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Adsorption of ions and thickness dependence of conductivity in liquid crystals

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Abstract. It is experimentally shown that, at thicknesses less than 100 μm, conductivity of planar oriented liquid crystals is a function of the thickness. The main reason for this effect is adsorption of ions on the surface of electrodes. The relation for estimation of changes in the conductivity has been theoretically obtained, and the value of the characteristic length for distribution of ions in a near-electrode area has been estimated.

Keywords: conductivity, planar oriented liquid crystal, adsorption of ions.

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1. Introduction

The value of conductivity σ is an important parameter that should be known when determining suitability of liquid crystals (LC) for scientific or practical needs. Therefore, it is important to establish conditions under which the σ value of LC is measured. In prospectuses of LC manufacturers, presented in most cases is the value of alternating current frequency (usually it is 1 kHz), at which the conductivity is measured. There are not any standards for the thickness of cells.

Since real measurements of the σ value in liquid crystals are performed in cells of certain thickness, it is important to know whether the cell thickness influences (and how, if there is such influence) on the value of LC conductivity.

It was shown in [1-3] that, after filling the cell with liquid crystal, some part of ions is adsorbed on the electrode surface. So, the total amount of charge carriers in LC will decrease, which in some way should affect the value of conductivity. Relative changes in concentration will be greater the smaller the thickness of the cell. Therefore, a priori it can be asserted that the value of change in conductivity should depend on the cell thickness. Analysis of publications has shown that detailed studies and theoretical analysis of the conductivity depending on the thickness of measuring cell are absent. In a rather long-published paper [4], considered was a thickness dependence of the conductivity of homeotropic oriented LC. These obtained small changes in the conductivity were explained by anisotropy of the LC conductivity and non-homogeneous orientation of LC molecules with the cell thickness (tilting one near the surface and strictly homeotropic in the bulk sample). A thickness dependence of the conductivity was obtained in [5] when studying the properties of liotropic LC. The authors considered injection of charge carriers as a possible mechanism to explain this effect. But it was only a hypothesis that was not accompanied by appropriate models and estimations.

Therefore, the purpose of this work was a detailed experimental study of the influence of cell thickness on the value of LC conductivity and theoretical analysis of these changes taking into account redistribution of the ion concentration in near-electrode area due to adsorption of ions.

2. Materials and methods

To measure the conductivity, for these studies we used standard cells of the sandwich type. Electrodes were layers of tin oxide transparent in the visible spectral range. These layers were deposited on glass plates. To avoid the influence of edge effects, using the etching procedure each electrode was separated by inner (measuring) and external (protecting) parts. When measuring, the protecting electrodes were connected to each other.

The thickness of the cell was set by teflon tapes that were placed on protecting electrodes. Since the cell thickness was one of the main parameters for the cell, its value was determined in two ways: the interenferential one and that based on measurements of cell conductivity that is not filled with liquid crystal. When measuring the thickness *d* by using the interference method, this value was estimated from place to places over the whole area of the cell. This enables one not to use a cell of the wedge shape for these researches.

Filling the cells with liquid crystals occurred due to forces of surface tension (at small thickness each cell is a capillary). In this case, when filling cells the LC flow is directed parallel to the surface, and at a small thickness independently of orienting surfaces it can create planar orientation of molecules (immediately after filling the cell). To eliminate the influence of this effect, studies were performed with cells in which the orienting surfaces themselves created the planar orientation of LC molecules. To create this orienting surface, a thin layer of polyimide was deposited on the electrode and rubbed with a cloth of velvet in a certain direction.

For researches, we used three kinds of liquid crystal mixtures: PKC1282 (НИОПИК, Russia), BL055 (Mark, Germany) and MJ961180 (Mark, Germany). This made it possible to establish whether the experimentally obtained dependences of conductivity on the LC thickness are common to all LCs.

Conductivity determination was based on analyzing the frequency dependence of the sample resistance. The value of resistance at various frequencies was determined by using the oscilloscopic method [6, 7]. The measuring signal voltage was 0.25 V and was an order of magnitude lower than the voltage of Fredericks transition. Therefore, changes in orientation of molecules with the cell thickness, which can be caused by electric field of the measuring signal, should not be taken into account. All measurements were performed at the temperature 293 K.

3. Results of the experiment

As we have mentioned when formulating the research problem, when ions are adsorbed on the electrode surfaces, the conductivity of samples should decrease, and its changes are the greater the smaller the thickness of the cell is. In general, it is confirmed by experimental data of this work. As to compare the results with theoretical estimations, one should know the relative change in the conductivity without account of changing its sign, we analyzed the thickness dependence of the relative change in the conductivity module ($|\Delta\sigma|/\sigma$).

The value $|\Delta\sigma|/\sigma$ was experimentally found from the equation

$$\frac{|\Delta\sigma|}{\sigma} = \frac{|\sigma_d - \sigma_\infty|}{\sigma_\infty},$$

where σ_d is the value of conductivity at a given thickness, σ_∞ is the conductivity at an infinite thickness extrapolated from the experimental data.

Shown in Fig. 1 are the thickness dependences $|\Delta\sigma|/\sigma$ for PKC1282 (1), BL055 (2), MJ961180 (3). It is seen that, with increasing the cell thickness, the value $|\Delta\sigma|/\sigma$ tends to zero. This effect is typical for all the samples. Our estimations showed that the obtained changes in the conductivity versus the cell thickness cannot be explained in the frameworks of the model proposed in [4]. Therefore, the main factor that defines the thickness dependence of conductivity was adsorption of ions on the surface of electrodes. As will be shown below, this approach made it possible to explain the presence of the conductivity peak for PKC1282 (curve 1). The presence of this peak cannot be explained in principle when being based on the work [4].

4. Model and estimation of parameters

Let we have the sample of sandwich type with the thickness d. Since the electric field is applied perpendicular to the surface of electrodes, to determine the dependence $\frac{|\Delta\sigma|}{\sigma}(d)$ it is important to find the distribution of charges in this particular direction. Choose the x axis in this direction and take one of the electrodes as its origin. To find the charge distribution, one can use a solution of the Poisson-Boltzmann equation for symmetric electrolyte [8-10], assuming that this condition is fulfilled for the LC. Since the sample thickness is specific, in a general case, one must take into account possible "overlapping" the distributions of ions that was formed near each electrode. This effect may be essential at very small thicknesses and, in general, can be described only qualitatively.

For quantitative estimations, we will consider the examples of such thickness, for which the distribution of ion concentrations near one of the electrodes does not effect on the distribution of ions near the opposite electrode. Then, the total distribution of ions with the thickness of the cell is as follows

$$n(x) = n_S\left[\exp\left(-\frac{x}{l_A}\right) + \exp\left(-\frac{d-x}{l_A}\right)\right], \qquad (1)$$

where n_S is the surface concentration of adsorbed charge, l_A is the characteristic length that describes distribution of ions near electrodes.

The total charge of adsorbed ions and ions in the near-electrode area of the sample equals

$$Q_S = eS\int_0^d n(x)\,dx = 2eSn_S l_A\left[1 - \exp\left(-\frac{d}{l_A}\right)\right], \qquad (2)$$

where S is the area of the electrode, e is the charge of ion.

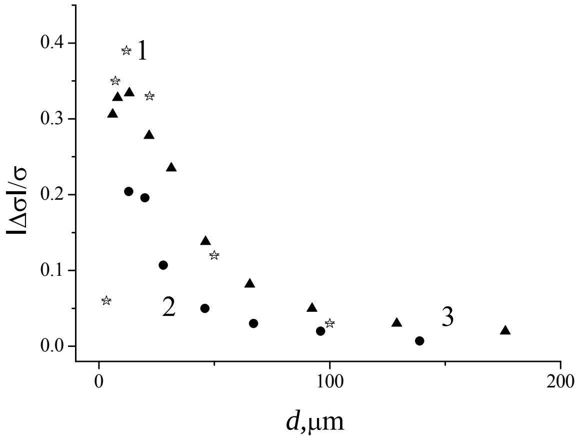

Fig. 1. The thickness dependence $|\Delta\sigma|/\sigma$ of planar oriented LC: PKC1282 (*1*), BL055 (*2*), MJ961180 (*3*).

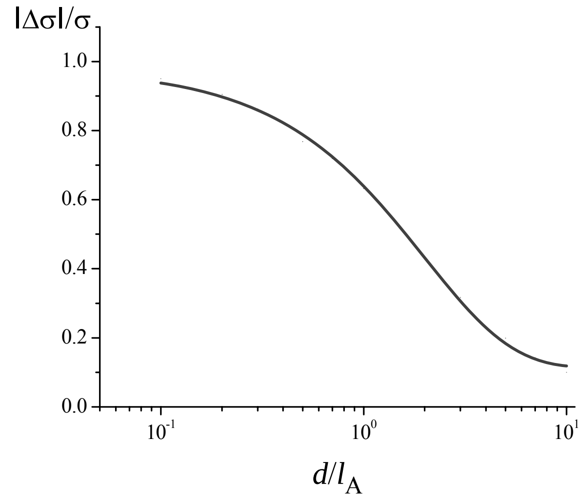

Fig. 2. Graphical view of the function (4) in the coordinates d / l_A.

Since the total charge of ions in the sample at the beginning of redistribution is

$$Q = Sden_0 \tag{3}$$

(n_0 is the bulk concentration of ions), the relative change in the conductivity caused by the process of adsorption of ions takes the form:

$$\frac{|\Delta\sigma|}{\sigma}=\frac{Q_A}{Q}=\frac{2eSn_S l_A\left[1-\exp\left(-\frac{d}{l_A}\right)\right]}{eSd\,n_0}= \frac{2n_S}{n_0}\frac{1-\exp\left(-\frac{d}{l_A}\right)}{\frac{d}{l_A}}. \tag{4}$$

The thickness dependence $|\Delta\sigma|/\sigma$ is expressed by a function that is in square brackets of the relation (4). This function is graphically depicted in Fig. 2. As it follows from this figure, the evident increase in $|\Delta\sigma|/\sigma$ should be observed when the sample thicknesses $l_A \approx 6l_A$, and when the thicknesses $d \approx l_A$ the change in $|\Delta\sigma|/\sigma$ should be quite sharp.

Extrapolation of experimental data based on Eq. (4) shows that in general these results can be described by the proposed model. Based on this analysis, estimated is the value l_A for the samples of various types: $l_A = 6.9 \pm 0.6$ μm for PKC1282, 3.0 ± 0.3 for BL055, and 6.4 ± 0.4 for MJ961180. As follows from the estimations, it reaches several micrometers and depends on the type of liquid crystal. Comparison of the value l_A with the Debay screening length l_D shows that it is more than two orders of magnitude higher than l_D.

The model proposed in this paper allows to explain not only the monotonous increase in the conductivity with increasing the LC thickness, but presence of the peak in the thickness dependence of the conductivity in the samples PKC1282 (Fig. 1, curve 1). In this model, the amount of ions in the near-electrode area of the sample is determined by using the distribution function found on the basis of the balance of diffusion and migration flows. At rather small thicknesses, these flows in the near-electrode areas of each electrode will overlap, which results in equalization of ion concentrations with the sample thickness and increase of the influence of the above-described effect of changes in the conductivity. As up to now these changes can be described only qualitatively, we will not analyze them in detail.

5. Conclusions

It is experimentally shown that the conductivity of planar oriented nematic liquid crystals depends on the thickness of the cell, and this dependence cannot be described by changes in orientation of molecules with the sample thickness. Proposed was the model of this effect where the main cause of the thickness dependence of conductivity is the adsorption of ions on electrodes and associated with this process of redistribution of ions in the near-electrode area of the sample.

For the sample thicknesses where overlapping the “tails” of charge distributions near each electrode is yet absent, considering LC as a symmetric electrolyte we have obtained the relation for the thickness dependence of the relative change in conductivity. It is shown that using this relation one can describe the obtained experimental results. Estimated was the value of the characteristic length l_A that is included in the function of distribution of ions in the near-electrode area of the sample. It has been shown that the value l_A reaches several micrometers and is more than two orders of magnitude higher than the Debye screening length.

Being based on the proposed model, the maximum of conductivity observed for PKC1282 at rather small thicknesses is explained by equalizing the concentration of ions with the thickness of the sample due to overlapping the "tails" of charge distributions near each electrode.

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