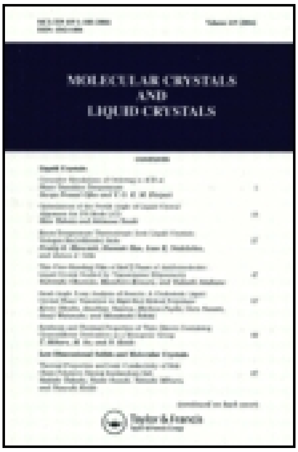

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DC Current in 4-N-Pentyl-4′-Cyanobiphenyl Liquid Crystal Cells

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DC Current in 4-N-Pentyl-4′-Cyanobiphenyl Liquid Crystal Cells

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Transient and steady electric currents through a pentyl-cyano-biphenyl nematic liquid crystal cell have been studied under and without external photo-irradiation. The importance of space-charge effects has been demonstrated.

Keywords DC conductivity; laser irradiation; pentyl-cyano-biphenyl liquid crystal; space charge

1. Introduction

The overwhelming majority of liquid crystals (LCs) are insulators, so their bulk electrical conductivity obeys the Arrhenius law typical of organic materials. However, various impurities, polarization effects, traps, and intrinsic-molecule ionization may drastically change this behaviour. Systematic studies of LC electrical conductivity started in 1970s, when nematics were proposed to be used in LC displays (LCDs) [1]. The application of an ac electric field to an LC cell was found to excite a very weak transient current through it, and ionic impurities detected by dielectric measurements [2] were suggested to be responsible for this phenomenon. Those impurities might arise either due to LC contamination from the surrounding environment or as aromatic fragments of LC matrix in the course of chemical synthesis and imperfect purification.

The transient current has a minimal effect on the performance of twist nematic mode, so that few studies of electric conduction in nematic LCs appeared until active-matrix LCDs, which require materials with an extremely low conductivity ($<10^{-12}$ S/m), emerged in the marketplace in 1980s. The origin of ions responsible for currents through LCs still remains a matter of discussion. Concerning the nematic LC pentyl-cyano-biphenyl (5CB), it may be impurity inorganic ions [3] or various charged fragments emerged due to spontaneous dissociation of 5CB

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molecules themselves [4]. Another conductivity mechanism is governed by electrochemical and photoelectrochemical reactions occurring near electrodes and activated by charge (electron or hole) injection [5].

To our knowledge, only one brief report [6] dealt with a weak steady electric current through a nematic LC (5CB) after the cell had been charged. The authors found that the current-voltage characteristics (CVCs) for the steady current, $I_s(U)$ contained linear sections, so that the role of near-electrode space charge was not crucial. However, the experiment was carried out at planar orientation of LC in the cell, and probable reorientation effects were not taken into account. We consider this circumstance to be responsible for the conclusion drawn, because our experimental data evidence just the opposite.

2. Experimental Part

We used 5CB-filled cells composed of two glass substrates covered with ITO layers and distanced at $L = 20\,\mu\text{m}$ from each other by polymer cylindrical spacers deposited outside of the electrode areas. The surface resistivity of ITO layers was $R_s = 50–100\ \Omega/\square$. Possible reorientations of LC molecules by an external electric field were avoided by their homeotropical alignment at electrodes. Two groups of 5CB-filled cells were fabricated. The cells of one group with the area of ITO coverage $S \approx 1\ \text{cm}^2$ were engaged in charge-discharge experiments, and the cells with $S \approx 0.0225\ \text{cm}^2$ in CVC measurements. In both cases, the electrode area was less than the area of corresponding sides of LC slab. The results obtained for different cells within each group turned out rather close to one another.

Currents through LC cells were measured with a picoammeter ($I_{\min} = 10^{-15}$ A). The applied dc voltage was controlled by a potential divider located in the measuring unit and the resistance of which (20 kΩ) was much lower than that of LC cell (2 MΩ). The whole measuring unit was grounded. The time-resolved analog signal from the picoammeter was digitized by a data acquisition card.

3. Results and Discussion

The application of dc voltage U across an LC cell resulted in an appearance of a sharp peak of non-stationary current $I(U,t)$, where t is the time, followed by a low but reliably measured plateau $I_s(U)$, which could remain constant within several days (see Fig. 1). The ratio between the $I_s(U)$-value and the peak amplitude was very small and allowed the peak to be considered as consisting of only transient current, $I(U,t) = I_t(U,t)$. The relaxation time of $I_t(U,t)$ was estimated as several tens of seconds. We observed a similar behavior in nematic mixture E7, where 5CB is a component, but the amplitude of the steady current was an order of magnitude lower. At the same time, no steady current, i.e., $I_s(U) = 0$, was observed for nematic mixture ZLI 4801, which does not contain cyano-biphenyl-based compounds.

The transient current could be associated with LC polarization in a capacitor composed of ITO electrodes, as it occurs in solid insulators. If only bound charges, which govern the dielectric constants of pure 5CB ($\epsilon_{\|} = 20$, $\epsilon_{\perp} = 18$), were responsible for cell polarization, their contribution could be evaluated as a charge $Q = CU$ accumulated in the cell-capacitor $C = \epsilon_{\|}\epsilon_0 S/L$ at the voltage U. The corresponding calculation gives Q of the order of 10^{-9} C at $U = 2.5$ V. But the real charge turned out much larger (of about 10^{-6} C), as was determined by integrating the discharge

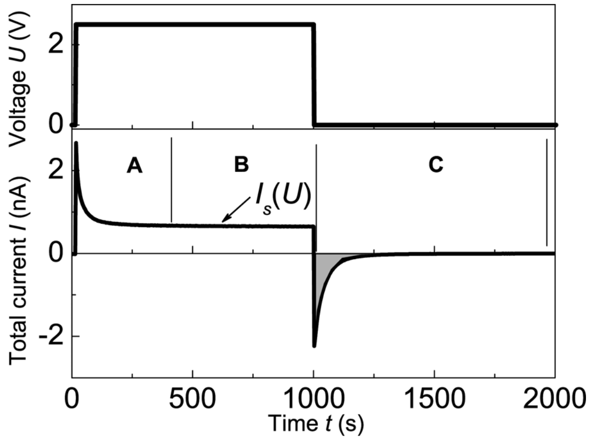

Figure 1. Charging and discharging currents $I(U,t)$ through an LC (5CB) cell of width $L = 20\,\mu\text{m}$ between ITO electrodes. The amplitude of the pulse bias voltage is $U = 2.5\,\text{V}$. $I_s(U)$ is the saturation current.

current measured after the cell had been short-circuited. The result obtained allowed us to conclude that 5CB also contains free charges and those charges strongly dominate the cell charge Q, so that the contribution of bound charges can be neglected here. The applied field inhomogeneously redistributes free charges between the Gouy-Chapman electrolytic double-layer region [7] and the cell bulk.

The dynamics of charge Q accumulation is depicted in Figure 2. Specifically, we measured the dependence of the accumulated charge Q on the charging time interval t_u, during which the voltage was applied. The corresponding Q-values were obtained by integrating the relevant discharging transient current curve. The analysis of the

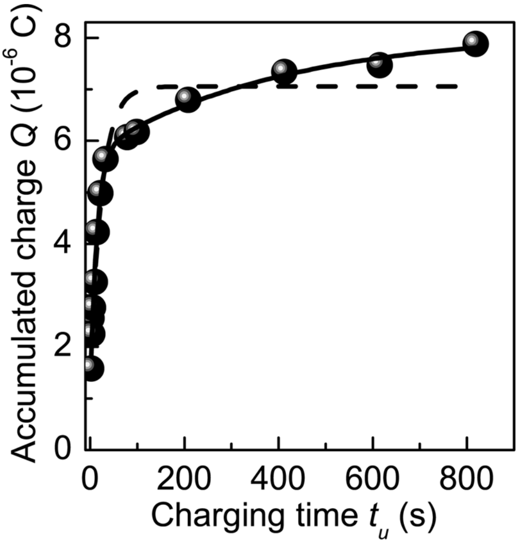

Figure 2. Experimental dependence (spheres) of the accumulated charge Q on the charging time interval t_u and its single- (dashed curve) and double-parameter (solid curve) fittings.

experimental dependence $Q(t_u)$ testifies that, to describe it properly, one should use at least a two-exponential approximation

$$Q(t_u) = A_0 + A_1\exp(-t_u/\tau_1) + A_2\exp(-t_u/\tau_2), \tag{1}$$

where A_i and τ_j are fitting parameters. The adequacy of Equation (1) is in agreement with a scenario, where the excess charge in the LC cell is generated in both the charged double-layer region (for the disconnected-circuit and steady-current regimes) and the space charge cloud extending into the LC bulk. Accordingly, associating the relaxation parameters τ_j in Equation (1) with characteristic times of double layer (τ_1) and space-charge cloud (τ_2) formation, we obtain $\tau_1 \approx 14$ s and $\tau_2 \approx 397$ s for those quantities at $U = 2.5$ V.

It might be, in principle, that two relaxation terms in Equation (1) are a simple reflection of two ionic groups [8], although it is difficult now to identify those groups unambiguously.

Long times of charge or discharge processes observed here correlate well with those for solid organic acenaphthalene crystals, where the steady-current regime was attained after 2-3 h [9].

Diffusion of free carriers governs the dynamics of cell charge/discharge. The same bulk diffusion coefficient $D \approx (2.5 \pm 0.3) \cdot 10^{-12}$ m^2/s was evaluated from both the characteristic decay time of the discharge transient current [10] and in the framework of the cell recharging method [11]. This value is by an order of magnitude lower than the self-diffusion coefficient of 5CB molecules, $D_0 = (6.5 \pm 0.5) \cdot 10^{-11}$ m^2/s [12,13]. This fact can be understood, if one adopts the hypothesis that free charges (electrons supplied by the negative electrode) are transported through 5CB by means of molecular aggregates. In the process, 5CB molecules *per se* did not change in the long run by any possible chemical reaction in the electrochemical cell. This suggestion is supported by the fact that the LC inside the cell did not alter its external appearance (color and transparency) during several days, when the steady current ran through. Besides, it means that electrons or protons engaged in the hydrogen bonds between LC molecules might be responsible for the latter to aggregate [14].

We also measured CVCs $I_s(U)$ for cells filled with 5CB. At low bias voltages U, they can be approximated by the power-law dependence $I_s(U) \sim U^k$, where the value $k = 1.64$ testifies that the current is governed, to a great extent, by a space charge accumulated in the cell at the transit stage. Otherwise, we would have obtained the Ohmic dependence $I_s(U) \sim U$. The latter regime was also attained, but at larger bias voltages, when, as we think, the space charge became depleted. It should be noted that various insulating solid organic materials usually demonstrate power-law conductivity with $1.1 < k < 1.4$ [9].

Conductivity processes in the cells with homeotropically aligned 5CB molecules were studied by laser irradiation (the wavelength $\lambda_{\text{irr}} = 440$ nm, the power density $P/S = 500$ W/m^2). The results obtained are shown in Figure 3 for different applied bias voltages. It is no wonder that current across the cell abruptly increases, when the laser is switched on. Then, while keeping the laser in the steady regime, the current gradually decreases, probably due to the interaction with traps. At lower voltage ($U = 1$ V), the reduction is relatively small and slow, whereas at $U = 2.5$ V, the current falls even below the initial level, which may mean a decrease in the number of charge carriers involved. In any case, it is difficult now to propose an adequate explanation for this puzzling phenomenon.

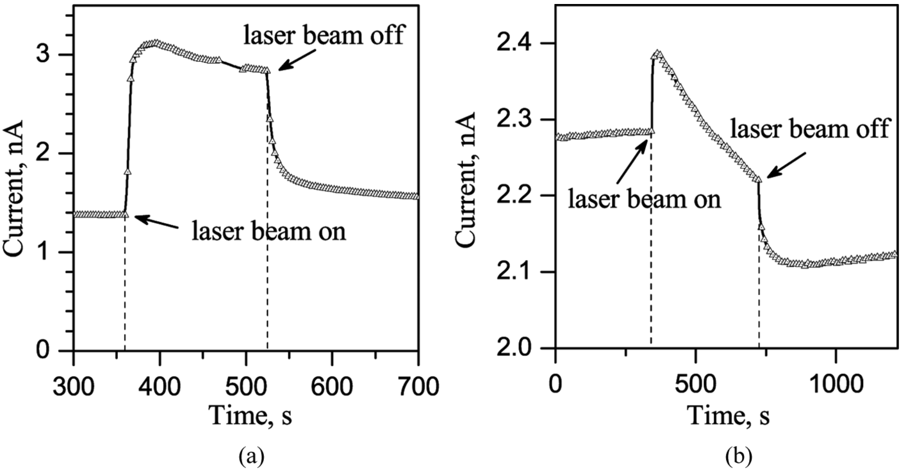

Figure 3. Experimental dependences (points) of dc current through an LC cell with 5CB subjected to a long irradiation with laser beam for various bias voltages $U = 1$ (a) and 2.5 V (b) across the cell. Curves are guides for eye. Dashed lines mark the boundaries of the time interval when laser irradiation is switched on.

After the laser is switched off, the current jumps downwards and then tends to its initial value for $U = 1$ V, which seems quite plausible. On the other hand, at $U = 2.5$ V, the current also jumps downwards and tends to its previous value. However, in the latter case, it means a current growth. This behavior will be studied further in more detail, but in any case it seems to be governed either by charged traps or modifications of current carrying molecular aggregates. The latter might be charge-transfer complexes. It should be noted that the observed relaxation of the currents to their initial values is extremely slow, which is in contrast, e.g., to the microsecond-order time characteristic of transient photocurrents in a charge transfer complex of trinitrofluorenone with a carbazole substituted discotic liquid crystal [15].

4. Conclusions

To summarize, we have studied transient and steady currents in the nematic LC cells and demonstrated that the space-charge effects are important. Specifically, we consider the nematic interlayer as an inhomogeneous medium with double layers near electrodes produced by adsorption of ions from the LC bulk. The LC bulk contains charge carriers of both signs, which might be either extrinsic (impurities) or intrinsic ones. In the latter case, they may be imagined as aggregates of LC molecules. In the steady-current regime, the CVCs are determined by the space charge generated in the near-electrode regions of nematic. At large enough biases U, the steady current dependence $I_s(U)$ is linear, since the space charge cloud is depleted. The observed transient phenomena testify that charge carriers of at least two kinds are engaged. They may originate, e.g., from the double-layer and the bulk region of the LC cell.

The currents across the LC cells were studied also under the influence of the laser irradiation, which revealed a complicated slow non-linear temporal behavior of I_s after laser irradiation was both switched on and switched off.

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