Liquid crystal cell as a model of a biological system: biosensor

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Abstract. The relevance of the work is determined by the constant search for new solutions in biology and medicine to create biomaterials and suspensions with specified physicochemical properties. The paper considers nematic liquid crystals of the class of two ringed ethers with different terminal groups. Thin layers (8 - 100 microns) of liquid crystals were affected by an electric field. In the case when the electric field was directed perpendicular to the molecules (homeotropic orientation), a torsion moment occurred. In the case of the planar orientation of the crystal molecules with the application of an electric field, the formation of a domain pattern of the type of concentric circles was observed. It is found that the magnitude of the wave vector changes in direct proportion to the applied field. The results of the presented studies can be used in biology and medicine. The proposed liquid crystal cell can be used as a cell model of a living organism, as a biosensor or for molecular imaging to study the issues of drug delivery to cells, tissue regeneration, and the creation of new biomaterials.

1 Introduction

The current rapid development of nanotechnology research resembles the boom in the field of information technology in the 70 - 80s or in the field of biotechnology in the 80 - 90s of the last century [1 - 20]. And this is quite understandable, given that nanotechnology provides a high potential for economic growth, on which the quality of life of the population, technological and defense security, resource and energy conservation depend. Now almost all developed countries have national programs in the field of nanotechnology. The attractiveness of nanotechnology for science, industry and medicine is, first of all, that they allow manipulating matter at the level of individual atoms and molecules, using them to create materials with a unique structure - carbon nanotubes, the thinnest semiconductor coatings, especially strong nanocomposites. The initial "raw material" for the production of nanoproducts can be not only carbon, silicon, metals, but also "building blocks" of biological nature [21]. In the process of evolution, biological molecules have acquired properties that make them very attractive for use in nanotechnology. Firstly, it should be noted the chemical diversity of biological "bricks" (amino acids, lipids, nucleotides). Secondly, they are prone to spontaneous formation of complex spatial structures. Thirdly, the regulated assembly of

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"building blocks" can go in different ways, which opens up the possibility of creating a variety of nanoconstructions.

The hierarchy of self-assembling biological structures begins with monomers, i. e. nucleotides and nucleosides, amino acids, lipids. They form polymers such as DNA, RNA, proteins, polysaccharides. Polymers are organized into ensembles (membranes, organelles), then cells, organs and whole organisms are formed. The use of biological molecules for the synthesis of artificial nanostructures based on the principles proposed by nature looks quite natural. As a result of self-assembly, it is possible to obtain substances with unique properties, in particular, to create chimeric molecules containing, for example, amino acids and synthetic organic chains. And this opens up fantastic opportunities for the construction of nanomaterials and the "transfer" of biopolymers from the world of biology to the world of technology. From the point of view of the convenience of nanosembly, nucleic acids are distinguished among the variety of biological compounds. Why them? Nucleic acids have several characteristic features. Short (50 - 100 nm long) two-stranded DNA and RNA molecules have a fairly high rigidity, and therefore they are convenient to use as "building blocks". At the same time, single-stranded nucleic acid retains flexibility and, in addition, has the ability to recognize its complementary chain. Two such chains easily "stick together" due to the formation of hydrogen bonds. If two stranded molecules have single-stranded "tails" at the ends (they are called sticky ends), then other chains can be attached and branching sites can be formed. And this allows you to create flat lattices and complex spatial structures. The properties of two-dimensional and three-dimensional structures made of nucleic acids can be easily adjusted by changing the environment in which the assembly takes place (using different solvents). Other elements can be embedded in DNA and RNA structures, for example, biologically active substances that attach to nitrogenous bases. The means of modern biotechnology make it possible to produce single-stranded and double-stranded nucleic acid molecules with predetermined sequences of nitrogenous bases on an industrial scale, therefore there is no shortage of "building blocks" for nanosembly.

There are two strategies for creating nanoconstructions, but regardless of which one is chosen, the structure of nucleic acid-based materials can be controlled with molecular precision. Construction "step by step". This approach, based on the sequential modification of the initial molecule of a two-chain nucleic acid or synthetic polynucleotide, was theoretically justified in 1982 in the work of American chemist Ned Ziman. The first step is to obtain DNA fragments with sticky single-stranded ends. This can be done by biochemical methods or by direct chemical synthesis. When the sticky ends of different DNA fragments stick together, a structure with small defects is formed - breaks in the sugar-phosphate chains. The breaks are stitched together by a special enzyme - ligase. The second step is to create the branching point necessary to form a cruciform structure. This is possible when using DNA fragments with a specific sequence of nitrogenous bases. Cruciform structures are not exotic at all. They are found in DNA molecules isolated from bacteria. An artificially created cross-shaped DNA molecule can have sticky ends with the help of enzymes. These ends provide a connection to the corresponding complementary fragments of other DNA molecules. As a result of sequential stitching of the sticky ends, a flat nanolattice is formed. Due to the mobility of the DNA molecule at the branching point, the rigidity of the resulting nanostructure is not very high. In order to increase it, nanoconstruction techniques have been developed, which can be called "additional" to N. Ziman's approach. So, in 1994, Christoph Niemeyer (Germany) proposed using DNA molecules to which fragments of biotin and streptavidin, a protein binding biotin, are sewn. This technique allows you to create nanostructures in the form of closed rings.

In 1997, American scientist Donald Bergstrom used synthetic molecules consisting of two chains of nucleotides, the ends of which are sewn together by a rigid hydrocarbon bridge, for nanoconstruction. From such details it is possible to create constructions in the form of

stars with several rays. The low rigidity of nanostructures of the flat lattice type also has an attractive side: such a lattice, with the correct selection of the nucleotide sequence, is easy to bend. In 1991, Ned Zeman obtained a nanostructure shaped like a cube with edges made of DNA molecules. You can also create other three-dimensional structures, such as interlocked octahedra and dodecahedra. Ziman's technology is beautiful, but it involves great economic costs. For its application, segments of nucleic acids with a given sequence of nitrogenous bases and a whole arsenal of enzymes - restrictases and ligases - are needed to cleave and stitch DNA fragments in the right places. The finished products must be carefully removed from the reaction mixture and a thorough analysis of their properties must be carried out. Modern control methods, in particular atomic force microscopy, are required at all stages of such nanoconstruction.

The authors of the work are continuously searching for the practical application of liquid crystals in various branches of human activity. Previously, it was proposed to use liquid crystals in solving technical problems to create devices, sensors, liquid media level monitoring systems for the oil and gas industry; the research results may be useful for the development of light modulators, displays [22 - 27]. In the presented article, it is proposed to use a cell with a liquid crystal as an analogue of a living cell of an organism. Its behavior under the action of an external field, for example, electric, is interesting from the point of view of the study of biological systems.

The paper presents the results of an experimental study of the gyration effect induced by an electric field. Electrogiration is the effect of spatial dispersion, which consists in the occurrence or change of optical activity (gyration) in crystals under the action of an alternating or constant electric field. Electrogiration, as a phenomenon of spatial dispersion, differs from the Faraday effect by the increment of optical activity when the sign of the wave vector changes, in other words, with the electrogiration effect, the increment of optical activity changes the sign when the sign of the wave vector changes, and with the Faraday effect does not change. The gyration effect induced by the electric field is proportional to the electric field strength (linear electrogiration), which is resolved in solid crystals belonging to all point symmetry groups, with the exception of three cubic ones — $m3m$, 432 $i\bar{4}3m$. If there is an effect proportional to the square of the electric field strength (quadratic electrogiration), then it is resolved by symmetry only in acentric crystals. For the first time, quadratic electrogiration was observed in quartz crystals. Linear and quadratic electrogiration effects have been studied in photorefractive and ferroelectric materials, as well as in dielectric semiconductor materials. The electrogiration effect is the first discovered effect of gradient nonlinear optics, since from the standpoint of nonlinear electrodynamics, frequency permutations are taken into account, as well as the gradient of the electric field of the light wave within small lengths corresponding to the macroscopic gradient of the external electric field [28].

With this effect, chiral phases are formed in liquid crystals, for example, when optically active additives are dissolved in LC. The simplest additives are sugar or cholesterol derivatives. Today, the scientific community focuses on the research and practical application of self-organizing systems, due to the fact that they are the basis of nanotechnology. Liquid crystal molecules have the ability to assemble themselves into ensembles, so they can be safely attributed to nanomaterials. The mechanism of self-organization depends on the structural features of nanomaterial molecules. It is well known that the difference between nematic liquid crystals (NLCs) and cholesterol (HCCs) consists in the presence of a twist in cholesterol, at the same time their local structure and properties are similar. Today, it has been proven that HCCs are found only in nematic molecular systems, which are characterized by the difference of molecules from their mirror image. To obtain spiral structures of nematic, it is enough to dissolve optically active substances in the LC matrix. Another method of obtaining is twisting one of the substrates with a planar orientation of the molecules. For the

first case, the wave vector of the induced spiral $\vec{q}$ is directly proportional to the concentration C of optically active substances: $\boldsymbol{q} = 4\pi\beta C$, where β is the microscopic torsion force. It should be noted that at the moment it is not clear how the magnitude of the optical activity of the solute is related to the spiral pitch, but it is reliably known that the macroscopic torsion force is proportional to the magnitude of the optical activity [29].

In liquid crystals, it is possible to have an effect called the optical activity effect induced by an electric field, which leads to a spatial twist of the LC, due to the fact that the symmetry of the LC allows its observation. It is known for ordinary solid crystals and is called electrogiration. The magnitude of optical activity can be expressed in terms of the third-rank axial tensor g_{ijk}, whose dependence on the magnitude of the electric field $\sigma_{ij} = g_{ijk}E_k$ is linear [30]. In the case of NLC, according to its symmetry, only two components of the g_{ijk} electrogiration tensor other than zero are allowed to exist: g_{xzy} and g_{xzx} for $g_{xzy} = -g_{xzx}$ [31]. Consider a nematic liquid crystal oriented in such a way that the NLC director is directed perpendicular to the electric field strength $\boldsymbol{E}\perp\boldsymbol{n}$, $\boldsymbol{n}\|OZ$, but $\boldsymbol{E}\|OX$. In this case, the NLC becomes optically active, and the angle of rotation φ_z of the plane of polarization of light propagating along the *OZ* axis will be equal to:

$$\varphi_z = g_{xzy}k_zE_x,$$

and along the *OX* axis:

$$\varphi_y = g_{xzy}k_xE_x,$$

where k_y – *y* is the component; k_x - *x* is the component of a unit vector along the direction of light propagation.

The appearance of optical activity in the NLC leads to the appearance of torsion moments π^*_{ij}, which are proportional to $g_{xzy}E_x$ and $g_{xzx}E_x$.They are compensated by elastic moments:

$$\pi_{xz} = K_{22}(n_x\frac{dn_z}{dy} - n_z\frac{dn_x}{dy}) \quad \text{or} \quad \pi_{yz} = K_{22}(n_z\frac{dn_z}{dy} - n_x\frac{dn_z}{dy}),$$

where K_{22} is the coefficient of elasticity; n_x- and n_z are the components of the director.
In both cases, the wave vector of the structure along the axis *OY* or *OX*:

$$q_y \sim \frac{g_{xzx}E_x}{K_{22}}, \quad q_x \sim \frac{g_{xzy}E_x}{K_{22}}.$$

So, two torsion moments appear: π^*_{xz} и π^*_{zy}. The first tends to twist the NLC in the *XZ* plane, and the second along the electric field. Therefore, it is necessary to create such conditions to exclude either π_{zy} or π_{xz}. In the presence of both torsion moments, the interpretation of the experiment is very difficult.

2 Materials and methods

To observe the gyration effect induced by an electric field, it is necessary to use liquid crystals with very low electrical conductivity and dielectric anisotropy. Such requirements are met by liquid crystals of the class of two ringed ethers with different end groups and with a COO group in the center, which have strong polarizability (end groups *X, Y: X_1=C_4H_9; X_2=$C_6H_{13}O$; X_3=C_4H_9OC; Y_1=OC_6H_{13}; Y_2=OC_4H_9; Y_3=OC_2H_5*). The resistivity of such crystals after purification is of the order of $6\cdot10^{10}$ Ohms·m, and the permittivity of

$\varepsilon_{\parallel} \approx \varepsilon_{\perp} \approx 5.75$, if $\varepsilon_{\parallel} - \varepsilon_{\perp} < 0.005$. For this mixture of LC flexoelectric coefficients have the values $e_{\parallel} \approx e_{\perp} \sim 10^{-6}$ units. CGS, i. e. they are an order of magnitude lower than, for example, for *n*–methoxybenzylidene-butaniline (MBBA).

The studies of the gyration effect induced by an electric field described below were carried out using a polarization microscope and its accessories. The spectral photometric attachment of the microscope had a rectangular probe of 5 × 1000 microns and allowed photometry and analysis of the double refraction of crystal sections of such sizes. Registration of signals from a photoelectronic multiplier for wavelengths of 200 - 800 nm was carried out by a digital voltmeter and a two-coordinate recorder; fast-flowing processes were studied using a memory oscilloscope with subsequent processing on a computer. The temperature of the sample placed in the thermostatic chamber was adjusted to an accuracy of 0.1 ºC. The electric field was set either by a signal generator of a special form, or by a constant voltage source. The double refraction and the orientation angle of the NLC director were determined from the analysis of the ellipticity of light using a Senarmon compensator with a constant stroke difference. Photographing was carried out using a digital camera followed by computer image processing.

The dielectric permittivity $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of mixtures and pure components were measured at frequencies up to 100 kHz using an alternating current bridge, and the electrical conductivity was measured by a DC bridge, the double refraction was determined by the magnitude of the difference in the course of a homeotropically oriented NLC in a plane–parallel cuvette tilted at an angle of 10º to the light rays. To create a dedicated orientation direction on one of the substrates, a microrelief was created with a sufficiently large step of 10^{-5} cm by polishing the substrate in the selected direction. After that, a transparent conductive layer of tin *Sn* was sprayed onto the substrate. With a small microrelief step of less than 10^{-5} cm, samples with only a planar orientation of molecules on one of the substrates were obtained. Also, it was thanks to the microrelief that the spinning of molecules along the *OX* axis did not occur (the prohibition condition). The experimental cell was assembled from two 10 × 20 mm glass plates made of slides. Between them were placed pads of cover glass, which set the thickness of the liquid crystal. Samples with a crystal thickness from 8 to 100 microns were studied. The experimental technique is described in detail in [32].

3 Results and discussion

Consider the behavior of a nematic liquid crystal and the dynamics of spiral structures formed by the action of electric fields on it (the axis *OX* is perpendicular to the plates of the capacitor, and $\boldsymbol{n} \| OZ$). Almost simultaneously with the application of the field (under weak boundary conditions), the reorientation of LC molecules begins. Here the torsion moments π^*_{xz} and π^*_{zy} are realized and a special picture of the domain structure is formed, in which the domains form a set of coaxial circles of different radius of spherulites. Each of these domain patterns observed in a microscope is associated with the formation of spiral structures having a special point from which the radial twist of the NLC begins in the *YOZ* plane. If there is a microrelief on one of the substrates, then the domain structure has the form of a system of parallel bands (Figure 1). The wave vector of the bands is directly proportional to the applied field, while, for different thicknesses of LC samples, the width of the domains is the same for equal electric field strengths (Figure 2). From the dependence for torsion moments, it can be seen that the orientation angle at a certain point of the *YOZ* sample should change to the opposite when the polarity is reversed. This effect takes place if you change the polarity of the electric field. In this case, the wave vector first decreases to zero (with a large step of domain structures), and then grows to the initial value (Figure 3). If the polarity is switched periodically, in this case, the hysteresis of the wave vector is observed, which depends on the

switching frequency. The hysteresis value depends on the temperature of the liquid crystal, as well as on the defects in the domain structure. That is, when the electric field is turned on, the wave vector will change from zero to some value $\boldsymbol{q}$. The formation time of structures depends on the boundary conditions of the elasticity and viscosity coefficients. If we increase the switching frequency of the electric field (E = const), then there is an increase in the width of the domains. If the electric field is abruptly turned off (for example, $E \approx 10^7$ V/m), then the helicoid structures gradually unwind and the pattern of domains repeats in reverse order. Typical domain promotion times are 5 - 20 s, they also depend on the thickness of the NLC layer and temperature. This limits their use in the design of displays, but makes it an ideal environment for creating systems for long-term display of information, for example, tables.

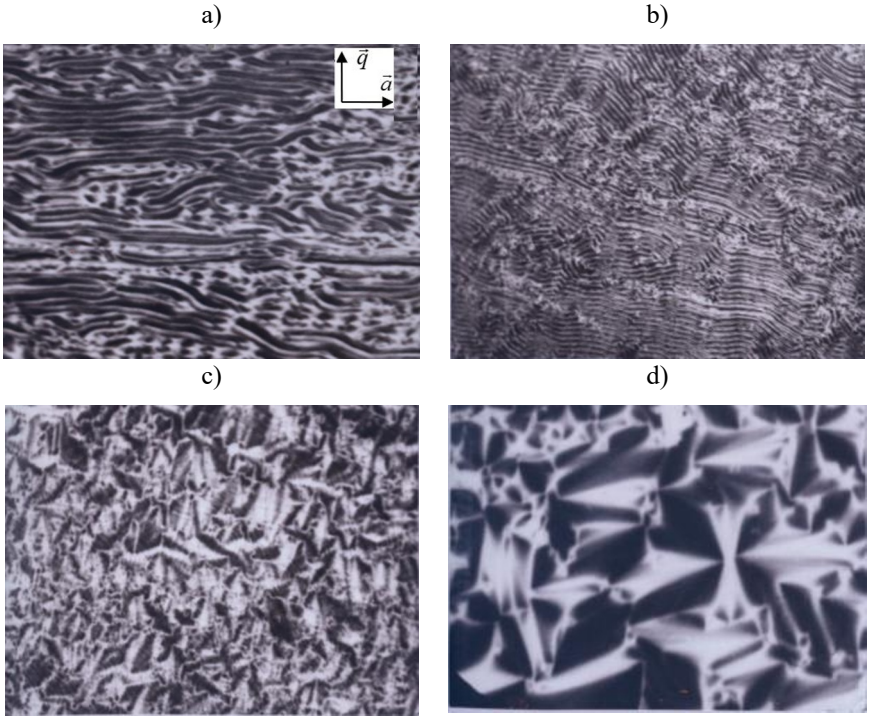

Fig. 1. Micrographs of domain structures at field strengths: a) -10^2 kV/m; b) -$3 \cdot 10^2$ kV/m; c) -$6 \cdot 10^2$ kV/m; d) -10^3 kV/m. In Figure (a), the arrow shows the direction $\boldsymbol{a}$ of the microrelief and $\boldsymbol{q}$ of the wave vector of spiral structures (scale 1:100).

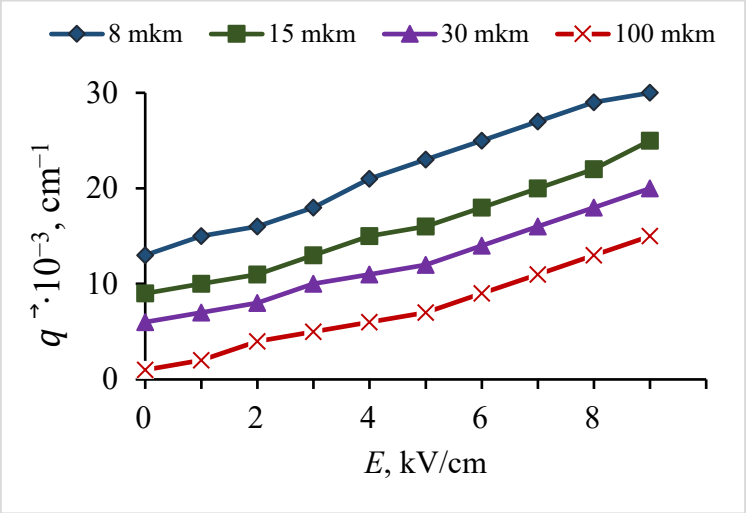

Fig. 2. The dependence of the wave vector of the LC spiral induced by an electric field on its intensity (for clarity, the values of the wave vector are shifted for 30 microns by $0.6 \cdot 10^{-6}$ m^{-1}, for 15 microns by $0.7 \cdot 10^{-6}$ m^{-1}, for 8 microns by $1.2 \cdot 10^{-6}$ m^{-1}).

The optical structure of individual domains is strongly determined by the magnitude of the double refraction, and they have the form of bands representing a system of major isohyres and isochromes. At low voltages, domain structures are not visible when the plane of polarization of the axis of the helicoid is parallel, domain structures are not visible. In this case, there is also no diffraction of light. When the field increases, a lot of defects are formed in the NLC layer.

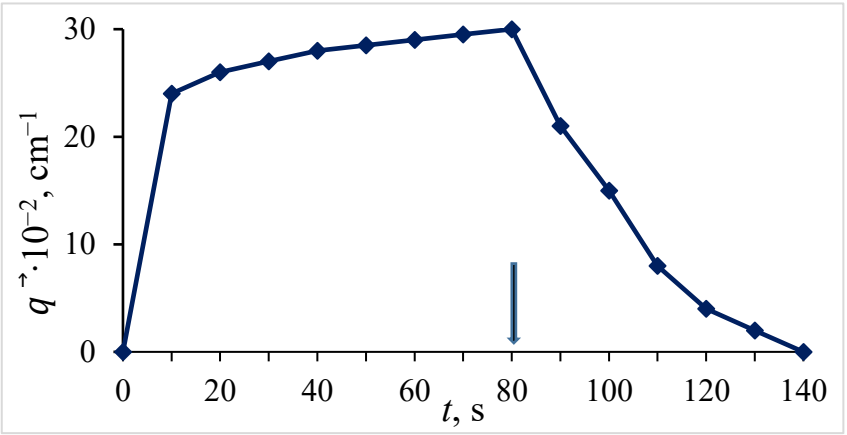

Fig. 3. Time dependence of the wave vector of the LC spiral when the electric field is switched on and off (shown by the arrow) ($E = 9 \cdot 10^2$ kV/m).

The orientation structure of LC molecules near defects, which was reconstructed from polarization-optical studies, makes it possible to attribute them to χ-disclinations of spiral structures. With an increase in the values of the electric field effect, the number of half-integer force disclinations increases, they decay according to the scheme $\chi(1/2) = \lambda^{-2} + \tau^{+}$ per $\lambda\tau$-pair ($P/2$ pair). With the growth of the wave vector $\boldsymbol{q}$, the number of $P/2$–pairs increases, while they form the boundary of the hyperbola that separates the layers, resulting in the formation of a confocal texture in the *YOZ* plane.

4 Conclusions

Thus, the effect of electrogiration in nematic liquid crystals under the action of an electric field has been experimentally investigated. This phenomenon was predicted on the basis of the NLC symmetry theory. The observation condition is a small value of the anisotropy of the dielectric constant, high purity of the liquid crystal itself. The existence of the effect of electrogiration is possible in solid crystals. However, linear or quadratic electro-optical effects in them do not allow it to be observed. It is found that the magnitude of the wave vector linearly depends on the strength of the applied field. Electro-optical phenomena are widely used to create optical radiation control devices (light modulators, deflectors, optical phase gratings) and optical indicators (liquid crystal displays, digital indicators), to register field strength, as well as to study the structure of matter, intramolecular processes, phenomena in solutions and crystals. The proposed liquid crystal cell can be used as a cell model of a living biological organism, as a nanosensor/biosensor, for molecular imaging. This is relevant for studying the issues of drug delivery to cells, tissue regeneration, and the creation of new biomaterials.quations

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