INFLUENCE OF FULLERENES ON DIELECTRIC AND CONDUCTIVITY PROPERTIES OF LIQUID CRYSTAL MBBA

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Influence of fullerenes C^{60} on dielectric and conductivity properties of liquid crystal MBBA has been investigated. It has been revealed that dielectric permittivity, dielectric losses and conductivity decrease in the frequency range of 20 Hz-1MHz at addition of fullerenes in liquid crystal. The activation energy has been defined from the temperature dependence of conductivity for both the pure liquid crystal and the colloid. It is established that the additive of fullerenes reduces the activation energy in both nematic and isotropic phases. Experimental results are explained by reduction of an order parameter and suppression of ionic conductivity at presence of fullerenes.

Key words: liquid crystal, MBBA, fullerenes, dielectric permittivity, electric conductivity
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1. INTRODUCTION

More recently, an alternative direction of physics and technology of liquid crystals (LC) has been the creation of hybrid liquid crystal systems and their application in various photonic devices. At this case a special role plays liquid crystal colloids. Herewith, not only properties of the liquid crystal are improved, but there are novel effects. Even at enough large sizes of particles the effect of an operated filtration and selective modulation of light [1-13] is observed. At the particle sizes of 100-600 nm, the electro-optical properties of liquid crystal are improved [14-32], and also generation of the second optical harmonic is observed in ferroelectric liquid crystal colloids [33]. Logically, to assume that there can be new effects when the particles sizes are very small. In particular, such particles may be fullerenes which are nanoparticles and have spherical form.

In the present work the results of investigation of influence of fullerenes on dielectric and conductive properties of nematic liquid crystal 4-methoxybenzilidene – 4’ – butylaniline (MBBA) are presented.

2. EXPERIMENTAL

We used the nematic liquid crystal 4-methoxybenzilidene – 4' – butylaniline (MBBA) (NIOPIK, Russia) as a matrix having negative anisotropy of dielectric permittivity. The fullerenes C^{60} (U.S. Research Nanomaterials, In.) was added into the liquid crystal with 0.5 wt.% and was shaken in a vortex mixer for 1 hour, followed by sonica3tion 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. The thin polyamide film rubbed in one direction was used for the planar orientation of LC molecules while a small amount of lecithin was added in the colloid and the pure LC for the homeotropic configuration. The cell thickness was fixed with calibrated 50 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 filled cell was kept in the special heater in which the copper-constantan thermocouple was used for temperature measurements. 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 18°C – 60°C.

3. RESULTS

Observation under the polarization microscope has shown that the presence of fullerenes in MBBA shifts the clearing point from 42.2°C to 41.6°C. It is necessary to notice that the clearing temperature increases and reaches 47 °C at keeping of the pure LC in vacuum for 6 days.

Fig. 1 and Fig. 2 show frequency dependences of real ε' and imaginary ε'' parts of dielectric permittivity in both the pure LC and the corresponding colloid in homeotropic and planar configurations, accordingly, at temperature 23□C. Apparently, the longitudinal component ε_{II}' of dielectric permittivity of the pure LC varies a little up to 150 kHz and it is equal to 4.72 at frequency of 10 kHz while it makes 4.12 in the colloid. The transverse component $\varepsilon_{\perp}'$ of dielectric permittivity in the pure LC is equal 5,22 at 10 kHz and remains almost invariable up to the highest frequencies while it makes 5.11 in the colloid at the same frequency. Namely, the real part of dielectric permittivity decreases in both cases at additive of fullerenes. Hereat, the parallel component decreases more than perpendicular component. The additive of particles also reduces an imaginary part of dielectric permittivity in both configurations.

Temperature dependence of parallel and perpendicular components of dielectric permittivity of both the pure MBBA and the colloid is resulted in Fig.3. As one can see, longitudinal component of dielectric permittivity of the pure LC increases from 4.72 (23□C) to 5.07 (41□C) while the transverse component changes from 5.22 to 5.07 at the same temperatures. As increasing temperature it decreases in the isotropic phase and reaches 4.99 at 49□C. Longitudinal component of dielectric permittivity

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of the colloid decreases from 4.12 (23°C) to 4.02 (41°C) then it increases up to 4.06 (49°C) in the isotropic phase. The transverse component decreases from 5.11 at 23□C to 4.06 near to transition in the isotropic state, then dielectric permittivity decreases and reaches 3.97 at 49□C.

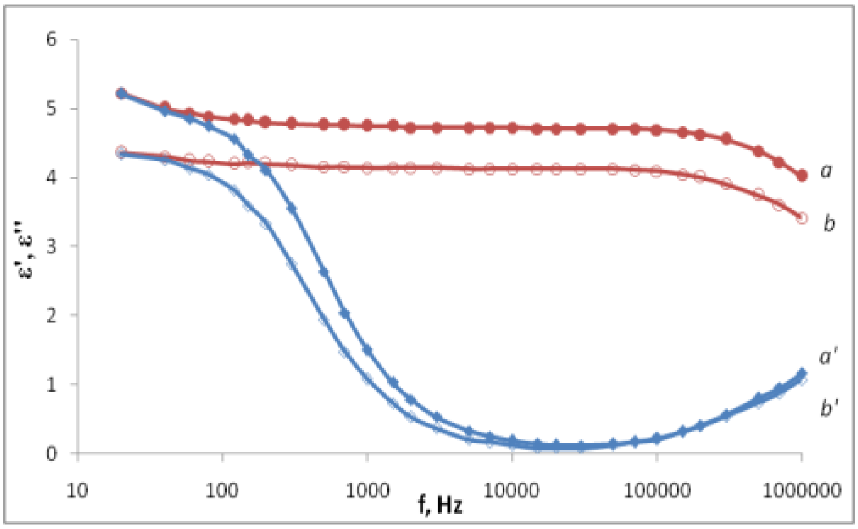

Fig.1. Frequency dependence of longitudinal components of dielectric permittivity and losses of the pure LC and the colloid: (a) ε' of LC; (b) ε' of the colloid; (a') ε'' of LC; (b') ε'' of the colloid.

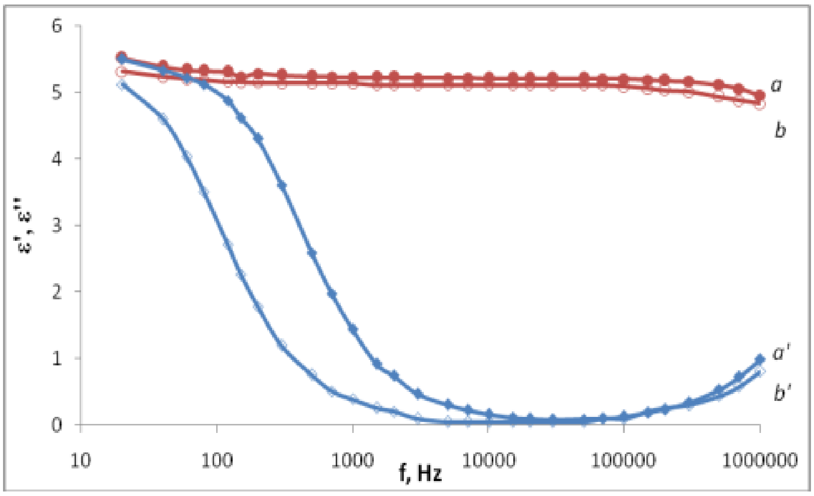

Fig.2. Frequency dependence of transverse components of dielectric permittivity and losses of the pure LC and the colloid: (a) ε' of LC; (b) ε' of the colloid; (a') ε'' of LC; (b') ε'' of the colloid.

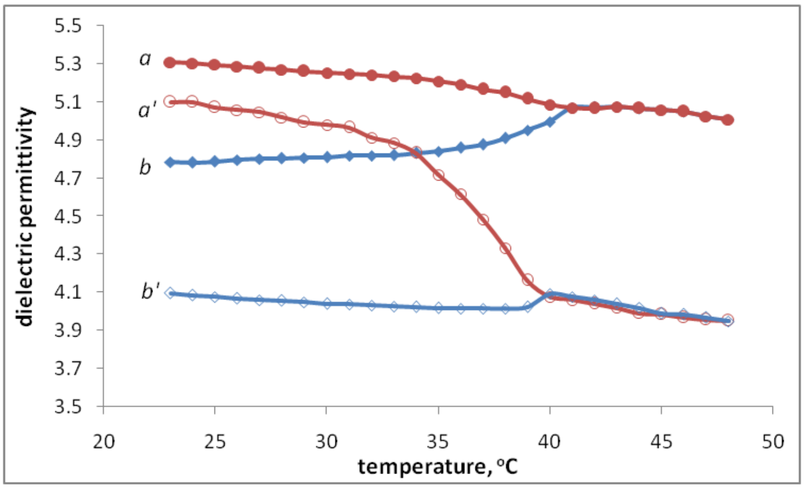

Fig.3. Temperature dependence of dielectric permittivity components of the pure LC and the colloid: (a) $\varepsilon_{\perp}'$ of LC; (b) ε_{II}' of LC; (a'); $\varepsilon_{\perp}'$ of the colloid; (b') ε_{II}' of the colloid.

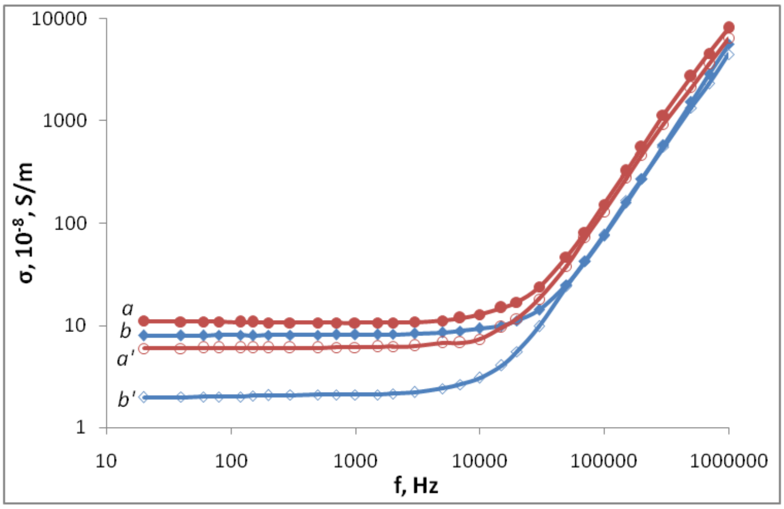

Fig.4. Frequency dependence of components of electric conductivity of the pure LC and the colloid: (a) σ_{II} of LC; (b) $\sigma_{\perp}$of LC; (a') σ_{II} of the colloid; (b') $\sigma_{\perp}$ of the colloid.

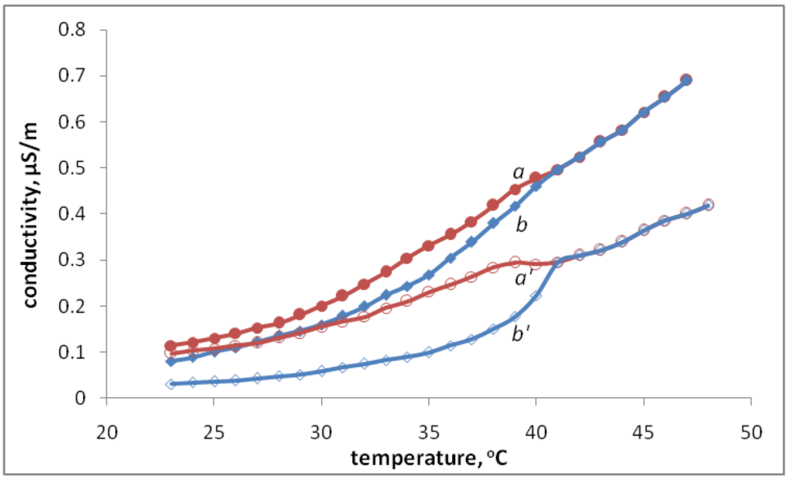

Fig.5. Temperature dependence of electric conductivity components of the pure LC and the colloid: (a) σ_{II} of LC; (b) $\sigma_{\perp}$of LC; (a') σ_{II} of the colloid; (b') $\sigma_{\perp}$ of the colloid.

The frequency dependences of conductivity of both the pure LC and the colloid at temperature 23C are presented in Fig.4. One can see, parallel component of the pure MBBA conductivity varies a little up to 10 kHz and equal to $1.1\cdot10^{-7}$ S/m, then it rises drastically and makes $6.5\cdot10^{-5}$ S/m at 1 MHz. At the additive of fullerenes conductivity remains almost unchanged and equal to $6.0\cdot10^{-8}$ S/m then it increases and also reaches $6.5\cdot10^{-5}$ S/m at 1 MHz. The transverse component makes $8.0\cdot10^{-8}$ S/m at low frequencies then also sharply increases after 10 kHz and reaches $4.5\cdot10^{-5}$ S/m at 1 MHz. The frequency dependence of conductivity has similar character at additive of fullerenes. But conductivity equals to $2.0\cdot10^{-8}$ S/m at low frequencies and it has the same value as well as for the pure LC. Therefore, values of conductivity of the colloid lower than for MBBA at low frequencies while it coincide for certain directions concerning the director. In addition, conductivity along the director is above than across.

An increase in temperature results to increasing of conductivity in both pure MBBA and the colloid (Fig.5). The parallel component of conductivity of MBBA rises from $1.3\cdot10^{-7}$ S/m (23°C) to $4.8\cdot10^{-7}$ S/m near the clearing point on the frequency of 10 kHz. The transverse component of conductivity varies from $1.1\cdot10^{-7}$ S/m to $4.8\cdot10^{-7}$ S/m at the same frequencies and temperatures. Then it increases up to $7.7\cdot10^{-7}$ S/m at 49°C in the isotropic phase. The parallel component of conductivity of the colloid increases from $9.5\cdot10^{-8}$ S/m (23°C) to $2.9\cdot10^{-7}$ S/m (40°C) while the transverse component does from $3.0\cdot10^{-8}$ S/m to $2.8\cdot10^{-7}$ S/m (40°C). In the isotropic state, it increases up to $4.0\cdot10^{-7}$ S/m at 49°C.

4. **DISCUSSION**

According to [34], particles do not disturb the director field of 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 a particle size and K is the LC average elastic constant. The value of anchoring energy is within 10^{-5} – 10^{-6} J/m^2, the elastic constant of LC has an order of 10^{-12} N, and the particles (fullerenes) have sizes of 0.6-0.7 nm. Simple calculations show that ζ has an order within 10^{-2}-10^{-3}, in other words, such colloid has to behave as a pure liquid crystal but with modified properties.

According to [35] embedded particles abate interaction between LC molecules. At this case, for the spherical form and low concentration of isotropic particles, the clearing temperature T_c of a colloid is defined by the expression:

$$T_c = (1- f)\, T_o$$

where f is the volume fraction of particles, T_0 is the clearing temperature of the pure LC. The fullerene particles are isotropic and have spherical form. Their volume fraction equals to 0.003. The simple calculations give the values of 42.0°C which are higher than the experimental data but they agree qualitatively with them.

Experiments have shown that the real part both parallel and perpendicular components of dielectric permittivity at addition of fullerenes decreases. In this case the longitudinal component ε_{II} decreases by 0.58 while the transverse component $\varepsilon_{\perp}$ by 0.11. According to the Mayer-Meyer theory for dielectric permittivity of liquid crystal, ε_{II} and $\varepsilon_{\perp}$ depend on number N of LC molecules in single volume, and also on the order parameter S. Inclusion of fullerenes between LC molecules reduces their number per unit volume but negligible degree. The order parameter S also decreases as it depends on an angle between the directions of long axes of individual LC molecules with the general direction field of the nematic phase. Imbedded nanoparticles increase corresponding angles and, accordingly, reduce the order parameters. Thus, N and S act similarly, namely, both parameters reduce the longitudinal components ε_{II} of dielectric permittivity. While a decrease in N and S have diverse effect on ε_{II}. As a result, the value of the longitudinal component decreases in a greater degree than the value of its transverse component of dielectric permittivity.

Dielectric anisotropy *Δε* of the pure LC at temperature 23°C and middle frequencies equals -0.50 while it does -0,99 in the colloid. That is the dielectric anisotropy increases almost in 2 times, namely, 1.98 times at addition of fullerenes. It is obvious, the similar increase in dielectric anisotropy will strongly reduce threshold voltages of the Freedericksz effect and formation of Williams' domens.

As it has been noted earlier, an inclusion of fullerenes into the liquid crystalline matrix reduces its conductivity. It proves to be true also reduction of dielectric losses. It is obvious, that the reason of reduction of conductivity consists that fullerenes suppress the ionic conductivity in the LC. It, its turn, indicates on a decrease of critical frequency of disappearance of the Williams' domens.

Arrhenius low for conductivity is defined by following expression:

$$\sigma = Ae^{-\frac{E_a}{k_B T}}$$

where E_a is activation energy, k_B is the Boltzmann constant, T is absolute temperature, and A is the parameter connecting with properties of the medium. Using this expression it is possible to calculate the activation energy for pure LC and the colloid. The activation energy along the long axis of molecules of the pure MBBA is equal to 0.87 eV while it does 0.58 eV for the colloid. The activation energy perpendicular to the long axis of molecules makes 1.1 eV for the pure LC while it is equal to 0.71 eV for the colloid. The additive of fullerenes also decreases the activation energy in isotropic phase from 0.54 eV to 0.35 eV. Apparently, a decrease of the activation energy connects with decreasing of ionic conductivity.

5. CONCLUSIONS

It is shown that the additive of fullerenes C^{60} into the liquid crystal MBBA decreases dielectric permittivity and losses, electric conductivity, and also the activation energy of both nematic and isotropic phases of liquid crystal. Experimental results are explained by reduction of the order parameter and suppression of ionic conductivity at presence of fullerenes.

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