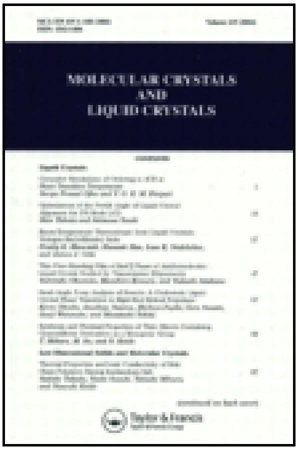

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DC Currents in Dye-Doped Liquid Crystals

O. V. Kovalchuk [a]

[a] Institute of Physics, Prospekt Nauki 46, 03650, Kyiv, Ukraine

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DC Currents in Dye-Doped Liquid Crystals

O.V. KOVALCHUK

Institute of Physics, Prospekt Nauki 46, 03650 Kyiv, Ukraine

Steday-state current-voltage characteristics have been measured in liquid crystals containing deliberately introduced non-dissociating dyes. A comparison with results of ac measurements demonstrates that the shapes of the characteristics are controlled by electrode processes. A simple model was put forward allowing one to describe qualitatively the shapes of the characteristics.

Keywords: Liquid crystal; dc current

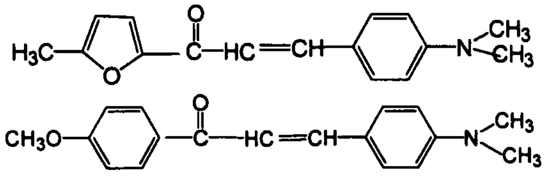
INTRODUCTION

Interest in studies of properties of dye-doped liquid crystals has been stimulated by emerging prospects of application of such systems in optical information processing. In most cases, liquid crystalline (LC) cells operate under a dc bias, thus a question arises concerning electrical properties of LC systems containing impurities inherently present or produced during storage, and/or dopants deliberately introduced in LC matrices. Analysis of a large number of papers on electrical properties of liquid crystals provides a convincing evidence for the ionic character of the dc electrical conductivity in LC: even in the purest materials the ionic conductivity exceeds the electronic one by several orders of magnitude.

Presence of mobile ions, their adsorption of electrode surfaces, possible irreversible electrochemical processes on the electrodes, result in an extreme complexity of the process, leaving several problems unresolved (see, e.g., [1-9]). One of important problems which should be considered is the effect of dopants, deliberately introduced into liquid-crystalline matrices. Early models assumed that the conductivity of LC can be substantially modified only by dissociable solutes. The main aim of the present work was to examine the effect of neutral (non-dissociating) or weakly dissociating dopants.

EXPERIMENTAL

Two commercially available LC mixtures have been used in the work reported in this paper: BL055 (*a*) and ZL1-4803-000 (*b*), both supplied by Merck. The electric permittivity determined for a planar orientation of molecules($\varepsilon_{\perp}$) and its anisotropy ($\Delta\varepsilon$) at 20 °C amount to 6.00 and 13.42 for *a*, and 11.3 and 51.5 for *b*, respectively. Two dyes were used: 1-(5-methylfuran-2-yl)-3-(4-dimethylaminophenyl)-propenon (*I*) and 1-(4-methoxyphenyl)-3-(4-dimethylaminophenyl)-propenon (*II*) (see Scheme 1). The construction of the measuring cell and the method of its filling with LC have been described in [10]. SnO_2 and Cu deposited on glass slides have been employed as electrodes. Both symmetric and asymmetric electrode configurations were used: in the former case, the cells contained SnO_2 electrodes with no orienting layers, whereas the latter configuration consisted of a Cu electrode, used in most cases together with an SnO_2 electrode covered with a thin rubbed polyimide layer (hereafter referred to as a P-electrode). The sample thicknesses varied between 10 and 50 μm, typically amounting to ca. 20 μm.



I

II

SCHEME 1 Dye molecules used in the present work

The discussion of the mechanism of the conduction in the samples under study is based on the analysis of steady-state current-voltage (*CV*) characteristics. Currents flowing in the samples after application of a biasing voltage were found to be a function of time, decreasing by more than one order of magnitude before steady-state values have been reached. The analysis of obtained results has shown that the shapes of *CV* characteristics depend not only on the material but also on the sample history.

Parameters of near-electrode regions were investigated using the low-frequency dielectric spectroscopy (LFDS) [10,11]. In most cases, such measurements were performed twice: before starting a series of experiments, and after concluding it. Such an approach allowed for taking into account of both, values of parameters of near-electrode regions, and their dependence on external electric fields in the analysis of the conduction mechanism. The LFDS method was also used to determine the ac conductivity (σ_{AC}); the latter parameter allowed one to draw conclusions about a possible dissociation of dopant molecules dissociate in LC matrices. Changes of σ_{AC}, detected after a series of measurements of *CV* characteristics, pointed to changes of bulk properties of LC-dopant mixtures resulting from dc currents flow.

The measurements were carried out at and above the room temperature, the accuracy of the temperature stabilisation being better than 0.2 K.

RESULTS

Typical experimental *CV* characteristics measured on pristine (undoped) ***a***, and on the same material containing 0.8 wt % of dye ***I***, are shown in Figure 1. To a first approximation, the curves can be fitted with a superposition of two exponentials intersecting at $U_J \approx 1.5$V; a justification of such a fit will be given in the subsequent section of this paper. It was found that the slope of the low-voltage section increases upon introduction of the dye as does the magnitude of the current at $U > U_J$. It should also be noted that the former finding is in an apparent disagreement with results obtained from LFDS: the dielectric measurements show that σ_{AC} of the dye-doped LC is 1.2 times lower than that of the pristine sample.

The experiments reported in this paper revealed the existence of an open-circuit electromotive force (EMF) in LC cells. Appearance of a potential difference if a well known phenomenon in electrolyte solution placed between electrodes made of different materials; in our experiments, however, such a potential (hereafter referred to as φ_d) was

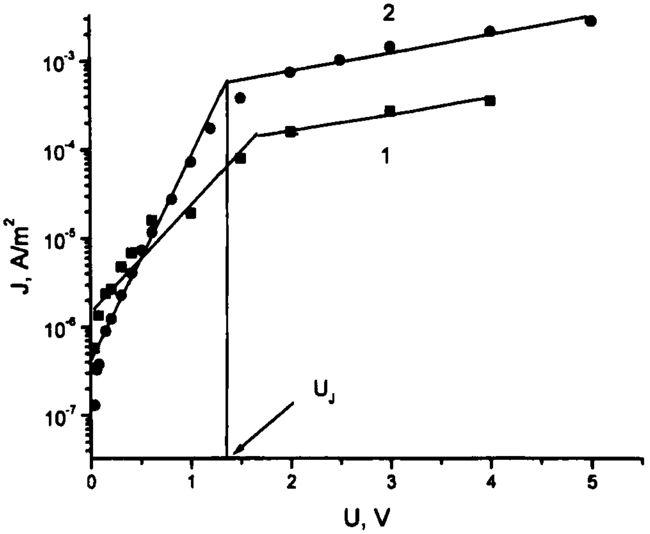


FIGURE 1 *CV* characteristics of pristine ***a*** (squares, curve 1), and of ***a*** doped with 0.8 wt % of ***I*** (circles, curve 2), measured at 292 K, both electrodes are SnO_2-covered glass.

found to appear persistently in samples consisting of pristine or dye-doped LC placed between two nominally indentical electrodes. Typically, room temperature values of φ_d amounted to 20-40 mV in virgin samples (irrespective of whether the electrodes used in the experiments were symmetrical or not), increasing by the factor of 2 or more in samples which had been previously biased. These values increase further if the temperature was raised to 310-320 K. In asymmetric samples, the magnitude of φ_d in samples previously biased was found to depend on the bias polarity: φ_d increased by the factor of 2-4 if Cu had been biased negative, whereas a 10-fold increase was observed with Cu biased positive.

Figure 2 shows a *CV* dependence measured on a sample containing 2 wt % of ***II*** in ***b*** placed in between asymmetric electrodes. The curve was measured after previous measurements performed with the Cu electrode biased positive. This feature demonstrates that application of an external bias results in formation of a galvanic cell with the opeccircuit voltage of ca. 0.4 V and short-circuit current of ca. 2.2×10^{-4} A/m^2.

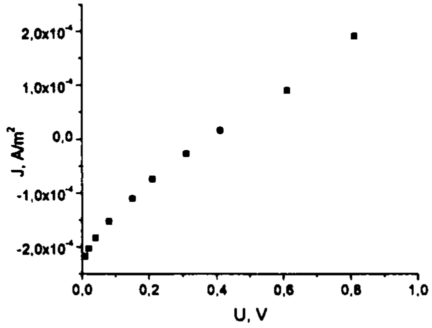


FIGURE 2 *CV* characteristics measured in a sample containing 2 wt % of ***II*** in ***b***, placed between asym-metric Cu-P electrodes.Sample thickness 28.6 μm, temperature 292 K. The polarity of the current is shown relative to the Cu electrode.

As was mentioned above, *CV* characteristics measured in virgin samples differ substantially from those measured in samples previously exposed to a voltage treatment. The differences depend on the nature of electrodes employed in the experiments: use of symmetric electrodes results in a decrease of the slopes of of the characteristics for $U < U_J$ and a decrease of the current for $U < U_J$.

DISCUSSION AND CONCLUSIONS

A comparison of the steady-state *CV* characteristics with results obtained from LFDS points to the importance of electrode processes in controlling currents in the system under study. In the conditions of our experiments, σ_{AC} is of the order of 10^{-7} $\Omega^{-1}m^{-1}$. A simple estimation shows that the currents, if limited by the bulk conductivity of the samples, would exceed those measured in the experiments reported here by at least one order of magnitude. The currents should therefore be limited by kinetic processes associated with energy barriers formed at the electrodes. Consequently, within a simple model, *CV* characteristics can be expressed by equations describing the current flow through the interface barriers (here approximated by two diodes in series, one forward biased, the other reverse biased) and a term expressing the conductivity of the sample bulk

$$J = J_0\{1 - \exp(-\frac{eU_1}{nkT})\}, \tag{1}$$

$$J = J_0\{\exp(\frac{eU_2}{nkT}) - 1\}, \tag{2}$$

$$U = U_1 + U_2 + \frac{Jd}{\sigma_{AC}}. \tag{3}$$

In the above equations, U_1 and U_2 are voltage drops on the barriers, J_0 is the saturation current, n is the non-ideality factor, and d stands for the sample thickness.

According to the model, at low voltages the current will be limited by the reverse biased barrier, and the current will be described by Eq. (1): at voltages for which $J < J_0$, the current should exponentially depend on the voltage applied, as indeed is the case (Figure 1). One should note, however, that the fits exhibit non-zero values of the current at zero voltage, the extrapolated current (J_B) being of the order of 10^{-6} A/m^2. This feature can be attributed to the fact that in reality the measuring cells are galvanic cells.

According to the above equations, at sufficiently high voltages ($U \sim U_J$), the resistance of the reverse biased diode becomes comparable with that of the forward biased one and with the resistance of the bulk. In this case, the course of *CV* characteristics should deviate from the exponential dependence predicted by Eq. (1) and one should expect appearance of an inflection point; in Figure 1 the position of such a point is determined from the intersection of two exponentials. The values of the voltage U_J determined from the measurements repoted in this paper amounts to ca. 1.5 V, whereas the saturation currents (J_0) were determined to be ca. 10^{-2}-10^{-1} A/m^2, respectively, depending on the electrode material, sample composition and sample history.

The results shown in the present paper (and many others, not presented here) clearly indicate that the shapes of *CV* characteristics in both, nominally pure LC, and in LC doped with neutral (non-dissociating) dyes is controlled by electrode processes and electrode barriers. The model put forward in the paper explains qualitative features of experimental characteristics. Further studies are, however, necessary to explain molecular mechanisms of the observed processes.

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