Saturation effect for dependence of the electrical conductivity of planar oriented nematic liquid crystal 6CB on the concentration of Cu_7PS_6 nanoparticles

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Abstract. The influence of Cu_7PS_6 nanoparticles with the average size 117 nm on the dielectric properties of planar oriented nematic liquid crystal 6CB has been investigated within the frequency range $10^1…10^6$ Hz and at the temperature 293 K. It has been shown that when changing the concentration of nanoparticles within the range 0 to 1 wt.%, the conductivity of the liquid crystal changes stronger than its dielectric permittivity. It has been shown that the electrical conductivity increases monotonously with increasing the concentration of nanoparticles. However, for this dependence a saturation effect is observed. The mechanism of this effect was proposed.

Keywords: nematic liquid crystal, superionic nanoparticles, electrical conductivity, dielectric properties, saturation effect.

1. Introduction

Nowadays, liquid crystals (LC) are mainly used for manufacturing the displays. The number of LC-based displays among the total number of displays of various types has already exceeded 80% and continues to grow. However, there are scientific forecasts that relatively soon liquid crystal displays can be replaced by organic electroluminescent displays. Such displays do not require backlighting, and it is technologically much easier to make them flexible. Therefore, an important scientific task is widening the functional capabilities of LC.

A promising method of expanding the functional possibilities of LC can be the use of different type nanoparticles. As it follows from the analysis of works [1-8], among these nanoparticles, the ferroelectric ones are the most promising for modification of the functional possibilities of LC. We believe that also nanoparticles of superionic conductors with a structure of argyrodite can significantly expand the functional properties of LC. Investigation of superionic conductors with the argyrodite structure has shown that they have a high electrical conductivity as well as ferroelectric and nonlinear optical properties [9, 10]. Therefore, it was

possible to predict that these properties will also be inherent to nanoparticles.

As we showed in [11], when conducting nanoparticles are available in the superionic conductor Cu_6PS_5I, the conductivity of the nematic liquid crystal 6CHBT increases. However, for a relatively small interval of changes in the concentration of nanoparticles (0.01 to 0.1 mg/ml), it was found that the concentration dependence of conductivity is a nonmonotonic function. To test whether this effect would be observed in liquid crystals other than 6CHBT, the task was to perform similar studies with a liquid crystal 6CB. The main difference between the liquid crystal 6CB and 6CHBT one lies in the value of the dipole moment. As follows from the table data, the value of the dipole moment of the 6CB molecules is greater than that for the 6CHBT molecules.

As shown in [12], changing the liquid crystal (from 6CHBT to 6CB) leads to a much greater influence of Cu_6PS_5I nanoparticles on the electrical conductivity. However, from coloring liquid crystal to green when the Cu_6PS_5I nanoparticles were introduced into the 6CB liquid crystal, it was concluded that in a more polar, than 6CHBT, 6CB liquid crystal some of the Cu_6PS_5I molecules dissociate. It is copper ions, as in the solution of copper sulfate, that were the main reason of the color of liquid crystal.

However, in order to still check how the type of liquid crystal affects the concentration dependence of conductivity, when introducing nanoparticles, it was logically to conduct studies with nanoparticles other than Cu_6PS_5I. For research, we used Cu_7PS_6 nanoparticles. According to the results of studies on Cu_7PS_6 single crystals, it was shown that the binding energy of copper atoms in Cu_7PS_6 is much larger than that in Cu_6PS_5I molecules, which made it possible to avoid dissociation of Cu_7PS_6 molecules in liquid crystal.

Therefore, the purpose of this work was to study the influence of Cu_7PS_6 nanoparticles on the dielectric properties of nematic LC 6CB, as well as to compare them with similar results of the effect of Cu_6PS_5I nanoparticles on 6CB. Our analysis of works on the properties of liquid crystals 6CB [13-15] without and with nanoparticles showed that the problem of this type was not considered before.

2. Materials and methods

A polar nematic liquid crystal belonging to the cyanobiphenyl family 4-cyano-4-n-hexylbiphenyl (6CB) (BDH Limited Poole England) was used. It is in the nematic phase between 14.5 and 29 °C.

The synthesis of Cu_7PS_6 compounds was performed from Cu, S, and P taken in accordance with the stoichiometry and placed in an evacuated ampoule of silica. The ampoule was heated at the rate 50 K/h to the temperature 673 ± 5 K and kept at this temperature for 24 h. Then, the temperature was increased to the value of 973 ± 5 K and the ampoule was kept at this temperature during 3 days. Further, the melting zone was heated up to 1380 ± 5 K that is by 50 K above the melting temperature with 24 h ageing. The ageing resulted in nucleation. The annealing of the formed seeds was performed for 48 h.

Cu_7PS_6 powders were milled with a planetary ball-mill (Fritsch Pulverisette 6). Cca. 2 g of powder was milled in a stainless steel vial of 80 ml volume using four stainless steel balls of 20 mm diameter in each run. The rotation speed was 400 rpm, and the milling atmosphere was 2 GPa Ar. The maximum milling time of the powder was 30 min.

6CB liquid crystals without/with Cu_7PS_6 nanoparticles were studied in a sandwich-type cell with transparent ITO electrodes. The electrodes were coated with an appropriately processed polymer layer to provide the planar orientation of the LC molecules. The concentration of nanoparticles of a near-spherical shape with the average size of 117 nm in the liquid crystal was 0.1, 0.5, 1 wt.%. The cell thickness was 10 μm. The LC cell was filled using the capillary method at a temperature by 5…10 K above the nematic-to-isotropic phase transition temperature.

The dielectric properties of the obtained sandwich cells were investigated within the frequency range $10…10^6$ Hz at the temperature 293 K using the oscilloscopic method [16]. The amplitude of the measuring signal of the sinusoidal shape was 0.2 V. Assuming that the equivalent scheme of the measuring cell is a parallel connected resistance and a capacitor, the values of the resistance R and the capacitance C of the samples at different frequencies were determined, and on the basis of these values and geometric cell sizes, the imaginary (ε'') and real (ε') components of the complex dielectric permittivity were determined. Using the value of the resistance R on the frequency dependence region, where the resistance did not depend on the frequency, the conductivity of the liquid crystal was determined.

3. Results and discussion

Fig. 1 shows the frequency dependences of ε' for planar oriented liquid crystal 6CB (*1*) and 6CB with the impurity of Cu_7PS_6 nanoparticles with the concentrations of 0.1 (*2*), 0.5 (*3*), 1 wt.% (*4*).

As follows from this figure, for the frequencies $f < 5 \cdot 10^2$ Hz and $f > 2 \cdot 10^5$ Hz, significant dependence of the value of ε' on the frequency is observed.

Previously, we showed that the low-frequency dispersion of dielectric permittivity is caused by electrode processes. As it was shown in [17], the relaxation process observed at $f < 5 \cdot 10^2$ Hz can be explained as based on the two-layer Maxwell–Wagner polarization. For this case, one of the layers is a near-electrode region, where for this frequency range the charge transfer occurs due to oscillations of the dipoles

of LC molecules within the angles corresponding to the fluctuations of the order parameter. The second layer is the bulk part of the sample, where the charge transfer occurs through the transfer of ions. In accordance with the Maxwell–Wagner polarization theory, the value of the relaxation time should be inversely proportional to the LC electrical conductivity. Therefore, the particular peculiarities of electrical conductivity of a liquid crystal 6CB with Cu_7PS_6 nanoparticles can be a determining factor for the difference between dielectric spectra without and with nanoparticles.

According to [18], the dispersion of ε' for $f > 2 \cdot 10^5$ Hz can be explained by the fact that the dipole moments of the molecules at these frequencies have no time to return to the electric field change cycle. Since the dipole component of the polarization of the molecules is the main component, it also leads to a significant change in the ε' value.

It also follows from Fig. 1 that within the frequency range $5 \cdot 10^2 < f < 2 \cdot 10^5$ Hz the ε' value is practically independent of the frequency. This dependence is typical for the samples, where the influence of near-electrode processes is minimal. Therefore, we can assume that the results obtained within the frequency range $5 \cdot 10^2 < f < 2 \cdot 10^5$ Hz characterize the bulk properties of the samples. It should also be added that even with the maximum concentration of Cu_7PS_6 nanoparticles the ε' value for 6CB varies insignificantly. Thereof, it can be concluded that the dielectric permittivity of the Cu_7PS_6 nanoparticles is not much larger than the dielectric permittivity of 6CB.

Fig. 2 shows the frequency dependences of ε'' for the planar oriented liquid crystal 6CB (*1*) and 6CB with the impurity of Cu_7PS_6 nanoparticles with the concentrations of 0.1 (*2*), 0.5 (*3*), 1 (*4*) wt.%.
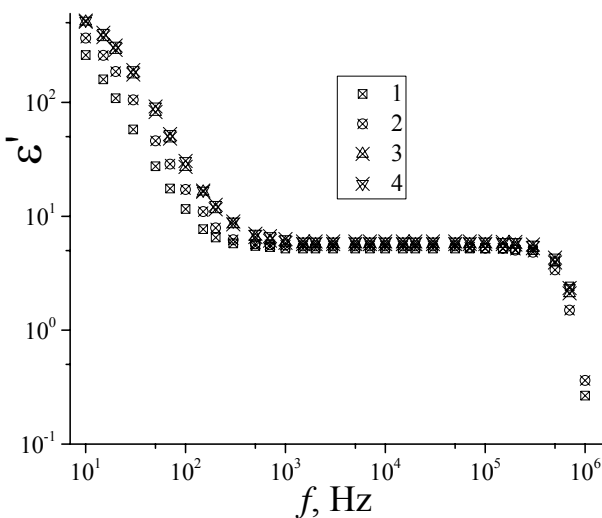
Fig. 1. Frequency dependences of the real component ε' of the complex permittivity for planar oriented liquid crystal 6CB (*1*), 6CB + 0.1 wt.% Cu_7PS_6 (*2*), 6CB + 0.5 wt.% Cu_7PS_6 (*3*) and 6CB + 1 wt.% Cu_7PS_6 (*4*). The sample thickness is 10 μm. The temperature is 293 K.
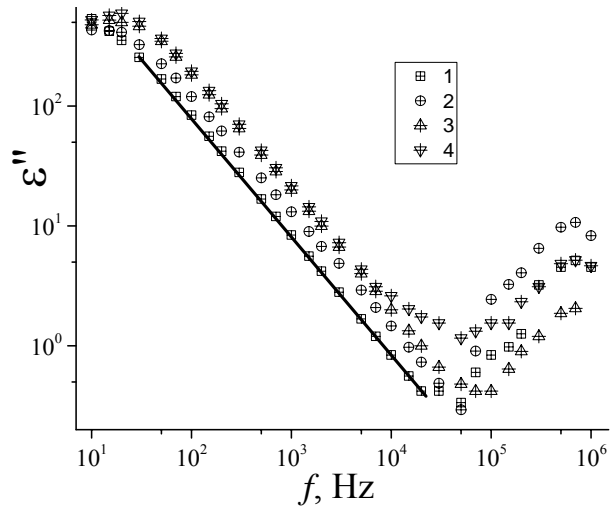
Fig. 2. Frequency dependences of the imaginary component ε'' of the complex permittivity for planar oriented liquid crystal 6CB (*1*), 6CB + 0.1 wt.% Cu_7PS_6 (*2*), 6CB + 0.5 wt.% Cu_7PS_6 (*3*) and 6CB + 1 wt.% Cu_7PS_6 (*4*). The sample thickness is 10 μm. The temperature is 293 K.

As follows from the data obtained, the inverse proportional dependence of ε'' on the frequency f is generally observed (the resistance value is independent of the frequency). The frequency region falls into the frequency range where this dependence takes place, where, as follows from Fig. 1, ε' does not depend on the frequency. The deviation from this dependence for $f < 50$ Hz can be explained by the influence of near-electrode processes, as it was done when analyzing the frequency dependence of ε'.

Deviations from the inverse proportional dependence of ε'' on the frequency f for the frequencies higher than $2 \cdot 10^4$ Hz, as in the case of the frequency dependence of ε', can be explained by substantial limitation of dipole polarization (for these frequencies, the dipole moments of the liquid crystal molecules do not have time to return to the cycle change in the magnitude of the electric fields).

From the analysis of the experimental data presented in Figs. 1 and 2, we can conclude that the frequency region $5 \cdot 10^2 < f < 2 \cdot 10^5$ Hz characterizes bulk properties of LC without/with nanoparticles. As it was shown above, for this region, often the ε' value is insignificantly dependent on the concentration of nanoparticles. More significant changes in the ε'' value on the concentration of nanoparticles within the frequency region $5 \cdot 10^2 < f < 2 \cdot 10^5$ Hz gave grounds to analyze the dependence of the electrical conductivity of LC on the concentration of nanoparticles.

Using the ε'' values obtained experimentally, the value of the electrical conductivity was estimated from the relation

$$\sigma = \varepsilon_0 \, \omega \, \varepsilon'',$$

where ε_0 is the electric constant, and $\omega = 2\pi f$ – the cyclic frequency.
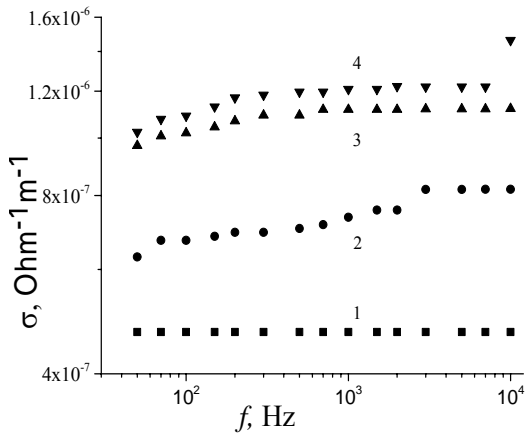
Fig. 3. Frequency dependences of the conductivity of planar oriented 6CB with the Cu_7PS_6 impurity of the concentrations: 0 (*1*), 0.1 (*2*), 0.5 (*3*) and 1 (*4*) wt.%. The sample thickness is 10 μm. The temperature is 293 K.

Fig. 4. The conductivity dependence of the planar oriented 6CB on the concentration of Cu_7PS_6 nanoparticles for the frequency 10^3 Hz. The sample thickness is 10 μm. The temperature is 293 K.

Fig. 3 shows the frequency dependences of the conductivity for planar oriented 6CB with the Cu_7PS_6 impurity of the concentrations: 0 (*1*), 0.1 (*2*), 0.5 (*3*) and 1 (*4*) wt.%.

As it follows from Fig. 3, with the exception of 6CB without nanoparticles (curve *1* in Fig. 3), the conductivity of LC with nanoparticles varies with the frequency. The reason for this effect may be introduction of additional (to those which are already present in LC) charge carriers by nanoparticles or charge transfer by the nanoparticles itself, when they can become charged in the liquid crystal, for example, due to the dissociation processes. The data obtained by us did not allow us to explain the main reasons for the change in conductivity with the frequency in the presence of nanoparticles. To analyze the dependence of the conductivity of 6CB on the nanoparticle concentration was more important for us.

Being based on the analysis of the experimental data shown in Fig. 3, we can conclude that the conductivity of 6CB with nanoparticles begins to be significantly less dependent on the frequency, starting with $f = 10^3$ Hz. Therefore, it was decided to analyze the dependence of the conductivity of the 6CB liquid crystal on the concentration of Cu_7PS_6 nanoparticles precisely for the frequency 10^3 Hz.

Fig. 4 shows the dependence of the conductivity of planar oriented 6CB on the concentration of Cu_7PS_6 nanoparticles for the frequency 10^3 Hz.

From the analysis of the experimental data shown in Fig. 4, it follows that within the range of concentrations of Cu_7PS_6 nanoparticles from 0 to 1 wt.%, the value of the electrical conductivity of 6CB nematic LC monotonically increases. However, even with such rather low concentrations of nanoparticles, the change in the electrical conductivity at the highest concentrations of Cu_7PS_6 goes to saturation.
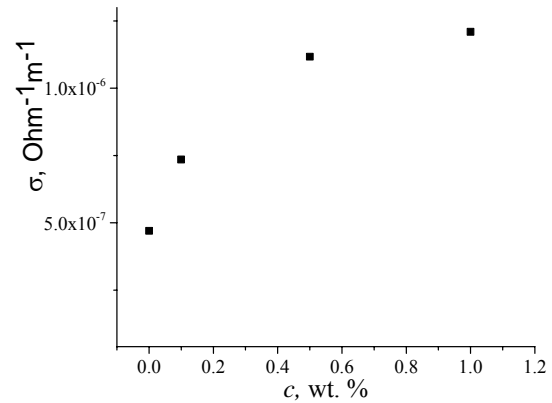
Earlier in [20], we observed the effect of saturation of the conductivity for the nematic liquid crystal E7, when diamond nanoparticles were introduced. This effect was explained by two competing mechanisms of changing the concentration of charge carriers in LC when introducing nanoparticles: (i) increasing the concentration of charge carriers in the liquid crystal mainly due to desorption of charge carriers from the surface of the nanoparticles and (ii) decreasing the concentration of charge carriers in the liquid crystal due to their adsorption on the surface of nanoparticles. It is important to note that precisely ions that are contained in LC can be adsorbed on the surface of nanoparticles. The first effect is obviously dominant at low concentrations of nanoparticles, and the second one – at high concentrations. The effect of saturation of electrical conductivity on the concentration of nanoparticles can be explained on the basis of the mechanism proposed in the work [20].

4. Conclusions

Within the range of concentrations from 0 to 1 wt.% the effect of Cu_7PS_6 nanoparticles on the dielectric properties of the nematic liquid crystal 6CB has been investigated.

1. It has been shown that the greatest influence of the nanoparticles on the real (ε') and imaginary (ε") components of complex dielectric permittivity is observed at low frequencies, under which the properties of samples are caused by the near-electrode processes.

2. For the frequencies at which the sample properties are caused by their bulk properties, it has been found that when introducing the nanoparticles the ε" value to a greater extent increases than the ε' one.

3. It has been shown that the conductivity of 6CB monotonically increases with increasing the concen-

tration of Cu_7PS_6 nanoparticles. However, for the highest concentrations of nanoparticles, the effect of saturation is observed. It has been proposed to explain this effect on the basis of the existence of competing processes of changing the concentration of charge carriers when introducing nanoparticles: generation of charge carriers additional to those existing in the liquid crystal due to their desorption from the surface of nanoparticles and the decrease of charge carrier concentration due to adsorption on the surface of nanoparticles.

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