

Influence of anion substitution on electrical conductivity of composites based on liquid crystal with $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X} = \text{I}, \text{Br}$) nanoparticles

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Abstract. Dielectric properties of composites based on planar-oriented 6CB liquid crystal with $\text{Cu}_6\text{PS}_5\text{X}$ ($\text{X} = \text{I}, \text{Br}$) nanoparticles at 293 K in the frequency range from 6 to 10^6 Hz have been studied. The concentration of nanoparticles varied from 0 up to 0.1 wt.%. It has been shown that $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles significantly less influence the conductivity of 6CB than the $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles. Moreover, at the concentrations 0.01 to 0.05 wt.% of $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles the conductivity of LC decreases. It has been assumed that the nonmonotonic dependence of 6CB conductivity on the concentration of $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles is caused by two competing mechanisms: an increase in conductivity due to the introduction of conductive impurities with nanoparticles and a decrease in conductivity caused by adsorption of impurities on the surface of nanoparticles.

Keywords: superionic conductors, liquid crystal, dielectric permittivity, electrical conductivity, concentration dependence.

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1. Introduction

$\text{Cu}_6\text{PS}_5\text{I}(\text{Br})$ crystals belong to the compounds with argyrodite structure [1]. These materials are known as superionic conductors or solid electrolytes. They have attracted great interest not only in the view of the possibility to apply them in a high-energy-density batteries and sensors, but also due to their remarkable properties.

Liquid crystals (LC) are now widely used in display technology. To significantly expand the limits of practical application of LC, it is necessary to be able to predictably change their properties. One of the methods for expanding the functional properties of LC is introduction of various types of nanoparticles [1-4]. As we have shown in Refs. [1-4], significant changes in the properties of LC are observed when introducing superionic nanoparticles. The introduction of $\text{Cu}_6\text{PS}_5\text{I}$ nano-

particles into 6CB leads to an increase in conductivity by almost two orders of magnitude, which is caused by dissociation of nanoparticles in LC with formation of Cu ions [1]. The purpose of this work was to investigate the influence of $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles on the dielectric properties of a planar-oriented nematic 6CB and to compare it with the results of the influence of $\text{Cu}_6\text{PS}_5\text{I}$ superionic nanoparticles on this LC.

2. Experimental

$\text{Cu}_6\text{PS}_5\text{Br}$ powders were milled with a planetary ball-mill. The maximum milling time of the powder was 30 min. 6CB without/with $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles was 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 close to 200 nm in LC was 0.01, 0.05, 0.1 wt.%. The cell thickness was 18 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 these sandwich cells were investigated in the frequency range from 6 up to 10^6 Hz at the temperature 293 K by using the oscilloscopic method [5].

3. Results and discussion

Fig. 1 shows the frequency dependences of the real component of the complex dielectric permittivity ϵ' of 6CB LC with different concentrations of $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles. It follows from Fig. 1 that $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles have a significantly less impact on the value of ϵ' than that of $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles [1]. It was shown that the influence of nanoparticles essentially depends on the frequency range. Therefore, for analysis, it is logical to separate the frequency dependence for ϵ' into two regions *A* and *B* (Fig. 1).

As it follows from Fig. 1, there is a sharp increase in the value of ϵ' with a decrease in frequency in the section *A* ($f < 10^3$ Hz). As we have shown in Ref. [5], this effect is due to the fact that in order to ensure the charge transfer in the electrode section, the intensity of the electric field in the sample is redistributed in such a way that almost the entire voltage of the measuring signal will be applied to a thin (dozens of nanometers) near-electrode layer. It was shown in Ref. [4] that the dispersion of ϵ' in the *A* region of dielectric spectrum can be described by the Debye equation. This dispersion is caused by the rotation of the dipoles of LC molecules at the angles corresponding to fluctuations of the order parameter. Since the electric field is mainly concentrated

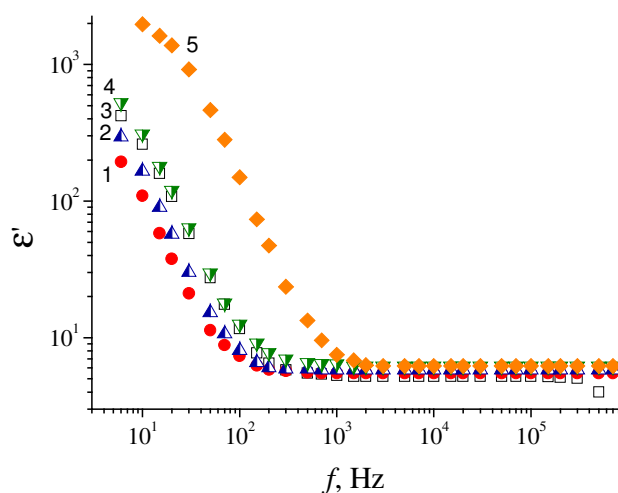


Fig. 1. Frequency dependences of the ϵ' real part of complex dielectric permittivity at 293 K in 6CB (*1*) and 6CB with different content of $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles: 0.01 (2), 0.05 (3) and 0.1 wt.% (4) and 6CB with 0.1 wt.% $\text{Cu}_6\text{PS}_5\text{I}$ superionic nanoparticles (5) [1].

in near-electrode section, it is there that the charge transfer occurs due to oscillations of the molecular dipoles. In the bulk of LC, charge transfer occurs due to motion of ions. Therefore, the parameters of the relaxation process in the *A* region depend not only on the parameters of the near-electrode section, but also on the conductivity of the sample.

Significantly less influence of $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles on the value of ϵ' of 6CB LC than the influence of $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles is obviously caused by the fact that $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles significantly less influence the conductivity of 6CB LC than $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles. As shown below, the lower influence of $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles on the conductivity of 6CB LC defines the essential difference between the frequency dependences of ϵ' at different concentrations of nanoparticles.

As it follows from the analysis of Fig. 1 for the frequencies $f > 10^3$ Hz (region *B* of the dielectric spectrum), the value of ϵ'' does not depend on the frequency. It corresponds to the condition where the electric field intensity in the thickness of the sample will be the same. In this case, the ϵ' value will be equal to the bulk dielectric permittivity. It is concluded that the presence of impurities of $\text{Cu}_6\text{PS}_5\text{Br}$ even at the maximum concentration (0.1 wt.%) results in a small (less than 20%) increase in dielectric permittivity of 6CB LC with nanoparticles (Fig. 1).

One more important conclusion can be drawn from the analysis of the frequency dependences of ϵ' in region *A*. At 0.01 wt.% and 0.05 wt.% of $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles, the dielectric permittivity is less than that of pure LC. According to Ref. [6, 7], this fact may be caused by the influence of nanoparticles on the LC conductivity. Therefore, it is logical to consider how the $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles influence the conductivity of 6CB LC.

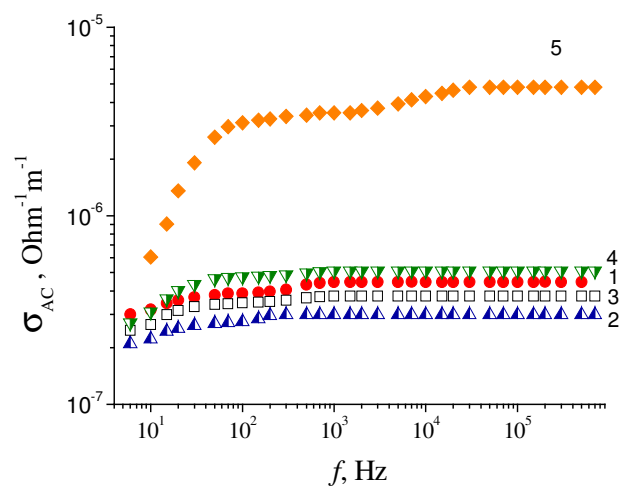


Fig. 2. The frequency dependences of the electrical conductivity σ_{AC} at 293 K for 6CB (*1*) and 6CB with a different content of $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles: 0.01 (2), 0.05 (3) and 0.1 wt.% (4) and 6CB with 0.1 wt.% $\text{Cu}_6\text{PS}_5\text{I}$ superionic nanoparticles (5) [1].

Fig. 2 shows the frequency dependence of conductivity σ_{AC} of 6CB LC with the different concentration of $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles.

It follows from the analysis of Fig. 2 that the frequency dependence of conductivity also can be separated into two regions A and B. In the A region ($f < 10^3$ Hz), the value of σ_{AC} decreases with decreasing the frequency. In fact, for these frequencies, one cannot talk about the conductivity since, as noted above, the electric field is applied not to the entire bulk of LC, but to a thin near-electrode layer. For the frequencies $f > 10^3$ Hz (region B of the dielectric spectrum), as it follows from Fig. 2, the conductivity does not depend on the frequency. It is these values of conductivity that correspond to the bulk conductivity. It is shown that the value of σ_{AC} of nematic LC is a nonmonotonic function of the content of $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles (Fig. 2).

Fig. 3 shows the dependence of 6CB LC conductivity on the concentration of $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles. From these data, it follows that the conductivity of 6CB LC is a nonmonotonic concentration function of $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles. At small concentrations of nanoparticles (0.01...0.05 wt.%), the LC conductivity decreases. However, with the maximum concentration, the LC conductivity becomes larger (almost by the factor 1.1). To explain this effect, it is reasonable to assume that $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles affect the 6CB LC via two different mechanisms. First, along with the nanoparticles, the certain impurities are introduced into LC, which can be the charge carriers. In addition, the LC conductivity can increase due to dissociation of nanoparticles in LC [1]. However, in the case of $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles this mechanism of conductivity increase is not observed (no color of LC was detected as for $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles [1]). Second, the conductivity of LC may decrease as a result of adsorption of ions that transfer the charge to LC on the surface of the electrodes. Each of the above mechanisms

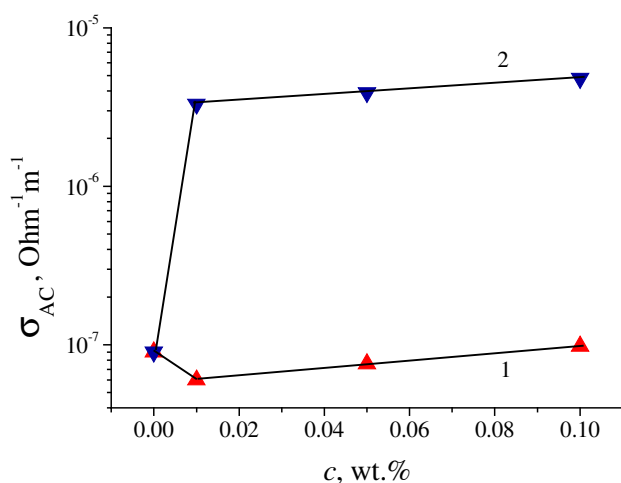


Fig. 3. Concentration dependence of the electrical conductivity σ_{AC} at 293 K for 6CB with $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles (1) and 6CB with 0.1 wt.% $\text{Cu}_6\text{PS}_5\text{I}$ superionic nanoparticles (2) [1].

may vary in different ways from the concentration of nanoparticles. It is obvious that in the case of a nonmonotonic dependence of the conductivity of 6CB LC on the concentration of $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles, both these mechanisms act simultaneously. At 0.01...0.05 wt.% of nanoparticles, adsorption of ions on the surface of nanoparticles is prevalent, and at 0.1 wt.% conductivity increase occurs due to the introduction of additional (to those existing in LC) ions.

From the comparison of the data obtained here with the data presented in Ref. [1], one can conclude that $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles significantly less influence the conductivity of 6CB LC (increasing the conductivity by only 1.1 times with a maximum concentration of 0.1 wt.%) than the nanoparticles of $\text{Cu}_6\text{PS}_5\text{I}$ (increase in concentration by almost two orders of magnitude). Thus, the substitution of I atoms with the Br ones in $\text{Cu}_6\text{PS}_5\text{X}$ (X = I, Br) nanoparticles leads to a significant difference in their effect on 6CB conductivity.

4. Conclusions

It has been shown that $\text{Cu}_6\text{PS}_5\text{Br}$ superionic nanoparticles significantly affect the conductivity of 6CB LC, stronger than they influence its dielectric permittivity. Conductivity of 6CB LC within the range 0...0.1 wt.% is a nonmonotonic function of the concentration of $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles. The mechanism of this effect is proposed with account of the existence of two competing and closely related processes: the increase of conductivity due to introducing the additional ions (to those existing in LC) and decrease of conductivity caused by adsorption of ions on the surface of nanoparticles, since these ions are charge carriers in LC. It has been shown that $\text{Cu}_6\text{PS}_5\text{Br}$ nanoparticles significantly less influence the conductivity of 6CB LC than $\text{Cu}_6\text{PS}_5\text{I}$ nanoparticles.

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