

# Electrooptical properties of metal organic ionic liquid crystals

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*Electrooptics of smectic liquid crystals has been drawing an increasing interest, especially for new classes of compounds, such as metal alkanoates which manifest as thermotropic as lyotropic smectic mesophases. In the present work, electric and electrooptic properties were studied in detail of pure and dye-doped (polymethine dye) potassium kaproate, a water mixture of which is forming a lyotropic Sm A type liquid crystalline phase at room temperature. As follows from experimental data, for frequencies  $f < 3 \times 10^4$  Hz, dispersion of the components of complex dielectric permittivity  $\epsilon'$  and  $\epsilon''$  is observed. Appropriate relaxation process is described by the Debye equation. On the basis of the analysis of frequency dependencies of  $\epsilon'$ ,  $\epsilon''$  for the frequencies  $f > 3 \times 10^4$  Hz the conductivity of samples on an alternating current was found. The introduction of dye in ionic lyotropic liquid crystals (ILLC) results in increase in conductivity (by 1.5 times) and reduction of relaxation time. The bleaching of the dye in ILLC under the action of a direct voltage ( $U > 5$  V) was observed. The mechanism explaining "threshold" character of such process was proposed.*

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**Keywords:** ionic liquid crystals, dielectric permittivity, relaxation process, conductivity, electrooptics.

## 1. Introduction

The majority of metal organic substances form ionic liquid crystals such as smectic A (Sm A) [1], which electric properties were investigated poorly. At the introducing into them of polymethine dyes [2,3] the absorption in the region of 550 nm and intensive fluorescence are observed. It allows realising the holographic grating recording in such systems. However, for an explanation of a number of spectral, nonlinear optical and electrooptical characteristics of dye-doped ILLC (DILLC) it is necessary to have the information on mobility of charges carriers, conductivity, interionic interaction. For this purpose the electric and electrooptic properties of ILLC and DILLC were investigated at influence of an electric field.

## 2. Materials and methods

To main goal was to investigate the electrooptical properties of ionic liquid crystals existing in a water solution of caproate-K, which at a room temperature forms smectic A [1]. Were investigated as pure ILLC and ILLC with an impurity of polymethine dye – tetracyanpentametin [2,3]. The concentration of an impurity was 0.11 weight %.

The samples had a sandwich-like structure. The transparent ITO layers were applied onto a glass substrate to make the electrodes. The thickness of ILCC film (20–50  $\mu\text{m}$ ) was given by stripe spacers, which were placed on a security electrode. The measurements were carried out at the temperature 293 K.

Dielectric properties of the samples have been studied at the applied alternating voltage of the triangular form. The peak value of the measuring voltage was established at 0.25 V. Frequency of the measuring signal was changed within the range of  $10^{-2}$ – $10^6$  Hz. For each frequency according to the technique described in [4,5], the values of the sample resistance  $R$  and capacity  $C$  were figured out from the recorded oscillograms. Thus, it was accepted that the equivalent scheme of a sample was a pair of parallel-connected resistance  $R$  and capacity  $C$ .

To distinguish the bulk and surface properties of the samples, the analysis based on the method of the low-frequency dielectric spectroscopy [5] has been carried out. For this purpose the components of the complex dielectric permittivity  $\epsilon'$  and  $\epsilon''$  were calculated from the known values  $R$  and  $C$ . On the basis of the analysis of frequency dependencies of  $\epsilon'$  and  $\epsilon''$  as well as from the dependence  $\epsilon'' = f(\epsilon')$  the parameters of the relaxation processes and the bulk electric properties of ILLC and DILLC were determined.

The parameters of samples at measurement on an alternating voltage were compared with similar data at the application direct voltage. It has enabled to define more precisely the changes of electric properties of ILLC caused by the introduction of dye.

The optical properties of the samples were investigated by means of the computerised spectral unit. The kinetics of the intensity of the passing through the DILLC-cell light at the application of direct electric field for the region of the maximum absorption ( $\lambda = 550$  nm) was investigated.

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### 3. Experiment and discussion

In Fig.1, the frequency dependencies of  $\epsilon'$  (1) and  $\epsilon''$  (2) for ITO-ILLC-ITO are given. The dispersion of  $\epsilon'$  is clearly observed for the frequencies  $f < 3 \times 10^4$  Hz, while the dispersion of resistance  $R$ , as the deviation of  $\epsilon''$  from linear frequency dependence is observed for  $f < 10^2$  Hz. From the analysis of  $\epsilon''(\epsilon')$  dependence follows that the Cole-Cole diagram for such low-frequency dispersion could be approximated with a semicircle. According to Ref. 6, such a relaxation process corresponds to the Debye dispersion and is described by a ratio

$$\epsilon^* = \epsilon_{1\infty} + \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau}, \quad (1)$$

where  $\omega = 2\pi f$  is the circular frequency,  $\epsilon_\infty$  and  $\epsilon_s$  is the dielectric permittivity at  $f = \infty$  and  $f = 0$ , respectively,  $\tau$  is the dielectric relaxation time.

One of the most essential features of such dispersion is very large values of  $\epsilon'$  and  $\epsilon''$  in the region of small frequencies. The basic reasons of this could be as nonlinear processes of polarisation as a non-uniform distribution of electric field in the sample. As soon as the measurements were carried out for different frequencies, it was possible to determine the frequency spectrum of the current been passing through the sample. It is known, that at nonlinear processes of polarisation the harmonics, multiple frequency of a measuring signal, should be observed. As it was shown in Ref. 7, the greatest amplitude in a frequency spectrum should have the harmonic on the double frequency of the measuring signal. Our researches have shown, that the peak value of this harmonic does not exceed the error of measurement (less than 1% of amplitude of the signal on the basic frequency). Hence, the basic reason of the large values of  $\epsilon'$  and  $\epsilon''$  is the non-uniform distribution of the electric field in the sample. For direct current for  $U < 1.5$  V practically whole voltage is enclosed in the near-electrode area. As the voltage peak value of the measuring signal  $U_o$  was set 0.25 V, it is reasonable to suggest, that at low frequencies whole voltage is enclosed to the boundary ITO-ILLC. For the frequencies, without low-frequency dispersion ( $f > 3 \times 10^4$  Hz), voltage distribution in the sample is homogeneous.

While frequency decreases, the lower is the value of  $f$  the thinner is the layer near the electrode where the field is enclosed. At zero value the frequency field will be enclosed to the near-electrode layer which thickness is equal to the dense part of the double electric layer (DEL). Capac-

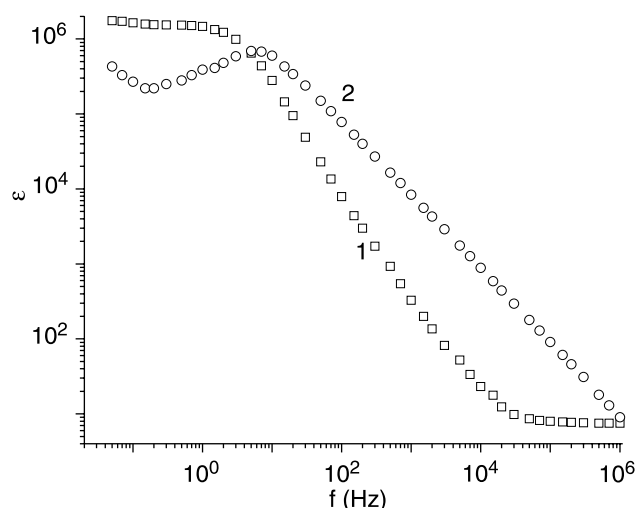


Fig. 1. Frequency dependencies of  $\epsilon'$  (1) and  $\epsilon''$  (2) for pure ILLC, film thickness 20  $\mu\text{m}$ , and temperature 293 K.

ity measured at such frequencies corresponds to that of the near-electrode area. Therefore in determination of  $\epsilon$  it is necessary to take into account only the thickness of that area where the electric field is enclosed. As the thickness of this area itself depends on the frequency, the values  $\epsilon'$  and  $\epsilon''$  were defined under condition of the homogeneous distribution of the electric field. This was also the reason of their large values at low frequencies.

Thus, the reduction of the value  $f$  in the region of the low-frequency dispersion results in reduction of the thickness of the near-electrode area to which the electric field is enclosed. Thus, the analysis of the frequency dependencies of  $\epsilon'$  and  $\epsilon''$  appeared actually to be the scanning of the near-electrode area over its thickness.

In the ratio (1)  $\epsilon_s$  corresponds to the capacity of DEL at  $f = 0$ . Therefore from this value the thickness of DEL,  $W$ , could be defined. Also in Refs. 5, 8, and 9 we shall make the following assumptions: in the samples (of thickness  $d$ ) with identical electrodes near each of electrodes DEL is formed with identical parameters, the dielectric permittivity in DEL is equal to the dielectric permittivity of the bulk of the sample. Then,

$$W = 2d \frac{\epsilon_\infty}{\epsilon_s}. \quad (2)$$

The values of  $W$ ,  $\tau$  for ITO-ILLC-ITO are given in Table 1. As it was already mentioned for  $f > 3 \times 10^4$  Hz  $\epsilon'$  does not depend on the frequency. In this area the resistance of

Table 1. Parameters received by the method of the LFS and on the basis of the analysis of the current-voltage characteristics for pure ILLC and for DILLC. Thickness of samples 20  $\mu\text{m}$ . Temperature 293 K.

	$\tau$ (ms)	$W$ (nm)	$\sigma_{AC}$ ( $\Omega^{-1}\text{m}^{-1}$ )	$\sigma_{DC}$ ( $\Omega^{-1}\text{m}^{-1}$ )	$d_d$ (nm)	$\mu$ ( $\text{m}^2/\text{Vs}$ )
ILLC	34.6	0.22	$5.0 \times 10^{-4}$	$9.0 \times 10^{-5}$	4.4	$4.8 \times 10^{-10}$
ILLC + 0.11 % of dye	17.2	0.31	$7.2 \times 10^{-4}$	$1.2 \times 10^{-4}$	7.2	$4.4 \times 10^{-10}$

the sample does not also depend on  $f\sigma_{AC}$ . Therefore it is possible to accept, that it corresponds to the volume resistance and one could define the conductivity on an alternating current  $\sigma_{AC}$  from its value. The value of  $\sigma_{AC}$  is also given in the Table 1. Besides, the values of conductivity on a direct current  $\sigma_{DC}$ , thickness of dielectric layer  $d_d$  and mobility of charge carriers  $\mu$  are given in Table 1. From the data obtained  $\sigma_{AC}$  appeared practically to be equal to  $\sigma_{DC}$ .

The comparison of the data for investigated ILLC with the data for usual liquid crystals (LC) shows, that the conductivity of ILLC is more than by three orders higher than LC conductivity mainly because of the greater concentration of ions. The important task of the work is the determination of the changes of electric parameters ILLC, which takes place at introduction of dye. The analysis of frequency dependencies of  $\epsilon'$  and  $\epsilon''$  for DILLC has shown, that for the ILLC-dye system low-frequency dispersion has been also described by the same ratio as for pure ILLC. The parameters describing low-frequency relaxation processes and charge transfer for DILLC are given in Table 1. It is clear that the introduction of the dissociating dye results (as was expected) in an increase in conductivity (almost by 1.5 times), insignificant increase of  $W$  and a two-fold reduction of the value of  $\tau$ . Moreover, as well as for pure ILLC  $\sigma_{AC}$  appeared to be of the same order as  $\sigma_{DC}$ .

In Fig. 2, the frequency dependence of the ratio  $\epsilon''_D/\epsilon''$  is given, where  $\epsilon''_D$  and  $\epsilon''$  correspond to doped and pure ILLC, respectively. As it can be seen, in the frequency region  $f > 10^2$  Hz it is practically constant and approximately equals 1.5. As it was already mentioned, this frequency range corresponds to the changes of the bulk properties of samples.

For  $f < 10^2$  Hz the value  $\epsilon''_D/\epsilon''$  goes through a minimum and finally increases with the change of frequency. According to the models of DEL such behaviour could be explained by different influence of dye on diffusion and the dense part of the double electric layer.

For the analysis of the changes of electric parameters at the introduction of the dye it is important to define a constant of dye dissociation  $K_D$ . The expression of  $K_D$  for our molecular system can be presented as follows

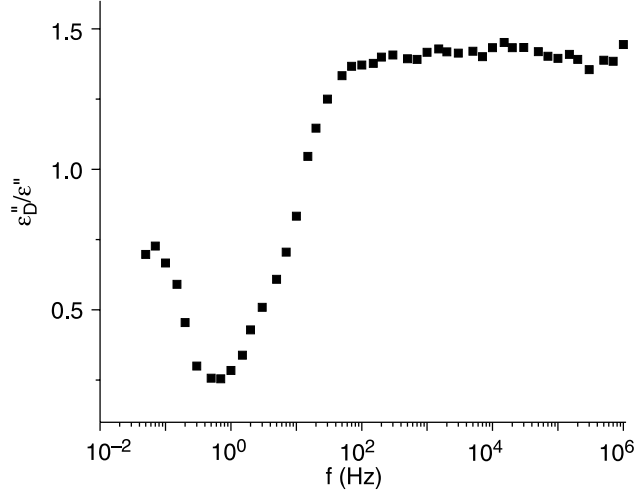


Fig. 2. Frequency dependence of the ratio  $\epsilon''_D/\epsilon''$  film thickness 20  $\mu\text{m}$ , temperature 293 K.

$$K_D = \frac{\Delta n_i}{n_D}, \tag{3}$$

where  $\Delta n_i$  is the change of ion concentration at the introduction of the dye, and  $n_D$  is the concentration of dye-molecules in a solution. Using a known ratio for conductivity, we receive

$$\Delta n_i = \frac{\sigma_D - \sigma}{ze\mu}, \tag{4}$$

where  $\sigma_D$  is the conductivity of the molecular system DILLC on an alternating current,  $\sigma$  is the pure ILLC conductivity on an alternating current,  $ze$  is the ion charge. Using the data of Table 1 we received, that  $\Delta n_i \approx 3 \times 10^{24} \text{ m}^{-3}$ .

Concentration of the molecules in a unit volume

$$n_D = \frac{\rho c N_A}{M}, \tag{5}$$

where  $\rho$  is the DILLC density,  $c$  is the dye weight concentration,  $N_A$  is the Avogadro constant,  $M$  is the dye molecular weight. Our estimations show that  $n_M \approx 3 \times 10^{24} \text{ m}^{-3}$  that means that  $K_D \approx 1$  and all molecules of dye dissociate in ILLC.

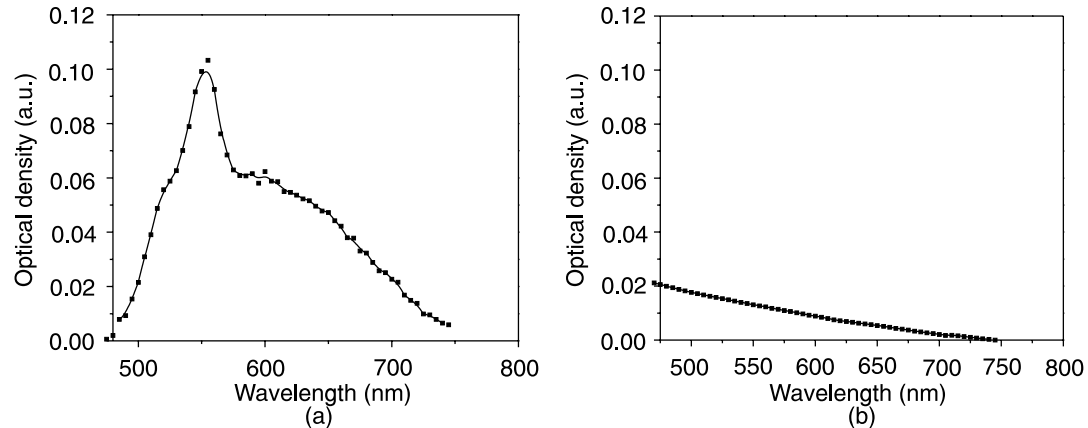


Fig. 3. Absorption spectrum of DILLC – before (a) and after (b) application of a stationary electric field ( $U = 5.5 \text{ V}$ ).

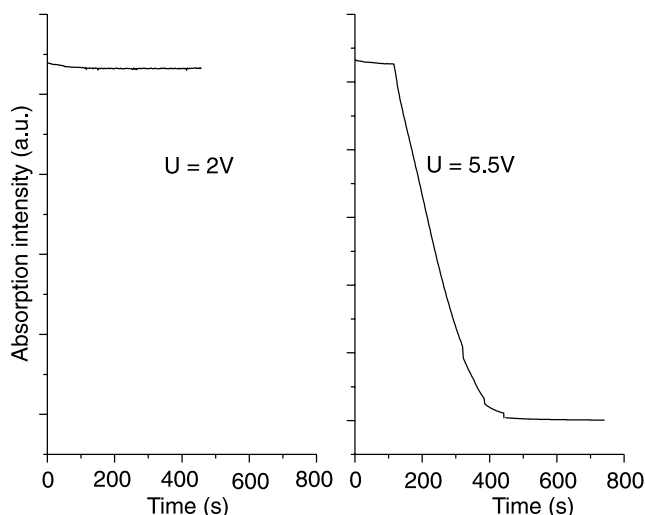


Fig. 4. Kinetics of the absorption intensity change of the DILLC on the wavelength 555 nm (maximum of absorption band) at different applied voltages.

The presence of the large concentration of ions in pure ILLC and the contribution of dye can result of the interaction between the ions of different types. Under the action of electric field this process can be efficiently amplified. Therefore, it seemed to be interesting to determine stability of the optical properties of DILLC at the application of a stationary electric field. According to spectral investigations of DILLC application to the samples of a stationary electric field drastically changed their absorption spectra (Fig. 3). Changes of absorption spectra pointed out at the formation of new substances, probably, with neutral molecules. Kinetics of this process at different values of applied voltage is shown in Fig. 4.

There are no essential changes light transmittance at the voltages lower 2 V. Application of the much higher voltage  $U = 5.5$  V results in a rather fast bleaching. While at  $U < 2$  V actually all voltage is applied at the near-electrode area the further increase in the voltage value leads to the increase in the bulk constituent of the electric field in the sample. Therefore it is possible to explain the “threshold” behaviour of bleaching in DILLC due to the stimulation of interionic interaction by the electric field. For such interaction it is necessary to overcome a power barrier. At  $U < 2$  V such interaction is poorly effective, as the electric field in the sample bulk is practically equal to zero.

#### 4. Conclusions

Thus, on the basis of the analysis of frequency dependencies of  $\epsilon'$  and  $\epsilon''$  for pure and dye-doped ILLC, it was shown, that the near-electrode processes caused their dispersion in the frequency range  $f < 3 \times 10^4$  Hz. Relaxation process causing this low-frequency dispersion is described by Debye equation with the relaxation time  $\tau = 34.6$  ms.

The value of conductivity on an alternating current was found for pure ILLC in the frequency range  $f > 3 \times 10^4$  Hz  $\sigma_{AC} = 5.0 \times 10^{-4} \Omega^{-1} \text{m}^{-1}$ . The introduction of the dye results in the increase in conductivity (by 1.5 times) and two-fold reduction of  $\tau$ . On the basis of the analysis of the experimental data was found that the constant of dissociation of the impurity in ILLC was approximately equal to 1.

It was shown that electric field application, above a certain “threshold” voltage, has caused the irreversible bleaching of the dye. The assumption was made that such a process was caused by the interaction of dye ions with the ions of the matrix. The character of the field redistribution in a sample caused the threshold behaviour of this process. Only over  $U > 2$  V, the field inside a sample begins sharply to increase. When the energy of ions becomes sufficient for overcoming power barrier efficiency of process of bleaching begins to grow.

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#### References

1. T.A. Mirnaya, V.D. Prisyazhnyi, and V.A. Shcherbakov, “The liquid-crystalline state of salt melts containing organic ions”, *Russ. Chem. Rev.* **58**, 1429–1450 (1989).
2. A.A. Ishchenko, *Structure and Spectral Luminescent Properties of Polymethine Dyes*, p. 232, Naukova Dumka, Kiev, 1994.
3. N. Volynets, N. Derevyanko, A.A. Ishchenko, G. Klimushcheva, T. Mirnaya, G. Yaremchuk, and L. Yatsenko, *Proc. SPIE* **4418**, 38–43 (2001).
4. F.J. Twarowski and A.C. Albrecht, “Depletion layer studies in organic films: Low frequency capacitance measurements in polycrystalline tetracene”, *J. Chem. Phys.* **20**, 2255–2261 (1980).
5. A.V. Koval’chuk, “Low-frequency dielectric spectroscopy as an investigation method of electrode – liquid interface”, *Functional Materials* **5**, 426–430 (1998).
6. T.L. Chelidze, A.I. Derevyanko, and O.D. Kurilenko, *Electrical Spectroscopy of Heterogeneous Systems*, p. 231, Naukova Dumka, Kiev, 1977. (in Russian).
7. S.G. Yudin, L.M. Blinov, N.N. Petukhova, and S.P. Palto, “Ferroelectric phase transition in Langmuir-Blodgett films of copper phthalocyanine”, *JETP Letters* **70**, 565–648 (1999).
8. A.V. Koval’chuk, “Low and infralow – frequency dielectric spectroscopy of the liquid crystal-solid substrate interface. Sliding layers”, *Ukr. J. Phys.* **41**, 991–998 (1996). (in Ukrainian).
9. A.V. Koval’chuk, “Generation of charge carriers and formation of antisymmetric double electric layers in glycerine”, *J. Chem. Phys.* **108**, 8190–8194 (1998).