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Influence of nanoparticles of Cu_7GeS_5I superionic conductor on dielectric properties of planar-oriented nematic liquid crystal 6CB

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Abstract. The influence of Cu_7GeS_5I nanoparticles on the dielectric properties of planar-oriented liquid crystal 6CB has been investigated within the frequency range 6…10^6 Hz at the temperature 293 K. The concentration of nanoparticles varied within the range 0 to 0.1 wt.%. It has been shown that the Cu_7GeS_5I nanoparticles considerably less increase the conductivity of the liquid crystal (only by 1.3 times at their maximum concentration) than Cu_7PS_6 ones, influence of which on the conductivity of the same liquid crystal we investigated earlier (24-fold increase in the conductivity at the same concentration of nanoparticles). It has been assumed that the main mechanism of conductivity changes when introducing Cu_7GeS_5I nanoparticles is the transfer of charge through nanoparticles. This mechanism of charge transfer is characterized by a rather strong dependence of the conductivity of the liquid crystal on the frequency and is experimentally observed especially at the maximum concentration of nanoparticles.

Keywords: superionic conductor, dielectric properties, planar-oriented nematic liquid crystal 6CB.

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1. Introduction

At this stage of industrial production, displays based on liquid crystals (LC) occupy leading positions and their proportion is continuously increasing. Unique property of liquid crystals is a liquid state, which provides the ability to change parameters depending on low voltages and the presence of order in location of molecules (at least in a certain direction (nematics) or in a certain plane (smectics)) gives the grounds for finding new (not only display) practical applications of LC.

To expand the limits of practical use 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 introducing the nanoparticles of various types [1-3]. As we showed in [4-6], significant changes in the LC properties, in particular electric and dielectric, are observed when nanoparticles of superionic conductiors are introduced. Investigation of superionic conductors in monocrystalline or polycrystalline state has shown that their properties can be changed in rather wide limits, depending on the chemical composition. Therefore, one should expect that superionic conductors different in properties will be in the form of nanoparticles that in different ways effect on the LC properties. Our previous studies [4-6] fully confirmed this hypothesis (in the first stages of the research). However, the analysis of the obtained data shows that it is not always possible, knowing the properties of the superionic conductor, to predict its effect in the nanocrystalline state on LC properties.

Obviously, such predictions can be made under conditions when there will be investigated and analyzed data in detail on the influence of nanoparticles of various types on LC properties. Therefore, studying the influence of various types nanoparticles of superionic conductors on LC properties has both practical and scientific significance.

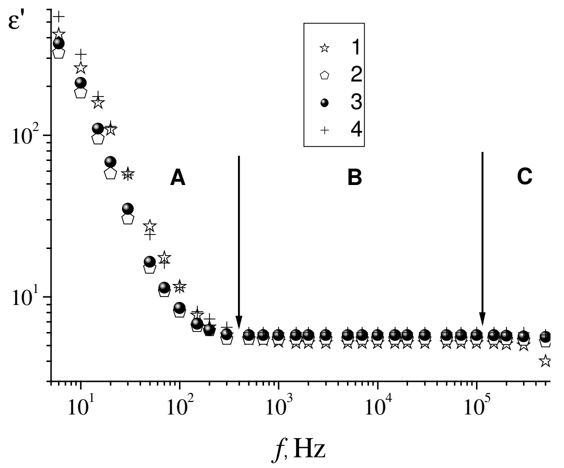

Fig. 1. Frequency dependences of the real part ε′ of complex dielectric permittivity for a planar-oriented nematic LC 6CB with the nanoparticles of Cu_7GeS_5I superionic conductor with the concentrations: 0 (*1*), 0.01 (*2*), 0.05 (*3*), and 0.1 wt.% (*4*). The temperature is 293 K (nematic phase of LC). The sample thickness is 20 μm. Vertical arrows mark the boundaries of three sections of the dielectric spectrum **A**, **B**, **C**.

The purpose of this work was to investigate the influence of nanoparticles of the Cu_7GeS_5I superionic conductor on the dielectric properties of the planar-oriented nematic LC 6CB.

2. Experimental

The studied samples were based on the thermotropic nematic LC 6CB (4-cyano-4-hexylbiphenyl) that was doped with the superionic nanoparticles Cu_7GeS_5I that were preliminary synthesised and milled. The maximum milling time of the Cu_7GeS_5I powder was 30 min. The LC was heated to the isotropic phase, and three different weight concentrations of nanoparticles (0.01, 0.05 and 0.1 wt.%) were added under continuous stirring. The average size of near-spherical shape nanoparticles was ~250 nm. The prepared samples were filled into the capacitor with ITO electrodes with the electrode area of approximately $0.5 \times 0.5\ cm^2$, and the distance between electrodes (the sample thickness) was 20 μm. Finally, the samples were filled into the cells in the isotropic phase due to capillary forces. A rubbed polyimide coating on the electrodes ensured initial planar orientation of liquid crystal molecules. *i.e.*, the director is parallel to the capacitor electrodes.

Dielectric properties of the obtained sandwich cells were investigated within the frequency range $6 \ldots 10^6$ Hz at the temperature 293 K by using the oscilloscopic method [7].

3. Results and discussion

Fig. 1 shows the frequency dependences of the real part of the complex dielectric permittivity ε′ of the planar-oriented nematic LC 6CB with the concentration of nanoparticles of the superionic conductor Cu_7GeS_5I: 0 (*1*), 0.01 (*2*), 0.05 (*3*), and 0.1 wt.% (*4*).

As it follows from Fig. 1, in the section **A** ($f < 10^3$ Hz) a sharp increase in the ε′ value with decreasing the frequency is observed. As we showed in Ref. [8], this effect is caused by the fact that, to ensure the charge transfer in the near-electrode area, 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 the thin near-electrode layer (tens of nanometers).

In Ref. [8], it was shown that in the section in the dielectric spectrum **A** the dispersion of ε′ can be described by the Debye equation. This dispersion is due to the rotation of the dipoles of LC molecules within the angles corresponding to the fluctuations of the order parameter. Since the electric field is mainly concentrated in the near-electrode area, it is precisely here that the charge transfer occurs due to oscillations of the molecule dipoles. In the volume of LC, charge transfer occurs due to the movement of ions. Therefore, the parameters of the relaxation process in the section **A** depend not only on the parameters of the near-electrode area, but also on the sample conductivity [8].

From the analysis of the section **A** of dielectric spectra at various concentrations of Cu_7GeS_5I nanoparticles, it follows that, unlike the data on the influence of the Cu_7PS_6 nanoparticles on 6CB dielectric properties, a significantly smaller difference between the dielectric spectra is observed. That is, already analyzing Fig. 1 one can conclude that the Cu_7GeS_5I nanoparticles less influence on the conductivity of LC 6CB than the Cu_7PS_6 nanoparticles. As it will be shown below, this assumption will be fully verified analyzing the frequency dependences of the imaginary part ε″ of complex dielectric permittivity.

As it follows from the analysis of Fig. 1, for the frequencies $10^3 < f < 10^5$ Hz (section **B** in the dielectric spectrum), the ε′ value does not depend on the frequency. It corresponds to the condition when the electric field strength along the sample thickness will be the same. In this case, the ε′ value will correspond to the dielectric permittivity of the sample volume. As shown in Fig. 1, the presence of Cu_7GeS_5I nanoparticles leads to a slight increase in the dielectric permittivity.

From the comparison with the analogous results obtained in the Ref. [6], we can conclude that the dielectric properties of Cu_7GeS_5I and Cu_7PS_6 nanoparticles are approximately the same.

As seen from Fig. 1, for the frequencies $f > 10^5$ Hz (section **C** of the dielectric spectrum) there is a decrease in the ε′ value with increasing the frequency. From the theory of relaxation processes, it is known [9] that the dispersion in the section **C** is inherent to all liquids and is caused by the fact that during the change of voltage within ¼ period of the measuring signal, the molecule dipoles have no time to rotate to a certain angle. Therefore, we will not analyze the influence of Cu_7GeS_5I nanoparticles on the parameters of dipole polarization of 6CB molecules.

Fig. 2 shows the frequency dependences of the imaginary part ε″ of the complex dielectric constant ε of the planar-oriented nematic LC 6CB with the concentration of nanoparticles of Cu_7GeS_5I superionic conductor: 0 (*1*), 0.01 (*2*), 0.05 (*3*), and 0.1 wt.% (*4*).

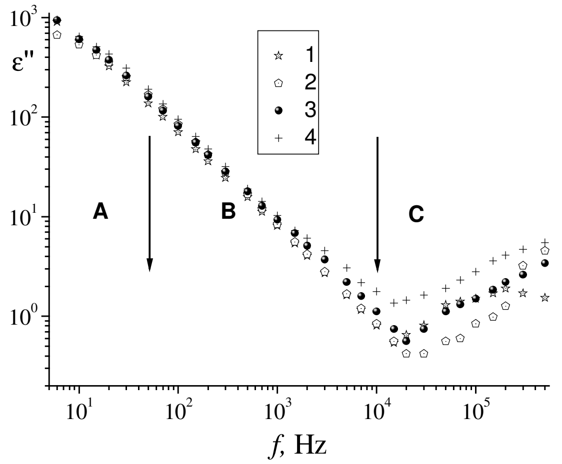

Fig. 2. Frequency dependences of the imaginary part ε″ of the complex permittivity for a planar-oriented nematic LC 6CB with the nanoparticles of Cu_7GeS_5I superionic conductor with the concentration: 0 (*1*), 0.01 (*2*), 0.05 (*3*), and 0.1 wt.% (*4*). The temperature is 293 K (nematic phase of LC). The sample thickness is 20 μm. Vertical arrows mark the boundaries of three sections of the dielectric spectrum **A**, **B**, **C**.

From the analysis of Fig. 2, it follows that, as in the case of ε′ (Fig. 1), the whole dielectric spectrum ε″ can be separated into three sections **A**, **B**, and **C**. Analysis of the section **A** of the dielectric spectrum and effect of the Cu_7GeS_5I nanoparticles on ε″ have already done by us when considering the frequency dependence ε′. Confirmation that the dispersion of dielectric permittivity in the section **A** is described by the Debye relation is that the frequency dependence in this section can be described with a small error by the relation

$$\varepsilon^*(\omega) = \varepsilon_\infty \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau}, \qquad (1)$$

where ε* is the dielectric permittivity, ε_0 and ε_∞ are the dielectric permittivities at the frequencies $f = 0$ and $f = \infty$, respectively, $\omega = 2\pi f$ is the cyclic frequency, and τ is the relaxation time.

As it was already noted above, since the Cu_7GeS_5I nanoparticles resulted in small changes in the values of ε′ and ε″, we did not investigate the influence of the concentration of Cu_7GeS_5I nanoparticles on the parameters of electrode processes in LC 6CB (in particular, on the magnitude of relaxation time).

From the analysis of the section **B** of the frequency dependence of ε″ it follows that for most concentrations of Cu_7GeS_5I nanoparticles, the ε″ value is proportional to f^{-1}. This dependence is typical for liquids in the case of homogeneous distribution of the electric field in the thickness of the sample and follows from the ratio

$$\sigma_{AC} = \varepsilon_v \varepsilon \omega \qquad (2)$$

(where ε_v is electrical constant) to find the conductivity of the sample on the alternating current σ_{AC}.

The frequency dependences of the conductivity for LC 6CB with various concentrations of the Cu_7GeS_5I nanoparticles are shown in Fig. 3.

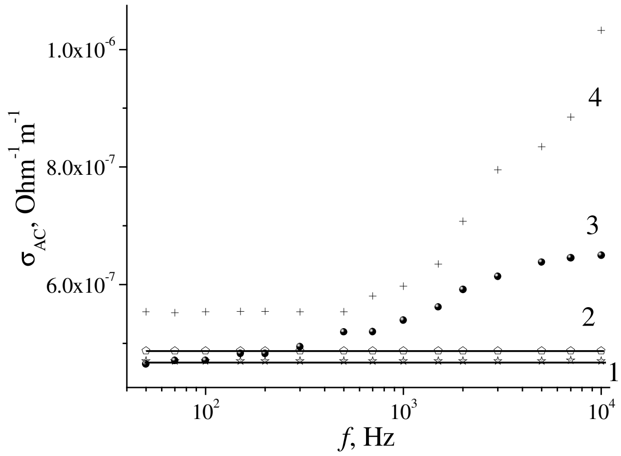

Fig. 3. Frequency dependences of the conductivity for LC 6CB with the concentration of Cu_7GeS_5I nanoparticles: 0 (*1*), 0.01 (*2*), 0.05 (*3*), and 0.1 wt.% (*4*). The temperature is 293 K (nematic phase of LC). The sample thickness is 20 μm.

From the analysis of Fig. 3, it follows that the conductivity of LC 6CB without nanoparticles (curve *1*) and 6CB + 0.01 wt.% of Cu_7GeS_5I nanoparticles (curve *2*) does not depend on the frequency. Regularities of this type are typical for pure liquids or liquids with a relatively low concentration of nanoparticles.

When introducing 0.05 wt.% of Cu_7GeS_5I nanoparticles and especially 0.1 wt.% of the nanoparticles, as it follows from Fig. 3, the conductivity begins to depend rather significantly on the frequency. As it was proposed in the Ref. [6], one can assume that at these concentrations of nanoparticles the electronic or ionic component of conductivity through the nanoparticle makes essential contribution. Since LC is placed between nanoparticles, then such a transfer mechanism involves overcoming barriers with variable lengths.

Considering the results of the influence of Cu_7PS_6 nanoparticles on the properties of LC 6CB in the Ref. [6], it was noted that nanoparticles can change the LC conductivity due to two mechanisms: conductivity through the molecules of nanoparticles and by introducing ions into LC. These ions can be impurities of various types that arise when synthesizing the nanoparticles.

In the Ref. [6], we observed lower changes in the conductivity with the frequency even at the maximum (0.1 wt.%) concentration of nanoparticles, but the overall increase in the conductivity, when introducing Cu_7PS_6 nanoparticles, was greater than in this work, when introducing the Cu_7GeS_5I nanoparticles into LC. Thereof, we can conclude that Cu_7GeS_5I nanoparticles, as compared with the Cu_7PS_6 ones, to a lesser extent influence on the ionic conductivity of LC 6CB (impurities that increase ionic conductivity are less introduced into the LC). In this case, the component of current through the Cu_7GeS_5I nanoparticles in this work significantly exceeds the component of current through the Cu_7PS_6 nanoparticles in the Ref. [6].

It is obvious that the difference in the influence of the nanoparticles Cu_7GeS_5I and Cu_7PS_6 [6] on the dielectric properties of LC 6CB should be manifested in the concentration dependences of the conductivity on the

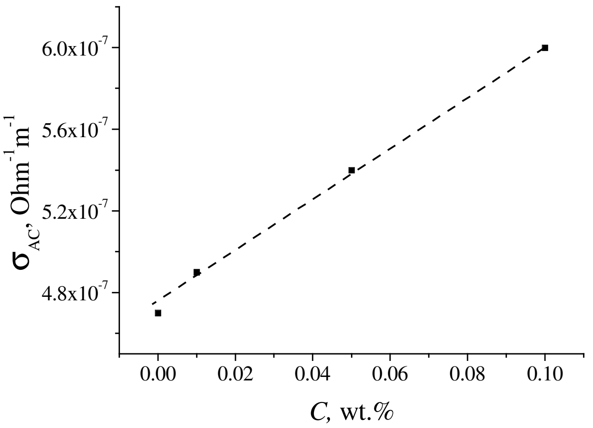

Fig. 4. Dependence of the conductivity of planar-oriented nematic LC 6CB on the concentration of Cu_7GeS_5I nanoparticles for the frequency 10^3 Hz.

frequency. Since for the concentrations $c > 0.05$ wt.% the conductivity essentially depends on the frequency, for the analysis we considered the frequency 10^3 Hz. The dependence of conductivity under the alternating current of planar-oriented nematic LC 6CB on the concentration of Cu_7GeS_5I nanoparticles is shown in Fig. 4.

As it can be seen in Fig. 4, observed is an almost linear dependence of the conductivity of LC 6CB on the concentration of Cu_7GeS_5I nanoparticles. In the Ref. [6], at the same concentrations of nanoparticles, for the dependence of the LC conductivity on the concentration of nanoparticles, the effect of saturation was observed. This difference between the concentration dependences of conductivity can be explained by the different contribution of each component of conductivity (ionic conductivity through LC and conductivity through the nanoparticles), when the Cu_7GeS_5I or Cu_7PS_6 nanoparticles are introduced into LC 6CB [6].

It is obvious in the case of introducing Cu_7PS_6 nanoparticle into LC, the main component of the change in conductivity under the influence of nanoparticles is an increase in the ionic component of the conductivity in LC itself. It is just for the ionic component and effect of saturation of conductivity on the concentration of nanoparticles, this situation is observed.

In the case when the ionic component of the conductivity change with introducing the nanoparticles is small (it is observed in this work), the contribution of conductivity components through the nanoparticles becomes more significant.

This assumption is confirmed by quantitative estimations of the change in the conductivity of LC 6CB when introducing the maximum concentration (0.1 wt.%) of Cu_7PS_6 nanoparticles [6] and the same concentration of Cu_7GeS_5I nanoparticles. As shown in Ref. [6], when introducing 0.1 wt.% of Cu_7PS_6 into LC 6CB, the conductivity is increased by 24 times, whereas when introducing the same concentration of Cu_7GeS_5I nanoparticles into LC 6CB (Fig. 4), the conductivity increases only by 1.3 times.

Obviously, for the case when Cu_7PS_6 nanoparticles were introduced into LC 6CB, the component of conductivity through nanoparticles also depended linearly on the concentration of nanoparticles. However, such an effect in the overall change in conductivity did not manifest itself, since the contribution of conductivity through nanoparticles was very low in this case.

4. Conclusions

1. The influence of Cu_7GeS_5I nanoparticles on the dielectric properties of a planar-oriented nematic LC 6CB has been investigated. It has been shown that, like to the case of the influence of Cu_7PS_6 nanoparticles on the same crystal [6], the entire frequency spectrum (within the range $6\ldots10^6$ Hz) of the complex dielectric permittivity can be separated into three sections. The most low-frequency section of the spectrum is caused by near-electrode polarization due to oscillations of the dipoles of molecules within the angles equal to fluctuations of the order parameter. For the middle frequency section, the dielectric spectrum depends on the bulk properties of LC, and for the highest frequencies ($f > 10^5$ Hz), the dispersion of the complex dielectric permittivity is due to the fact that the dipoles of the molecules have no time to rotate to a certain angle during the change in the voltage of the measuring signal.
2. It has been found that the conductivity of LC 6CB when introducing the maximum (0.1 wt.%) from the chosen Cu_7GeS_5I concentrations for studies is increased only by 1.3 times, while at the same concentration of Cu_7PS_6 nanoparticles the LC conductivity is increased by 24 times.
3. It has been shown that, unlike the influence of Cu_7PS_6 nanoparticles on the conductivity of LC 6CB, the influence of Cu_7GeS_5I nanoparticles on the conductivity of the same LC depends more on the frequency.
4. It has been assumed that, if introducing Cu_7PS_6 nanoparticles into planar-oriented LC 6CB, the main reason for the change in conductivity is the increase of ion concentration in LC, then in the case of the introduction of Cu_7GeS_5I nanoparticles into LC 6CB, the conductivity increases due to charge transfer through the nanoparticles. At the low concentrations of nanoparticles in this charge transfer mechanism, one has to take into account the charge transfer from one nanoparticle to another through LC. Since the distance between the nanoparticles was different, this led to the frequency dependence of the conductivity of LC with nanoparticles in that frequency range where the conductivity of LC without nanoparticles did not depend on the frequency.

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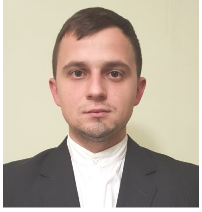

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