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NUMERICAL STUDY OF IONIC CURRENT IN A DIELECTRIC LIQUID LAYER SUBJECTED TO SQUARE WAVE VOLTAGE

Ionic current flowing in a thin layer of dielectric liquid under the action of square wave voltage was studied numerically. Quasi-blocking electrodes and equal mobilities of anions and cations were assumed. Field dependent dissociation and recombination were taken into account. The spatial distributions of ion concentrations and the ionic current density during a single voltage cycle were calculated as functions of time. A bump of the current was observed at suitably high voltage, low ion content and low frequency. This effect resulted from redistribution of ions which occurred in the whole layer. Two gradually diffusing groups of ions wandering across the layer, one formed by cations and the other formed by anions, could be distinguished. There was no unambiguous relationship between the moment at which the bump occurred and the value of ions mobility.

Keywords: dielectric liquid, ionic current, polarity inversion.

1. INTRODUCTION

The studies of time dependent and transient currents in dielectric liquids are of considerable attention. This is partially due to the role which is played by the ions in liquid crystal displays [1-6]. The display cells are filled with liquid crystal mixtures which usually contain ions and can be treated as weak electrolyte [7]. The ions are due to impurities introduced to the liquid unless special precautions are taken. The ion concentrations, N^{\pm} , vary between 10^{19} and 10^{21} m^{-3} for pure and contaminated materials respectively [8]. Their mobility μ^{\pm} is typically of order $10^{-10} - 10^{-9} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$ [9,10] The electrical conductivity σ is of order $10^{-10} - 10^{-8} \text{ } \Omega^{-1}\text{m}^{-1}$ [8,9,11]. The aligning coatings necessarily

deposited on the pixel electrodes are insulating. Therefore the liquid crystal layer may be considered as limited by quasi-blocking electrodes which significantly hinder the carrier migration. As a result, ions separated by external voltage accumulate at the electrodes [1,2]. The arising space charges form the double electric layers. The transport of ions and accumulation of them at the electrodes can influence the quality of the LCD performance.

Director reorientations following the changes of bias voltage lead to time variation of the current because of dielectric anisotropy and conductivity anisotropy of the nematic [8,11-13]. Such effect is known also in other systems e.g. in antiferroelectric liquid crystals [14]. In order to obtain the current caused solely by the ions redistribution and to avoid the current induced by the director changes, the isotropic liquid is considered here. The same approach was used in the previous paper [15] where the electrical properties of the isotropic liquid layer under the action of sinusoidal ac voltage were studied numerically.

In this paper, the electrical properties of the isotropic liquid layer under the action of square wave voltage are studied by means of numerical solution of the set of equations describing the charge transport in the layer. In particular, the spatial and time dependencies of ion concentrations and electric potential were determined.

The results show that under the influence of the constant external field acting during a half of the cycle, the ions of different signs are separated and accumulated at the opposite electrodes. The reverse voltage applied during the second half of the cycle causes the space charge redistribution. The ionic current resulting from this redistribution has a peculiar time dependence. In general the current decreases with time, but under suitable circumstances, the bump of the current is visible. Such behaviour is often found in experiments [16-20]. The main aim of the present simulation is to elucidate the problem of movements of ions under the action of the electric field, to relate these movements with the ionic current observed in external circuit and to verify the relation between the current bump and the mobility of the ions.

2. ASSUMPTIONS AND METHOD

2.1. Geometry and parameters

The system under consideration was the same as described in the previous paper [15]. A liquid layer of thickness d was confined between two infinite plates parallel to the xy plane of the Cartesian coordinate system. They were positioned at $z = \pm d/2$ and played the role of electrodes. The square wave

voltage of amplitude U_0 was applied between them. The frequency f was chosen from the range 1-10 Hz in order to ensure the appearance of the bump of the current. The model substance was characterized by the dielectric constant $\varepsilon = 7$. The weak electrolyte model [7] was adopted. A constant concentration of dissociable molecules, $N_d = 10^{24} \text{ m}^{-3}$ was assumed. The transport of the ions under the action of an electric field was characterized by their mobility and diffusion coefficients. Equal mobilities of the positive and negative ions were assumed. Their values corresponded to typical results of mobility measurements in isotropic phase of various liquid crystals: $\mu^+ = \mu^- = 10^{-9} \text{ m}^2 \text{ V}^{-3} \text{ s}^{-1}$ [9,10]. The Einstein relation was assumed for the diffusion constants: $D^\pm = (k_B T / q) \mu^\pm$. Quasi-blocking electrodes determined the boundary conditions, i.e. the effective resistance of the electrode contacts was much higher than the bulk resistance of the layer. This feature was due to high energy barriers which limited the charge transfer between the molecules or ions in the liquid and the electrodes [21,22].

The ion concentrations was determined by the generation and recombination constants. The recombination constant α was calculated from the formula $\alpha = \frac{2q\bar{\mu}}{\varepsilon_0 \varepsilon}$, [23], where $\bar{\mu} = (\mu^+ + \mu^-) / 2$, hence $\alpha = 5.2 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$.

The generation constant β depended on the electric field strength E according to the formula: $\beta = \beta_0 \left(1 + \frac{q^3}{8\pi\varepsilon_0 \varepsilon k_B^2 T^2} |E| \right)$ [23]. Two values of β_0 corresponding to the absence of the field, were considered: 10^{18} and $10^{20} \text{ m}^{-3} \text{ s}^{-1}$. The average concentration of anions and cations, $N_0 = \sqrt{\beta_0 / \alpha}$, was therefore equal to 4.4×10^{18} or $4.4 \times 10^{19} \text{ m}^{-3}$ respectively.

2.2. Method

All the quantities considered in this paper are assumed to depend on one coordinate z perpendicular to the layer. In the following, the reduced coordinate, $\zeta = z/d$, is used. The spatial and time dependence of the ion concentrations $N^\pm(\zeta, t)$ and of the electric potential $V(\zeta, t)$ during one period of the external voltage were calculated. The model of phenomena taking place in the bulk and at the electrode-liquid interfaces, which was used to describe the behaviour of ions in the layer, was given in detail in [15]. It can be expressed by the set of seven equations: two equations of continuity of the ion fluxes governing the transport of ions in the bulk, four equations describing the boundary conditions

for ion transfer across the electrode contacts and the Poisson equation. The boundary conditions for the potential were $V(-1/2, t) = 0$ and $V(1/2, t) = U(t)$. The set of equations was solved numerically. The electric potential $V(\zeta, t)$ and the ion concentrations $N^\pm(\zeta, t)$ were calculated as functions of coordinate and time for chosen sets of parameters of the layer. Periodic initial conditions were assumed: $V(\zeta, 0) = V(\zeta, \tau)$, $N^\pm(\zeta, 0) = N^\pm(\zeta, \tau)$ where $\tau = 1/f$. They ensured that the results corresponded to the behaviour which becomes stabilized after long time of application of voltage. The results allowed to determine the ionic current flowing in the layer. Since the current in the external circuit is proportional to the area S of the sample, the current densities are used in the following.

The total current (of density $j_i(t)$) has two components: the ionic current, of density $j_r(t)$, due to transport of ions in the liquid and the capacitive current, of density $j_c(t)$. The capacitive component was calculated according to the formula $j_c(t) = (C/S)(dU/dt)$. The ionic current was determined as an average of the net

$$\text{flux of charges over the layer thickness: } j_r(t) = q \int_{-1/2}^{1/2} [J_z^+(\zeta, t) - J_z^-(\zeta, t)] d\zeta$$

3. RESULTS

The main result of this paper concern the ionic current and are as follows. The time variation of the ionic current depended on the amplitude and frequency of bias voltage, on the thickness of the layer and on the ion content. In general, the ionic current was a decreasing function of time. If the voltage cycle was sufficiently long, the current stabilized after some time and achieved a constant value j_{stab} . However, an excess component in the form of a bump was observed under suitable circumstances as shown in the figures below presenting the current density for the single half of the cycle. The time dependence of the current can be characterized by the maximum value j_{max} , the stabilized current j_{stab} and by the time at which the bump appeared t_{max} (counted from the beginning of the voltage cycle). The bump became less distinguishable when the ion concentration was enhanced. The bump was observed in the low-frequency regime, e.g. between c. 0.1 and 10 Hz. It became weaker when the frequency was increased and disappeared above c. 10 Hz (Fig. 1). The time at which the bump appeared decreased with increasing frequency.

The bump became invisible at sufficiently low voltage. The influence of voltage amplitude is shown in Fig. 2. The time at which the bump appeared

became slightly shorter when U_0 increased. The maximum current j_{max} was practically proportional to the voltage (Fig. 3).

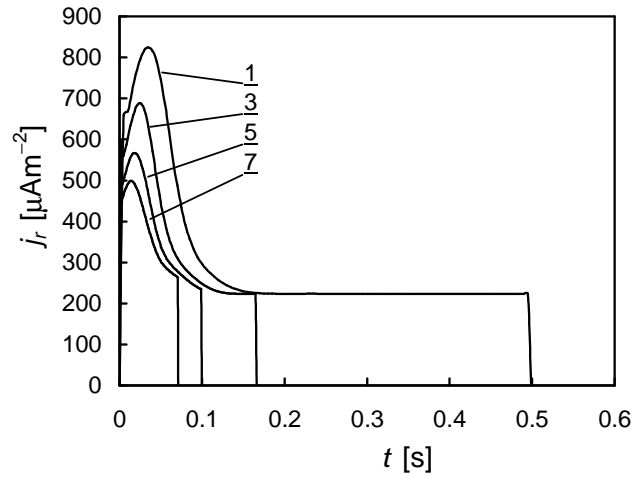


Fig. 1. Ionic current density calculated for four frequencies of the bias voltage indicated in Hz at the curves, $U_0 = 5$ V, $d = 20$ μm , $\beta_0 = 10^{20}$ $\text{m}^{-3}\text{s}^{-1}$

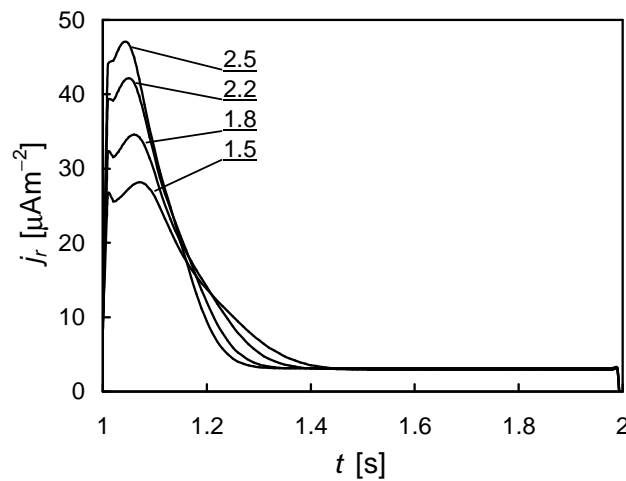


Fig. 2. Ionic current density calculated for four voltage amplitudes indicated in volts at the curves, $f = 0.5$ Hz, $d = 20$ μm , $\beta_0 = 10^{18}$ $\text{m}^{-3}\text{s}^{-1}$

The role of the layer thickness is illustrated in Fig. 4. The maximum current j_{max} decreased with increasing thickness of the layer (Fig. 5). The time t_{max} increased with the thickness.

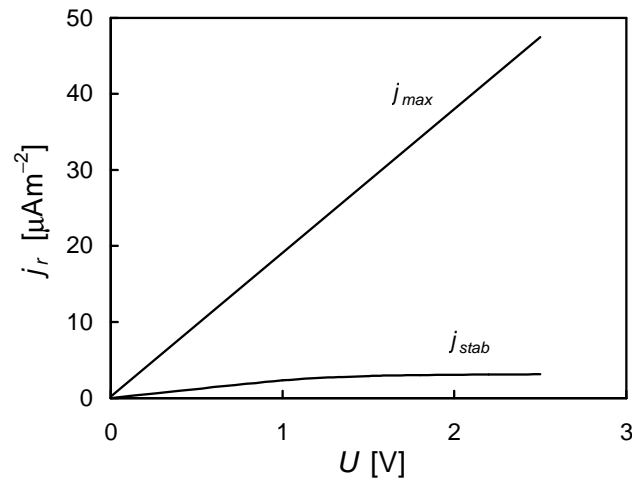


Fig. 3. Maximum current and stabilized current as functions of voltage amplitude, $f = 0.5$ Hz, $d = 20$ μm , $\beta_0 = 10^{18}$ $\text{m}^{-3}\text{s}^{-1}$

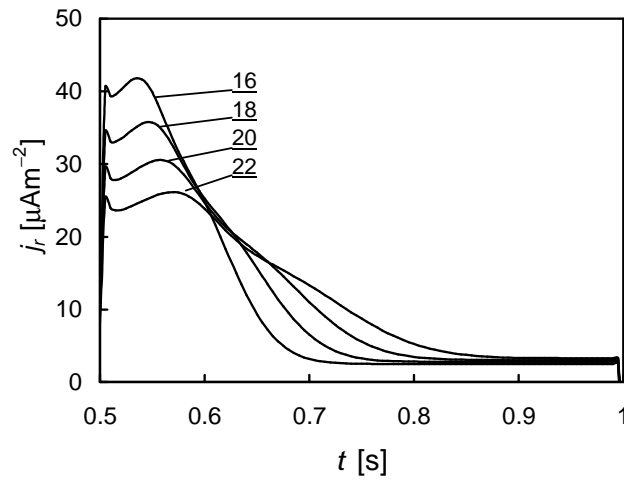


Fig. 4. Ionic current density calculated for four layer thicknesses indicated in micrometers at the curves, $f = 1$ Hz, $U_0 = 2$ V, $\beta_0 = 10^{18}$ $\text{m}^{-3}\text{s}^{-1}$

The stabilized current saturated with increasing voltage amplitude (Fig. 3) and weakly increased with the thickness (Fig. 5).

The time dependence of the current resulted from the redistribution of ions accumulated at the electrodes. The properties of the ionic current described above resulted from the time variation of the spatial dependence of the ion concentration, $N^\pm(\zeta, t)$. In the low-frequency regime, the prevailing part of ions of given sign was accumulated at the counter electrode during one half of the period, with concentration increasing with time. During the next half of the period, these ions moved out from the vicinity of this electrode. The changes of ion concentration occurred in the whole layer. Two regions with enhanced ion concentrations could be noticed. They corresponded to two gradually diffusing groups of ions wandering across the layer, one formed by cations and the other formed by anions. Figure 6 illustrates the displacement of the positive ions. The negative ions formed analogous group, but their spatial distribution was reflected symmetrically with respect to the mid-plane of the layer. Both groups moved in the opposite directions and gave identical contributions to the ionic current. Comparison of $j_r(t)$ function with $N^\pm(\zeta, t)$ dependence shows that evolution of the groups of ions coincided with the occurrence of maximum of the current bump. However, the bump of the ionic current cannot be considered as a result of movement of group of ions.

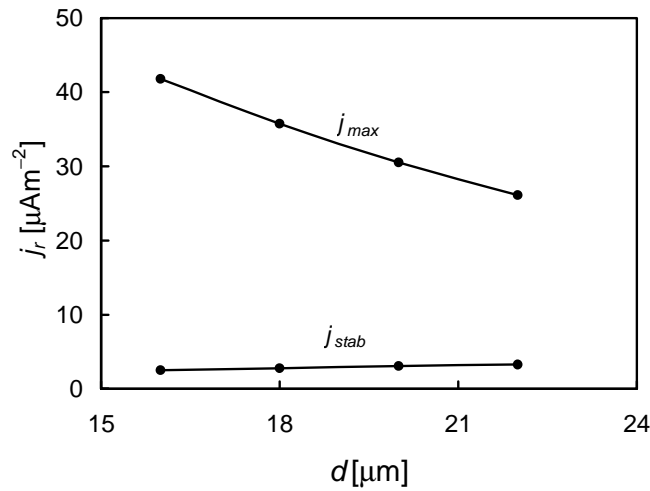


Fig. 5. Maximum current and stabilized current as functions of thickness, $f = 1$ Hz, $U_0 = 2$ V, $\beta_0 = 10^{18} \text{ m}^{-3} \text{ s}^{-1}$

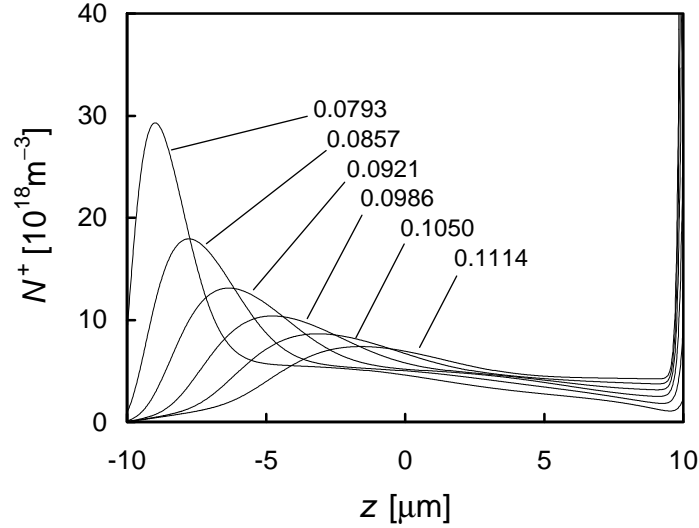


Fig. 6. Redistribution of the cation concentration; the time which elapsed after beginning of the cycle is indicated in seconds at the curves, $f = 7$ Hz, $U_0 = 5$ V, $d = 20$ μm , $\beta_0 = 10^{20} \text{ m}^{-3} \text{ s}^{-1}$.

4. SUMMARY

The ion concentrations and the electric potential distributions result from complex and time dependent mutual interactions between space charges and electric field. These relationships are difficult to qualitative analysis. Numerical solution of the set of nonlinear equations seems to be the only way to recognize the properties of the layer. The result presented here are coherent with numerical results reported in [19]. Additional computations showed very good agreement between the calculated $j_r(t)$ function and experimentally registered dependence for some nematic liquid crystals presented in [17,18]. This seems to validate the adopted model of ionic transport in the layer.

This peculiar time dependence of the ionic current can be considered as a result of redistribution of ions which occurs in the whole layer with various rate. The rather weak dependence of t_{max} on the thickness and voltage amplitude indicates that this time cannot be interpreted as the time of flight of ions across the layer. Therefore, the formula $\mu = d^2 / (U_0 t_{max})$ which is sometimes proposed [12], is inapplicable in the considered case and the t_{max} value cannot be related with the value of mobility of ions.

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**NUMERYCZNE BADANIA PRĄDU JONOWEGO
W WARSTWIE CIECZY DIELEKTRYCZNEJ
PODDANEJ DZIAŁANIU NAPIĘCIA
W FORMIE FALI PROSTOKĄTNEJ**

Streszczenie

Zbadano numerycznie prąd jonowy płynący w cienkiej warstwie cieczy dielektrycznej poddanej działaniu zewnętrznego napięcia w formie fali prostokątnej, przyłożonego między elektrodami silnie blokującymi. Założono równe ruchliwości anionów i kationów. Uwzględniono procesy dysocjacji i rekombinacji. Obliczono przestrzenne rozkłady koncentracji jonów oraz gęstość prądu jonowego w ciągu pojedynczego okresu zmian napięcia jako funkcje czasu. Stwierdzono wystąpienie maksimum prądu pojawiającego się przy odpowiednio dużej amplitudzie napięcia, niskiej koncentracji jonów i niskiej częstotliwości. Zjawisko to spowodowane było zmianami rozkładu ładunku w warstwie. Wykazano, że czas wystąpienia maksimum prądowego nie może być jednoznacznie powiązany z ruchliwością jonów.