

## LIQUID CRYSTAL MATERIALS WITH REGULATED OPTICAL PROPERTIES

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**Abstract.** In this work we present the results of structural and electrooptical investigations of the new-created composites based on lyotropic liquid crystals (LLC) of potassium caprylate and viologens. Provided structural analysis showed the presence of a Smectic ordering in the investigated samples and allowed to determine its main parameters. It was shown that the electrochromic properties of viologens are preserved after their solution in the liquid-crystalline matrix. They reveal themselves as a coloration of the samples under applying of an electric field and are proved by the optical absorption spectra. Also we analyzed the processes taking place in LLC-viologen composites in the case of an electric field applying.

**Keywords:** lyotropic liquid crystals; viologens; structural analysis; electrochromism; electronic spectra.

### Introduction

The idea of creation of new liquid crystal materials with regulated optical properties lays in doping lyotropic liquid crystals (LLC) with photo- and electrochromic admixtures. Molecules that belong to the class of viologens obtain needed properties, e.g. they are able to change their colour in the case of ultraviolet radiation or external electric field application [1]. These properties remain completely at solving viologens in different solutions. Thus, the same result should be observed at solving viologens in water-containing LLC. High viscosity of LLC might facilitate the prolongation of coloured states lifetime in comparison with the liquid solvents.

### Analysis of investigations and publications

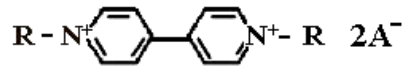
Liquid crystals investigations are in the first line of research in the field of display and optoelectronic technologies. Such investigations are particularly effective and acknowledged in the area of thermotropic and polymeric liquid crystals. As for the lyotropic liquid crystals, it should be mentioned that these materials are not used so widely and their investigations are still not full. However, there is a set of articles [2–4] devoted to the investigations of impurity LLC, whose mesophases gain new optical properties peculiar to the admixture materials.

The aim of the present work lays in following:

- creation of electrochromic composites based on lyotropic liquid crystals and species of viologens class;
- developing working cells for studying the created materials;
- ascertainment the structure of the LLC-viologen composites;
- realization of complex investigations with purpose to reveal electrooptical properties of LLC-viologen systems.

### Materials and methods

Lyotropic liquid crystalline phase was formed at mixing powder of a Potassium caprylate ( $C_7H_{15}COO K^+$ ) with water in 1:1 weight proportion at the room temperature ( $T = 293 K$ ). Then samples of LLC were doped by the viologens of two types: the first one  $N,N'$ -diheptyl-4,4'-dipyridilium dibromide ( $HD^{2+}2Br^-$ ), and the second one is  $N,N'$ -di(2-carboxyethyl)-4,4'-dipyridilium dichloride ( $CED^{2+}2Cl^-$ ). The viologens differ in substitutes at Nitrogen atoms and counterions. The general structural formula for both viologens is given as:



where  $R$  is a substitute,  $A$  is a counterion. In the case of  $HD^{2+}2Br^-$   $R = C_7H_{15}$ ,  $A^- = Br^-$ ; for the  $CED^{2+}2Cl^-$   $R = (CH_2)_2COOH$ ,  $A^- = Cl^-$ . Viologens content in the samples amounts to 2 % by weight.

Sandwich cells (fig. 1) were used for the investigation of the created samples. Samples were placed between two glass plates whose inner surface was covered with ITO electrodes. Then the plates were fastened and pasted together to avoid air access and further spoiling of the samples. The thickness of the sample was set with using teflon pads. The voltage was applied using constant voltage source.

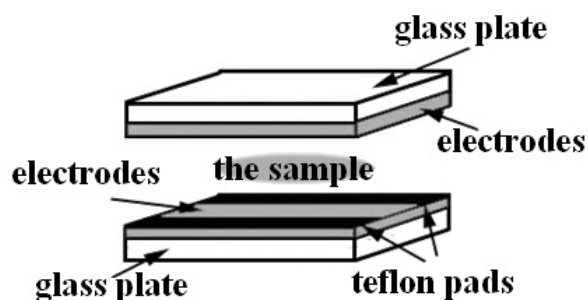


Fig. 1. The experimental sandwich-cell

### Structural investigations

The method of small-angle X-ray scattering was applied for the studying the structure of LLC on the base of aqueous solution of Potassium caprylate. X-ray experiments were carried out for both pure and viologen-doped LLC. They allowed determining the type of the formed mesophase and the impact of viologens solved in LLC on a liquid crystal ordering.

The obtained radiographs are presented in the fig. 2. The presence of an intense maximum in the small-angle area is a distinctive feature of Smectic liquid crystals. This maximum points at the existence of bilayer ordering of molecules for the investigated samples.

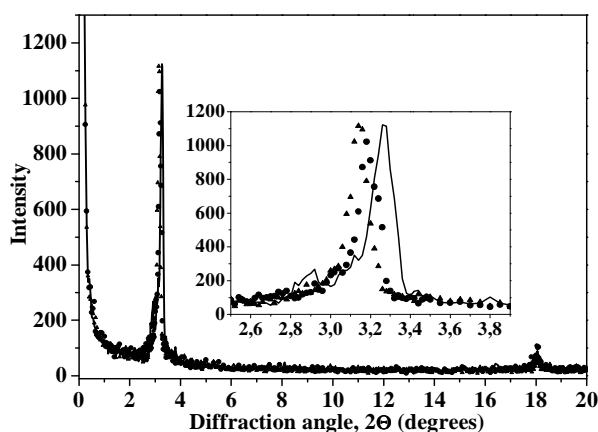


Fig. 2. Radiograph of pure LLC samples (solid line), LLC- $\text{HD}^{2+}2\text{Br}^-$  composite (dots), and LLC- $\text{CED}^{2+}2\text{Cl}^-$  composite (triangles)

The width of Smectic bilayers was calculated from the small-angle peak position using Wulff-Bragg formula. For pure LLC it comes up to  $d = 27,1 \text{ \AA}$ , for LLC- $\text{HD}^{2+}2\text{Br}^-$  and LLC- $\text{CED}^{2+}2\text{Cl}^-$  composites  $d = 27,8 \text{ \AA}$  and  $d = 28,5 \text{ \AA}$  correspondingly. Therefore, doping LLC matrix with viologens doesn't break its structure in general but leads to a little broadening of bilayers. In addition we determined the distance between hydrocarbon chains within one layer ( $s = 4,9 \text{ \AA}$ ) and correlation length of Smectic ordering for non-oriented samples ( $\xi_{\text{H}} \approx 350 \text{ \AA}$ ).

Basing on the obtained data we made a model of the LLC-viologen arrangement (fig. 3), which takes into account Smectic A ordering and bilayer structure with cation-anion interlayers consisting of water molecules, Potassium ions and negatively charged Oxygen atoms of caprylate carboxyl groups. Hydrocarbon chains of the caprylate molecules are perpendicular to the cation-anion interlayers. Estimation of the interlayers width gives following values:  $\Delta l = 8,8 \text{ \AA}$  for pure LLC,  $\Delta l = 9,3 \text{ \AA}$  and  $\Delta l = 10 \text{ \AA}$  for LLC- $\text{HD}^{2+}2\text{Br}^-$  and LLC- $\text{CED}^{2+}2\text{Cl}^-$  composites correspondingly.

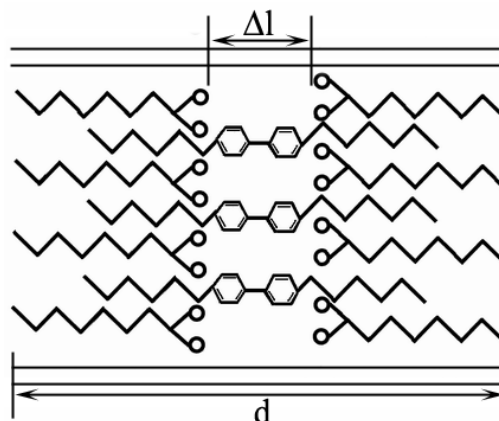


Fig. 3. Schematic representation of bilayer structure of LLC Smectic mesophase with built-in viologen molecules

Most probably viologen molecules are located in LLC matrix so that their central units and anions ( $\text{Br}^-$  or  $\text{Cl}^-$ ) are situated in cation-anion interlayers. With that the substitutes are located along similar hydrocarbon caprylate chains (fig. 3). Such a location is the most advantageous from the energetic point of view. Also it is proved additionally by the similarity in sizes of electrostatic LLC layer and central viologens units.

### Electrooptical investigations

It is known that application of an electric field leads to the reduction of viologen molecules and formation of coloured radical cations and dimers [5, 1]. Investigations of volt-ampere characteristics of LLC-viologen composites presented in the article [6] showed that viologens  $\text{HD}^{2+}2\text{Br}^-$  and  $\text{CED}^{2+}2\text{Cl}^-$  being contained in lyotropic liquid crystal reduce under the action of an electric field in two stages. On the first stage they turn into blue-coloured radical cations, on the second stage radical cations reduce to biradicals. The last ones join together with initial viologen molecules and thus form dimers with characteristic red colouring. In the case of  $\text{HD}^{2+}2\text{Br}^-$  it is possible to distinguish both reduction stages. In the case of  $\text{CED}^{2+}2\text{Cl}^-$  reduction processes are so quick that radical cations and dimers occur almost simultaneously. According to the data of volt-ampere characteristics reduction of viologens in LLC is a reversible process. This fact points at a possibility of a multiple repetition of colouring-decolouring cycles.

It should be mentioned that reduction takes place at the LLC-cell cathode, which serves as an electron donor for viologen molecules are able to catch electrons. Thus, after the application of an electric field one observes formation of a bilayer cell, which consists of the thin insoluble film of viologen reduction products and liquid crystal layer.

It was determined that both pure LLC and coloured LLC-viologen composited are characterized by dichroism [7]. In the first case it is explained by dichroic properties of the liquid crystal itself. In the second case it points at the ordering of a viologen reduction products film.

Data obtained with using methods of voltammetry were proved and completed by optical spectroscopy experiments. Electrooptical characteristics of LLC-viologen samples were studied basing on electron absorption spectra in visible region.

Both pure and viologen-doped LLC in the initial state do not absorb in the visible region (fig. 4, curve 1).

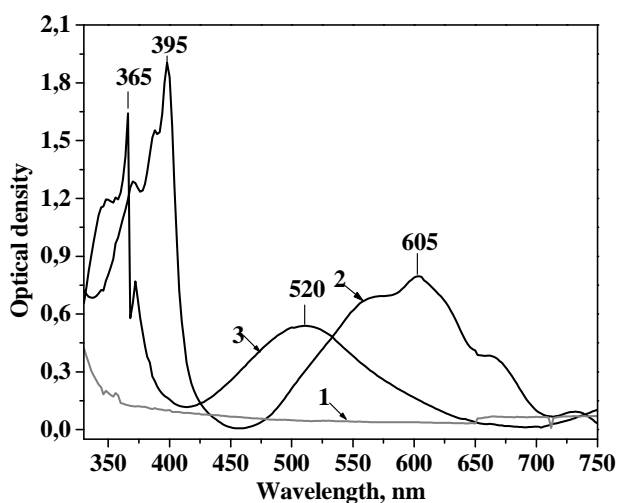


Fig. 4. Absorption spectra of LLC-HD<sup>2+</sup>2Br<sup>-</sup> composite without voltage application (curve 1); after application of voltage  $U = 2,5$  V (curve 2) and  $U = 4,0$  V (curve 3)

When studying LLC-HD<sup>2+</sup>2Br<sup>-</sup> samples in sandwich cells one-electron reduction and formation of blue-coloured radical cations were observed at voltage value of  $U = 2,5$  V. Absorption spectra are characterized by bands with optical density maxima at  $\lambda = 395$  nm and  $\lambda = 605$  nm (Fig.4, curve 2). The first band is stipulated by  $\pi$ - $\pi'$  electron transition polarized along the long axis of radical cation. The second band is stipulated by electron transition polarized in the plane of the dipyrilium core and perpendicular to the long axis of radical cation.

Two-electron reduction of viologen molecules that leads to decolourization of a sample occurs at voltage value of  $U = 3$  V. Dimerization takes place at  $U = 4$  V; absorption bands of the dimers have maxima at  $\lambda = 365$  nm and  $\lambda = 520$  nm (fig. 4, curve 3) and correspond to the red colouring of the samples.

The samples of LLC-CED<sup>2+</sup>2Cl<sup>-</sup> gradually colour in violet after voltage application starting from  $U = 2$  V. Optical density maximum is observed at voltage value of  $U = 3$  V. The spectra has a wide absorption band with two maxima at  $\lambda = 525$  nm and

$\lambda = 595$  nm (fig. 5, curve 1). Factorization of the spectrum by Gauss profile allows distinguishing two separate absorption bands, which belong to radical cations ( $\lambda = 600$  nm, fig. 5, curve 2) and dimers ( $\lambda = 515$  nm, fig. 5, curve 3) as well. Therefore, spectral investigations prove simultaneous formation of radical cations and dimers in LLC-CED<sup>2+</sup>2Cl<sup>-</sup> samples.

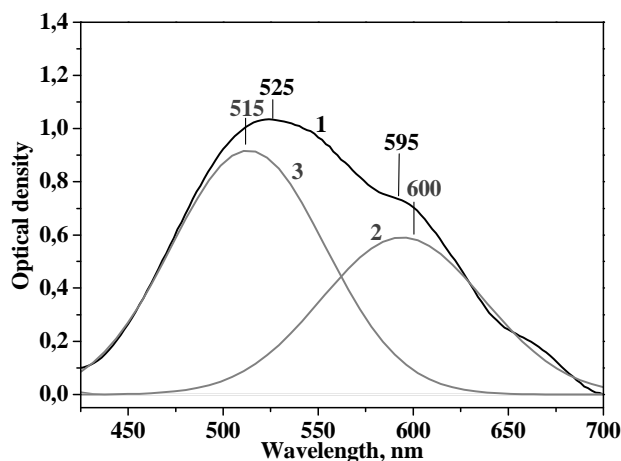


Fig. 5. Absorption spectrum of LLC-CED<sup>2+</sup>2Cl<sup>-</sup> composite after application of voltage  $U = 2,5$  V (curve 1); factorized spectrum (curves 2 and 3)

The lifetime of coloured radical cations and dimers of viologens in LLC medium depends on the value of voltage applied and duration of its action. In such a way the lifetime could be varied from seconds to hours. Besides, this time is much bigger in comparison with liquid solvents for which the lifetime of viologen reduction products amounts to 10-100  $\mu$ s [8]. Thus, from the point of view of controlled colouration processes LLC-viologen composites are promising for their further usage in optoelectronic technologies.

## Conclusions

1. New composite materials were created on the base of lyotropic liquid crystals doped by viologen impurities. Having liquid crystal ordering they obtain electrochromic properties peculiar to viologen molecules.

2. Methods of small-angle X-ray scattering detected the presence of bilayer Smectic ordering of molecules in lyotropic liquid crystals – viologen composites. Furthermore, impurity molecules are organically built into LLC matrix without breaking its structure. We evaluated space characteristics of LLC structure such as Smectic bilayers and cation-anion interlayers widths and correlation ordering length.

3. It was determined that during the voltage application the reversible reduction of viologens in

LLC medium takes place. It leads to the formation of coloured radical cations and dimers whose presence was fixed by optical absorption spectra. We showed the possibility of managing colouration processes in LLC-viologen samples and mentioned the prospects of their further usage.

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Received 24 September 2013.

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### Г. Б. Бордюг. Рідкокристалічні матеріали з керованими оптичними властивостями

Наведено результати структурних та електрооптичних досліджень новостворених композитів на основі ліотропних рідких кристалів каприлату калію та віологенів. Проведено структурний аналіз, який показав наявність у досліджуваних зразках смектичного впорядкування та дозволив визначити його основні параметри. Показано, що електрохромні властивості віологенів зберігаються і при розчиненні в рідкокристалічній матриці, що проявляється в забарвленні зразків під дією зовнішнього електричного поля і підтверджується оптичними спектрами поглинання. Проаналізовано процеси, які проходять в ліотропних рідких кристалах – віологен композитах у разі прикладання електричного поля.

**Ключові слова:** ліотропні рідкі кристали; віологени; структурний аналіз; електрохромізм; електронні спектри поглинання.

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Напрямок наукової діяльності: фізика молекулярних та рідких кристалів.

Кількість публікацій: 14.

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**А. Б. Бордюг. Жидкокристаллические материалы с управляемыми оптическими свойствами**

Приведены результаты структурных и электрооптических исследований недавно созданных композитов на основе лиотропных жидких кристаллов каприлата калия и виологенов. Проведен структурный анализ, который показал наличие в исследуемых образцах смектического упорядочения и позволил определить его основные параметры. Показано, что электрохромные свойства виологенов сохраняются и при растворении их в жидкокристаллической матрице, что проявляется в окрашивании образцов под воздействием внешнего электрического поля и подтверждается оптическими спектрами поглощения. Также были проанализированы процессы, которые проходят в лиотропных жидких кристаллах – виологен композитах в случае приложения электрического поля.

**Ключевые слова:** лиотропные жидкие кристаллы; виологены; структурный анализ; электрохромизм; электронные спектры поглощения.

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Количество публикаций: 14.

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