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FILLING INITIATED ION TRANSPORT PROCESSES IN LIQUID CRYSTAL CELL

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The ion adsorption/desorption processes initiated by LC filling in liquid crystal (LC) cells are studied. The LC we used was 5CB and the aligning substrates were UV irradiated polyvinylcinnamate (PVCN) films providing planar alignment of LC. It is shown that intensity of adsorption/desorption processes is strongly determined by purity of LC and irradiation associated parameters, such as exposure dose τ_{exp} *and time period between irradiation and LC filling* $\tau_{\mathrm{f-i}}$. *To fill the cells we used both 5CB kept in air and 5CB vacuumed at* 10^{-2} *Torr over 1 h. The ion concentration in first portion of LC was estimated to be higher by factor 2 compared with the second one. The cell filling with LC kept in atmosphere is associated with intensive ion adsorption from LC bulk to aligning substrates (when exposure time is zero or when* $\tau_{\mathrm{f-I}} > 1h$*) or with both adsorption and desorption of ions (in case when* $\tau_{\mathrm{f-i}} \ll 1h$*). In contrast, cell filling with vacuumed LC mainly initiates ions desorption from the polymer substrates. The latter effect is observed for non-irradiated cells too. This shows that even non-irradiated substrate charges, more likely by adsorption of air ions. The following UV irradiation just increases charging of aligning substrates.*

Keywords: liquid crystal; ion transport; conductivity; photoalignment

1. INTRODUCTION

The liquid crystal (LC) photoalignment method suggested about ten years ago, as alternative for traditional rubbing procedure, was a breakthrough in technology of LC displays (LCD). This method brought opportunity to simplify different technological processes, developing new LCD modes and new LCD applications. Avoiding direct mechanical contact with the aligning substrate the photoalignment method diminishes drastically the static charges generation on the aligning substrate. At the same time, the surface

*Corresponding author: olegyar@iop.kiev.ua charging is not completely removed, since UV light irradiation causes generation of ions in the aligning polymer films and in the molecular layers adsorbed on this films [1,2]. The generated charges may strongly influence ion transport processes in LCD modifying its performing characteristics, such as volt holding ratio and residual DC connected with image sticking problem [3]. In addition, generated charges cause distortion of applied electric field at the aligning substrates and modification of LC anchoring [4]. Owing to this, study of charge transport processes in the cells based on photoaligning substrates is of great importance for understanding of the performance characteristics of this type of LCD.

First results devoted to this problem we published in [5]. The objects of our studies were LC cells based on ITO and PVCN photoaligning layers. The time period between irradiation and LC filling, $\tau_{\mathrm{i-f}}$, was equal to one hour. The ion transport processes in LC layers starting just after the cell filling were investigated by measurement of sample conductivity. These measurements reviled adsorption of ions from LC bulk on the aligning substrates. The parameters of this process (characteristic time, concentration of adsorbed ions *etc.*) were practically independent on the irradiation time. Moreover, the obtained values were close to the values obtained for the cells based on non-irradiated substrates. To explain this surprising fact, we measured photoinduced change of surface potential of PVCN substrates. The measurements showed that photoinduced increment of the surface potential, $\Delta\Phi_{\mathrm{s}}$, relaxes with characteristic time τ_{Φ} shorter then 1 h, i.e. for the time shorter then $\tau_{\mathrm{i-f}}$. So, UV generated charges on the substrates were compensated (most likely because of absorption of ions and neutral atoms from air) before cell filling with LC. At these conditions, influence of surface generated charges on the charge transport characteristics can be neglected.

In the present research we consider the case when $\tau_{\mathrm{i-f}}$ is considerably lower than τ_{Φ}. It is shown that non-compensated part of surface ions causes qualitatively new charge transport processes in LC cells. The concurrence of the processes of ion adsorption and ion desorption determines complex kinetic of sample conductivity after LC filling. It is concluded that the efficiency of the concurring processes of ion transport can be controlled by irradiation conditions as well as by purity of LC material.

2. EXPERIMENTAL PART

2.1. Samples

The cells were made from ITO covered glass slides. To prevent any cell edge effects, ITO coating on one slide was designed to obtain two pixels in the center of the slide as it is shown in Figure 1. In this way two different sites in each experimental cell were simultaneously investigated. Both cell

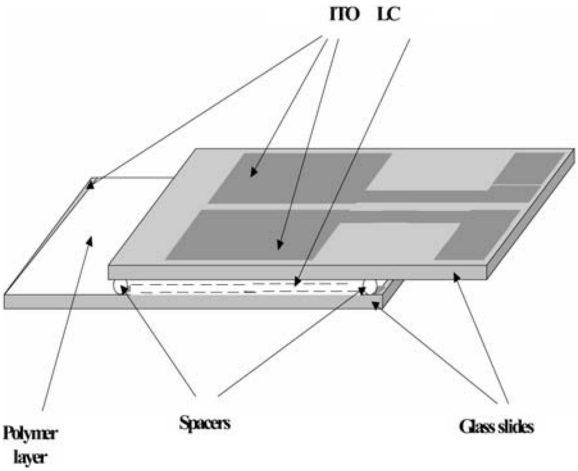

FIGURE 1 Design of LC cell.

substrates were spin coated by polyvinylcinnamate (PVCN), classical photoaligning polymer. The cell gap 13.5 µm was maintained with glass spacer balls and independently controlled by interference method. The cell sticking was provided by epoxy glue.

In contrast to [5], where substrates were irradiated before sample assembling, in present experiments the glued cells were irradiated. The sample preparation procedure was modified to shorter time period between irradiation and LC filling. The irradiation was carried out by polarized integral UV light of metal halogenide lamp (Panacol, Germany). The light intensity was about $8\,\mathrm{mW/cm^2}$. The irradiation time was varied within 0 and 60 min. During irradiation the cell alternately faced the light by different sides to provide uniform irradiation.

After finishing irradiation procedure the cell was filled with nematic LC 5CB purchased from Merck. The time period between irradiation and filling, $\tau_{\mathrm{i-f}}$, was about 1 min. The conductivity measurements were started in 4 minutes after the filling. The short pause between filling and measurements was necessary to reach equilibrium in LC alignment.

Several regimes of sample irradiation and filling were used. The main of them are the following:

1. The cell was irradiated and filled with LC kept in air.
2. The cell and LC were subjected to vacuum 10^{-2} Torr over 1 h. Subsequently, cell irradiation and filling were realized at the same vacuum conditions.

The additional conditions will be described below.

2. 2. Method

In electric circuits LC cell can be substituted by combination of parallel capacitor C and resistor R. The value of C and R in our experiments were measured by oscilloscope method described in [6–8]. The measurements were carried out in the frequency range 0,1—10^4 Hz. Based on these results the components ε' and ε'' of complex dielectric constant were calculated and its dependence on the field frequency was analyzed. The sample conductivity was measured in the frequency range corresponding to constant value of ε' (linear part of $\varepsilon''(t)$ curve). The alteration of the sample conductivity preceding equilibrium states has been studied. Since concentration of ions in LC is low (typically $10^{20}\,\mathrm{m}^{-3}$ [9]) and so recombination of ions can be neglected, the mentioned conductivity change is mainly caused by adsorption/desorption processes in LC cells. This approach was first time applied to study ion transport processes in [10]. All our measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. Frequency Dependencies

Figure 2 shows frequency characteristics obtained for two regimes of cell filling described above. The dependencies can be well described by Debye relaxation law. The low frequency relaxation process ($f_r \approx 10$ Hz) corresponds to orientational relaxation of LC molecules from the interface area [11]. The relaxation process is completely finished at $f > 30$ Hz.

Since measured dependencies $\varepsilon''(f)$ are linear at $f > 30$ Hz, the following formula can be applied:

$$\sigma = \varepsilon_0 \varepsilon'' \omega \tag{1}$$

and so conductivity of 5CB in air and in vacuum can be estimated. These values are $\sigma = 4{,}6*10^{-8}$ Ом$^{-1}$*м$^{-1}$ and $\sigma = 2{,}6*10^{-8}$ Ом$^{-1}$*М$^{-1}$, respectively. So, vacuuming of LC leads to substantial reduction (almost in two times) of sample conductivity and, hence, concentration of ions. This result is in good agreement with the fact of LC boiling during vacuuming which also shows that dissolved gases (including neutral molecules and ions as well) intensively leave LC. Taking into account lower concentration of dissolved gases in vacuumed LC one can also explain slightly higher values of ε' obtained for this case (Fig. 2). So, presented results show that concentration of ion impurities in LC strongly depends on the storage conditions. The materials kept in atmosphere intensively adsorb

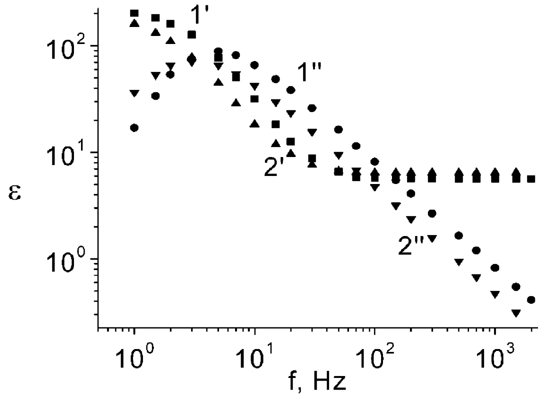

FIGURE 2 The frequency dependencies of real ε' ($1'$, $1''$) and imaginary ε'' ($2'$, $2''$) parts of dielectric permittivity for two regimes of cell filling. In regime 1 (curves $1'$ and $1''$) the cell is irradiated and filled with LC in air. In regime 2 (curves $2'$ and $2''$) the cell was irradiated and filled with LC in vacuum 10^{-2} Torr. The cell gap is 13.5 μm.

gases containing various types of ions. This is a reason why conductivity value is not included to the list of physical parameters of commercially available LC.

In the following, conductivity measurements were carried out at the frequency corresponding to linear part of $\varepsilon''(f)$ curve. Since oscilloscope method requires comparable resistance and reactance of LC cells, the field frequency was adjusted at 200 Hz for the cells of first type and at 70 Hz for the cells of second type.

3. 2. Kinetic of Conductivity

3. 2. 1. LC Filling in Atmosphere

Dependencies of the sample conductivity on the time passed after the LC filling are presented in Figure 3. The Figure 3a corresponds to non-irradiated cell, whereas the Figure 3b to irradiated one. As can be seen, in case of non-irradiated cells σ(t) curve monotonously decreases. The same behavior of σ(t) curve was earlier observed for the case when $\tau_{i-f} = 1$ h [5]. It can be explained with the ion adsorption from LC bulk onto the cell substrates. The σ(t) curve is fitted well with the mono-exponential function

$$\sigma(t) = \sigma_0 - \Delta\sigma(1 - \exp(-t/\tau)) \qquad (2)$$

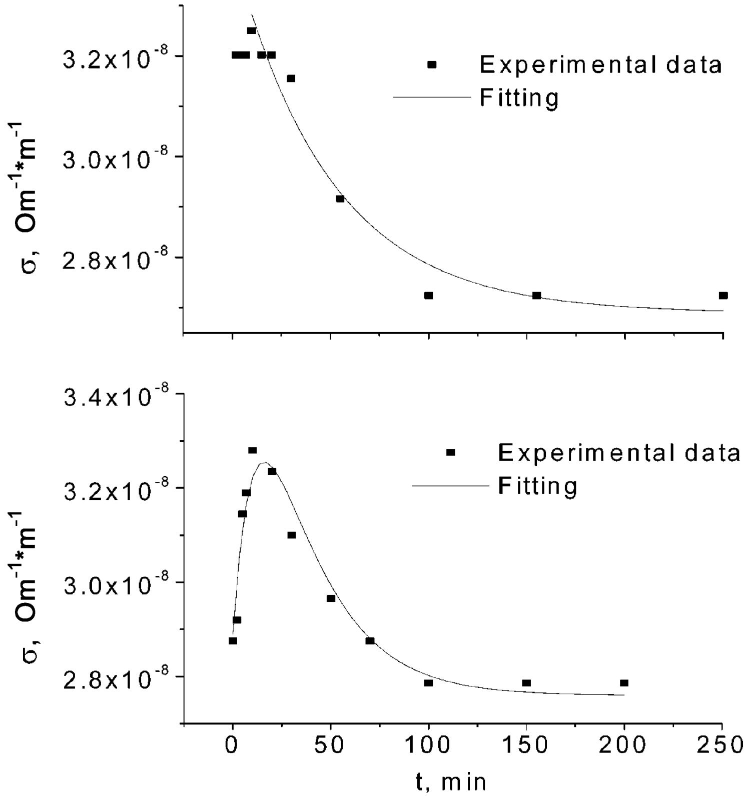

FIGURE 3 Experimental and fitting curve $\sigma(t)$ corresponding to the cell irradiated and filled in air. a) non-irradiated cell; b) cell irradiated 20 min.

In result of fitting we obtain $\sigma_0 = 3.6{*}10^{-8}$ $\mathrm{Om}^{-1}\mathrm{m}^{-1}$, $\Delta\sigma = 0.73{*}10^{-8}$ $\mathrm{Om}^{-1}\mathrm{m}^{-1}$, $\tau = 50\,\mathrm{min}$. The value of $\Delta\sigma$ can be used to estimate surface density of adsorbed ions n_s from the formula [12]:

$$n_S = \frac{\Delta\sigma d}{e\mu} \tag{3}$$

where *e* is an electron charge, μ is ion mobility, *d* is a thickness of LC layer. At $\Delta\sigma = 0.73{*}10^{-8}$ $\mathrm{Om}^{-1}\mathrm{m}^{-1}$ and $\mu = 10^{-10}\,\mathrm{m}^2/\mathrm{Vs}$ taken from [13], the value of the ion density on the substrates is $n_s = 6.1\ 10^{15}\,\mathrm{m}^{-2}$. Note, that this estimate is correct when the ion recombination in not essential.

In contrast to non-irradiated cell, the σ(t) curve obtained for irradiated cell goes through maximum (Fig. 3b). This curve can be fitted with two exponents as below

$$\sigma(t) = \sigma_0 + \Delta\sigma_1(1 - \exp(-t/_1)) - \Delta\sigma_2(1 - \exp(-t/_2)) \tag{4}$$

For the curve presented in Figure 3b the fitting parameters are $\sigma_0 = 2.82*10^{-8}$ $\mathrm{Om^{-1}m^{-1}}$, $\Delta\sigma_1 = 0.83*10^{-8}$ $\mathrm{Om^{-1}m^{-1}}$, $\Delta\sigma_2 = 0.88*10^{-8}$ $\mathrm{Om^{-1}m^{-1}}$, $\tau_1 =$ 7 min, $\tau_2 = 33$ min. The value of $\Delta\sigma_1$ sharply increases within first several minutes of irradiation and goes to saturation. In contrast, parameters $\Delta\sigma_2$, τ_1 and τ_2 weakly depend on the irradiation time.

The observed decrease of σ(t) curve, same as in the case above, can be explained by ion adsorption onto aligning substrates. On the other hand, initial grow of σ can be the result of ion income from the polymer substrates due to the process of ion desorption. The fitting results show that characteristic time of ion desorption, τ_1, is considerably shorter then the time of ion adsorption, τ_2. So, non-monotonous character of σ(t) curve can be explained assuming concurrence of ion adsorption and desorption processes characterizing by different time constants.

3. 2. 2. Cell Filling with Vacuumed LC

The typical σ(t) curve corresponding to this case of filling characterizes by monotonous grow (Fig. 4). It can be well fitted with the function:

$$\sigma(\mathrm{t}) = \sigma_0 + \Delta\sigma(1 - \exp(-\mathrm{t}/\tau)) \qquad (5)$$

In case of the curve presented in Figure 4 fitting parameters are $\sigma_0 = 1.66*10^{-8}$ $\mathrm{Om^{-1}m^{-1}}$, $\Delta\sigma = 0.76*10^{-8}$ $\mathrm{Om^{-1}m^{-1}}$, $\tau = 28$ min. These parameters weakly depended on the irradiation dose.

The monotonous grow of σ suggests that the process of ion adsorption playing important role at the air filling is effectively suppressed. This can be caused by strong reduction of ions in LC bulk due to the vacuum evacuation. As we showed above the concentration of ions is reduced by the factor of 2.

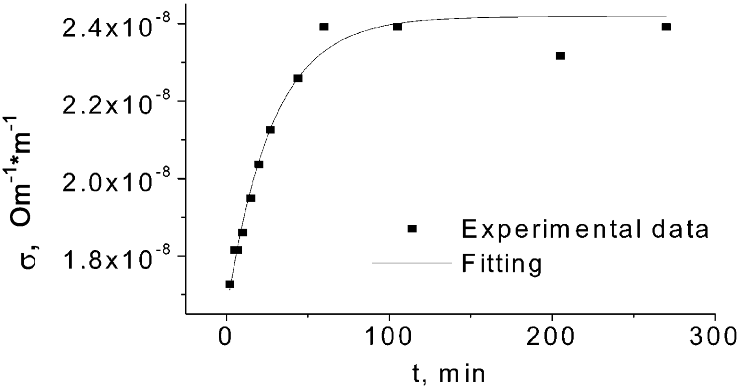

FIGURE 4 Experimental and fitting curve $\sigma(t)$ corresponding to the cell irradiated and filled in vacuum 10^{-2} Torr. Irradiation time is 20 min.

It is the most naturally to assume that obtained growing of σ is determined by the same ion desorption process which causes growing part of σ(t) curve in Figure 3b. However, we also considered other opportunities, for instance, σ increase due to diffusion of air ions in vacuumed LC layer. To check this, the σ(t) curves were measured in both LC cells thoroughly glued and not glued after filling. No difference in the obtained data was detected. From this we concluded that characteristic time of air penetration into LC is considerably higher then the growing time of σ(t) curve.

We also showed that UV irradiation of the aligning substrates in vacuum is not the principle point to realize ion desorption regime discussed above. The monotonously growing σ(t) curve was also obtained for the cell irradiated in air and filled with vacuumed LC. So, the main feature of σ kinetic, i.e., monotonous growing, observed for the case of vacuum filling, is determined by deionization of LC due to evacuation of dissolved gases.

The surface density of the desorbed ions can be estimated from (3) using value $\Delta\sigma = 0.76*10^{-8}\,\mathrm{Om}^{-1}\,\mathrm{m}^{-1}$ obtained from the fitting of σ(t) curve (Fig. 4). This estimation gives $n_s = 6.5\,10^{15}\,\mathrm{m}^{-2}$. The obtained value is comparable with the value of adsorbed ions estimated above. This confirms that conductivity kinetic is caused by ion redistribution within LC cell and the ion exchange with outside can be neglected.

The weak dependence of the σ(t) curve on irradiation dose, which is observed for the cells irradiated and filled in vacuum, may be explained by low concentration of gases supplying ions under UV irradiation. As we noticed, this dependence is considerably stronger for the cells irradiated in air and filled with vacuumed LC. However, this regularity was not systematically studied.

CONCLUSIONS

Thus, LC filling into the cell based on photoaligning substrates initiates ion redistribution within the cell, which is associated with the concurring processes of ion adsorption and desorption. The efficiency of these processes depends on the substrate irradiation conditions and concentration of ions in LC material. The cell filling with LC enriched with ions is accompanied with ion adsorption from the LC onto aligning substrates (non-irradiated substrates) or both ion adsorption and desorption (irradiated substrates). In contrast, at the filling with ion purified LC only the ion desorption from aligning substrates is detected.

The observed ion transport processes causing transient of conductivity of LC layers are shown to be associated with the ions, which can be easily removed from LC by vacuuming and desorbed from the substrates by LC filling. These ions are mainly supplied from the air.

Based on the conductivity change, surface density of the adsorbed (desorbed) charges is calculated. These estimates should be taken into account at the consideration of surface phenomena in LC depending on electric field.

It is important to note that applied method is not sensitive to the charges generated with UV light in the aligning polymer substrates. Since polymer is practically insoluble in LC, these charges can not diffuse to LC and so influence results of our measurements.

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