Contributed paper

# Electric properties of ionic metal alkanoate smectics with different dyes

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*The comparison analysis of electric properties of dye-doped ionic lyotropic liquid crystals before and after applying dc voltage was studied experimentally. The contributions both of the electrode – liquid crystal boundary layers and of electrochemical processes to electric effects are estimated.*

## 1. Introduction

Our recent experimental researches of ionic lyotropic liquid crystals (ILLC) pure and doped ones have showed that these materials posses some interesting spectral, electro- and nonlinear optical properties [1] and they are considered to be perspective media for applications in optical information technologies. ILLC form a smectic mesophase at a room temperature, possess high intrinsic ionic conductivity as well as they can be used as universal solvents (matrices) for many inorganic and organic doping substances (e.g. polymethine dyes, electro-chromic impurities, transient and rare-earth metals). The luminescence, holographic recording, and laser generation have been already obtained in ILLC doped by polymethine dyes and a fluorescein. However, to well understanding spectral, nonlinear optical and electro-optical characteristics of DILLC it is necessary to have the information about mobility of charge carriers, conductivity, and interionic interactions. The influence of external electric fields of different voltages on the changes of electrical and dielectric parameters in DILLC samples is studied in the presented paper. It was shown that the applied dc electric field, which increased a certain "threshold" voltage ($U \geq 6$ V), causes an irreversible bleaching of dyes. At the smaller dc voltage ($U \leq 2$ V), practically the whole voltage is enclosed in the near-electrode areas, as it is followed from the current-voltage characteristics [2]. For the higher voltages $U > 2$ V, the field inside a sample begins sharply to increase. The analysis of contribution of the electrode – DILLC boundary layer as well as electrochemical processes to the electric effects was one more goal of this study.

## 2. Materials and methods

The more typical representatives of ionic class of mesogenes are alkanoates with a uni- or divalent metal [3]

$$[C_nH_{2n+1}CO_2]^- Me^+, \qquad Me = K, Na, ...$$
$$[C_nH_{2n+1}CO_2]^- Me^{2+}, \qquad Me = Mg, Cd, ...$$
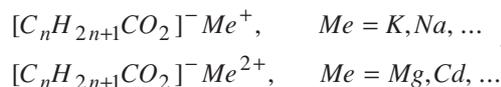
In this work a water solution of potassium kaproate ($C_9H_{19}COOK$) with different ionic polymethine dyes [cation type (N1) and anion type (N2)] and fluorescein [4] were investigated at a room temperature. The structural formulae of dye molecules are shown in Fig. 1. The impurity concentration was 0.01wt. %. The structure of DILLC corresponds to that of a thermotropic smectic A. The water molecules settle down in electro-static charged cation-anion layers.

The samples of DILLC films had a sandwich-like structure. Transparent ITO layers were covered onto the glass substrates to make the electrodes. A thickness of DILLC films (60 μm) is given by the stripe spacers. The electric properties of dye-doped ILLC were studied at the application of a stationary as well as an alternating voltage.

## 3. Influence of a stationary voltage on dielectric permittivity in DILLC

Like in the work [5], we measured the values of the resistance $R$ and the capacity $C$ of the samples by the oscilloscope method within the range of the frequency of the electric field of $10^{-3}$–$10^6$ Hz. On the basis of the obtained data, dependence of the complex dielectric permittivity components $\varepsilon'$ and $\varepsilon''$ versus frequency has been carried out. These measurements were made before and after applying

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Fig. 1. The structural formulae of dye molecules: 1 – cation type of a polymethine dye, 2 – anion type of a polymethine dye, 3 – fluorescein.



Fig. 2. Dependencies of $\varepsilon'$ (1) and $\varepsilon''$ (2) versus frequency of electric field for DILLC with the fluorescein obtained by experimental measurements of capacity and resistance of samples. The frequency region where the conductivity is not dependent from $f$ is showed by a straight line. The arrow points out the frequency at which the conductivity kinetics was measured.

a stationary voltage of 6 V on the samples. After action of 6-V voltage, the coloured DILLC samples become transparent. In the process, the DILLC absorption band is vanished in a visible spectrum [5]. This effect is connected with electro-chemical destruction of the doped molecules in DILLC.

In Fig. 2, the frequency dependencies of $\varepsilon'$ (curve 1) and $\varepsilon''$ (curve 2) for DILLC with fluorescein are presented. Analogous dependencies were obtained for DILLC with polymethine dyes. Like in the case for pure ILLC [5], the dispersion of $\varepsilon'$ is observed for the frequencies $f < 10^5$ Hz. From the analysis of $\varepsilon''(\varepsilon')$ functional dependence (the Cole-Cole diagram), it follows that such low-frequency dispersion can be approximated by an arc. According to

Ref. 6, the relaxation process corresponds to the Cole-Cole diagram and is described by the ratio

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

where $\varepsilon^*$ is the complex dielectric permittivity, $\varepsilon_\infty$ and $\varepsilon_s$ are the dielectric permittivities at $f = \infty$ and $f = 0$ respectively, $\omega = 2\pi f$ is the cyclic frequency, $\tau$ is the dielectric relaxation time, and $\alpha$ is the Cole-Cole parameter.

As it follows from Fig. 2, $\varepsilon''$ depends on the frequency linearly at $f > 5 \times 10^2$ Hz. Therefore, it can be used for calculation of the ac conductivity $\sigma$ at this frequency region from the next ratio

$$\sigma = \varepsilon_0 \varepsilon'' \omega \qquad (2)$$

where $\varepsilon_0$ is the dielectric constant of the vacuum. The obtained values of $\sigma$, $\tau$, and $\alpha$ for studied samples are listed in Table 1. It can be seen that a small dye concentration changes the sample conductivity insignificantly.

Table 1. Parameters characterizing near-electrode relaxation processes for ILLC and DILLC before and after long-time action of the stationary voltage (6 V).

| Sample | $\sigma$ ($\Omega^{-1}m^{-1}$) | $\sigma$ (6 V) ($\Omega^{-1}m^{-1}$) | $\tau$ (ms) | $\tau$ (6 V) (ms) | $W$ (nm) | $W$ (6 V) nm | $\alpha \pm 0.02$ | $\alpha$ (6 V) $\pm 0.02$ |
|---|---|---|---|---|---|---|---|---|
| ILLC | $2.7 \times 10^{-3}$ | $2.4 \times 10^{-3}$ | 1.1 | 3.5 | 3.1 | 1.7 | 0.04 | 0.07 |
| ILLC+N1 | $4.0 \times 10^{-3}$ | $1.6 \times 10^{-3}$ | 2.1 | 4.4 | 1.4 | 1.3 | 0.04 | 0.06 |
| ILLC+N2 | $7.2 \times 10^{-3}$ | $9.4 \times 10^{-4}$ | 2.9 | 40 | 1.9 | 1.1 | 0.06 | 0.04 |
| ILLC+Fl | $3.6 \times 10^{-3}$ | $2.6 \times 10^{-4}$ | 3.5 | 500 | 1.5 | 3.6 | 0.04 | 0.09 |

As it follows from Fig. 2, the values $\varepsilon'$ and $\varepsilon''$ become very large in the region of small frequencies. The basic reason of this could be a non-uniform distribution of electric field in the samples [6,7], since the absolute values of $\varepsilon'$ and $\varepsilon''$ are inversely proportional to a thickness of a layer of the actual field stress. Practically, the whole voltage is enclosed in the near electrode area.

To determine an average thickness of the near-electrode area $W$, we take on two following assumptions:

- parameters of near-electrode areas are exactly the same for the every electrodes,
- dielectric permittivity of a near-electrode area is equal to that one of a sample volume.

Then [6,7]

$$W = \frac{d}{2} \frac{\varepsilon_\infty}{\varepsilon_s} \qquad (3)$$

where $d$ is the sample thickness. The values of $W$ for different samples are listed in Table 1. One can see that they are rather small.

We can assume that a relaxation process is connected with charge exchange on the electrode-DILLC boundary layer, as it was shown for others LC [8,9]. Ions that take part in this process accumulate at near-electrode areas and the relaxation of this near-electrode charge after the field broke down corresponds to the measured relaxation time $\tau$ in Eq. (1). To simplify the analysis of such relaxation, like in Ref. 8 we assume no external electric field. The primary equation characterized the charge relaxation is the continuity equation

$$\frac{\partial \rho}{\partial t} + div J = 0 \qquad (4)$$

where $\rho$ is the near-electrode charge density and $J$ is the current density.

The charge carrier tunneling across the electrode/liquid interface is described as [9,10]

$$J = J_0 \exp(\beta \sqrt{U}) \qquad (5)$$

where $J_0$ and $\beta$ are the parameters of the process, $U$ is a voltage. Since the charge field is localized mainly in the near-electrode layer, we have

$$U = E d_d \qquad (6)$$

where $E$ is the electric field strength, $d_d$ is the thickness of the dielectric layer where the charge tunneling occurs.

Let the coordinate system be chosen so that $x$ and $y$ axes lie in a plane parallel to a sample substrate. Since the external field is applied perpendicularly to that plane, the charge relaxation can be considered along the only coordinate $z$. Taking into account Eqs. (5) and (6) we can write

$$\frac{\partial \rho}{\partial t} + \frac{d}{dz}[J_0 \exp(\beta \sqrt{E d_d})] = 0 \qquad (7)$$

The variables $\rho$ and $E$ in Eq. (7) are related according to the Poisson equation

$$\frac{dE}{dz} = \frac{\rho}{\varepsilon' \varepsilon_0} \qquad (8)$$

Equation (7) is a non-linear one and can be solved, in general, only numerically. On the basis of Eq. (7), it is interesting to consider the relaxation dynamics of the charge density. At the initial moment, when the internal electric field is strong, the tunnel current is also high. Therefore a rather fast drop of the charge density takes place. The internal electric field strength drops in time, thus resulting in a substantial (due to exponential dependence) retardation of the charge relaxation process. That is, the relaxation time is not constant but shows a certain statistic distribution. This qualitative conclusion is confirmed by an experimental Cole-Cole diagram with $\alpha \neq 0$ in Eq. (1).

Taking into account Eqs. (7) and (8) for non-linear relaxation process, $\tau$ must depend on the $\rho$ value at the initial moment of time $t = 0$. Since the charge density at the near-electrode area is formed due to ion transport from the sample volume [5], $\rho$ should be proportional to the sample conductivity $\sigma$. The higher is $\sigma$, the greater is $\rho$ and $E$ values at $t = 0$ and the faster is the charge relaxation.

After long time action ($t \sim 10^3$ s) of a stationary electric field ($U = 6$ V) the value of $\sigma$ is decreased (see Table 1). The analysis of frequency dependencies of the values $\varepsilon'$ and $\varepsilon''$ after a long time action of the stationary electric field shows that these values can be described by Eq. (1) but with the distinctive $\alpha$ parameters. These parameters are also given in Table 1. From the qualitative analysis of the Eqs. (7) and (8) it is followed that the time of the relaxation process $\tau$ increases with decrease of $\sigma$ that makes the relaxation process slower. This increasing of $\tau$ is rather considerable for the DILLC contained the fluorescein. As one can see from Table 1, the decreasing $\sigma$ leads only to the smaller changes of the values $W$ and $\alpha$ in comparison with $\tau$. So, it follows from the experimental results that the applied dc electric field (6 V) caused the destruction of doped molecules in DILLC leads to noticeable changes of parameters of all system.

## 4. The effect of dc electric field on the conductivity kinetics

One can see from Fig. 2, that $\varepsilon'' \gg \varepsilon'$ in the frequency range $10^4 < f < 10^6$, i.e., the conductivity current is much more than the displacement current. Therefore just the conductivity current will give the main contribution to the ac current. In such a case the kinetics of the ac current will correspond to the kinetics of the conductivity. But as it was noted above, the conductivity of DILLC is decreased at long-time action of dc voltage. It leads to the frequency range of the condition $\varepsilon'' \gg \varepsilon'$ to be reduced. To investigate the conductivity kinetics and satisfy the required con-

ditions at dc electric field action, in our experiments we use the medium frequency equal to 90 kHz (in Fig. 2 this frequency is marked by an arrow).

The conductivity kinetics normalized on the value $\sigma_0$, where $\sigma_0$ is the conductivity without the electric field, for the DILLC with the impurity N1 is shown in Fig. 3. One can see, that under the action of the dc voltages $U = 2$ V and $U = 4$ V the conductivity is not changed with the time. In the case of applied $U = 6$ V, the value $\sigma$ is rapidly decreased. As it is followed from Fig. 3, this kinetics of $\sigma$ can be presented as a sum of two exponential functions with different time constants

$$\frac{\sigma_t}{\sigma_0} = 1 - \frac{\Delta\sigma_1}{\sigma_0}$$
$$\times \left[1 - \exp\left(-\frac{\tau}{\tau_1}\right)\right] - \frac{\Delta\sigma_2}{\sigma_0}\left[1 - \exp\left(-\frac{\tau}{\tau_2}\right)\right], \quad (9)$$

where $\sigma_t$ is the conductivity value at the moment time $t$, $\Delta\sigma_1$ and $\Delta\sigma_2$ are the absolute values of conductivity changes for the first and the second processes accordingly, $\tau_1$ and $\tau_2$ are the time constants of those processes.

The obtained values $\Delta\sigma_1/\sigma_0$, $\Delta\sigma_2/\sigma_0$, $\tau_1$ and $\tau_2$ are shown in Table 2. It is followed from the experimental data that one can observe the two processes of the conductivity changes with different time constants not only for dye doped ILLC, but also for pure ILLC. It means that physical mechanism of these processes should be the same for doped and pure ILLC, but the presence of dyes will influence on the parameters of the processes.

Table 2. Parameters of conductivity kinetics at applied dc electric field (6V).

| Sample | $\Delta\sigma_1/\sigma_0$ | $\Delta\sigma_2/\sigma_0$ | $\tau_1$ (s) | $t_2$ (s) |
|---|---|---|---|---|
| ILLC | 0.23 | 0.74 | 5.16 | 5016 |
| ILLC+N1 | 0.07 | 0.6 | 21.16 | 1049.15 |
| ILLC+N2 | 0.31 | 0.66 | 4.18 | 620.92 |
| ILLC+Fl | 0.88 | – | 10.34 | – |
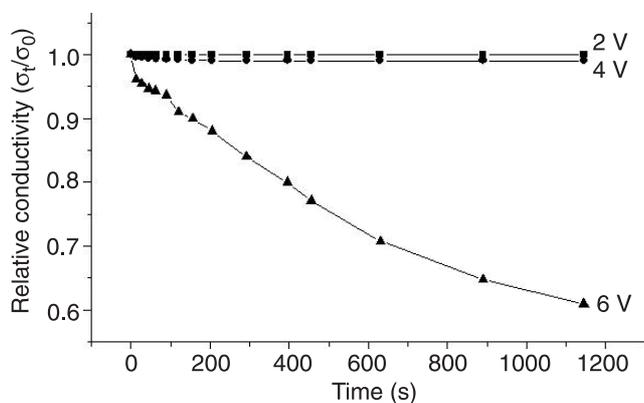


Fig. 3. The conductivity kinetics for DILLC with the polymethine dye N1 at action of the stationary voltages 2, 4, and 6 V.

According to the conventional knowledge about the conductivity in liquids, the decreasing of the $\sigma$ can be explained by electrolytic deposition of ions on electrodes. If the voltage is less than 6 V, the double electric layers located near the electrodes prevent to the deposition because of the electric barrier of these near-electrode layers. It is known that a near electrode layer consists of diffuse and dense parts. Therefore one can consider, that the faster change of the $\sigma_t$ is determined by the "break" of the diffuse layer, and the slower processes is determined by "break" of the dense layer.

Aside from the mechanism described above, the observed kinetics of the $\sigma_t$ in the DILLC can be explained by the presence of ions having essentially different mobility (by one order and more). In the DILLC, the cations of the potassium are more mobile, and the anions of the kaproate have much less mobility.

## 5. Formation of asymmetric double electric layer after the action of dc electric field

It is obtained from the oscillograms at low frequencies ($f < 0.1$ Hz) that the action of dc electric field leads to the sample capacity becomes to depend on the value and polarity of the voltage. Similar dependence was observed previously for the glycerin [11] but its conductivity increased after the action of electric field in contrast to the effects observed in DILLC. For glycerin, explanation of the effect of conductivity changes was based on formation of asymmetrical double electric layers (DEL) which had distinct parameters because of the ion desorption occurred only from the surface of one electrode to a sample volume. For DILLC, such a reason for emerging an asymmetric DEL is not suitable, as the conductivity decreases after the action of dc electric field.

As it was shown for the first time in Ref. 10, a barrier is formed on the interface of LC-electrode and prevents to the charge exchange between ions and electrodes. The higher voltage has the barrier which is localized near the anode and it is connected with the electron transfer from a neutral molecule to the electrode. Hence, the largest changes of parameters should be for such a DEL which is near the "+" power source. Just this mechanism is responsible for distinctive parameters in opposite DEL after the action of dc electric field and it is more reasonable to explain the dependence of the DILLC capacity on the voltage polarity.

The voltage-capacity (C-V) characteristic of DILLC doped by the dye N1 is shown in Fig. 4 in the coordinate $C^{-2}(U)$. It is seen that experimental data for most applied voltages get on a straight line. With frequency increasing, this straight line is moving up along the ordinate axis. As in the case of the glycerin, this effect can be explained by the influence of a series resistance which leads to the displacement of the C-V curve relative to the curve at the $f = 0$ and can be described by the following expression [10]

$$\Delta(C^{-2}) \approx 2\omega^2 r^2 \qquad (10)$$

where $r$ is the series resistance of the sample and $\Delta C^{-2}$ is the displacement value of the C-V curve.

On the basis of the data presented in Fig. 4 and from Eq. (10) we have obtained the value $r = 2.8$ MΩ that was more than one order less to compare with the glycerin. On the basis of the conductivity value for DILLC doped by the dye N1 we found the resistance of the sample volume being equal to 200 Ω. Therefore, like in the case of the glycerin, the series resistance is not determined by the volume resistance of the sample, but it is defined by the resistance of such DEL layer which has less barrier height and it prevents to current transport much more than in the sample volume.

With the help of the known value $r$; we can find the location of the C-V curve at $f = 0$ (curve 3 in Fig. 4). The point of intercept of this curve with the ordinate axis gives the capacity of the dense part of DEL being equal to $4.2 \times 10^{-5}$ F. Taking into account the known geometric parameters and according to the formula of the plane capacitor, we found that the thickness of the dense part of the DEL is $W_B = 0.34$ nm. It was in 6 times less than for the glycerin samples. By crossing of the C-V curve at the extrapolation frequency $f = 0$ with the abscissa axis, we obtained the barrier height on the DILLC-electrode boundary equal to $\varphi_B = 0.3 \pm 0.02$ V, that was on 0.1 V less than it was obtained for the glycerin.
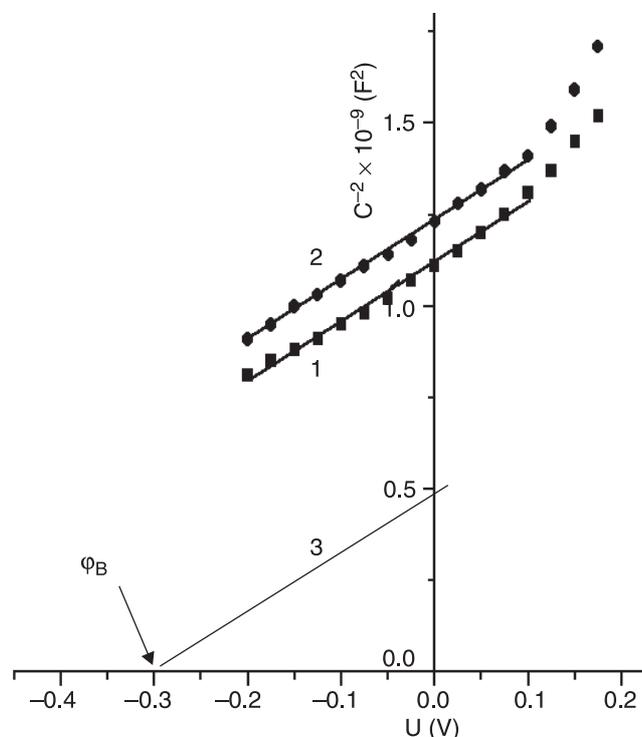
Likewise in Ref. 11, from the incline of the C-V curve, and according to the expression

$$\frac{d(C^{-2})}{dU} = \frac{2}{\varepsilon_0 \varepsilon_\infty e N_B S^2} \qquad (11)$$

where $e$ is the electron charge, $N_B$ is the ion concentration in the dense part of the DEL and $S$ is the electrode area, we obtained the value $N_B = (3.0 \pm 0.5) \times 10^{27}$ m$^{-3}$. Such large value $N_B$ shows that practically all molecules in the dense part of the DEL are ionised.

The electrolysis of water solutions of alkanoic acids includes two main electro-chemical reactions, namely the oxidation of water molecules and the oxidation of the carbonyl acid anions. The later reaction is known as the anode condensation or Kolbe electro-synthesis that results in creation of hydrocarbons with doubling carbon atoms compared to initial compound. The reaction can be described by the following scheme:

$$2C_nH_{2n+1}COO^- + 2e \rightarrow$$
$$\rightarrow 2C_nH_{2n+1}COO^\bullet \rightarrow 2C_nH_{2n+1} + 2CO_2 \rightarrow C_{2n}H_{4n+2}.$$
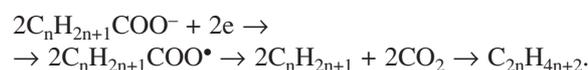
The process is dominant for the voltages being more than 2 V, but at the low voltages there are water oxidation reactions which pick up hydrogen and oxygen. Alkanoic radicals are created by the electrolysis as interim products. They provoke generation of new radicals, by this way to initiate chin radical reactions that leads to creation of high-molecular compounds (resine-like substance). The deposition of such phase on the anode was observed at application of the stationary voltage (6 V) on DILLC.

## 6. Conclusions

In pure ILLC and DILLC doped by polymethine dyes and fluorescein, the dielectric dispersion is observed at low frequencies and can be described by the Cole-Cole equation. It was shown the relaxation process is caused by charge exchange on the electrode-DILLC boundary. Long-time action of a stationary voltage leads to decrease in conductivity as well as to significant increase in the time of relaxation process. The mechanism of the relaxation process is the same as without the voltage.

On the basis of an analysis of dielectric spectra, the method to investigate the conductivity kinetics in ILLC under the action of dc electric field is proposed. It was shown that the behaviour of conductivity decreasing both in pure ILLC and in DILLC with polymethine dyes can be described by two exponent functions which have different time constants distinguished by more than one order.

It was shown, that long-time action of dc electric field leads to different changes of DEL parameters near the cathode and near the anode that leads to creation of non-symmetrical DELs. The DEL of higher barrier voltage is formed near the anode. From the analysis of C-V character-



Fig. 4. C-V characteristics of DILLC with the polymethine dye N1 at the frequencies $10^{-3}$ Hz (1) and $1.5 \times 10^{-3}$ Hz (2). Straigt line 3 corresponds to the theoretical C-V characteristics at $f = 0$, calculated according to Eq. (10).

istics, obtained for DILLC with the dye N1, the parameters of the dense part of the DEL are estimated: the thickness $W_B$ = 0.34 nm, the barrier height $\varphi_B$ = 0.30 + 0,2 V, the concentration of ionised molecules $N_B$ = (3.0 ± 0.5) $\times 10^{27}$ m$^{-3}$. The deposition of a new polymer-like phase on the anode was observed after application of the stationary voltage (6 V) to DILLC.

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