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EFFECT OF ELECTRIC FIELD MODULATION ON CHARGE PROPAGATION IN A LOW-CONDUCTING POLAR LIQUID

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Unsteady processes of current propagation and formation of charge structures in a low-conducting polar liquid in the electric field of a horizontal capacitor are considered. Free charges are assumed to form in the liquid only owing to unipolar injection from the anode, which arises if the field strength on the anode is greater than a threshold value. The charge distribution in time and space and the evolution of the density of the current through the capacitor and the field strength on the anode are analyzed. It is demonstrated that the time intervals between two charge injections in a variable field (injection periods) may vary depending on the external field period. The density of the current through the capacitor is obtained as a function of the frequency and amplitude of the external field.

Key words: *low-conducting liquid, unipolar injection, charge waves, variable field.*

Introduction. Investigations of the processes of current propagation in low-conducting liquids are of interest in studying the behavior of liquid dielectrics, in particular, in analyzing the current motion in high-voltage devices. On the other hand, the knowledge of laws that describe the charge kinetics in multispecies media subjected to electric fields may be used to design non-mechanical switches.

Current oscillations in a constant field induced by a capacitor filled by a low-conducting liquid were experimentally observed if the voltage applied was greater than a certain critical value [1]. One possible mechanism of the emergence of current oscillations in the capacitor was considered in [2]. This mechanism is based on the difference in mobility of ionized admixtures of the carrier medium (proper ions) and of injected charges, and also on the threshold character of ion injection. Ionization of a liquid dielectric in the near-electrode layer occurs only if the electric field strength near the anode is greater than a certain critical value. Polyansky and Pankrat'eva [2] observed and studied the oscillatory modes of current propagation through the dielectric in a constant field and analyzed the effect of the ratio of mobilities of the injected and proper ions and the threshold value of the field strength on the system dynamics.

The subject of research of the present work is the current propagation processes and the existence of self-sustained charge waves in a plane capacitor filled by a polar liquid under a constant or variable electric field. In contrast to [2], the parameters of surface recombination of the injected ions on the anode and cathode are assumed to be different. In addition, the effect of the variable external field on the charge distribution in the interelectrode gap is studied. It is demonstrated that the action of the variable external field violates the periodicity of charge injection from the anode surface, and the sum of the injection periods equals the period of the external field. The effect of the amplitude and frequency of the variable field on the mean current density in the capacitor is determined.

1. Formulation of the Problem. Method of the Solution. Let us consider a low-conducting polar liquid (bromobenzene, iodobenzene, or chlorobenzene) filling a plane capacitor of thickness L (the x axis is directed perpendicular to the capacitor plates; the anode coordinate is $x = 0$). The liquid medium consists of neutral molecules of the dielectric and admixtures. The dissolved admixtures dissociate, thus, generating free charges and

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ensuring a low intrinsic conductivity of the liquid $\sigma_0 \approx 10^{-11}$ S/m [3]. Moreover, positive ions of another form arise on the anode surface as a result of complicated electrochemical processes.

Charge generation in the near-electrode region [4, 5] is a process of ion formation in reactions of the following type:

$$\mathrm{M} + (\mathrm{X}^+\mathrm{Y}^-) \to \mathrm{M}(e) + (\mathrm{X}^+\mathrm{Y}) \to \mathrm{X}^+_{\text{free}}. \tag{1}$$

Here M is the metal of the electrode, which captures the electron e from the ion pair $(\mathrm{X}^+\mathrm{Y}^-)$. The ion component X^+ is called the injected component, and the conductivity generated by reaction (1) is called the injection conductivity. This scheme is the classical example of unipolar injection: positive ions are generated on the anode. Repelling from the anode, these ions propagate in the interelectrode space.

Depending on particular test conditions, various models that describe the charge injection in a dielectric liquid can be used (see [2, 5, 6]). As in [2], injection is assumed to occur if the field strength in the near-anode region is greater than a certain critical value. Note that the model developed in [2] is used to describe and explain various experimental data: oscillations of current in a capacitor [1] and luminescence of flows of liquid dielectrics [7].

The concentration of ions injected into the volume from the anode surface is denoted by n_1; the concentrations of positive and negative ions arising in the interelectrode gap owing to volume dissociation of admixtures are n_2 and n_3, respectively. The system of equations that describe the one-dimensional behavior of the fields of the ion concentration and the potential includes the equations of evolution of ions of each kind and Poisson's equation (the charge fluxes in the volume of the dielectric have two components: diffusion and drift components; there is no charge transfer caused by the flow, and the dielectric as a whole is motionless):

$$\begin{gathered}
\frac{\partial n_1}{\partial t} + \frac{\partial (n_1 U_1)}{\partial x} = -\beta n_1 n_3, \qquad \frac{\partial n_2}{\partial t} + \frac{\partial (n_2 U_2)}{\partial x} = w - \alpha n_1 n_3, \\
\frac{\partial n_3}{\partial t} + \frac{\partial (n_3 U_3)}{\partial x} = w - \alpha n_2 n_3 - \beta n_1 n_3, \\
n_i U_i = -D_i \frac{\partial n_i}{\partial x} - \operatorname{sign}(e_i) b_i n_i \frac{\partial \varphi}{\partial x}, \qquad i = 1, \ldots, 3, \\
\Delta \varphi = -\frac{q}{\varepsilon \varepsilon_0}, \qquad q = \sum_{i=1}^{3} e_i n_i, \qquad E = -\frac{\partial \varphi}{\partial x}, \qquad e_{1,2} > 0, \quad e_3 < 0.
\end{gathered} \tag{2}$$

Here e is the electron charge, D_i and $b_i = eD_i/(kT)$ are the ion diffusion and mobility coefficients characterizing the kinetic and transport properties of ions of the ith kind, k is the Boltzmann constant, φ is the electric potential in the liquid dielectric, E is the electric field strength, q is the bulk charge density, and ε is the dielectric permeability of the medium. To characterize the processes in the capacitor, we use the total charge Q in the capacitor and the total current density J including the displacement current:

$$Q(t) = \int\limits_0^L q(x,t)\, dx, \qquad J(t) = \sum_{i=1}^{3} e_i n_i U_i + \varepsilon \varepsilon_0 \frac{\partial E}{\partial t}.$$

The issue of the boundary conditions on the electrodes injecting the charge is one of the most difficult aspects in the theory of electric convention of liquid dielectrics. This problem was analyzed in [4, 8]. We only note here that the macroscopic analysis of the charge transfer through the metal–liquid dielectric interface is much more difficult than that through the electrode-vacuum, metal–metal, or metal–semiconductor interfaces, because of the lack of the far order in liquids. Various phenomenological versions of the boundary conditions are used in the hydrodynamic description of the processes of charge propagation in liquid dielectrics [2, 5, 8].

Following [2], we write the boundary conditions for problem (2) on charge propagation in the interelectrode gap. The electrochemical process of formation and disappearance of ions occurs on the electrodes. This phenomenon is described with the use of the balance relation between the total flux of ions from the volume and the difference in ion fluxes formed and disappeared on the electrodes. Ionization is assumed to occur on the anode only. Ions of all types recombine on the electrode surfaces. The intensity of the flux of injected ions is determined by the strength of the electric field near the anode E_a, which depends both on the external difference of the potentials E_0 and on the bulk charge distribution in the interelectrode space. As the injected charge becomes accumulated near the anode, the electric field in the near-anode layer becomes weaker, and the injection ceases at a certain critical value of the field strength $E_{\rm cr}$. With allowance for the assumptions made above, the boundary conditions acquire the following form:

— on the anode ($x_a = 0$),

$$\varphi = \varphi_0, \qquad n_1 U_1 = AE - K_1 n_1, \qquad n_i U_i = -K_i n_i, \qquad i = 2, 3,$$

$$E < E_{\rm cr}: \quad A = 0, \qquad E \geq E_{\rm cr}: \quad A = \text{const};$$

— on the cathode ($x_c = L$),

$$\varphi = 0, \qquad n_i U_i = K_i n_i, \qquad i = 1, \ldots, 3$$

(K_i and A are parameters characterizing the electrochemical processes on the surface). The characteristic values of K_i and A can be estimated by analyzing the measured current density in the case of electrization of liquid dielectrics in metallic pipes [9]. The surface recombination rate constant K_i essentially depends on the properties of the substance used to produce the electrodes. The values of this parameter can be different for the anode and cathode. The injection intensity coefficient A is determined by the properties of the electrode–liquid system, for instance, by the surface concentration of ion pairs ($\mathrm{X}^+\mathrm{Y}^-$) and by the rate of redox reactions on the electrodes [2, 5]. In experiments, one can deliberately add an admixture (e.g., crystalline iodine [4]) into the carrier liquid to change the level of injection. The value of $E_{\rm cr}$ depends on the properties of the electrode–liquid system, but is mainly determined by the character of anode-surface treatment. Real electrode surfaces (e.g., of steel electrodes) have roughness elements (microscopic spikes) where the field initiating electrochemical reactions of ion formation in a dielectric with an admixture becomes much more intense [8]. The parameter $E_{\rm cr}$ is an integral characteristic of these processes.

In polar liquids, admixture ions dissociate almost completely. In the absence of the electric field, the interelectrode space contains only internal ions n_2 and n_3. The distribution of ions n_2 and n_3 is uniform; therefore, the dielectric liquid is electrically neutral (the total charge in the volume equals zero). In the presence of the electric field, the internal ions migrate to the electrodes and then leave the capacitor: electrical cleaning from admixture ions occurs. Thus, the polar liquid is characterized by system (1) with coefficients $\alpha = \beta = w = 0$. In non-polar liquids, where the right sides of the system differ from zero, the mechanism of self-sustained charge oscillations in the interelectrode gap remains basically unchanged [2]. The volume processes of ion recombination and dissociation are not considered further.

We introduce dimensionless variables with the use of the scales of length L, charge relaxation time $t_r = \varepsilon_0\varepsilon/\sigma_0$, field strength $kT/(eL)$, potential kT/e, charge density en_0, and concentration $n_0 = \sigma_0/(2eb_0)$. We write the system of equations of charge evolution and the boundary conditions in dimensionless form:

$$\begin{gathered}
R\,\frac{\partial n_{1,2}}{\partial t} - \frac{\partial^2 n_{1,2}}{\partial x^2} - \frac{\partial n_{1,2}}{\partial x}\,\frac{\partial \varphi}{\partial x} - n_{1,2}\,\frac{\partial^2 \varphi}{\partial x^2} = 0, \\
R\,\frac{\partial n_3}{\partial t} - \frac{\partial^2 n_3}{\partial x^2} + \frac{\partial n_3}{\partial x}\,\frac{\partial \varphi}{\partial x} + n_3\,\frac{\partial^2 \varphi}{\partial x^2} = 0, \\
2R\,\frac{\partial^2 \varphi}{\partial x^2} = -n_1 - n_2 + n_3, \\
x = 0, \qquad \varphi = F_0, \qquad \frac{\partial n_1}{\partial x} + \frac{\partial \varphi}{\partial x} = A_1 E - B_1 n_1, \\
\frac{\partial n_i}{\partial x} + \operatorname{sign}(e_i) n_i\,\frac{\partial \varphi}{\partial x} = B n_i, \qquad i = 2, 3, \\
x = 1, \qquad \varphi = 0, \qquad \frac{\partial n_i}{\partial x} + \operatorname{sign}(e_i) n_i\,\frac{\partial \varphi}{\partial x} = -B n_i, \qquad i = 1, \ldots, 3.
\end{gathered} \tag{3}$$

System (3) contains the following dimensionless parameters: ratio of the charge relaxation time to the diffusion time $R = D_0\varepsilon_0\varepsilon/(L^2\sigma_0)$, parameters of surface reactions $B_i = K_i L/D_0$, injection intensity coefficient $A_1 = 2Ae/\sigma_0$, and dimensionless anode potential $F_0 = e_0\varphi_0/(kT)$.

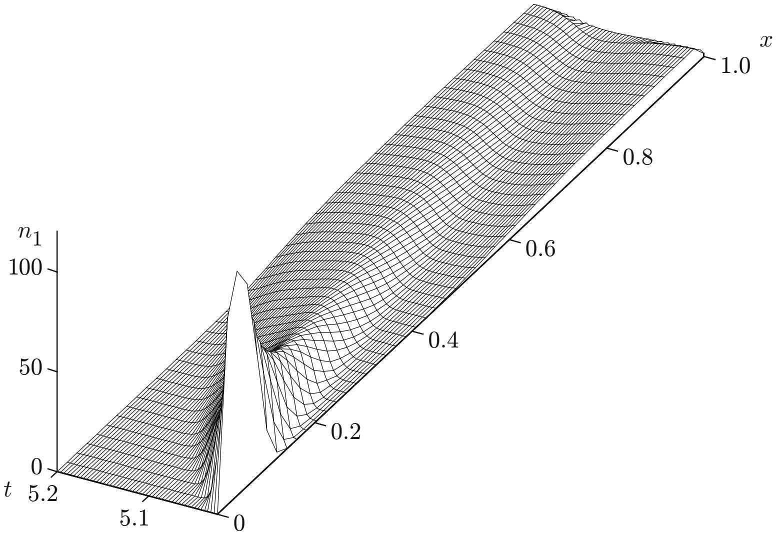

Fig. 1. Time evolution of the charge distribution in a constant field of a capacitor.

The unsteady nonlinear problem (3) in constant and variable fields was solved by the finite-difference method. An implicit (in time) scheme with the grid refined near the electrodes was used. The nonuniform grid was defined analytically by the formulas

$$x_j = \frac{1}{2}\,\frac{\exp(jC/N_j) - 1}{\exp(C/2) - 1}, \qquad j = 0, \ldots, N_j/2,$$

$$x_j = \frac{1}{2}\Big(2 - \frac{\exp((N_j - j)C/N_j) - 1}{\exp(C/2) - 1}\Big), \qquad j = N_j/2 + 1, \ldots, N_j,$$

where C is the refinement parameter, N_j is the number of grid nodes, and j is the node number. As the most essential diffusion boundary layers appear near the electrodes, the grid was refined to the maximum possible extent in these areas. The number of nodes in the interelectrode gap was normally $N_j = 100$, and the refinement parameter was varied in the interval $8 < C < 10$. Thus, the minimum step was $\Delta x_j = 3.6 \cdot 10^{-4}$ (the step in the core was $\Delta x_j = 5 \cdot 10^{-2}$), which allowed us to study the diffusion boundary layers near the electrodes in much detail.

To study the processes in the capacitor, we chose the following values of parameters: distance between the plates $L = 0.002$ m and anode potential $\varphi_0 = 260$ V. If the dielectric is pre-cleaned iodobenzene or bromobenzene, the following physical and chemical characteristics of the dielectric can be used: residual conductivity of the liquid $\sigma_0 = 2 \cdot 10^{-11}$ S/m corresponding concentration of carriers $n_0 = 2 \cdot 10^{15}$ m^{-3}, dielectric permeability $\varepsilon = 4.4$, temperature $T = 300$ K, and diffusion coefficient $D_0 = 10^{-9}$ m^2/sec. In this case, the time of relaxation of the bulk charge is $t_r \approx 2$ sec; $R = 5 \cdot 10^{-4}$ and $F_0 = 10^4$. In addition, we used the coefficient of injection intensity $A_1 = 10^5$ and the coefficient of surface recombination $B_1 = 5 \cdot 10^3$ and $B = 5 \cdot 10^4$ corresponding to the case of liquid oscillations in a constant field [2].

2. Constant Field. We consider the case with a constant external field. A physically important difference of this work from the case considered in [2] is the difference in the coefficients of surface recombination of the injected ions on the cathode and anode: $B_1 \neq B$. This situation can be provided by using electrodes with different physical and chemical properties.

We consider charge wave propagation between the capacitor electrodes in a constant field (Fig. 1). The critical voltage $E_{\rm cr}$ at which injection begins is assumed to be $0.9E_0$ [$E_0 = F_0/L$ is the field strength in the capacitor without the dielectric (we will call it the external field)].

The results presented here are qualitatively similar to those obtained in the case with identical coefficients of surface reactions, which was considered in [2]. If the voltage applied is only slightly greater than the critical value, conditions for existence of self-sustained charge waves in a dielectric liquid are created. The physical mechanism supporting the self-sustained charge waves can be described as follows. When the external field is applied,

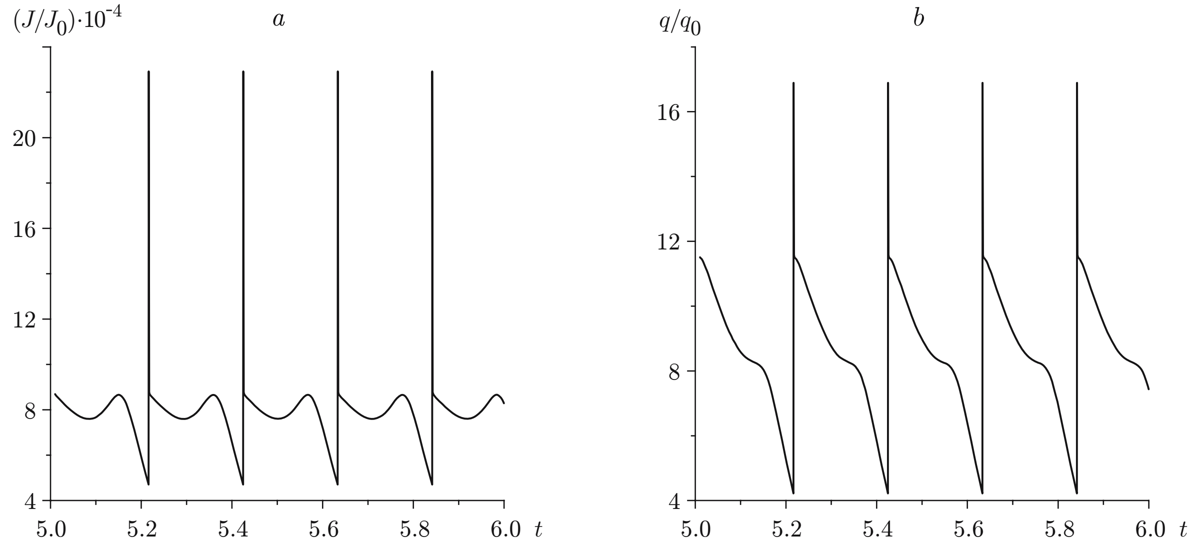

Fig. 2. Time evolution of the total current density (a) and the charge in the capacitor (b) in a constant field.

electrochemical cleaning occurs for a certain time interval: the internal ions reach the electrodes and are discharged on the latter, while a pure injected charge is fed into the volume. The positive injected charge arising on the anode does not have enough time to leave and generates its own electric field compensating for the external field in the near-anode region. When a sufficiently large charge is accumulated, the field strength becomes lower than the critical value, and injection ceases. Part of the charge formed near the anode disappears because of surface recombination reactions. The remaining charge starts to move in the interelectrode space under the action of the electric field. As this charge approaches the cathode, the field on the anode becomes stronger. At a certain time, the field strength again exceeds the critical value, thus, initiating the next injection of ions.

The time evolution of the total current density on the anode and the bulk charge in the capacitor are illustrated in Fig. 2 [$J_0 = \sigma_0 kT/(eL)$]. The peaks on the curves correspond to moments of charge injection. After injection, there occurs an intense outflow of ions through the anode, which becomes weaker as the charge in the near-anode region decreases. Then, a group of ions separates from the anode and propagates into the capacitor. As the ions move through the interelectrode space, the charge in the system remains almost unchanged: the ion concentration near the electrodes is rather low, and there are no surface recombination reactions (the gently sloping segment on the curve of the bulk charge density versus time). At this moment, the electric field strength and, as a consequence, the current density increase. When the charge reaches the cathode, the total charge and the current density decrease owing to surface recombination, which leads to even more intense amplification of the field near the anode. When the critical strength is reached, the process is repeated. It is seen in Fig. 2 that ion injection occurs with a constant period $T_0 = 0.2$.

3. Variable Field. Let us consider the case of a modulated external field:

$$\varphi = F_0(1 + \eta \sin(2\pi t/T)).$$

Here η and T are the amplitude and period of modulation of the external field, respectively.

Let the period of the external field coincide with the injection period: $T = T_i$. The behavior of the field strength in the near-anode region $E_a = E|_{x=0}$ in a steady-state regular regime is shown in Fig. 3a. When the field strength on the anode reaches the critical value, injection occurs: a large number of ions are formed near the anode. At the moment of injection, the field strength in the near-anode region drastically decreases and reaches a minimum value (point A in Fig. 3a). A further increase in the field strength near the anode (segments AB and CD in Fig. 3a) is determined by an increase in the external field strength. The emergence of a gently sloping segment BC on the curve $E_a(t)$ (see Fig. 3a) is caused by the fact that the decrease in the external field is compensated by the field induced by the charge propagating in the capacitor. The bulk charge in the capacitor and the total current density change with the external field period T.

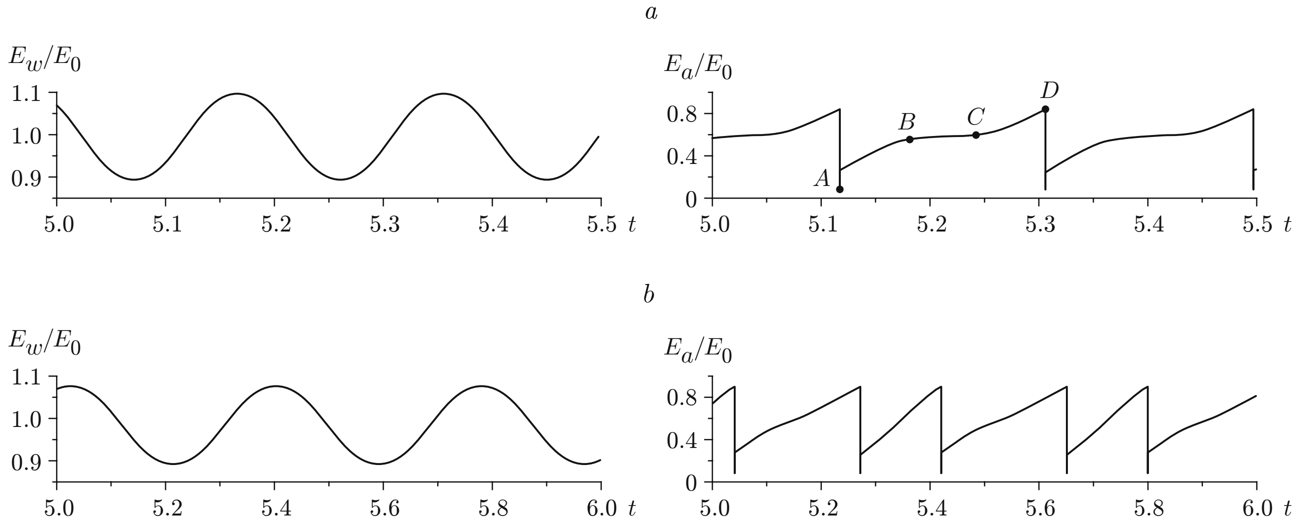

Fig. 3. Strength of the external field E_w and of the field on the anode E_a ($\eta = 0.1$) for $T = T_i$ (a) and $T = 2T_i$ (b).

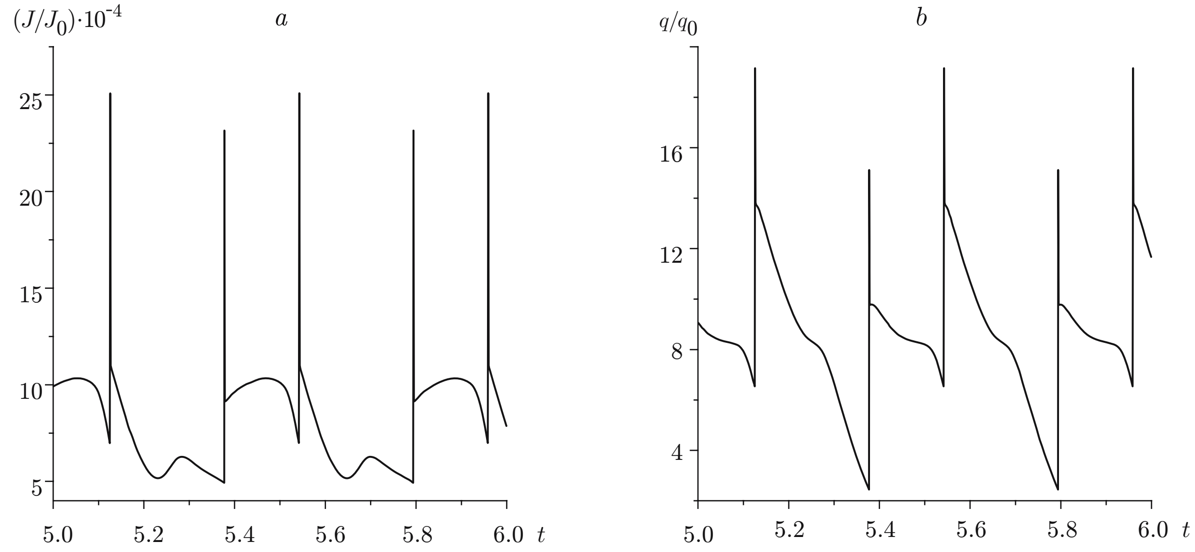

Fig. 4. Time evolution of the total current density (a) and the charge in the capacitor (b) in a variable field for $T = 2T_i$ ($\eta = 0.1$).

Let us consider the case $T = 2T_i$ (Fig. 3b). During the period considered, injection occurs three times, and the time interval between the first and second injections (first period T_1) is always smaller than the interval between the second and third injections (second period T_2): $T_1 < T_2$. The following relation holds: $T = 2T_i = T_1 + T_2$. The shorter period T_1 corresponds to the interval where the external field strength increases. The interval T_2 is longer than T_1 because it corresponds to the change in the external field strength near its minimum.

In contrast to the case of a constant external field (or to the case where the field period coincides with the injection period), the total charge in the capacitor and the current density in the intervals T_1 and T_2 in a variable field with $T = 2T_i$ are different (Fig. 4). This is fairly understandable from the physical point of view. During the first (short) period T_1, all ions do not have enough time to reach the cathode and recombine until a new charge is added into the system from the anode. During the second (longer) period of injection T_2, a low charge stays in the interelectrode space. Its minimum is always smaller than the charge minimum in a constant field because of a rather long process of surface recombination of ions that reached the cathode and because of the absence of

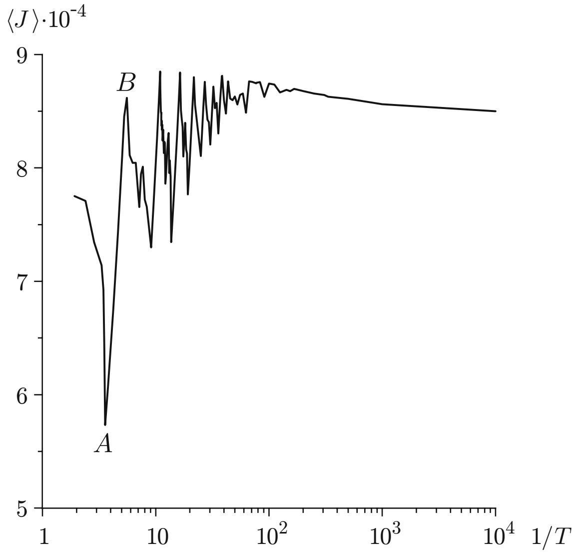

Fig. 5. Mean current density versus the external field period ($\eta = 0.1$).

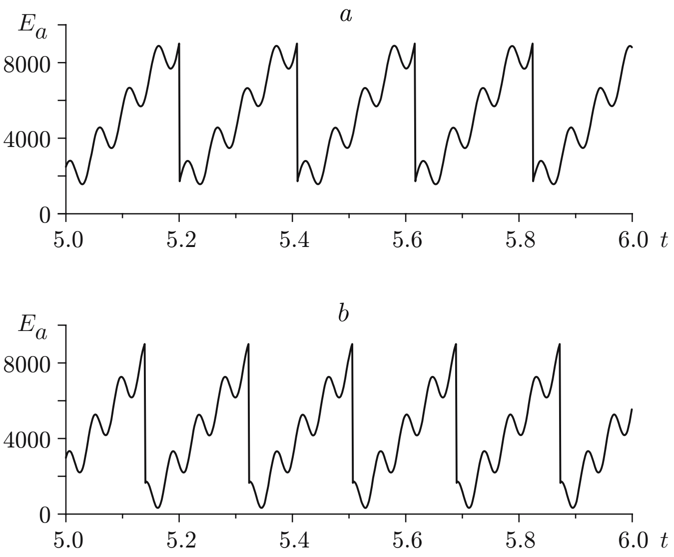

Fig. 6

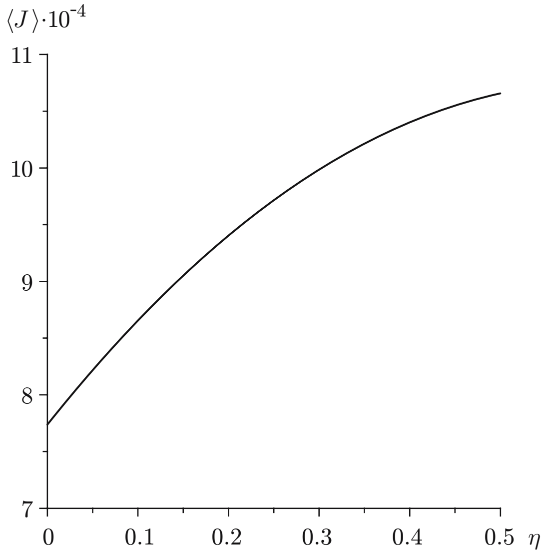

Fig. 7

Fig. 6. Field on the anode at the points of the local minimum (a) and local maximum (b) of the dependence of the mean current on the external field frequency for $T = 0.0520$ (a) and 0.0458 (b).

Fig. 7. Mean current density versus the amplitude of modulation of the external field at $T = T_i/32$.

injection of new ions. In the case with $T = 3T_i$, there are three injections of ions: $T = T_1 + T_2 + T_3$. The longest period T_2 coincides with the time interval during which the external voltage decreases.

The dependence of the period-averaged density of the current through the capacitor $\langle J\rangle$ on the external field frequency has a complicated character (Fig. 5): segments of the linear growth of the current density alternate with intervals of the decreasing current density. This dependence is essentially different from the curves of the parametric resonance in a variable electric field [10], which is caused by the initially nonlinear character of the physical processes considered, the threshold character of injection, and interaction of electric fields and concentration fields. The qualitative behavior of this dependence can be explained by analyzing the field on the anode (Fig. 6).

A rapidly growing field is subjected to high-frequency modulations between two consecutive injections. The period of modulation of the external field decreases on the segments of the linear growth of the mean current density, e.g., on the segment AB (see Fig. 5). At the point A of the local minimum of the mean current, the moment of injection beginning coincides with the moment when the external field strength starts growing (Fig. 6a). In this case, the charge formed on the electrode moves with a moderate velocity. If the moment of injection beginning coincides with the moment when the maximum strength of the external field is reached (Fig. 6b), the charge injected into the capacitor is accelerated during the same time to high velocities, and the maximum of the period-averaged current density is reached (point B in Fig. 5). The mean current density in the high-frequency region changes monotonically. During the injection period T_i, the external field changes many times, the time of acceleration of the injected charge near the electrode drastically decreases, and the system dynamics is determined by averaged fields. Under such a high-frequency action, the density of the current passing through the capacitor substantially depends on the amplitude of the external forcing and changes approximately by 40% (Fig. 7).

Conclusions. The processes of propagation of a charge injected from the anode in a constant field or a modulated field of a capacitor filled by a liquid dielectric are studied. Regimes of existence of self-sustained waves with different degrees of surface recombination on the electrodes are found in a constant field. In the case of a harmonic modulation of the external field with $T > T_i$, several periods of injection are observed, with the total duration of these periods being equal to the external field period T. The mean current density is found as a function of the modulation frequency and amplitude.

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