particularly, ε_{II}' changes from 19.54 to 16.99 while $\varepsilon_{\perp}'$ reduces from 6.48 to 5.10 in the middle frequency region. As a result, dielectric anisotropy changes from 13.06 up to 11.89. A presence of fullerenes also decreases the value ε''. In addition, a peak of dielectric absorption is observed (the maximum value of ε'') at homeotropic configuration of the sample. At this case, the additive of fullerenes shifts a maximum of dielectric absorption from 590 kHz to 230 kHz at 23°C.
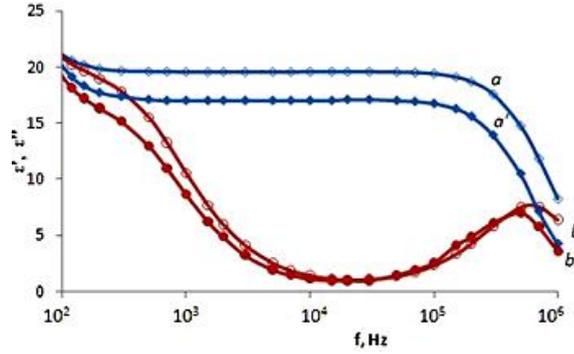
Fig. 1. Frequency dependence of the real ε' and imaginary ε'' parts of the dielectric permittivity at the homeotropic configuration: (a) ε' of pure 5 CB, (a ') ε' of the colloid, (b) ε'' of the pure 5 CB, (b ') ε'' of the colloid.
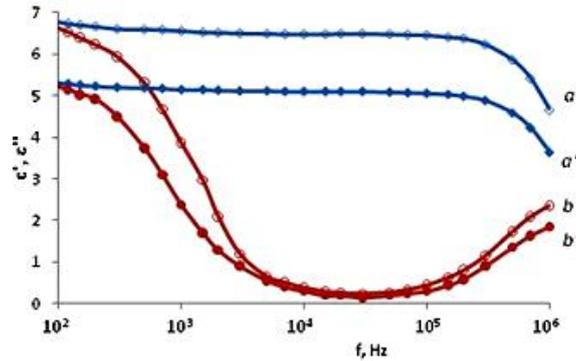
Fig. 2. Frequency dependence of the real ε'and imaginary ε'' parts of the dielectric permittivity at the homeotropic configuration: (a) ε' of pure 5 CB, (a ') ε' of the colloid, (b) ε'' of the pure 5 CB, (b ') ε'' of the colloid.

The observed experimental facts can be explained by the Maier-Meier theory for anisotropic liquids, according to which the expression for both components of the dielectric permittivity are defined as follows [7]:

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

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

Dielectric anisotropy is the difference of these quantities:

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

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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. 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 slightly. A different matter the order parameter S which is defined as follows:

$$S = \frac{1}{2}(3\langle\cos\theta\rangle - 1)$$

The embedded particles increase the instantaneous angle θ between the individual molecules and the preferred direction of the molecules (director). In this regard, the order parameter is significantly reduced. The second term in the curly brackets of the expressions for components of dielectric permittivity containing the order parameter has opposite sign. As a result, the longitudinal component decreases more strongly than its transverse component at the presence of fullerenes. Moreover, the anisotropy of the dielectric permittivity $\Delta\varepsilon'$ is directly proportional to the order parameter S and the number of molecules N per unit volume. Hereat, it also decreases. It is consistent with our experimental data.

Fig. 3 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 LC at all temperatures. The frequency of the dielectric absorption peak of the pure LC varies from 590 kHz (23°C) to 750 kHz (30°C) while it increases from 230 kHz (23°C) to 650 kHz (30°C) for the colloid.

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 fullerenes increases the relaxation time from $2.7\cdot10^{-7}$ to $7.3\cdot10^{-7}$ s at 23°C and from $2.4\cdot10^{-7}$ sec to $6.9\cdot10^{-7}$ sec at 30°C. Obviously, the increase in the relaxation time connects to the originated obstacles to the flip-flop motion of LC molecules. 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.
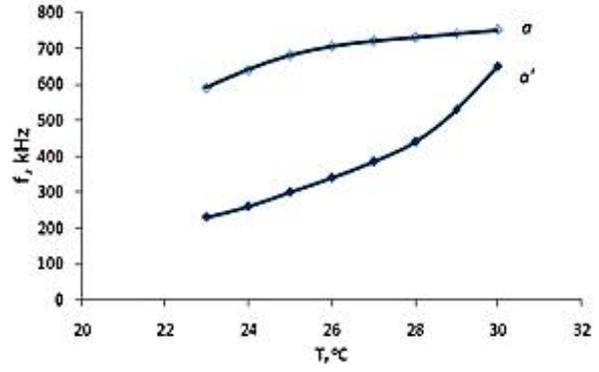
Fig. 3. Temperature dependence of the frequency of a local maximun of ε'': (a) the pure 5 CB, (a') the colloid.
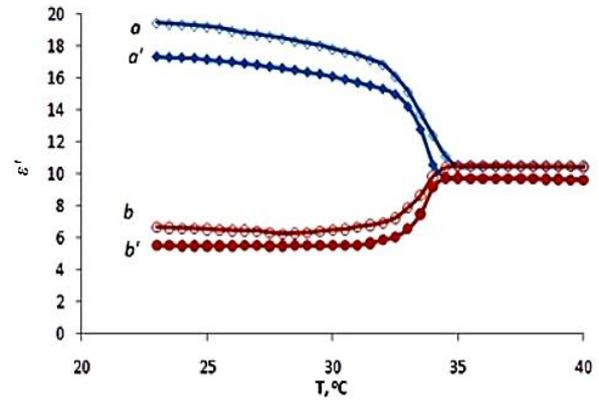
Fig. 4. Temperature dependence of the longitudinal and transverse components of the dielectric permittivity at the frequency of 10 kHz: (a) ε_{II}' of the pure 5CB, (a') ε_{II}' of the colloid, (b) $\varepsilon_\perp'$ of the pure 5CB, (b') $\varepsilon_\perp'$ of the colloid.

The temperature dependence of the parallel and perpendicular components of the dielectric permittivity of both the pure LC and the colloid at frequency of 10 kHz is shown in fig. 4.

As can be seen, the longitudinal component of the dielectric permittivity of the pure LC decreases from 19.48 (23°C) to 13.81 (34°C) while the transverse component changes from 6.68 (23°C) to 10.60 (34°C).

The dielectric permittivity of the colloid is shifted to lower values at all temperatures. In this case, the longitudinal component of the dielectric permittivity of the colloid decreases from 17.35 (23°C) to 10.60 (34°C). The transverse component increases from 5.53 (23°C) to 9.18 (34°C). In the isotropic phase, the dielectric permittivity slightly decreases from 10.53 (36°C) to 10.47 (40°C). In the fourth term, the dependence of the longitudinal and transverse components of the dielectric permittivity in the Maier-Meier equations also includes the temperature of the sample. With increasing temperature, the values of these quantities decrease. It agrees with the experiment.

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