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Transient and steady electric currents through a liquid crystal cell

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This paper presents a study of the transient and steady electric currents through a pentyl-cyano-biphenyl (5CB) nematic liquid crystal (LC) cell. It is demonstrated that space-charge effects are important, contrary to what has been observed before. Specifically, the nematic interlayer can be considered as an inhomogeneous medium, with near-electrode double layers emerging due to adsorption of ions present in the LC. The bulk of the LC contains charge carriers of both signs, which might be either extrinsic (impurity-induced) or intrinsic. In the latter case, they could consist of heavy fragments of LC molecules or anion and cation radicals, induced by redox processes near the electrodes. In the steady-current regime, the current–voltage characteristics are, most probably, governed by a space charge distributed in the nematic. For large enough biases U, the steady current approaches the Ohmic regime due to the depletion of the space-charge cloud. The observed transient-current phenomena suggest at least two types of charge carriers.

Keywords: 5CB; dc conductivity; space charge

1. Introduction

The majority of liquid crystals (LCs) are insulators, with the electrical conductivity in the bulk obeying the Arrhenius law [1]

$$\sigma = \sigma_0 \exp\,(-E_a/k_B T), \tag{1}$$

typical of organic materials [2, 3]. Here, T is the temperature, σ_0 a material-dependent parameter, k_B the Boltzmann constant and E_a the activation energy. Impurities, polaronic effects, traps and intrinsic-molecule ionisation may drastically change this behaviour both for solid and LC insulators [2, 4–10]. Systematic studies of the mesophase electrical conduction date back to the beginning of the 1970s, when a twist nematic mode was proposed for implementation in LC displays (LCDs) [11–14] (see also the review [15]). The application of an ac electric field to an LC cell was found to excite a very weak transient current through it. Ionic impurities, which were also detected by dielectric measurements [16], were suggested to be the source of this phenomenon. Those impurities might arise owing to LC contamination resulting either from the surrounding environment or as aromatic fragments of the LC matrix, which emerge in the course of chemical synthesis followed by imperfect purification.

The transient current turned out to have 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 emerged in the marketplace in the 1980s. Active-matrix displays required LC materials with extremely low conductivity ($<10^{-12}$ S m^{-1}), providing an impetus for new detailed studies of electric conductivity in LCs – in particular, nematic LCs (see, e.g., [17–21]). Measurements of transient currents and the complex, low-frequency dielectric constant in LCs allowed the mobilities and the diffusion coefficients of ions along and perpendicular to the LC director, as well as the properties of the electric double layer that forms at the electrode–LC interface, to be determined.

The origin of ions that are responsible for currents through LCs still remains a matter of discussion. Some authors [22–24] suggested that inorganic ions play an important role in the formation of charge carriers in the nematic LC pentyl-cyano-biphenyl (5CB) LC. Naito *et al.* [25] suggested the presence of positive ions in 5CB and concluded that they mainly formed from a spontaneous dissociation of 5CB molecules. It was inferred from experiment that there are many ionic species in 5CB cells [19]. This conclusion was based on the fact that ultraviolet irradiation increased the ion concentration in 5CB, leaving the ion mobility the same. It might also happen that ions, which govern conductivity in the LC cell, are generated by electrochemical and photoelectrochemical reactions occurring near electrodes and activated by charge (electron or hole) injection [26, 27].

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It should be noted that electrochemical oxidation and/or reduction at the cell electrodes is possible for other organic LC materials, leading to the appearance of anion and cation radicals under the influence of the applied electric field, so that the LC itself becomes conducting [28]. For instance, such electrolytic processes were observed for *p*-methoxybenzilidene–*p*-*n*-butylaniline (MBBA) [29], a 1:1 mixture of MBBA with *p*-ethoxybenzilidene-p'-butylaniline (EBBA) [30] and tolanes [31]. In practical situations, charge carriers in LCs may result from the joint action of several factors, as indicated above.

Besides the transient electric current, Mada and Yamada [32] reported that they revealed a weak steady current flowing through the LC 5CB after the cell had been charged. The authors found that, in a cell composed of two substrates covered with indium tin oxide (ITO) electrodes and an LC in between, the steady current, I_s, was proportional to the applied voltage, U, only in the low-voltage regime, whereas nonlinear current–voltage characteristics (CVCs) were observed when the voltage across the cell exceeded a few volts. The magnitude and shape of the CVC turned out to depend substantially on the presence of an additional aligning polyimide layer between the LC and the electrode. Mada and Yamada [32] suggested that the steady current across the cell resulted from charge-carrier recombination or a redox reaction at the electrode surface. They concluded that the observed CVC cannot be described by a space-charge-limited current. The linearity of their $I_s(U)$ dependences at low U indicates the absence of screening of the applied electric field by space charge. Nevertheless, we believe that the CVC nonlinearity at higher U testifies to the existence of a space-charge cloud (see the description of the corresponding phenomena in a vacuum [33–35], gas-discharge or electron (ion) beam plasma [36–38], and insulating solids [39–43]). It seems plausible that, in the experiments [32], the charge injection into an LC cell is small at low U so that the screening cloud appears only at higher U. However, in our present measurements, we find that the CVCs are nonlinear even at the lowest measured voltages, and that the space-charge phenomena manifest themselves over a broader range of U. The origin of the differences between CVCs in these two studies needs to be resolved.

To the best of our knowledge, the brief report [32] is the only one that describes the observation of a steady electric current in nematic LCs. The flow of the steady current implies that the electrode layers play an active role in the electric conductance of cells filled with nematic LCs, at least in the case of 5CB. While describing such behaviour, the role of the adsorption phenomena at the relevant interfaces should be considered [44, 45]. This includes the influence – sometimes decisive – of the image forces [46].

Charge transfer processes at the electrode–LC interface have special importance because a number of surface-driven light-controlled effects have been found recently in nematic LCs [47–49]. These effects are caused by light-induced changes of the ion concentration in the vicinity of the electrode–LC interface. Therefore, the response of an LC cell to light irradiation should be strongly affected by processes at the interface in the steady-current mode.

In this paper, we describe our experiments that were aimed at studying steady and transient electric currents across LC cells filled with 5CB. The corresponding analysis has revealed details concerning the formation and characteristics of an electric double layer near the ITO.

2. Experimental details

We used LC cells composed of two glass substrates covered with ITO layers with the LC 5CB in between. The surface resistivity of the ITO layers was $R_s = 50 - 100\Omega/\square$. The LC thickness $L = 20\ \mu$m was fixed by polymer cylindrical spacers deposited outside of the electrode areas. To avoid possible reorientations of the LC by an external electric field, the LC was homeotropically aligned on the ITO electrodes. Homeotropic alignment was achieved by the following treatment. First, the substrates were washed out with ethyl alcohol. After washing, they were rinsed in deionised water, the residuals of which were removed from the ITO surfaces by nitrogen blow-off. The whole treatment was performed at room temperature. Then, the LC cell was put into a grounded measuring unit connected with a picoammeter, which could measure electric currents larger than 10^{-15} A. The applied dc voltage was controlled by a potential divider located in the measuring unit. The total resistance of the potential divider (20 kΩ) was much lower than the resistance of the LC cell (2 MΩ). The time-resolved analogue signal from the picoammeter was digitised by a data acquisition card.

To study the effects described in this paper we used two groups of LC cells filled with 5CB. The cells of one group were used in charge–discharge experiments, the cells of the other for CVC measurements. The difference between those groups concerned the area of ITO coverage (it was reasonable to fabricate cells intended for charge–discharge experiments with considerably larger coverage areas). The results obtained for different cells within each group turned out to be rather close to one another. So, below, we have restricted our consideration to two LC cells (one from each group), which demonstrated results typical of each research regime. The area of ITO coverage was $S = 1\text{cm}^2$ in the cell engaged in the charge–discharge experiments and $S = 0.0225\ \text{cm}^2$ in the cell used for the CVC measurements. In both cases, the electrode area was less than the area of the corresponding sides of the LC slab.

2.1 Charging and transient phenomena

Application of the dc voltage U across an LC cell resulted in a non-stationary current $I(t)$ including a transient current contribution $I_t(t)$ with a relaxation time of tens of seconds (Figure 1, interval A). While the transient current magnitude vanished after a certain time, $I(t)$ reached a very small but reliably measured, finite steady value I_s of about 1 nA (Figure 1, interval B). The steady current I_s did not change in time over several days. A later short-circuit resulted in a discharge current in a direction opposite to the charging current (Figure 1, interval C). Similar behaviour was observed in the nematic mixture E7, 5CB being one of its components; however, the amplitude of the steady current was an order of magnitude smaller than that in 5CB. At the same time, no steady current was observed at all for nematic mixture ZLI 4801, which does not contain cyano-biphenyl-based compounds (the discharge current through the cell filled with ZLI 4801 is depicted in Figure 1 by the dotted curve). Similar extended transient currents were observed earlier for other insulating objects, for instance corona-charged polyethylene films [50].

These results suggest that the transient current is caused by the LC polarisation in a capacitor composed of ITO electrodes, as it occurs in solid insulators [51]. Both bound and free charges in the cell contribute to the cell polarisation. The bound charges are responsible, in particular, for the dielectric constants of pure 5CB ($\varepsilon_\| = 20, \varepsilon_\perp = 18$). The charge q, which can be accumulated in our cell capacitor with the capacitance $C = \varepsilon_\| \varepsilon_0 S/L$ (ε_0 is the vacuum dielectric constant, $\varepsilon_\perp = 18, S = 1\ \text{cm}^{-2}$, and $L = 20\ \mu\text{m}$) is due to the displacement of the bound charges and is of the order of 10^{-9} C at $U = 2.5$ V. At the same time, we integrated the discharging curve depicted in Figure 1 (shadowed area) and obtained a much larger value, $Q \approx 10^{-5}$ C. Therefore, we draw a conclusion that free charges dominate the cell charge Q. The applied field inhomogeneously redistributes those charges between the double-layer region and the cell bulk.

The dependence of the charge Q accumulated in the cell on the applied voltage U is depicted in Figure 2. This dependence was obtained by integrating the discharging transient current curve over the discharge time. We found that the accumulated charge Q increases approximately linearly up to $U \approx 2$ V, and then a less steep, but also linear, growth of Q follows. The initial increase of Q is most probably connected with an enrichment of the near-electrode layers by charges injected into the cell and accumulated in it later. The formation of the charged double layer apparently terminates at $U \approx 2$ V, and the slow increase of the accumulated charge with growing U should be connected with other processes. For instance, one may suggest that large voltages $U \gtrsim 2$ V lead to ionisation of traps associated with defects or impurities.

Both an initial and a modified double layer play a dual role with respect to injected charges. On the one hand, the double layer itself may substantially increase the energy barrier for injected (and/or extracted) electrons. On the other hand, the application of an external field modifies the spatial charge distributions in the near-cathode and near-anode double layers. In essence, the external field turns out to be harmful for the near-

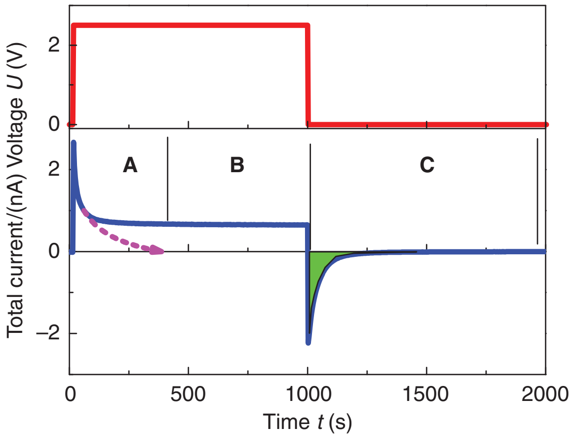

Figure 1. Charging and discharging currents through a LC (5CB) cell of width $L = 20\ \mu\text{m}$ between indium-tin-oxide (ITO) electrodes. The applied bias voltage is $U = 2.5$ V.

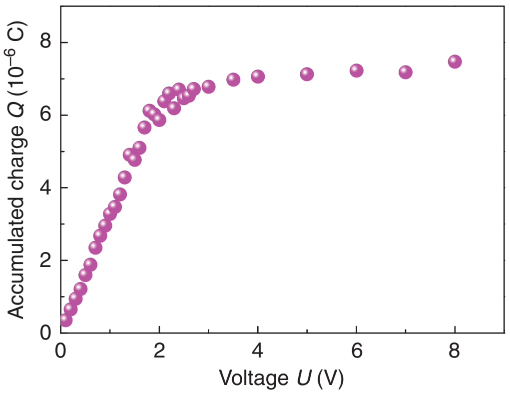

Figure 2. Accumulated charge Q in the cell versus applied bias voltage U.

cathode double layer, which may bring about an enhancement of the injected charge. One may also suggest that the double-slope shape of the curve $Q(U)$ in Figure 2 reflects the occurrence of two sorts of traps, namely deep and shallow traps. The existence of two distinct groups of traps was demonstrated for solid organic materials, for example, in experiments on the electrostatic potential decay of the corona charged polyethylene [52] and tetracene single crystals [53]. Note that traps in at least smectic or discotic mesophases should be dynamic in nature [54, 55], as opposed to those in the crystalline state. The nature of traps in our LC cell cannot be elucidated from our transport measurements, so that another technique should be applied, such as, in particular, optical methods.

The twofold character of the transient phenomena in LC cells is confirmed by a detailed analysis of the temporal behaviour of the excess charge. Specifically, we measured the dependence of the accumulated charge Q on the time interval t_u, during which the voltage was applied (Figure 3). The Q-values were obtained at different t_u by integrating the discharging transient current curve over the discharge time. The analysis of the experimental dependence $Q(t_u)$ testifies that the single-exponential approximation

$$Q(t_u) = A_0 + A_1 \exp\left(-\frac{t_u}{\tau_1}\right), \qquad (2)$$

where $A_0, A_1,$ and τ_1 are fitting parameters, poorly describes the experimental dependence (dashed curve). However, the two-exponential approximation

$$Q(t_u) = A_0 + A_1 \exp\left(-\frac{t_u}{\tau_1}\right) + A_2 \exp\left(-\frac{t_u}{\tau_2}\right) \qquad (3)$$

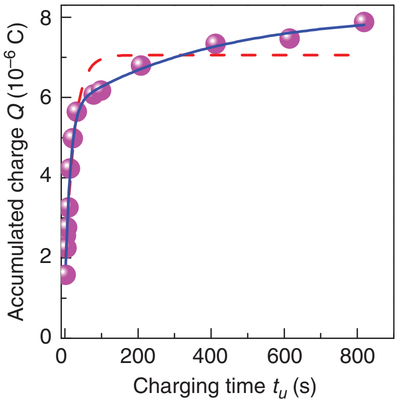

Figure 3. Experimental dependence (spheres) of the accumulated charge Q on the charging time t_u and its single- (dashed curve) and double-parameter (solid curve) fitting.

fits much better (solid curve) and this enabled us to evaluate the characteristic times of both the double layer ($\tau_1 \approx 14$ s) and space-charge cloud ($\tau_2 \approx 397$ s) formation at $U = 2.5$ V. The success of Equation (3) 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. The doubleness of the relaxation might alternatively be associated with the suggested existence of two kinds of traps, i.e. the bulk and surface traps.

It should be noted that the experimental curve is better fitted by a two-exponential dependence [3] rather than a more general stretched one-exponential (Kohlrausch) one, proportional to $\exp\left[-(t_u/\tau_K)^{\beta}\right]$ [56, 57], which describes a disordered glassy state of the relaxing system and is appropriate to a number of organic glasses and supercooled liquids [58]. Hence, in our case, the character of the electrical conductivity was not dictated by a wide distribution of trap depths. It should be kept in mind that, in principle, the two relaxation terms in Equation (3) might be a simple reflection of having two groups of ions [59], although it is difficult in our case to unambiguously identify even one such group. As for the description of electrolyte conductivity with two ion species as a whole [59], this is based on the diffusion model [44, 60], which, being fruitful *per se*, cannot explain the CVC nonlinearities observed in our experiments (see later).

The dynamics of the cell discharge is governed by the diffusion of free carriers from the charged double layer into the cell bulk to restore the initial spatial distribution. We estimated the diffusion coefficient of the carriers in the bulk, $D \approx (2.5 \pm 0.3) \times 10^{-12}$ m^2 s^{-1}, from the characteristic decay time of the discharge transient current [61]. The same value was obtained in the framework of the cell recharging method [62]. This value is an order of magnitude lower than the self-diffusion coefficient of 5CB molecules, $D = (6.5 \pm 0.5) \times 10^{-11}$m^{2}s^{-1} [63, 64]. This fact can be understood if one adopts the hypothesis that the steady current in 5CB is maintained by spontaneously dissociated LC molecules [25, 65]. Then, the decreased magnitudes of the diffusion coefficient for the charged 5CB ions in comparison to the self-diffusion coefficient of the neutral 5CB molecules are naturally explained by the solvation of 5CB ions in a medium consisting of neutral molecules and their charged fragments (in the spirit of the modern colloid theory [66]). As a matter of fact, this phenomenon results in an increase in the charge-carrier effective mass.

It should be noted that dielectric spectroscopy measurements reported in [21, 22] led to the values

$D = (1.9 \times 10^{-12} \div 1.2 \times 10^{-11})\,\mathrm{m^2\,s^{-1}}$, and the carriers responsible for conductivity in 5CB were suggested to be positive and negative inorganic ionised impurities. The ion sizes were estimated to range from 0.25 to 1.5 times the Stokes radius, which suggested to the authors that those ions – naked, hydrated or solvated by polar 5CB molecules – are the majority charge carriers in 5CB. In our opinion, one should not exclude the possibility that highly disassociated heavy 5CB molecules give a contribution to the steady charge transfer in a cell filled with 5CB. Nevertheless, a contribution of impurity inorganic ions to the total conductivity cannot be excluded from consideration.

The concentration of 5CB ions in the cell can be evaluated by the formula

$$c_v = \frac{Q - q}{keSL}, \tag{4}$$

where $q = CU$ is the bound charge accumulated in the cell at the applied voltage U, $e > 0$ is the elementary charge and ke is the average effective charge per ionised molecular fragment. For the actual cell parameters, at $U = 2.5$ V and $Q = 6 \times 10^{-6}$C, and provided $k = 1$, one can estimate the average ionic concentration to be $c_v \approx 2 \times 10^{16}$ cm^{-3}, which is considerable.

2.2 *Current–voltage characteristics*

As was pointed out previously, after the charging process accompanied by the inevitable transient current had completed, we observed a steady-state current I_s through the cell. Steady-state measurements were made after transient currents had decayed, namely, every CVC point was obtained 43 s after the transition from the initial $I(t = 0)$ to the relevant steady current value I_s was completed. The measured CVC for the steady current is presented in Figure 4(a) (spheres). It demonstrates a strongly nonlinear behaviour in the range of low and average applied voltages, and an almost linear (Ohmic) dependence $I_s(U)$ at $U > 5$V. We would like to emphasise that a similar steady current was found for the conductivity of the nematic mixture E7, where 5CB was one of its components; however, no steady current was observed in the nematic mixture ZLI 4801 free of cyano-biphenyl-based compounds. This suggests that in some LCs, such as 5CB, free charges can appear predominantly in the bulk, whereas the double layer develops in any LC cell [44].

On the other hand, there are mechanisms of ion creation in the interface regions, triggered by charge injection [26, 27]. The very nonlinearity of CVC in electrolyte solutions (and our LC samples can be described as such [44]) is hardly surprising, bearing in mind, for example, that the electric field provokes chemical species dissociation [2, 67, 68]. The theory of this ionisation mechanism (usually named after Onsager) has been elaborated for isotropic solids, and it is a more sophisticated version [69–71] of the thermal ionisation of neutral donors (traps) substantially enhanced by an external electric field (the so-called Poole–Frenkel effect [2, 6, 72–74]). Nevertheless, Onsager dissociation (ionisation) is neither the sole nor even a dominant reason for substantial deviations from Ohm's law in organic materials. Our observations in LCs, described later in more detail, gives new evidence of the steady-current nonlinearity.

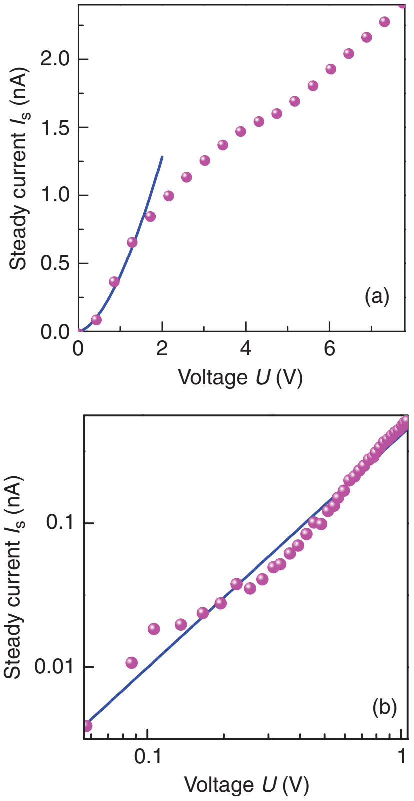

Figure 4. (a) Experimental current–voltage characteristic of a steady current I_s through the LC cell (spheres) and its power-law fitting (solid curve); (b) low-voltage section of the same dependences in log–log scaled-up coordinates.

To gain some insight into the CVC nonlinearity depicted in Figure 4(a) one should pay attention to the fact that the very non-Ohmic character of the steady current through an insulator at low voltages implies the existence of a space charge with a finite density, which limits the magnitude of this current. Our estimations given above testify that rather a considerable extra charge ($Q \approx 10^{-5}$ C) does exist in the LC cell bulk. This charge can hinder current flowing through the cell and gives rise to negative-feedback deviations of the CVC from Ohmic behaviour. Let us analyse the concave CVC section, bearing in mind a possible influence of the space charge, whatever its nature. We note that the conventional treatment of charge motion driven by an external field through a vacuum gap or an insulating slab between metallic electrodes covers both the situation when charge carriers are emitted into the slab through an energy barrier [33, 34], and the case when the barrier is absent and carriers are injected into the space between electrodes [39, 40].

If ones neglects the thermal distribution of charge carriers over their energies (it does not change the dependence *I*(*U*) qualitatively [34, 75]), the CVC can be described analytically [33, 34, 36, 39]. To illustrate this, we shall restrict our scrutiny to two typical cases, which might be realised in our LC cells. The first one has been originally introduced to describe an inviscid flow of positive ions [36] or electrons [33] in a vacuum gap between metallic electrodes. In this model, the CVC is determined by a set of three equations (see, e.g., [34]),

$$\Delta\varphi(\mathbf{r}) = -4\pi\rho(\mathbf{r}), \tag{5}$$

$$\mathbf{j}(\mathbf{r}) = \mathbf{v}(\mathbf{r})\rho(\mathbf{r}), \tag{6}$$

$$\frac{1}{2}m\mathbf{v}^2(\mathbf{r}) = e\varphi(\mathbf{r}). \tag{7}$$

Formula (5) is the Poisson equation, where $\varphi(\mathbf{r})$ is the varying voltage in the gap at the point $\mathbf{r}$ (φ is reckoned from its cathode value adopted as zero), and $\rho(\mathbf{r})$ is the charge density distribution. Formula (6) is the relationship between the current density $\mathbf{j}(\mathbf{r})$ and the charge velocity $\mathbf{v}(\mathbf{r})$. Recall that, for simplicity, we assume the thermal Maxwell distribution of charge carriers to be infinitely narrow. The third equation describes the electron (ion) acceleration in the electrostatic field, and the parameter m in this equation is the charge-carrier mass. As a consequence, at low voltages and in the plane geometry, the CVC follows the Child–Langmuir law

$$j = \frac{2}{9\pi L^2}\sqrt{\frac{e}{2m}}U^{\frac{3}{2}}. \tag{8}$$

In the adopted notation, $U \equiv \varphi(r = L) - \varphi(r = 0) = \varphi(r = L)$. The current density versus voltage dependence (8) is, therefore, a benchmark of the space-charge accumulation in the gap, so that the resulting current is a space-charge-limited one. At large U, the charge carriers are driven away from the cathode immediately after injection, and the current is no longer described by Equation (8), tending instead to saturation. In particular, in the cold emission case, the dependence *j*(*U*) for large enough U obeys the Fowler–Nordheim law [34, 35]. At the same time, the CVC form for a space-charge-limited current through a gas-discharge plasma [37, 38] is substantially influenced by collisions and collective excitations, the flow being viscous.

On the other hand, if charge carriers are emitted or injected into an insulator [39, 40, 76, 77], their motion is no longer accelerated and is described by Equation (7). Instead, one should take into account a material relationship between $\mathbf{v}(\mathbf{r})$ and the electrostatic field $\mathbf{F}(\mathbf{r}) = -\nabla\varphi(\mathbf{r})$:

$$\mathbf{v}(\mathbf{r}) = \mu(\mathbf{F}(\mathbf{r})). \tag{9}$$

Here, μ is the charge-carrier mobility (which is, generally speaking, field-dependent), and Equation (9) describes a charge-carrier viscous drift in the external field *F*(*r*) determined by collisions with fluctuations, impurities and imperfections. As a first approximation, we can neglect the diffusion current component, although it should be taken into account in the general case [39, 40, 78].

Thus, in the model, where an insulator has no traps, polaron effects are absent and μ does not depend on $\mathbf{F}(\mathbf{r})$, the current density obeys the Mott–Gurney law at low U [39]:

$$j = \frac{9\varepsilon\mu}{32\pi L^3}U^2. \tag{10}$$

Here, ε is the dielectric constant of an isotropic insulator. One should expect that Ohm's law $j \propto U$, appropriate to the charge flow in a resistive environment, is to be observed at large U. If $\mu = \mu(\mathbf{F})$, the exponent power in Equation (10) changes [40]. In particular, it might be equal to 3/2, as in Equation (8), the nature of the conductivity being different in both cases.

Equations (5)–(10) were obtained in the framework of a simplified approach, with only the drift current component taken into account and the diffusion component $-\mu k_B T\nabla\rho(\mathbf{r})/e$ totally neglected [79]. This approximation is not valid in the close vicinity of the electrode (electrodes), where the injection takes place. However, this layer is very thin and does not govern the total conduction. Furthermore, an analysis of the full non-linear equation system with the diffusion term retained showed that the current magnitude and the power-law behaviour of space-charge-limited currents in semiconductors with traps are similar at bias voltages $U > k_B T/e$ in the simplified and more complicated theories [40, 80]. Therefore, according to the model [40, 78–80], the diffusion-limited regime at low U gives way to the space-charge-limited regime at higher *U*s, the overall CVC being highly non-linear (see, in particular, [81]).

There is another approach, belonging to Macdonald, who calculated a good many properties of semiconductors and electrolyte solutions in a slab between electrodes [60, 82–85]. He considered the diffusion processes as a dominant factor that governs the conductivity of objects concerned in the cases of ohmic electrodes, partially or completely blocking. The results of Macdonald and co-authors are pertinent to small currents, when injected or emitted charges do not form clouds that are dense enough to impede the current flow. In our case, when high voltages are applied to a thin LC cell, leading to strong space-charge effects and, consequently, to non-linear CVCs, the model [33, 36, 40, 79, 80] is undoubtedly more adequate.

It should be noted that high acting electrostatic fields ($\geq 10^5$ V cm^{-1}) might extract charge carriers from traps, if any, (the Poole–Frenkel effect [6, 73]), making the whole picture more involved [86]. This possibility will be discussed later.

For the completeness of our analysis, one should bear in mind a possible influence of image forces near both electrodes on the current, the problem recognised both for solid organic materials [87–89] and LCs [46]. It may turn out that, in a thin LC cell, the Coulomb attraction between a given charged particle and its own image would be strong enough to compete with the Coulomb repulsion of the particle concerned with its distant counterparts for conspicuous near-electrode areas (see the considerations in [89]). Of course, it will influence the overall CVCs.

Although the described basic models cannot be uequivocally applied to the conductivity of the LC cell, the power-law nonlinearity in the observed $I_s(U)$ dependence strongly suggests that space-charge phenomena are important here. Therefore, it is reasonable to analyse the CVCs on the basis of the scenario with currents limited by a spatially inhomogeneous Coulomb field in the cell. While doing this, we fully recognise that the microscopic justification of the applied approach based on the space-charge concept is still lacking. Nevertheless, more traditional interpretations of the LC conductivity are not able to explain our results, so that our hypothesis at least has its right to exist.

Indeed, looking at the experimental CVC (the spheres in Figure 4(a)), it becomes evident that, besides the Ohmic behaviour at high voltages, there are also other types of conductivity. One of them appears at low voltages $U < 1.5$ V, while the other dominates in the intermediate *U* range. It is expected that all the factors mentioned above should alter the CVC, so that the latter can only be calculated numerically. Nevertheless, one can consider Equations (8) and (10) as useful relationships, which provide some insight into the problem. Namely, we suppose that a space charge that arises in the near-electrode regions leads to deviations of $I_s(U)$ from the linear (Ohmic) behaviour. Therefore, taking all the aforesaid into account, we attempted to describe the steady currents through our LC cells *at low voltages* by a power-law dependence $I_s \sim U^\alpha$, where α is a fitting parameter. The results of our calculations are shown in Figure 4(b). The fitting curve is a linear dependence (solid line) in log–log coordinates with the slope $\alpha \approx 1.64$, whereas experimental points are denoted by spheres. Hence, the value of α falls into the interval from 1.5 (Equation (8)) to 2 (Equation (10)). The observed deviation of α from 2 means that the charge-carrier mobility in the cell depends on the effective electrostatic field, i.e. on the applied voltage.

The fitting dependence is also depicted in Figure 4(a) (in the natural *I*–*U* coordinates) as a solid curve. The success of our approximation means that it is quite plausible to consider the low-*U* CVC region as a space-charge-limited current. At the same time, Ohmic behaviour is observed at large $U > 4.5$ V, which is also in agreement with our picture.

The remaining range of the CVC between 1.5 and 4.5 V seems most probably to be a transition region between two regimes. Alternatively, it may be governed by some types of trap for moving ions [40]. At the same time, the observed transition is similar, for example, to that for a system consisting of the nematic mixture E7 and the dye disperse red 1 [27]. In this different LC composite, the exponent power α is approximately equal to 3. The same exponent $\alpha \approx 3$ was shown to be appropriate for the dc conductivity of diodes formed by solid organic materials. For instance, it was inferred from data for solid films 200 nm in thickness of the organic polymer poly(4-dicyanomethylene-4H-cyclopenta[2,1-b:3,4-b']dithiophene) (PCDM) on the ITO-covered glass substrates and with Al counterelectrodes [90]. A voltage-driven space charge was revealed there at the ITO/PCDM interface. A current through a sandwich of lead phthalocyanine between ITO and Al is another example of such a behaviour [91]. At the same time, exponents in the range from 1.9 to 5 were found for Au/CuPc/Al Schottky diodes (here, CuPc stands for copper phthalcyanine) [92]. We emphasise that further experimental studies and theoretical analyses are needed to confirm or disprove our assumption that our CVC for LC cells in the transition *U* region is a simple transformation change-over between non-linear and Ohmic regimes.

Thus, bearing in mind the double-slope dependence $Q(U)$ in Figure 2, the charge transport across the cell seems to be governed by injected electrons captured and released by two types of traps. The latter might be of impurity origin and/or formed by polarised configurations of LC molecules [55]. Note that impurity charges, either extrinsic (T-independent) or induced by thermal ionisation, should manifest themselves as an Ohmic region at the lowest U [40]. Nevertheless, the observed deviations of I_s from the fitting dependence $U^{1.64}$ at U within the interval $0.05\ \mathrm{V} < U < 0.3\ \mathrm{V}$ are rather scattered (see Figure 4(b)), so that the linear, at low U, dependence $I_s(U)$ cannot be inferred unequivocally from our measurement results. Anyway, additional conductivity and/or optical measurements should be made to distinguish between the injected charge cloud and an already existing charge-carrier background, whatever its role. It would also be of importance to study CVCs at extremely low U, where space-charge effects are not so important and the conductivity is governed by more or less conventional diffusion-driven processes or/and the LC–electrode interfaces, the latter indicated many years ago [93]. In any case, as was mentioned above, the 'diffusion-limited-current' model for the charge transport through electrolyte-based systems is merely an approximation [94].

To the best of our knowledge, since the corresponding, essentially non-linear, equation systems [44, 94–97] have not been solved so far, there exists no theoretical description of conductivity in electrolyte cells. At the same time, power-law CVCs have been found theoretically for electrolyte-based configurations in particular cases for currents across thin electrolyte films [94], anion-impermeable membrane boundary with the electrolyte solution [98, 99] and ion-selective nanochannels [100, 101].

All the analyses of $I_s(U)$ given above were based on the assumptions that the electrode surface (i) is homogeneous and smooth and (ii) has a plane geometry. Nevertheless, there is a possibility that hot spots appear at the interfaces, thus governing CVCs. In this case, in particular, the geometry of the current source patch might be close to hemispherical or conic, so that the I_s magnitude and the dependence $I_s(U)$ would change [102].

We note that our experimental CVCs differ qualitatively from those of Kovalchuk [103, 104] which were obtained for cells with a ZL1-4803-000 LC. He found an exponential dependence

$$I_s(U) \propto \exp\left(C\sqrt{U}\right), \tag{11}$$

C being a constant, and interpreted it to be a Richardson–Schottky attenuation [34] of the tunnel barrier located in the double layer near the electrodes. This dependence can also be judged to be the Poole–Frenkel lowering [2, 6, 73, 74, 105] of the tunnel barrier for carrier emission from traps into the bulk. The distinctions between those phenomena was analysed in detail [72, 106, 107], and the main difference is hidden in the coefficient C, which depends on the compensation degree between donors and acceptors in semiconductors. Such effects in LCs have not been studied.

Equation (11) was derived theoretically by Frenkel [73]. Earlier, the original experimental researches of mica conductivity in strong electrostatic fields F by Poole [105] led to a different, although also exponential, formula for the electrical conductivity:

$$\sigma = \sigma_0 \exp\left(C'F\right). \tag{12}$$

In most cases, the numerical analysis of electrical measurements is based on either of two possibilities (11) or (12), being simply a phenomenological procedure. Moreover, since space-charge current effects are ubiquitous in organic solids and charge-carrier mobilities entering Equation (10) may exhibit the Poole–Frenkel behaviour (11), one should combine Equation (10) with the empirical dependence

$$\mu(F) = \mu_{ZF} \exp\left(C''\sqrt{F}\right) \tag{13}$$

to describe the experimental data [108]. Zero-field mobility μ_{ZF} in Equation (13) should be regarded as an effective one

$$\mu_{ZF} = \mu_0 \frac{\theta}{1+\theta}, \tag{14}$$

where θ is the free-to-trapped carrier ratio [109]. In principle, similar reasonings should be applied to LC cells, where the space-charge build-up governs the conductivity in the circuits involving LCs, the effect being not only interesting from a fundamental point of view but also of practical importance for LCDs [110].

It is also necessary to mention the well-known process of bulk phonon-assisted trap ionisation [111, 112], which leads to a current versus voltage equation of another type:

$$I_s(U) \propto \exp\left(C'''U^2\right). \tag{15}$$

It comes about from Figure 4 that neither Equation (11) nor Equation (15) can describe our experiments. Thus, the space-charge scenario will remain the most probable one, whatever the origin of the charge carriers and traps involved, although a thorough account of additional factors indicated above must be made to obtain quantitative agreement.

3. Conclusions

To summarise, we have studied transient and steady currents in nematic LC cells and demonstrated that space-charge effects are important, contrary to previous conclusions. 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 can be imagined to be heavy fragments of LC molecules. In the steady-current regime, the CVCs are determined by the space charge generated in the near-electrode regions of the nematic. For 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, for example, from the double-layer and bulk regions of the LC cell.

We fully recognise that it is difficult to reconcile the existence of long-lived charged traps in the bulk of LC fluid with the slowness of charging processes suggesting the possibility of bound surface traps. At the same time, a trap-free plasma-like conduction across the cell can hardly take place owing to the observed complex character of the transient processes and the discrepancy between the observed CVCs, on the one hand, and the limiting Child–Langmuir (8) and Mott-Gurney (10) laws, on the other hand. One should also keep in mind the possibility of phase separation in the system, the charged molecular clusters being large long-living traps, as has been found in correlated colloidal systems [66].

Further experiments are needed to clarify those subtleties and the effects of the charged double layer in the conduction, which determine the intriguing behaviour of the multi-layer conducting cell. In particular, to excite trapped charge carriers, optical studies might be especially useful. Moreover, the latter would also be helpful to elucidate the very nature of charge carriers distributed over the LC cell, which determine the conductance in the circuit.

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