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Dielectric spectroscopy of liquid crystal doped with Fe₃O₄ nanoparticles

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Abstract

The influence of Fe₃O₄ nanoparticles on dielectric properties of planar oriented liquid crystal were studied at the frequency range 10⁻¹-10⁶ Hz and in temperature interval of 292 - 345 K. It was shown that the dielectric spectrum of doped liquid crystal can be divided into two areas. Parameters obtained from the dielectric spectrum for frequencies lower than 10 Hz characterize near electrode processes, and parameters obtained for frequencies more than 10 Hz characterize the bulk properties of the sample. The relaxation time and near-electrode area thickness have been estimated. It was experimentally shown that magnetic nanoparticles change the near-electrode area parameters.

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1. Introduction

Experimental studies showed that the behaviour of liquid crystals (LCs) can substantially change under the influence of electric and magnetic fields. These particular LC properties allowed to make good use of them in practical applications. Most devices including LCs (mainly displays) are based on different types of electro-optical

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effects [1, 2, 3]. One of important limitations of these systems is a necessity to use electrodes. It complicates not only the fabrication technology of functional elements of these devices, but requires the development of methods for diminishing the influence of those near-electrode effects that affect the operating characteristics of the devices (adsorption of ions on orienting surfaces, decrease of response time due to the influence of double electric layers, etc). All these effects can be avoided when the LC is under the influence of a magnetic field, as in this case there is no need to use electrodes. Their practical usage is restrained by the fact that the anisotropy of the magnetic susceptibility of LCs is far less than that of the dielectric one. Therefore, a rotational motion of LC molecules can be induced under the influence of fairly strong magnetic fields. The magnetic anisotropy of LCs can substantially be increased by the incorporation of magnetic impurities (mainly iron oxides). As it was shown in [4, 5], in these LCs (ferronematics), the magneto-optical effects take place at lower magnetic fields. In most papers, studies on the influence of magnetic nanoparticles (MNs) on the Freedericksz transition under the action of a magnetic field [4, 5] or on the reorientation of molecules under the simultaneous action of electric and magnetic fields were reported. In doing so the influence of MNs on the characteristics of the near-electrode layers was not taken into account, even though the near-electrode layers can substantially influence the re-orientation of molecules in electric or magnetic fields. As was shown in [6, 7, 8, 9], dielectric spectroscopy is an effective method to study the characteristics of the near-electrode areas of the sample. Therefore, the aim of this paper was to study the influence of MNs on the dielectric spectra of LCs and it was important to find out, how the changes of the dielectric properties depend on the phase of the LC and on the magnetic field. We investigated in particular the initial stage of the Freedericksz effect, carrying out the measurements at voltages and magnetic fields which were sufficiently lower than those needed for complete reorientation of molecules. To our knowledge such experimental studies have not been performed before.

2. Experiment

The studied ferronematic samples were based on the thermotropic nematic 4-(trans-4-n-hexylcyclohexyl)-isothiocyanatobenzene (6CHBT). 6CHBT is a low-melting enantiotropic LC with high chemical stability [10]. The temperature of the nematic-to-isotropic transition (clearing point) of the studied nematic is $T_{N-I} = 42.8\text{ }^{\circ}\text{C}$ ($= 316\text{K}$). The nematic samples were doped with a magnetic suspension consisting of nearly spherical Fe_3O_4 magnetic particles coated with oleic acid as a surfactant. The frequency dependence of the resistance R and the capacitance C of the sample was measured by using the oscilloscopic method [7] under condition that the equivalent circuit of the sample is a resistance and a capacitance connected in parallel. The measuring signal had a triangular shape, the amplitude was 0.25 V. The frequency of measuring signal was varied within the range 1×10^{-1} - 10^6 Hz. From the measured R and C the real and imaginary parts (ϵ' and ϵ'') of the complex dielectric permittivity have been determined. Magnetic field was created by two or four SaCo magnets which were located on each of the two glass substrates that bounded the liquid crystal from both sides. In this case, the magnetic field was directed along the electric field.

3. Results and discussion

Figures 1 and 2 show the frequency dependences of complex dielectric permittivity components ϵ' and ϵ'' of the planar oriented pure 6CHBT and 6CHBT doped with Fe_3O_4 nanoparticles at different temperatures. The analysis of experimental data gives grounds to divide the dielectric spectrum into two parts: part A (at frequency $f < 10$ Hz) and part B (at $f > 10$ Hz). In part A of the dielectric spectrum, a strong change (by a few orders of magnitude) of ϵ' and ϵ'' with increasing frequency are observed indicating the presence of a low frequency dispersion characterized by a relaxation time τ and a dielectric increment of ϵ_s . In contrast to that, in part B of the dielectric spectrum ϵ' is frequency independent providing the bulk permittivity ϵ_b , while ϵ'' diminishes linearly with increasing frequency on a log-log scale (i.e. the specific resistance ρ of the sample is frequency independent). As was shown in [7], part B refers to those frequencies at which the near-electrode processes do not influence the behaviour of the sample.

Part A of the dielectric spectrum is caused by the influence of near-electrode processes. Namely, an electric double layer develops owing to adsorption of ions at the electrode surfaces; its thickness l_s is about the Debye screening length. Due to this charge accumulation, almost all external voltage applied to the cell falls on the near-electrode area, yielding almost no potential drop on the bulk part of the sample. Hence the sample is actually divided into three parts (two near-electrode and one bulk regions). The observed low f relaxation is related to the dynamics of adsorption, desorption of ions and the charge transport in the near-electrode layer. In [6, 7, 8, 9] it was shown that

the large values of the complex dielectric permittivity components at low frequencies (i.e. the large dielectric increment ϵ_s) are caused by the heterogeneous distribution of the electric field in the sample. As the bulk region is almost potential free, the cell capacitance is about the net of that of the double layers. Assuming that the parameters (capacitances) of the near-electrode areas at both electrodes are identical and the dielectric permittivity of the near-electrode area equals ϵ_v , the thickness l_s can be estimated from the dielectric increment of the low f dispersion (obtained from the analysis of the Cole-Cole diagram) via

$$l_s = \frac{d\epsilon_v}{2\epsilon_s} \quad (1)$$

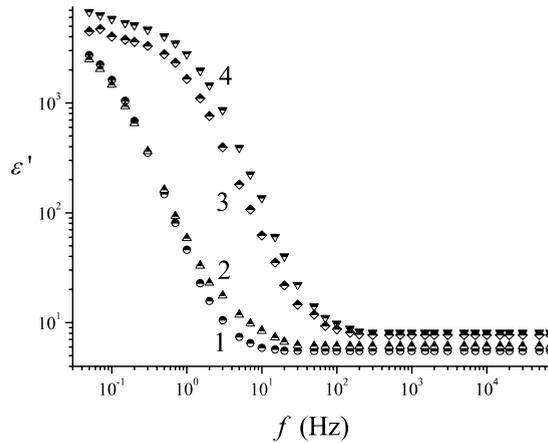


Figure 1: Frequency dependences of the real part (ϵ') of the complex dielectric permittivity for planar oriented 6CHBT (1, 2) and 6CHBT with Fe_3O_4 nanoparticles (2, 3) at different temperatures: at $T = 292$ K (1, 2) in the nematic phase; at $T = 338$ K (4) and at $T = 342$ K (3) in the isotropic phase. The thickness of the samples was $20 \mu\text{m}$.

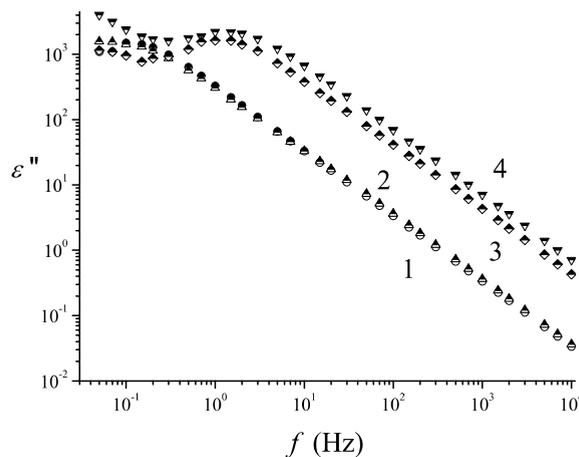


Figure 2: Frequency dependences of the imaginary part (ϵ'') of the complex dielectric permittivity for planar oriented 6CHBT (1, 2) and 6CHBT with Fe_3O_4 nanoparticles (2, 3) at different temperatures: at $T = 292$ K (1, 2) in the nematic phase; at $T = 338$ K (4), $T = 342$ K (3) in the isotropic phase. The thickness of the samples was $20 \mu\text{m}$.

These near-electrode processes were shown [11] to play an important role in the anchoring properties of planar-oriented LCs with positive anisotropy of the dielectric permittivity (like for the 6CHBT under study).

Before analyzing the dielectric spectra within a wide temperature range it is expedient to consider how Fe₃O₄ nanoparticles influence the dielectric spectra of 6CHBT at fixed temperatures. The results obtained on the basis of dielectric spectrum analysis at the temperature 292 K using Eq. (1) are listed in Table 1 (first two rows).

From the analysis of the variation of τ and l_s caused by the incorporation of Fe₃O₄ nanoparticles into the LC it is evident that the relative variation of near-electrode parameters (l_s and τ) is considerably larger than that of the bulk ones (ϵ_v and ρ). For example, if after incorporation of Fe₃O₄ nanoparticles the ϵ_v value increases by 10%, the τ value increases by 60%. Such effect to some extent can be caused by the non-uniform distribution of Fe₃O₄ nanoparticles as a result of their partial adsorption onto the electrode surface. Exactly due to adsorption of nanoparticles the angle of pre-orientations of molecules is variable and thus the value of dielectric permittivity increases.

Table 1: The influence of magnetic field on the dielectric properties of 6CHBT and 6CHBT with Fe₃O₄ at temperature 292 K. Sample thickness was 20 μm .

sample	B (T)	ρ (m)	ϵ_v	l_s (nm)	τ (s)
6CHBT	0	5.3×10^7	5.5	18	1.0
6CHBT+Fe ₃ O ₄	0	5.3×10^7	6.1	21	1.6
6CHBT	0.45	5.6×10^7	5.8	21	1.5
6CHBT+Fe ₃ O ₄	0.45	5.3×10^7	6.6	24	1.8
6CHBT	0.60	5.3×10^7	5.8	21	1.4
6CHBT+Fe ₃ O ₄	0.60	4.8×10^7	6.6	25	1.8

Table 1 presents also the results about the influence of nanoparticles on the parameters of bulk and near-electrode areas for pure 6CHBT and 6CHBT with Fe₃O₄ subjected to a static magnetic field B at a temperature of 292 K. In the case of pure LC, the magnetic field leads to an increase of ϵ_v . The variation of ϵ_v determined for two different magnetic fields does not depend on B within the experimental error. Similar results were obtained when analyzing the magnetic field influence on ϵ_v for 6CHBT with Fe₃O₄ nanoparticles. It follows that with changing the magnetic field from 0.45 to 0.6 T, no change of ϵ_v is observed within the experimental error either for the pure 6CHBT or for the 6CHBT with Fe₃O₄ nanoparticles. It should be noted that the specific resistance depends on the magnetic field (Table 1). The relative changes are larger for 6CHBT with Fe₃O₄ nanoparticles than for the pure LC. The analysis of the parameters of the near-electrode relaxation process shows that both in the pure LC and in the LC with MNs the action of the magnetic field results in an increase of the relaxation time and the thickness of the near-electrode layer (Tables 1). It is thus important to mark that l_s depends on the magnetic field B .

4. Conclusions

It is shown that a small amount (volume concentration of magnetic nanoparticles 10^{-4}) of magnetic nanoparticles (Fe₃O₄) incorporated into the liquid crystal 6CHBT causes a change of its dielectric spectrum. Within the frequency range of 10^{-1} - 10^6 Hz the dielectric spectrum of planar oriented 6CHBT can be divided into two regions. For $f > 10$ Hz frequencies, the ϵ_v value does not depend on frequency, and ϵ'' linearly decreases with increasing frequency on a log-log scale (i.e. the sample resistance does not depend on frequency). Parameters obtained in this region characterize the bulk properties of liquid crystal. For $f < 10$ Hz, in the dielectric spectrum of the samples the rather abrupt increase of ϵ' and ϵ'' with decreasing frequency is observed. It is shown that such changes can be caused by near-electrode relaxation process.

The essence of the process is the formation of an electric double layer at the electrode-liquid crystal interface; thickness of which is about the Debye screening length. Almost all external voltage applied to the cell falls on this near-electrode area of the sample. The low f relaxation might be related to the dynamics of the ionic charge transfer; the huge dielectric increment is the result of the heterogeneous electric field distribution and originates from the near-electrode region. It is found that the relaxation process caused by the double layer in the near-electrode area is well approximated by the Debye equation. From the measurements the relaxation time and the thickness of the

nearelectrode area were estimated. It is shown that incorporating magnetic particles into the liquid crystal increases both the relaxation time and the thickness of the near-electrode area. It is remarkable that thickness of the near-electrode area depends on the applied magnetic field.

Acknowledgments

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