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THE STUDY OF THE EFFECT OF SILVER NANOPARTICLES ON THE PHYSICAL PROPERTIES OF 4-CYANO-4'-PENTYLBIPHENYL LIQUID CRYSTAL

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This research is devoted to a comprehensive analysis of the structural, dielectric, and electro-optic modifications of the nematic liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) upon the incorporation of silver (Ag) nanoparticles. The primary aim of the study is to investigate how silver nanostructures (approximately 20–80 nm in size) alter the fundamental properties of the 5CB medium, and to compare the obtained results with those arising from the influence of other metals. The main focus of the work is on changes in dielectric anisotropy (Δε). It has been established that the addition of silver nanoparticles at relatively low concentrations (around 0.5–1%) leads to significant modifications in key parameters such as dielectric permittivity and dielectric losses of 5CB. The distinctive distribution of silver within the 4-cyano-4'-pentylbiphenyl matrix plays a decisive role in controlling the system's conductivity. Comparative analyses demonstrate that silver-doped composite materials exhibitenhanced *electro-optic sensitivity, which distinguishes them from composites doped with other metals.*

Keywords: 5CB; metal nanoparticles; nematic ordering; dielectric anisotropy; electrical conductivity

INTRODUCTION

Liquid crystals (LCD) are considered a fascinating class of materials that combine molecular-level ordering with fluidity. These materials are attractive both for fundamental scientific research and for their wide range of applications in modern technologies [1, 2]. Among LC phases, nematic liquid crystals (NLC) possess the simplest structure and form the basis of everyday devices such as liquid crystal displays (LCD) and many other systems. With technological progress, the need has arisen to improve LCD in terms of energy efficiency, faster response times, and enhanced image quality (viewing angle).

In recent years, particular attention has been paid to modifying LC properties by incorporating various non-mesogenic substances (dyes, polymers, nanoparticles, carbon nanotubes, etc.) [6–9]. Liquid crystals enriched with nanoparticles (NPS) of different sizes and shapes are highly significant for sensor technologies, fast electro-optic devices, memory elements, and optical filters [11–14]. The interplay between the anisotropic structure of LC and the conductive or magnetic properties of nanoparticles provides additional advantages for these technologies. Therefore, controlling the interaction between nanoparticles and LC

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molecules is essential for tuning macroscopic properties to the desired level.

Due to their unique optical properties, metal nanoparticles—particularly silver (Ag) NPs—have become a major research focus. Silver's high conductivity, chemical stability, and biomedical applications make it one of the most preferred materials [3–5]. Studies by Vimal et al. demonstrated that incorporating Ag NPs significantly affects phase transitions and molecular ordering in ferroelectric LCs [15]. Singh and colleagues showed that adding small amounts of silver to NLCs increases the transition temperature and reduces the required operating voltage [12]. Tripathi's experiments revealed that Ag NPs decrease dielectric anisotropy and elastic constants [7]. Our own research group has also shown that LC ordering can be tuned using different silver composites [17]. Furthermore, Ag/Pd mixtures have enabled the fabrication of cells with faster response times [16]. A recent review by Shen et al. provides a detailed explanation of how various nano-dopants influence the physical parameters of LCs [10].

The reaction of metal atoms with cyanobiphenyl monomers or dimers can lead to complexes of different geometries (linear or "sandwich"-type). Experimental IR spectra show a sharp decrease in the vibrational frequency of the C≡N group compared to pure 5CB, confirming that silver forms π-complexes with 5CB in a cooled environment. Since liquid crystals often exist in condensed dimeric structures [7–10], it is likely that a silver atom resides between two 5CB molecules, forming a complex.

The cyanobiphenyl molecule contains two active centers—polar cyano groups and aromatic rings. This structural feature allows transition metals to form σ-complexes through direct coordination with the cyano group, as well as π-donor/π-acceptor complexes via the aromatic rings [2].

In this study, nematic liquid crystals belonging to the alkyl-cyanobiphenyl group (e.g., 4-n-pentyl-4'-cyanobiphenyl) were used. These materials are characterized by positive dielectric anisotropy (Δε) and homeotropic molecular alignment [20]. Homeotropic orientation occurs in LCs with positive dielectric anisotropy ($\Delta\varepsilon > 0$). In this state, LC molecules with dipole moments aligned along their long axis orient parallel to the applied field and perpendicular to the cell plane.

The fundamental theoretical model describing the dielectric properties of nematic liquid crystals was proposed by V. Mayer and G. Meyer, who introduced the following equations to characterize the system.

$$\varepsilon_{\parallel} - 1 = \frac{4\pi\rho}{M} N_A hF\left[\overline{\alpha} + \frac{2}{3}\Delta\alpha_1 S + \frac{Fg}{3k_BT}\left(1 - \left(1 - 3cos^2\beta\right)S\right)\right)\right]$$

$$\varepsilon_{\perp} - 1 = \frac{4\pi\rho}{M} N_A hF\left[\overline{\alpha} + \frac{1}{3}\,\Delta\,\alpha S + \frac{Fg}{3k_BT}\left(1 + \frac{1}{2}\left(1 - 3cos^2\beta\right)S\right)\right)\right]$$

$$\Delta\varepsilon = \frac{4\pi\rho}{M} N_A hF\ \left[\overline{\Delta}\alpha - \frac{Fg}{2k_BT}\left(1 - 3cos^2\beta\right)\right]S$$

In the Mayer–Meyer theory, M- represents the molar mass, ρ- the density, N_A- the Avogadro constant, and k- the Boltzmann constant. This model is able to describe both positive and negative dielectric anisotropy cases, as well as the temperature dependence of the quantities ε‖ and ε⊥ with sufficient accuracy.

A decisive parameter in this process is the degree of ordering, S: in the solid crystalline state S = 1, in the isotropic liquid phase S = 0, and in the liquid crystal state 0 < S < 1. This parameter fully determines both the electrical and optical anisotropy properties of the liquid crystal. Elasticity and viscosity in liquid crystals are also direction-dependent. As S → 0, both optical anisotropy (Δn) and dielectric anisotropy (Δε) decrease monotonically.

Nematic liquid crystals are anisotropic condensed media in which the long axes of molecules are aligned in a common direction. The dielectric permittivity of such media is expressed by a tensor consisting of ε‖ and ε⊥ components. Dielectric anisotropy is defined as

$\Delta\varepsilon = \varepsilon\parallel - \varepsilon\perp$, and its sign depends directly on the chemical structure of the molecules. The behavior of liquid crystals in an electric field is determined by the sign of $\Delta\varepsilon$: when $\Delta\varepsilon > 0$, the director (n) aligns along the field direction; when $\Delta\varepsilon < 0$, the director aligns perpendicular to the field.

A liquid monocrystal, due to both dielectric and conductivity anisotropy, experiences a torque in an external field. Because of the low internal friction and viscosity of the material, this torque enables the director to reorient within a short time[18,19].

The anisotropic shape of molecules leads to different refractive indices for ordinary (n_o) and extraordinary (n_e) rays. This difference is related to whether the polarization direction of light is parallel or perpendicular to the director. Optical anisotropy is calculated as $\Delta n = n_e - n_o$. Under the influence of an electric field, molecular rotation changes the director, which modifies the n_e component along the field vector and causes oscillations in the intensity of light transmitted through the liquid crystal layer.

EXPERIMENTAL

Physical mesauraments

The composite was observed using a Polarized Optical Microscope (POM). The dielectric permittivity of the obtained composite was measured with an Immittance E7-20 device.

The nanocomposite samples under investigation were prepared on the basis of the liquid crystal pentylcyanobiphenyl (5CB), which exhibits a nematic phase at room temperature. Into this matrix, a small amount (1% by weight) of silver nanoparticles (AgNPs) with an average diameter of approximately 20–80 nm was incorporated. The nematogen 5CB, produced by Merck, was used without additional purification.

At room temperature, this compound remains in a stable nematic state, and upon controlled heating it undergoes the following phase transitions: Crystal–Nematic at 22.5 °C and Nematic–Isotropic at 35.3 °C. At 20 °C and a frequency of 1 kHz, the dielectric anisotropy of 5CB is positive ($\Delta\varepsilon \approx 10$) (Figure 1).

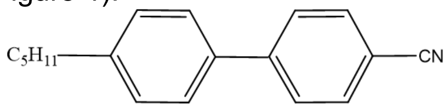

Figure 1. Chemical structure of 5CB

The prepared AgNPs/5CB nanocomposite mixture was introduced into the cells in the isotropic state via capillary action. In the study, cells consisting of parallel glass plates were used. These glass substrates, with a thickness of 1.1 mm, were coated with a conductive indium–tin–oxide (ITO) layer of 20–40 nm thickness. The cells were also separated by a dielectric layer (Teflon spacer).

To ensure planar orientation, the electrode surfaces were coated with a polyimide layer. The preparation of the polyimide coating was carried out in the following sequence: 1. Polyimide was dissolved in dimethylacetamide at 5% weight ratio and filtered. 2. The resulting solution was dropped onto the ITO-coated cell, and a special device was used to form a 0.1 µm thick layer on the glass surface. 3. The added solvent was evaporated in a heater to avoid interference with the experimental results.The effective working area of the cells was 1 × 1 cm, with a thickness of d = 25 µm. For comparative analysis, analogous cells were also filled with pure 5CB.

RESULTS AND DISCUSSION

Transition metals such as silver form complexes with 5CB (cyanobiphenyl) molecules through two main mechanisms: π-donor and π-acceptor mechanism – the metal atom interacts with the aromatic rings of the biphenyl fragment, σ-complex mechanism – the metal atom directly coordinates with the cyano (C≡N) group.

It is known that cyanobiphenyls form head-to-tail type dimers in the condensed phase. The silver atom enters the center of this dimer structure, thereby stabilizing the system. Theoretical calculations and charge distribution analyses show that the most stable configuration in the 5CB–silver system is a "sandwich"-type complex. In this case, the silver atom, with a charge of +0.8, polarizes the cyano group and alters the dielectric properties of the system. This demonstrates that silver nanoparticles strengthen molecular ordering in the nematic matrix and generate a local electric field (Figure 2).

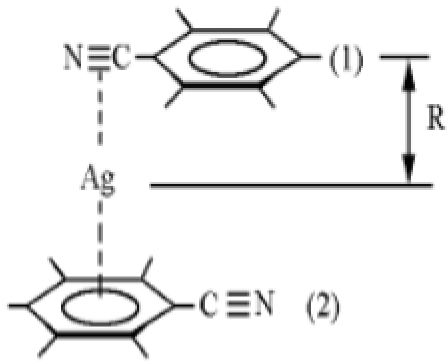

Figure 2. Schematic representation of the coordination model formed between the silver atom and 5CB molecules

The frequency dependence graph of the dielectric permittivity (ε′) of the AgNPs/5CB nanocomposite obtained in our study (Figure 3) shows complete qualitative agreement with the literature data (Figure 4) [20]. In both cases, a sharp increase in dielectric permittivity is observed in the low-frequency region (up to 10^2 Hz). This increase is explained by the additional ionic polarization created by the silver nanoparticles incorporated into the matrix and by charge accumulation at the electrode–sample interface.

However, in our samples, the differences observed in ε′ values with an increase in spacer thickness from 20 µm to 60 µm allow for a deeper analysis of the orientation properties of nanoparticles under different geometric conditions.

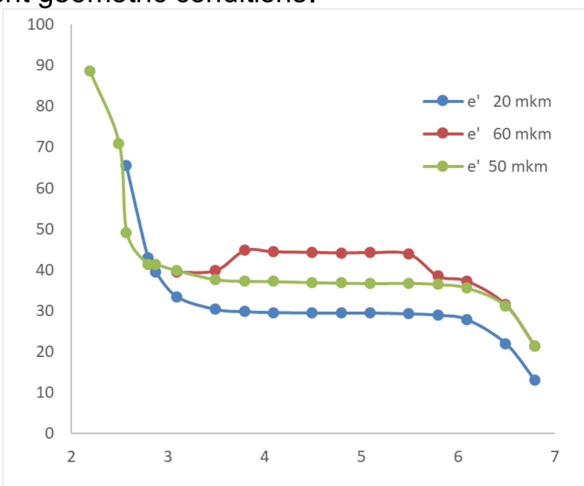

Figure 3. Graph of the frequency dependence (lg ω) of the dielectric permittivity (ε′) of the nanocomposite prepared using Teflon spacers of different thicknesses.

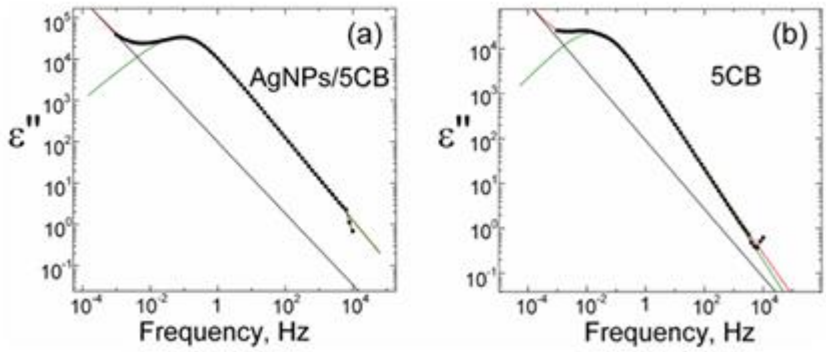

Figure 4. Graphs of the frequency dependence of the imaginary part of the dielectric permittivity [4]

According to literature data, dielectric relaxation in the AgNPs/5CB system follows the H–N function as shown in Figure 4, which is in full agreement with our experimental results (Figure 3).

CONCLUSION

Within the scope of this study, nanocolloid systems based on the nematic liquid crystal 5CB with incorporated silver nanoparticles (AgNPs) were synthesized, and their dielectric properties were analyzed. It was determined that silver atoms interact with 5CB molecules through both σ-bonding and π-donor/acceptor mechanisms. Measurements carried out using dielectric spectroscopy show that silver dopants significantly affect the overall dielectric permittivity (ε′) of the system. A sharp increase in dielectric permittivity was observed at low frequencies.

It was found that in composite samples with a 20 μm thick Teflon spacer, surface effects are more dominant, leading to fluctuations in ε′ values. In contrast, in cells with 60 μm thickness, the frequency dependence of dielectric permittivity exhibits a more stable character. This stability is explained by the volumetric distribution of silver nanoparticles compensating for surface polarization.

By optimizing the concentration of silver and the geometry of the cells, it is possible to reduce the operating voltage of liquid crystal devices. The high dielectric permittivity observed in the nanocomposite system enhances their potential applicability in sensor technologies. The results of the study demonstrate that AgNPs dopants modify the optical and electrical properties of the nematic phase at the molecular level.

The findings open up broad prospects for the application of these hybrid materials in next-generation tunable optical sensors, high-speed display technologies, soft electronics, multi-segment devices, and photonic systems. Ultimately, the results obtained may serve as both theoretical and practical foundations for the synthesis of new electro-optic materials.

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