

SPECTRAL AND ELECTRIC CHARACTERISTICS OF IONIC LIQUID CRYSTALS DOPED WITH VIOLOGEN

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We present the results of study of the electrooptical and dielectric properties of a liquid crystal composition on the base of a lyotropic ionic liquid crystal (LILC) of K caprylate with the electrochromic admixture of diheptyldipyridyl dibromide (viologen). Under the treatment of the electrostatic field, the colouring of samples takes place. It depends on the applied voltage and manifests itself in absorption spectra. The obtained cyclic voltage-current characteristic of the LILC composition allows us to interpret the processes running inside the sample under the action of an external electric field. The investigation of the permittivity showed that the transition to a coloured state with increase of the applied voltage is accompanied by the general decrease of the sample's conductivity.

Introduction

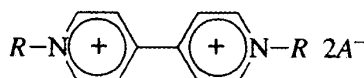
First of all, the scientific and practical interest in LC was connected with the possibility of their use in different electrooptical devices. The latest years, researches showed that liquid crystals are nonlinear optical and photorefractive media. One of the ways to create such materials is to dope an LC-matrix with electro- and photochromic admixtures. It seems to be promising that dipyridyl quaternary salts, which are usually called viologens, could be used as such admixtures. Their important peculiarity is the ability to take part in reversible redox reactions and to generate strongly coloured cation-radicals (CRs) whose absorption spectra lay in the visible region [1]. In the initial state, viologens are colourless.

As a matrix, we chose lyotropic ionic liquid crystals which appear to be the high-concentrated solutions of the salts of carbon acids in water and are characterized by the intrinsic conductivity and high viscosity [2]. The last fact is very essential because the CRs' lifetime is longer in a viscous medium.

Earlier, we investigated LILC doped with viologen as a medium for holography grating recording [3]. The aim of this work consists in the detailed study of the electrooptical and dielectric properties of LILC on the base of a potassium caprylate solution doped with viologen and in the determination of peculiarities of the processes taking place inside the sample under the action of an electric field.

Experimental Methods

As a material for investigations, we chose the lyotropic liquid crystal composition of K caprylate with water (1:1 by weight) doped with diheptylviologen dibromide (2 wt. %), whose formula is



$R = C_7H_{15}$; $A^- = Br^-$

Upon the observation on an optical polarization microscope, the sample had confocal-conical structure which is typical of smectic A.

For the investigations of electrooptical characteristics of the sample, we used sandwich cells whose inner surface was covered with ITO-electrodes. The thickness of the layer in such a cell varied from 3 to 50 μm by teflon gaskets.

Absorption spectra in the UV and visible regions were obtained with using a spectrometer based on a monochromator MDR-6.

Electrochemical investigations were carried out by using the method of cyclic voltamperometry on a potentiostat PI-50-1.1 with a programmer PR-8.

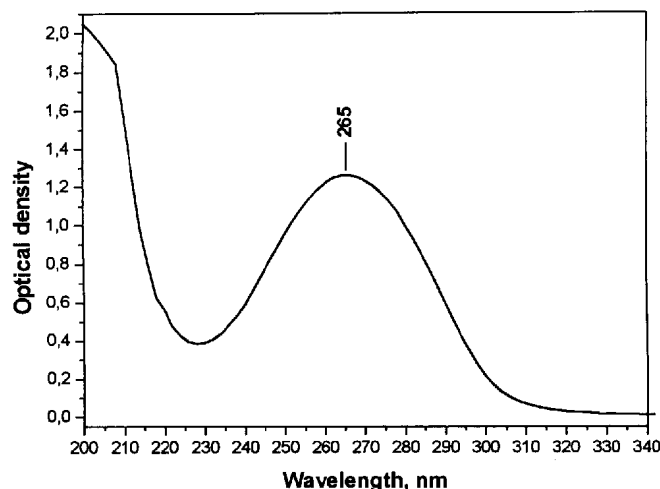


Fig. 1. Absorption band of the LILC composition in UV-region before the action of the electric field. Thickness of a sample is 3 μm

Current-potential curves were registered by a self-recording potentiometer PDP. The scanning rate was 20 mV/s. The electrochemical cell consisted of two glass plates covered with a thin transparent conducting layer of tin dioxide (SnO_2 ; $\delta=20 \mu\text{m}$). A platinum wire served as the reference electrode.

Using the oscilloscopic method, we measured the capacity (C) and resistance (R) of samples in the frequency region of 10^{-1} – 10^6 Hz in the alternating field. On the base of the data obtained, we analyzed the frequency dependences of complex dielectric permittivity components (ϵ' , ϵ'') before and after applying the direct voltage and calculated the conductivity of the samples.

All the measurements were performed at room temperature ($T = 293 \text{ K}$).

Results of Measurements and Discussion

A. Cyclic Voltage-Current Characteristic

The conductivity of the investigated LILC composition is ionic. The passage of a current in such a sample is followed by oxidation-reduction reactions which take place near electrodes. Upon the electrochemical reduction of viologens, strongly coloured CRs [5] are formed in the cathode region (owing to violet colour of CRs, dipyrindyl quaternary salts obtained the name of viologens).

Two reduction maxima with potentials of -0.448 and -0.580 V characterize the cyclic voltage-current dependence of the investigated sample. Two-charge dipyrindyl cation reduces in two steps when only one electron takes part in each stage.

At the first stage ($E_1 = -0.448$ V), CRs coloured in intense blue colour appear to be a product of the one-electron reduction of a dipyrindyl dication. Their appearance was registered by EPR and seen in electron absorption spectra.

At the second reduction stage ($E_2 = -0.580$ V), a CR catches one more electron and transforms into a biradical which instantly turns into a neutral molecule of heptylviologen characterized by the plane quinoid structure [6, 7].

The backward running of the voltage-current curve is characterized by the presence of only one oxidation maximum with potential $E_{\text{rev}} = -0.543$ V which differs from the first reduction potential ($E_1 = -0.448$ V) at 0.095 V. This testifies to the quasireversible process of one-electron reduction of a dipyrindyl dication. The second stage of the two-electron dipyrindyl dication's reduction is irreversible in the water-salt liquid crystal medium, whereas it is known that both stages are reversible in other solvents (dimethyl formamide and acetonitrile) [8].

B. Spectral Investigations

It is known that viologens are characterized by electron absorption spectra with one band in the region of $\lambda = 260 \div 270$ nm which is specified by the $\pi - \pi'$ electron transition [9]. The injection of viologens into media of different nature practically doesn't influence the position of this band. Without applying the electric field, the initially colourless LILC composition absorbs in the short-wave spectral region at a wavelength of $\lambda = 265$ nm (Fig. 1). The one-electron reduction of viologen molecules to CRs takes place on applying the voltage beginning from 1.5 V. In the course of this process, the sample obtains the typical blue colour. The formation of CRs is followed by the appearance of characteristic bands in the electron absorption spectra in the region of 395 nm and 605 nm (Fig. 2, a, curve 2).

With increase in the voltage applied to the sample, the absorption intensity in the long-wave region becomes larger and reaches its maximum at 2.3–2.5 V (Fig. 2, b, curves 2, 3). The observed absorption bands correspond to the transitions which are localized on the dipyrindyl part of the molecule. The long-wave absorption band with $\lambda = 605$ nm is caused by the transition polarized in the xy plane, where the x -axis coincides with the long axis of a viologen's cation-radical and the y -axis is perpendicular to it. The short-wave absorption band with $\lambda = 395$ nm is stipulated by the $\pi - \pi'$ electron transition polarized along the x -axis. This transition is

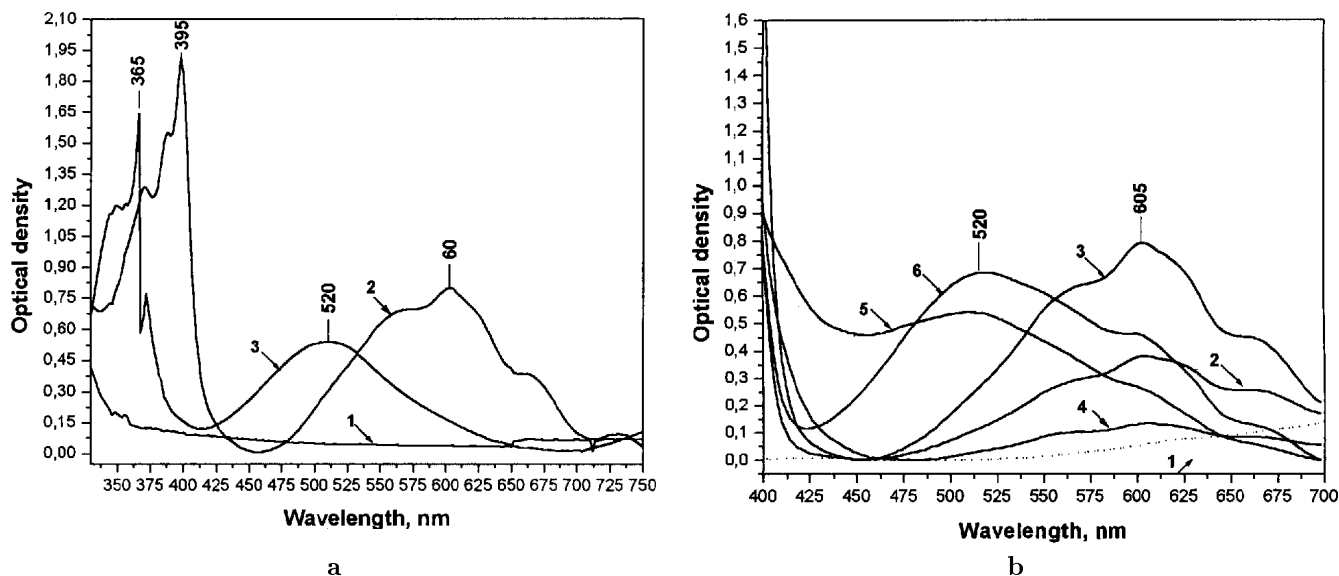


Fig. 2. *a* — absorption spectra (300–750 nm) of the LILC composition before the action of the electric field (1) and after the action of $U = 2.5$ V (2) — blue state; $U = 4.0$ V (3) — red state. *b* — absorption spectra of the LILC composition in the long-wave region before (1) and after applying the voltage: $U = 2.0$ V (2); 2.5 (3); 3.0 (4); 3.5 (5); 4.0 (6). Thickness of a sample is $33 \mu\text{m}$

almost fully localized on the pyridine ring (“a half of dipyridyl”).

At first, CRs are generated in the immediate proximity to the cathode, where the electron-deficient dipyridyl dication of viologen can capture an electron. The presence of an unpaired delocalized electron on the dication determines paramagnetic properties of CRs, whose formation is confirmed by EPR.

On the subsequent increase in voltage from 3 to 3.5 V, we observe a shift of the absorption band from $\lambda = 395$ nm to the short-wave region and the drastic fall of the band intensity at $\lambda = 605$ nm (Fig. 2b, curve 4). The sample again became almost transparent in the visible region. Coming closer to $U = 3.5$ V with increase in the concentration of CRs, the bands in the region of 365 and 520 nm appear. At $U = 4$ V, these bands have pronounced maxima (Fig. 2, *a*, curve 3); the sample gets red colour. The position of these bands practically coincides with that of the bands of the dimeric form of viologen cation-radicals described in the literature [1, 10]. This allows us to suppose that, inside the sample in addition to paramagnetic CRs, there are diamagnetic dimers which appear due to the spin-spin interaction of two CRs [11]. Increasing the number of dimers is associated with increasing the intensity of the band with $\lambda = 520$ nm (Fig. 2, *b*; the transition from curve 5 to curve 6). Indeed, during the accumulation

of CRs, the formation of dimers should intensify while the probability of a contact of two CRs increases. At the same time, when the intensity of the band at $\lambda = 520$ nm grew (accumulation of dimers), the EPR signal practically didn't change. This is in agreement with the fact that the process of dimerization is equilibrium [1]. That is, along with the formation of dimers, the inverse process takes place: dimers break into CRs; in this case, the EPR signal should be stable.

At least, a further increase of voltage to $U \geq 5$ V led to the decolouration of samples, which is stipulated by the two-electron reduction of viologen dications.

We mention that blue colour of the sample which appeared at the beginning ($U = 1.5 \div 2.0$ V) wasn't stable. In 10–20 min, the sample decolorized. The transition to a stable coloured state takes place under condition that the applied voltage was supported during about 10 min. This fact can be related to the presence of oxygen molecules in recently prepared samples, since samples were prepared under ordinary atmospheric conditions. It is well known that oxygen molecules are paramagnetic particles and are able to capture electrons from CRs. In other words, they are very effective quenchers of CRs [1]. So, being under a direct voltage ($U \approx 2.0 \div 2.5$ V) for 10 min, oxygen that was inside the cell originally burned out; after that, the sample passed in a stabler blue-coloured state.

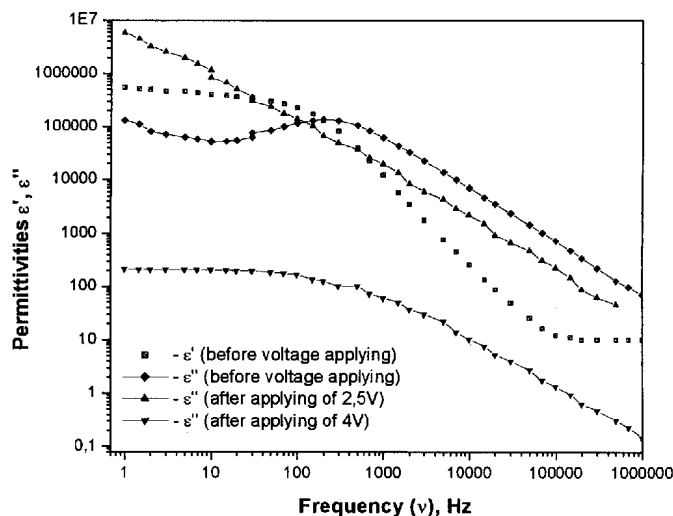


Fig. 3. Frequency dependences of permittivities ε' , ε'' for the LILC composition before and after applying the electric field

It is seen from Fig. 2, *b* that the most drastic changes occur when the voltage applied reaches $U \approx 3.0$ V (curve 4). This can be concerned with electrolysis of the water-salt matrix. It is known that, upon electrolysis of the water solutions of alkanolic salts, two main reactions run: oxidation of water molecules and oxidation of alkanolate-anion [12]. The last process is known as the reaction of anode condensation or Kolbe electrosynthesis which results in the creation of carbohydrates with the double number of carbon atoms in comparison with the initial compound. Probably, with voltage increase from 2.5 to 3.0 V, the processes of water oxidation with the segregation of hydrogen and oxygen prevail. As mentioned above, molecular oxygen is an effective quencher of CRs and is able to capture an electron from a viologen's CR by returning it to the initial state (from blue to colourless). That's why curve 4 is close by intensity to the initial curve 1 (Fig. 2, *b*).

Probably, under applying the voltage higher than 3.0 V, the processes of anodic condensation of matrix's alkanolate-anions begin to prevail (the number of oxygen molecules is sharply reduced). As a result, alkyl radicals are formed as intermediate products of electrolysis. The last ones are able to generate new radicals (additional sources for electron capture by viologen), initiating the running of chain radical reactions in the system. Thus, from the moment when water hydrolysis stops, CRs are generated again. At the voltage of $U > 3$ V, their accumulation is so quick that the formation of the dimer associates of viologens' CRs takes place at once (Fig. 2, *b*, curves 5 and 6). In addition, various high-molecular

compounds are formed (resinous substances) as by-products. In fact, after applying the voltage ($U > 3$ V), we observed the generation of a polymer film on the anode which hampered the current passage.

C. Dielectric Properties

In Fig. 3, the permittivities of the investigated object vs the frequency of the electric field applied are shown. The analysis of ε'' (ε') of the sample before applying the voltage has shown the existence of relaxation processes which are described by the Cole–Cole dispersion [13],

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

where ε^* is the complex permittivity, ε_s and ε_∞ are the permittivities for the frequencies $\nu = 0$ and $\nu = \infty$, respectively, $\omega = 2\pi\nu$ is the angular frequency, τ is the dielectric relaxation time, and α is the Cole–Cole parameter.

For the initial sample not exposed to the action of an electric field, we have obtained the following parameters: $\tau = 0.5$ ms; $\varepsilon_\infty = 11$; $\varepsilon_S = 2.95 \cdot 10^5$; $\alpha = 0.05$. These values are quite close to the values obtained for the pure LILC without admixtures [4, 14].

As is seen from Fig. 3, the dispersion region ($\nu < 10^3$ Hz) is characterized by quite great values of ε' and ε'' . This may be connected to the fact that a low-frequency field is heterogeneous; this determines, in turn, a heterogeneous distribution of the electric field intensity [15, 16]. The most essential changes of the electric field occur in the near-electrode region as a result of restriction on charge exchange between ions and electrodes.

While determining the average width of the near-electrode region W_ν , we supposed that double electrical layers approximately equal by parameters are formed near each electrode. In such a case, this width is [15, 16]

$$W_\nu = \frac{1}{2} d \frac{\varepsilon_\infty}{\varepsilon_S}, \quad (2)$$

where d is the distance between capacitor plates. Taking into account the parameters obtained above, we got $W_\nu = 0.85$ nm, i.e., the average width of the near-electrode layer, in which the relaxation processes take place.

The frequency dependences of ε'' obtained for the blue and red states of the sample (Fig. 3) noticeably differ from similar dependences of the sample before applying the voltage. Thus, the linearity of the dependence for the blue sample's state testifies to that,

after applying the electric field ($U = 1.5 \div 2.5$ V), the sample became homogeneous over all the volume of the cell.

For the frequencies $\nu > 10^3$ Hz, the permittivities for all three sample's states (transparent, blue, and red) fall linearly with increase in the frequency (Fig. 3). This allowed us to find the conductivity of the sample in different states, using the formula

$$\sigma_{AC} = \varepsilon_0 \varepsilon'' \omega, \quad (3)$$

where ε_0 is the electrical constant. Thus, for the transparent composition (without applying the electric field), $\sigma_{AC} = 3.8 \cdot 10^{-3} \text{ Ohm}^{-1} \cdot \text{m}^{-1}$; for the blue state (after the application of 2.5 V), the conductivity falls almost by three times: $\sigma_{AC} = 1,2 \cdot 10^{-3} \text{ Ohm}^{-1} \cdot \text{m}^{-1}$; and the most abrupt fall of conductivity is observed for the red state of the sample ($U \approx 4$ V): $\sigma_{AC} = 5.7 \cdot 10^{-6} \text{ Ohm}^{-1} \cdot \text{m}^{-1}$.

Thus, under the action of a constant electric field, the conductivity of the sample decreases with increase in the voltage. This is stipulated by electrochemical processes and by irreversible electrolysis processes which are running in the sample and result in the formation of various molecular associates and resinous substances which reduce the number of charge carriers and their mobility.

Conclusions

1. We have established that diheptylviologen put into the LILC matrix generates CRs under applying an electric field ($U \approx 1.5 \div 2.5$ V); as a result, the initially transparent sample obtains blue colouring. With increase in the voltage ($U \approx 3.0 \div 4.0$ V), the concentration of CRs rises, and this leads to the formation of dimer associates. Dimers' appearance in the sample is accompanied by the change in its colour from blue to red.

2. In electron absorption spectra, the initially colourless sample has only one band with $\lambda = 260 \div 270$ nm. The generation of CRs is characterized by the presence of two absorption bands in the regions of 400 and 600 nm. The formation of dimers is followed by the appearance of bands in the regions of 350 and 520 nm.

3. Using the method of dielectric spectroscopy, we evaluated the thickness of near-electrode layers and the conductivity of the LILC composition before and after applying the electric field. The transition to the coloured state is accompanied by the drop in sample's conductivity.

1. Vannikov A.V., Grishina A.D. Photochemistry of Polymeric Donor-Acceptor Complexes. — Moscow: Nauka, 1984 (in Russian).
2. Mirnaya T.A., Prisyazhnyi V.D., Shcherbakov V.A.// Uspekhi Khim. — 1989. — **58**. — P.1429–1450.
3. Iljin A.G., Klimusheva G.V., Yatsenko L.P. et al.// Proc. SPIE. — 1998. — **3488**. — P.16–19.
4. Klimusheva G.V., Koval'chuk A.V., Volynets N., Vakhnin A.// Opto-Electron. Rev., — 2002. — **10**. — P.39.
5. Shelepin I.V., Ushakov O.A.// Zh. Fiz. Khim. — 1975. — **49**, N7. — P.1736–1740.
6. Elofso R.M., Edsberg R.L.// Canad. J. Chem. — 1957. — **35**, N7. — P.646–650.
7. Bokman T.M., Kochi J.K.// J. Org. Chem. — 1990. — **55**, N22. — P. 4127–4135.
8. Grachev V.N., Zhdanov S.I., Supin G.S.// Elektrokhim. — 1978. — **14**, №9. — P.1353–1362.
9. Krainov I.P., Tsyguleva O.M., Kramarenko S.F.// Teor. Eksp. Khim. — 1984. — **20**, №6. — P.663–668.
Ivanov V.F., Shapiro B.I.// Izv. AN SSR. Ser. Khim. — 1976. — N 10. — P.1383–1385.
10. Kosover E.M., Gotter J.L.// J. Amer. Chem. Soc. — 1964. — **86**, N14. — P.5524–5527.
11. Tomilov A.P., Mairanovsky S.G., Fioshin M.Ya., Smirnov V.A. Electrochemistry of Organic Compounds. — Leningrad: Khimiya, 1968 (in Russian).
12. Jonscher A.K.// J. Mol. Liq. — 2000. — **86**. — P.259–268.
13. Volynets N., Klimusheva G., Koval'chuk A. et al.// Ukr. Fiz. Zh. — 2002. — **47**. — P.365.
14. Koval'chuk A.V.// Pis'ma Zh. Eksp. Teor. Fiz. — 2000. — **72**. — P.377.
15. Koval'chuk A.V.// J. Phys.: Condensed Matter. — 2001. — **13**. — P.10333.

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СПЕКТРАЛЬНІ ТА ЕЛЕКТРИЧНІ ХАРАКТЕРИСТИКИ ІОННИХ РІДКИХ КРИСТАЛІВ З ДОМШКОЮ ВІОЛОГЕНУ

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Резюме

Досліджено електрооптичні та діелектричні властивості рідкокристалічної композиції на основі ліотропного іонного рідкого кристала (ЛІРК) каприлату калію з електрохромною домшкою дигептилдипіридилдіброміду (віологену). При прикладанні постійного електричного поля відбувається забарвлення зразків, яке залежить від величини напруги, що прикладається, і яке відбивається на спектрах поглинання. Отримана циклічна вольт-амперна характеристика ЛІРК-композиції дозволила інтерпретувати процеси, що протікають усередині зразка внаслідок впливу зовнішнього електричного поля. Діелектричні дослідження показали, що перехід у забарвлений стан із збільшенням прикладеної напруги супроводжується загальним зменшенням провідності зразка.