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## **Method and estimation of parameters of dense part of double electrical layer at the interface electrode-solution of the dye in liquid crystal**

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**Abstract.** First estimated were the parameters of dense part of double electrical layer (DEL) at the interface electrode – solution of the dye in liquid crystal, based on analysis of capacitance-voltage characteristics obtained at low frequencies, taking the series resistance into account. DELs with various parameters near each electrode were obtained owing to their different chemical compositions. It was shown that the obtained difference in the DEL parameters is caused not only by different chemical composition of the electrodes, but also different orientations of molecules near each of them (planar orientation near one electrode and homeotropic one near another). It was estimated the barrier height, thickness of near-electrode layer, and concentration of ionized states in the dense parts of DEL near each electrode. It was shown that these parameters differ by 2 to 3 times, and an assumption was made about the reasons that can cause this difference.

**Keywords:** liquid crystal, double electric layer, planar and homeotropic orientation.

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### **1. Introduction**

Analyzing electro-optical characteristics of liquid crystal (LC), it should be considered near-electrode processes in most cases. In LC, as in electrolytes, these processes are caused by double electric layers (DEL) [1-4] that are mainly formed due to different mechanisms of conductivity in liquid (ion conductivity) and electrode (electron one). As known, the DEL structure at the interface electrode-liquid is complex and includes a diffuse (Gouy layer) and dense (Helmholtz layer) parts [5]. Parameters of the diffuse part of DEL in LC were estimated in a large number of articles (for example, see [3, 4]). The parameters of the dense part are much less studied.

From literature [5, 6], it is known that even for strong electrolytes determination of parameters for the dense part of DEL is a complex task. As it was demonstrated by our researches, the methods that were developed to estimate the Helmholtz layer parameters for strong electrolytes are unusable for analysis of DEL in LC.

In the study of dielectric spectra in LC, we also showed that, at low frequencies (tens of Hz or less) and amplitudes of the measuring signal  $U_0 < 2$  V, the voltage

applied to thin near-electrode layers at each electrode is almost equal to the voltage applied to the sample [7]. This gave grounds to use the analysis of capacitance-voltage characteristics (CVC) to estimate the parameters of the dense part of DEL. For LC, like to all liquids but unlike semiconductors, it is impossible to create an ohmic contact at least with one of the electrodes. Therefore, analyzing the CVC, one always should take account that he deals with a two-barrier structure. Theoretical analysis of this structure can be essentially simplified provided that the parameters of barriers are different.

Formation of barriers with different parameters near each electrode was first realized by us in glycerol [8] through a long-term (several hours) action of direct electric field at the temperature 340 K. Obtained in these samples were the CVC asymmetric as to the direction of electric field, and evaluated were the barrier parameters (height, thickness and concentration of ionized states). Unfortunately, this method to form different parameters of DEL could not be used for LC. Therefore, it was decided to use a method traditional for contact phenomena metal-semiconductor to form DEL with different parameters through using the electrodes with different chemical compositions.

The aim of this work was to develop technology of creating the LC structures with asymmetric DELs based on electrodes of different chemical composition and to estimate parameters of the dense part of DEL in these structures.

## 2. Materials and methods

For researches, we used a mixture of LCD ZLI4803. From the electrodes that would be the most neutral as to its interaction with molecules of liquid, the platinum Pt electrode was chosen. We chose another electrode out of Al, Ni, Cu, metal oxides  $\text{In}_2\text{O}_3$ ,  $\text{SnO}_2$ , and mixtures of these oxides ITO. The best results regarding asymmetry of CVC were obtained for the Cu electrode. However, for “pure” LC mixture ZLI4803 (without implemented impurities), to obtain CVC, by using which one could clearly separate the contribution of each of the barriers, was impossible. This effect was obtained for 2 wt.% solution of dye D in LC.

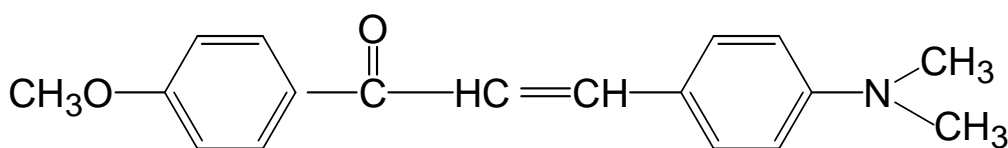
The structural formula of the dye D is shown in Fig. 1. It is seen that its high solubility (compared to that of other dyes) in liquid crystal is caused by the fact that the structure of molecules D is close to that of LC molecules.

The main part of our researches was performed using the structures Pt/ZLI4803 + 2 wt.%D/Cu. In addition, we investigated the structures Pt/ZLI4803 + 2 wt.% D/Pt and Cu/ZLI4803 + 2 wt.% D/Cu.

At the initial stage, we created a flat capacitor of a Pt plate that was purified in organic solvents and polished as well as a Cu plate that was buffed and cleaned with organic solvents, too. The thickness of this capacitor was specified by using teflon spacers with the thickness 25  $\mu\text{m}$ . Long-term fixation of the electrodes was provided by gluing the electrodes along the edges. With this aim, used were the electrodes possessing the same dimensions.

In order that the teflon spacers did not effect the capacity of the cells, there used Cu films deposited on glass fiber plastic, and by etching in the Cu electrode, created was a central part (measuring electrode) and a peripheral part (guard electrode). Since the teflon spacer was on the guard electrode, which was connected to ground when measurements were carried out, it did not effect the value of capacitance. The factual thickness of the cell was estimated in the value of capacitance of an empty cell. It was equal to 30  $\mu\text{m}$ .

After measuring its capacitance, the cell was filled using the capillary effect with liquid crystal. To speed up this process fillup took place at the temperature 340 K.



**Fig. 1.** Structural formula of D dye.

When measuring the frequency dependences for the components of the complex permittivity and CVC, we used the oscilloscopic method [9] within the frequency range  $10^{-4} - 10^6$  Hz. The measuring signal amplitude was equal to 0.5 V. At the frequencies  $f < 0.01$  Hz, oscillograms were recorded by using the self-recording device N307. Then, the obtained oscillograms were digitized and analyzed by computer. According to the results of this analysis, CVC were plotted.

Based on the analysis of these oscillograms at the frequencies  $10^{-2} - 10^6$  Hz determined was the value of the permittivity and conductivity of the bulk part of samples. All the measurements were performed at 293 K.

## 3. Results and analysis

When studying LC or solutions of certain substances in LC, it is important to know orientation of the molecules. Essentially, the orientation is fitted by using an observation in polarization microscope or an analysis of images of this microscope. In this case, at least one of this plates that creates this flat capacitor must be transparent to light. In our case, the electrodes were not transparent. Therefore, a conclusion about orientation of liquid crystal near the Pt and Cu electrodes was made using measurements of permittivity for the structures Pt/ZLI4803 + 2 wt.%D/Pt and Cu/ZLI4803 + 2 wt.%D/Cu.

Our analysis of the obtained results showed that the permittivity for the structures Pt/ZLI4803 + 2 wt.%D/Pt is close to that of ZLI4803 at planar orientation of molecules, and the permittivity for Cu/ZLI4803 + 2 wt.%D/Cu is close to that of ZLI4803 at homeotropic orientation of molecules. From these results, it was concluded that near the Pt electrode the LC molecules have planar orientation and near the Cu electrode – homeotropic one, for the samples Pt/ZLI4803 + 2 wt.% D/Cu hybrid orientation of LC molecules is realized.

Shown in Fig. 2 are CVC for the structure Pt/ZLI4803 + 2 wt.%D/Cu at various frequencies of the measuring signal. It is clearly seen that the obtained CVC are asymmetrical concerning the polarity of the electric field. It can be mainly caused not only by different materials of electrodes, but by different orientation of molecules near each of the electrodes.

Based on the analysis of Fig. 2, one may make the following conclusions. In the dependence  $C^{-2}(U)$ , there are straight-line portions, with increasing the frequency

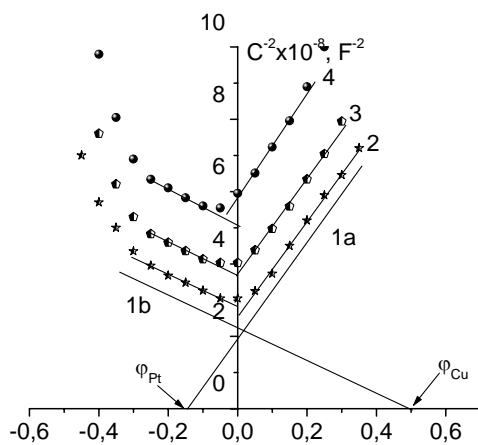
these portions are shifted towards larger values of  $C^{-2}$  (lower values of capacity), the slope of straight-line portions does not change at different frequencies. The presence of the straight-line portion in  $C^{-2}(U)$ -characteristics makes it possible to assert that, in the space charge region (SCR), electrically active centers (in our case, these are ionized molecules of near-electrode layer) are distributed uniformly.

Based on the results presented in [10, 11], one can conclude that the main cause of displacement of straight-line portion in  $C^{-2}(U)$ -characteristics when changing the frequency is an effect of series resistance  $R_S$ . In this case, the value of displacement of  $C^{-2}(U)$ -characteristics relative to its position at  $f=0$  is proportional to the frequency squared [11]

$$\Delta C^{-2} \approx 2\omega^2 R_S^2. \quad (1)$$

Our analysis of Fig. 2 showed that the displacement of CVC relative to the axis  $C^{-2}$  in the left and right sides may be described by Eq. (1) with a small error. As a result of this analysis, the value  $R_S$  was estimated. Like to the case of glycerol [8], it reaches tens of MOhm, which by more than 5 orders of magnitude exceeds the resistance of the sample bulk part. Because these structures is two-barrier, one can foresee that the series resistance for each barrier is the resistance of another barrier providing a current flows in the forward direction.

Analyzing the CVC in Fig. 2, by using Eq. (1) estimated was a position of  $C^{-2}(U)$ -characteristics at  $f=0$  (curves 1a and 1b). This enabled us to determine the height of barriers near each electrode. The obtained data are listed in the table. It is seen that the barrier height near the Pt electrode is almost three times lower than that near the Cu electrode.



**Fig. 2.** Capacitance-voltage characteristics of the Pt/ZLI4803 + 2 wt.% D/Cu structure for various frequencies  $f$ , Hz:  $1.2 \times 10^{-4}$  (2),  $2.0 \times 10^{-4}$  (3),  $3.0 \times 10^{-4}$  (4). The sign of voltage is indicated relatively to the Cu electrode. Curves 1a and 1b are obtained using extrapolation of experimental data to the frequency  $f=0$  via Eq. (1).

**Table. Parameters of the dense part of DEL near Pt and Cu electrodes as based on our analysis of CVC for the structures Pt/ZLI4803 + 2 wt.% D/Cu. For comparison, the data for glycerol [8] are listed.**

Substance	Electrode	$\phi$ , V	$W$ , nm	$n$ , $m^{-3}$
Glycerol [8]	SnO <sub>2</sub>	$0.40 \pm 0.02$	2.0	$(3.0 \pm 0.5) \times 10^{26}$
ZLI4803 + 2 wt.% D	Cu	$0.50 \pm 0.02$	1.6	$(3.2 \pm 0.5) \times 10^{27}$
ZLI4803 + 2 wt.% D	Pt	$0.14 \pm 0.02$	0.50	$(6.0 \pm 0.5) \times 10^{27}$

By using the intersection of the curves 1a and 1b with the axis  $C^{-2}$  drawn through the point  $U=0$ , estimated were the capacities at zero displacement for each of the barriers. Based on the formula for capacitance of flat capacitor, we estimated the thickness of space charge region  $W$  for each of the barriers. These data are also shown in Table.

It is seen that this thickness, as for glycerol, is a few monolayers, and the  $W$  value of near-electrode area at the Pt electrode is approximately three times lower than that near the Cu electrode. For each of the barriers, values of the concentration inherent to ionized states  $n$  were estimated via the slopes of curves 1a and 1b by using the ratio

$$\frac{d(C^{-2})}{dU} = \frac{2}{\epsilon_0 \epsilon n S^2}, \quad (2)$$

where  $\epsilon_0$  is the electric constant,  $\epsilon$  is the permittivity of the solution, and  $S$  – area of the sample. It follows from the table that the difference in the  $n$  value for each barrier is smaller than that observed for the values of the barrier height and thickness of the near-electrode layer  $W$ . In contrast to glycerol [8], it was difficult to estimate the concentration of molecules in the near-electrode area, because a mixture of liquid crystals was used, and it was not known what part of the total amount of the molecules in solution comprise the dye molecules in near-electrode area. However, based on comparison of the  $n$  values for the structure studied in this work with the results of [8], we can assume that almost all the molecules of the near-electrode layer are ionized. The main reason that leads to this effect is rather high value of electric field in the dense part of DEL. To estimate its magnitude, we assume that the voltage 0.1 V is applied to the dense part of DEL. The thickness of the dense part of DEL according to Table is approximately equal to 1 nm. Then, we get that the electric field value in the dense part of DEL is  $10^8$  V/m. Long-term action of this field is in principle sufficient to ionize the molecules.

#### 4. Conclusion

We first show that being based on analysis of CVC at low frequencies one can estimate the parameters of the

dense part of DEL at the interface electrode – solution of a dye in liquid crystal. To implement this method, created were the samples with different parameters of DEL near each electrode by using the electrodes of different chemical compositions. From the analysis of properties of these samples, the difference in parameters of DEL near each electrode is caused by not only different chemical composition of the electrodes, but by different orientations of LC molecules near them (planar orientation near the Pt electrode and homeotropic one near the Cu electrode).

It is shown that, like to glycerol, the obtained barriers that are asymmetric relative to polarity of the applied voltage can be evaluated taking the series resistance into account. For each of the barriers, the series resistance is the resistance of another barrier, if the current flows in the forward direction.

Through the analysis of CVC for the structures Pt/ZLI4803 + 2 wt.% D/Cu, estimated were the parameters of the dense part of DEL separately near Pt electrode and Cu one. It was shown that the barrier height and thickness of near-electrode layer at the Pt electrode differs triply from those at the Cu electrode. It is obvious that this difference in the parameters is mainly caused by different orientation of LC molecules near each electrode.

Also it was shown that the concentration of ionized centers near the Pt electrode is almost two times higher than that near the Cu one. The very value of the concentration of ionized centers is close to the concentration of LC molecules. So, we can assume that the majority of molecules in the dense part of DEL is ionized. This may be caused by rather high value (about  $10^8$  V/m) of external electric field in the dense part of DEL.

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