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Numerical study of the current-voltage characteristics of a weakly conducting liquid between extended parallel electrodes

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The article presents the results of solution of the problem of direct electric current flow through a weakly conducting liquid located between two flat metal electrodes. This solution takes into account the influence of spatial inhomogeneity of concentration and the degree of dissociation of ion pairs on electromigration processes. The behavior of ions and ion pairs is described using electrokinetic equations. This system of equations, combined with boundary conditions for concentration fluxes, allows one to model the redox process at the electrodes, during which steady-state concentration and electric potential profiles are established in the volume between the electrodes. It is shown that the significant nonlinearity of the processes under consideration leads to topologically different current-voltage characteristics, which continuously transform into one another as the parameters of the problem change. From a practical standpoint, this study allows for a more in-depth analysis of the phenomena occurring during the technological process of protonation of a lithium niobate crystal immersed in molten benzoic acid. This process is used to create channel waveguides in photonic integrated circuits. The proposed approach to describing electrical conductivity makes it possible to exclude abstract boundary conditions used in earlier works.

Keywords: Current-voltage characteristics, liquid dielectric, numerical simulation.

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Introduction

Currently, liquid dielectrics have many technical applications. They are used as insulators in such electrical devices as transformers, capacitors, etc. However, liquid dielectrics have weak conductivity, the nature of which is very complex. The assessment of the applicability of weakly conductive media in a particular device requires an in-depth study of their properties, which determine the operating range of the dielectric. In this regard, it is necessary to carry out many tests, which becomes especially relevant when miniaturizing devices. In addition to direct experiments, the behavior of a dielectric in certain situations is studied by theoretical methods, which are becoming more and more effective with the development of computing technologies. The solutions to the problems posed in this way make it possible to demonstrate the behavior of liquid dielectrics in various systems and to detect patterns that are not recorded in experiments due to various limitations. Often, in some cases, a very complex behavior of the dielectric is manifested, which raises many questions due to the inconsistency of experimental results with previously known data.

Even a seemingly simple task in which a liquid dielectric is placed between two electrodes on which a constant potential difference is maintained, resulting in an orderly movement of ions between them, is still very non-trivial from the point of view of observed phenomena. The fact is that a detailed study of the process of passing an electric current through a weakly conductive medium reveals a wide variety of physico-chemical mechanisms that affect the passage of current even in such a simple geometry [1,2]. The difference in formulation is reflected primarily in the chemical processes taking place both in the volume of the dielectrics and in the area of their contact with the electrodes. Depending on the choice of materials, the presence of impurities, the presence of ionizing radiation, and other factors, the interaction of a dielectric-electrode pair in one experiment may differ greatly from another. Thus, the passage of an electric current can be accompanied by the dissolution of the electrodes or the electrodeposition of dissolved substances on them [2]. Mass transfer during the passage of current is primarily associated with diffusion and electromigration, however, it can be complicated by such more subtle effects as spatial inhomogeneity of the dielectric constant of the medium, as a result of which several additional terms arise in the ponderomotor force, leading, under certain conditions, to electrohydrodynamic flows [2–4]. In a number of cases, the behavior of these flows is complicated by the presence of interfacial surfaces [5]. In addition, it is often necessary to deal with the non-stationarity of processes associated with a variety of factors, including electroplating [6].

One of the most important characteristics of electrically conductive systems is the dependence of the current in the circuit on the applied potential difference (volt-ampere characteristic, VAC). The generalized form of the VAC of liquid dielectrics was proposed in Ref. [7] and consisted of three sections: a linear dependence of current strength on voltage at small potential differences, reaching the limiting current at moderate voltages, and a pre-breakdown region characterized by a sharp increase in current strength with a further increase in voltage. Later, carefully conducted experimental studies revealed significant deviations from the proposed generalized form. So, according to Ref. [8], often in the area corresponding to the limiting current, a linear increase in current strength is observed with an increase in the potential difference. This phenomenon is called current exaltation. Its theoretical explanation was proposed in Ref. [9,10], in which an increase in the concentration of ions at the electrodes was found, which contributes to an increase in the intensity of migration currents. In addition, serious deviations are also observed at low voltages. And exactly in contrast to Ref. [7], where the linear section smoothly turns into saturation, the VAC experiences an additional bend [1,11]. The presence of convective transport also significantly complicates the shape of the VAC [12].

The desire to obtain a correct explanation of the deviations of the VAC from the initial linear law led to the writing of quite a large number of theoretical papers. If we are talking about a liquid dielectric in mechanical equilibrium, then in the framework of weak electric fields, ionic conductivity is described using the transport equations and the equations of electrostatics. Various methods of analytical solution of the specified system of equations were implemented in Ref. [1,2,11,13] and the dependences of current strength on voltage were obtained. These dependencies are superimposed with good accuracy on some experimental curves, the shape of which is close to that proposed in Ref. [7]. Nevertheless, obtaining such analytical dependencies involves a significant simplification of the system of equations describing the flow of current. The presence of more complex forms of VAC suggests that these approaches are insufficient for a comprehensive understanding of the electrical conductivity process. In this regard, numerical modeling is increasingly used to solve the problem of electrical conductivity in various systems. At the moment, there are several approaches for the numerical solution of the problem of the passage of an electric current through a weakly conductive liquid. In one of the approaches used, [14–16], the region of relatively large electric field strengths is always considered, which makes it possible to greatly simplify the boundary value problem, namely, to lower the order of the transport equations by eliminating diffusion terms. Despite the widespread use of this approach to describe electroconvective flows, it cannot be used in the case when not only the electromigration current plays a significant role in expressing the ion flux density, but also the diffusion current, i.e. in the area of low VAC voltages.

The conservation of the diffusion term in the transfer equations is associated with great computational difficulties. To simplify the numerical model, in some cases, among other things, it is proposed to use model boundary conditions for the flow of matter [17–19], including the coefficients of ion generation and destruction on the electrodes. This approach makes it possible to model the complex competition of diffusion and electromigration fluxes, and even gives results from which it is possible to construct a VAC [18], which is qualitatively consistent with some experiments. Despite this, these results are essentially very abstract, since it is difficult to directly compare the phenomenological coefficients under boundary conditions with the parameters of a real experiment.

A similar [17–19] system of equations, including diffusion and electromigration fluxes, as well as the effects of volumetric dissociation and recombination, is solved by simulating the passage of electric current through membrane systems [20–22]. The peculiarity of the boundary value problem formulated in such cases is that the membranes are brought into contact with the electrolyte, which is a source of ions. Due to the high concentration of ions at the entrance to the membrane, in such tasks it is acceptable to use boundary conditions of the first kind for concentration. This approach makes it possible to obtain VAC that are very consistent with experiments and have a large number of inflection points [23,24], the interpretation of which is based on the complexity of the membrane system. In a number of cases, mathematical modeling of the effect of convective flows on the VAC of membranes is carried out, which gives stochastic deviations from linear sections [25,26].

Nevertheless, despite all the richness and diversity of the results obtained so far, there is still no complete understanding of all aspects of the electrical conductivity of liquid dielectrics. Thus, many questions arise about the correctness of the description of the mechanisms of recombination and dissociation [27,28]. If, to describe recombination, a term is introduced in the transport equations that is proportional to ion concentrations and corresponds to their „flow“ in volume, which is very logical in the first approximation, then the description of dissociation, as a rule, boils down to the appearance in the same equations of a volumetric „source“ ions, in no way related to the local the concentration of ion pairs [14]. In this regard, the question arises about the completeness of the mathematical description of the electrical conductivity of liquid dielectrics in cases where the distribution of ion pairs is heterogeneous for various reasons.

The relevance of this question is very significant, since often a seemingly insignificant deviation in the parameters of a liquid dielectric entails serious changes in a particular technological process. An example is the technology of creating optical waveguides using a proton exchange reaction. To carry out this reaction, a lithium niobate crystal is brought into contact with a benzoic acid melt [29,30]. Under certain conditions, acid molecules that directly come into contact with the crystal dissociate. The hydrogen ions released during this dissociation penetrate deep into the crystal and replace lithium ions. The latter penetrate into the melt and, together with benzoate ions remaining from benzoic acid molecules, form an ionic boundary layer in it [31–33]. Experiments show that the water content in the benzoic acid melt has a significant effect on how many protons will penetrate into the crystal [34] and, accordingly, on the final characteristics of the waveguide. The use of not only X crystal sections as a substrate, but also Zsections, actually means that proton exchange will be carried out in the presence of a strong electric field [35] and may be accompanied by an electric current. It should be noted that pre-dried benzoic acid is often used in proton exchange [36], and the potential flow of current in the melt will be complicated by a small number of ion pairs capable of dissociation. Therefore, a physico-mathematical model is proposed in this paper that allows for a multiparametric analysis of the VAC of a weakly conductive liquid between extended electrodes when a limited number of ion pairs are contained in the volume.

1. Problem statement

We study the behavior of a weakly conductive liquid when a direct electric current is passed through it, taking into account the influence of spatial heterogeneity of the concentration of ion pairs on electromigration processes and, accordingly, taking into account the degree of their dissociation. Let us consider an infinite layer of a weakly conductive liquid enclosed between two flat metal electrodes at room temperature. The problem is isothermal, the liquid is in a state of mechanical equilibrium. The electrical conductivity of the liquid is ensured by the presence of neutral ion pairs in it. In the mathematical description of the processes of electrical conductivity, a model is proposed in which conduction ions appear due to the volumetric dissociation of ion pairs. The further disappearance of ions is due to two mechanisms: recombination in volume and neutralization on electrodes charged opposite to ions. We assume that in both cases, either immediately after recombination or after intermediate chemical reactions near the electrode surface, the initial ion pairs appear in the volume. Electrode processes are not explicitly considered in the model. Ion concentrations are considered to be significantly lower than the concentration of benzoic acid molecules. In this regard, the recombination of ions with a high probability does not lead to the formation of more complex molecules than the initial ion pair. From the results of solving the problem, it will be seen that the superimposed potential differences and, as a result, the resulting current densities are significantly less than those necessary to activate Kolbe processes, and therefore they do not appear in the model. In addition, we assume that the overvoltage of electrode reactions tends to zero, adsorption can be neglected, and the products of electrochemical reactions do not change the concentration profile in the electrode space.

As an example, we will investigate the behavior of a model liquid mixture similar in properties to a benzoic acid melt with a low water content. Ion pairs of the 1:1 type in such a mixture are present in the form of complexes of benzoic acid and water molecules [36]. After dissociation, negative benzoate ions and positive hydroxonium ions appear in the melt volume. Their transfer can be related to both the concentration gradient and the presence of an external electric field. In this regard, the ion flux densities are given by the following relations:

$$\vec{j}_\pm = -D_\pm \nabla n_\pm \mp k_\pm n_\pm \nabla \varphi, \tag{1}$$

where φ, $n_\pm$ are fields of electric potential, as well as positive and negative ions, $D_\pm$ and $k_\pm$ are coefficients of diffusion and mobility of the corresponding ions.

Thus, in the one-dimensional case, the transfer equations of the components involved in the redox process take the following form [14]:

$$\begin{aligned}\frac{\partial n_\pm}{\partial t} =& D_\pm n''_\pm \pm k_\pm (n'_\pm \varphi' + n_\pm \varphi'') - k_R n_+ n_- \\ &+2k_D \frac{I_1(z)}{z} n_0,\end{aligned} \tag{2}$$

$$\frac{\partial n_0}{\partial t} = D_0 n''_0 + k_R n_+ n_- - 2k_D \frac{I_1(z)}{z} n_0, \tag{3}$$

where n_0 is the ion pair concentration field, $I_1(z)$ is a modified Bessel function of the first kind. In turn, ion concentrations are inextricably linked to the electric field in the interelectrode space through the equation of electrostatics:

$$\varepsilon_0 \varepsilon \varphi'' = e(n_+ - n_-). \tag{4}$$

In equations (2)−(4), the parameters e, ε, ε_0 are the electron charge, the dielectric constant of the carrier fluid, and the electrical constant. The diffusion coefficient of ion pairs, as well as the coefficients of recombination and dissociation, are denoted, respectively, D_0, k_R, and k_D. To account for the effect of the electric field on the dissociation processes [14], a correction factor is introduced in the term responsible for the influx of ions, depending on the dimensionless value $z = L_b/L_e$:

$$L_b = \frac{e^2}{2\pi\varepsilon_0\varepsilon kT}, \quad L_e = \sqrt{\frac{e}{4\pi\varepsilon_0\varepsilon|\varphi'|}}.$$

Here k is the Boltzmann constant, and T is the temperature. The value z is determined by two characteristic scales. The Bjerrum length L_b is determined by the distance at which the energy of the electrostatic interaction between ions is comparable to their thermal energy. In turn, on the L_e scale, the force of the electrostatic interaction between ions is comparable to the force applied to ions from the external field. As will be seen later from the results of solving equations (2)−(4), the electric field in the interelectrode space will not be homogeneous. In this regard, taking into account the importance of the intensity of mutual transformations of ions and ion pairs in the present formulation, the term responsible for dissociation is adjusted using the Bessel function. This correction was proposed in Ref. [37], and shows an increase in the intensity of dissociation with an increase in the value of the electric field strength.

The strokes indicate the derivative of the coordinate x. The coordinate axis is directed along the normal to the electrodes in such a way that the anode is located at the origin of the coordinates, and the cathode is located at a distance of h from it. A potential difference φ_0 is maintained on the electrodes. The electrodes in the considered model process are not subjected to dissolution or deposition of additional chemical reaction products on them, including for the reason that the action of an electric field may take a limited time. The problem simulates a redox reaction in which the left and right boundaries are impervious to positive and negative ions, respectively. At the same time, ions of opposite signs are neutralized at these boundaries. This process is included in the physico-mathematical model in the form of ion runoff when they reach oppositely charged electrodes. The flux density associated with ion neutralization is defined as $\sigma\varphi'/e$, where σ is the electrical conductivity of a liquid dielectric. In turn, the outflow of ions, due to their neutralization at the boundaries, must be compensated by the influx of reduced ion pairs in order to fulfill the conservation law in the redox process. Thus, the boundary conditions for all values introduced into the problem are presented in the following form:

$$x = 0: \quad -D_+ n'_+ - k_+ n_+ \varphi' = 0,$$

$$-D_- n'_- + k_- n_- \varphi' = \frac{\sigma\varphi'}{e}, \quad D_0 n'_0 = \frac{\sigma\varphi'}{2e} \quad \varphi = \varphi_0, \tag{5}$$

$$x = h: \quad -D_+ n'_+ - k_+ n_+ \varphi' = -\frac{\sigma\varphi'}{e},$$

$$-D_- n'_- + k_- n_- \varphi' = 0, \quad D_0 n'_0 = -\frac{\sigma\varphi'}{2e}, \quad \varphi = 0. \tag{6}$$

We assume that ion pairs and negative ions are similar in their kinetics. In this regard, the value of the diffusion coefficient of ion pairs was considered close to the value of the diffusion coefficient of negative ions: $D_0 = D_-$.

The initial conditions for the system of equations (2)–(4) were

$$n_\pm(t=0) = 0, \quad n_0(t=0) = \overline{n}_0, \quad \varphi(t=0) = \varphi_0\left(1 - \frac{x}{h}\right).$$

The specific current strength for the construction of the VAC was calculated as the sum of the contributions of all ions to the total current density based on the ratios (1):

$$i = \int_0^h (j_+ - j_-)dx.$$

The physical and mathematical model (2)–(4) is based on equations containing spatial derivatives, temporal derivatives, and nonlinear terms with unknown functions themselves (n_+, n_-, and n_0). These concentrations are always unambiguously determined. Unambiguity at each subsequent moment of time follows from the imposition of certain initial conditions on these concentrations, which are set, among other things, at the boundaries. Thus, despite the use of the Neumann conditions (5), (6), at all subsequent points in time, the distributions of the components are described by a single solution.

Boundary value problem (2)–(6) was solved in dimensionless variables. The units of measurement for distance, time, concentration, and electric potential were h, h^2/D_+, $\overline{n}_0$, and φ_0, respectively. After the transformation to a dimensionless form, the system of equations, boundary and initial conditions take the following form:

$$\frac{\partial n_\pm}{\partial t} = A_\pm n''_\pm \pm B_\pm(n'_\pm\varphi' + n_\pm\varphi'') - Cn_+n_- + 2D\,\frac{I_1(z)}{z}\,n_0, \tag{7}$$

$$\frac{\partial n_0}{\partial t} = A_- n''_0 + Cn_+n_- - 2D\,\frac{I_1(z)}{z}\,n_0, \tag{8}$$

$$\varphi'' = E(n_+ - n_-), \tag{9}$$

$$x = 0: \quad -A_+ n'_+ - B_+ n_+ \varphi' = 0,$$

$$-A_- n'_- + B_- \varphi' = \overline{\sigma}\varphi', \quad A_- n'_0 = \frac{\overline{\sigma}\varphi'}{2}, \quad \varphi = 1, \tag{10}$$

$$x = 1: \quad -A_+ n'_+ - B_+ \varphi' = -\overline{\sigma}\varphi',$$

$$-A_- n'_- + B_- \varphi' = 0, \quad A_- n'_0 = \frac{\overline{\sigma}\varphi'}{2}, \quad \varphi = 0, \tag{11}$$

$$A_\pm = \frac{D_\pm}{D_+}, \quad B_\pm = \frac{k_\pm\varphi_0}{D_+}, \quad C = \frac{k_R\overline{n}_0 h^2}{D_+},$$

$$D = \frac{k_D h^2}{D_+}, \quad E = \frac{e\overline{n}_0 h^2}{\varepsilon_0\varepsilon\varphi_0}, \quad \overline{\sigma} = \frac{\sigma\varphi_0}{e\overline{n}_0 D_+},$$

$$n_\pm(t=0) = 0, \quad n_0(t=0) = 1, \quad \varphi(t=0) = 1 - x. \tag{12}$$

2. Solution method

Obtaining a numerical solution to the boundary value problem (7)–(12) is associated with certain computational difficulties. Thus, the presence in equations (7) and (8) of the term responsible for dissociation, together with the initial conditions (12), leads to a rapid increase in the concentration of ions in the volume at the initial time points, which requires a very small time step. However, in this case, the calculation until the establishment of stationary profiles will be unreasonably long due to the significantly slower diffusion process. Moreover, the formation of boundary layers near the electrodes, the thickness of which, as will be found later, will in some cases be ~ 0.0001 of the size of the calculated area, imposes serious restrictions on the choice of the coordinate step. Thus, in order to save machine time, a gradual increase in the time step and a significant thickening of the grid in the near-electrode regions are required.

To overcome all the numerical difficulties that accompanied the task and obtain a solution, the authors selected the mathematical package Comsol Multiphysics 6.1. The formulated equations (7) and (8) are new in the sense that they are absent from the pre-defined physical models in this mathematical package. A standard partial differential equation solver was used to integrate them, in which all equations and boundary conditions were manually written. The boundary value problem was solved using the MUMPS algorithm (MUltifrontal Massively Parallel sparse direct Solver). In the course of the solution, an uneven computational grid was generated, symmetrical relative to the center of the area under consideration, the elements of which were condensed near the borders. The convergence of the results was analyzed. In contrast to studies [18,19], in order to resolve the boundary layers, it was necessary to increase the density of the grid by several orders of magnitude due to spatial inhomogeneities in ion concentrations. The number of elements into which the calculated area was divided was increased to 200,000. It was found that 150,000 elements are sufficient to resolve the formed near-electrode boundary layers and convergence. In the algorithm used, the time step was set automatically for reasons of maximum saving of computing resources.

There are many parameters in this task, the values of which have not changed in the calculations.:

$$k_+ = 0.5\cdot 10^{-7}\,\mathrm{m^2/(s\cdot V)},\ k_- = 10^{-8}\,\mathrm{m^2/(s\cdot V)},$$

$$D_+ = 0.5\cdot 10^{-8}\,\mathrm{m^2/s},\ D_- = 0.5\cdot 10^{-9}\,\mathrm{m^2/s},$$

$$k_R = 10^{-16}\,\mathrm{m^3/s},\ k_D = 3\cdot 10^6\,\mathrm{s^{-1}},\ \varepsilon = 10,$$

$$\sigma = 10^{-12}\,\mathrm{S/m},\quad T = 300\,\mathrm{K}.$$

The mobilities, diffusion coefficients, and permittivity were estimated by analogy with Ref. [33,38]. In turn, the relations for calculating the coefficients of recombination and dissociation were borrowed from Ref. [14]. It should be noted that the value of the electrical conductivity coefficient is noticeably less than the value obtained in the experiment with real benzoic acid [36], which makes the liquid dielectric in question a model one and allows us to qualitatively transfer the results obtained to many other substances. The dimensionless parameters of the problem assumed the following characteristic values:

$$A_+ = 1,\quad A_- = 0.1,$$

$$B_+ = 10^{-1}\ldots 10^4,\quad B_- = 2\cdot 10^{-1}\ldots 2\cdot 10^3,$$

$$C = 2\ldots 2\cdot 10^8,\quad D = 6\cdot 10^6\ldots 6\cdot 10^8,$$

$$E = 2\cdot 10^{-6}\ldots 2\cdot 10^9,\quad \overline{\sigma} = 10^{-4}\ldots 0.1.$$

3. Numerical simulation results

Calculations show that at the initial time points in the interelectrode space, an active rearrangement of the concentration and electric potential profiles is observed. As a result of the dissociation of ion pairs, ions appear in the carrier liquid, which, under the influence of an electric field, begin to migrate towards electrodes with an opposite charge. This process is counteracted by diffusion, which, as profiles are established, makes an increasing contribution to the density of flows due to increasing concentration gradients. Eventually, the system comes to a stationary state, which is characterized by a balance of four mechanisms: electromigration, diffusion, recombination and dissociation. With the growth of φ_0, the initial stages of current generation become more violent and require more time to establish (Fig. 1). The parameters used in the calculations assumed values such that all profiles in dimensional units become stationary after a time $\sim 1-100\,\mathrm{s}$. The following figures demonstrate the profiles corresponding to the stationary state of the system.

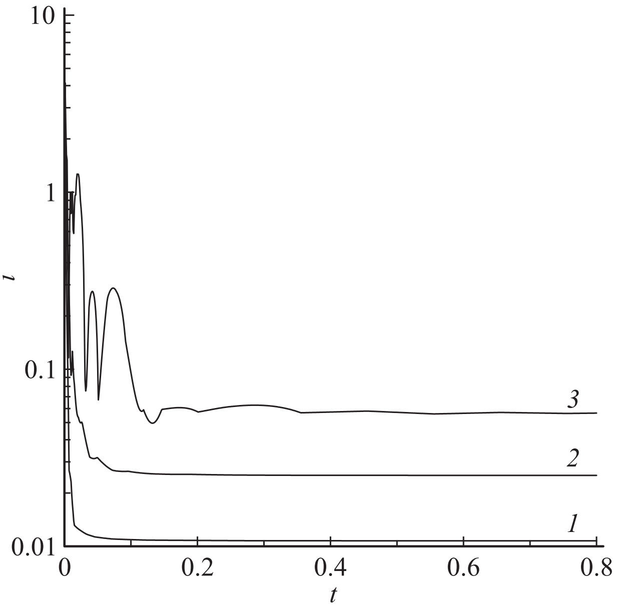

Figure 1. Dependences of the dimensionless specific current strength on time at $h = 0.001\,\mathrm{m}$ and $\overline{n}_0 = 10^{20}\,\mathrm{m^{-3}}$. φ_0: *1* — 0.5, *2* — 0.75, *3* — 1 V.

By the time the ion concentration profiles are established, they have common features. Under the action of an electric field, positive ions accumulate near the cathode, and negative ions accumulate near the anode. On the other hand, for the same reason, depleted regions of ions of the same signs are formed near the electrodes. Thus, concentration ionic boundary layers appear at the boundaries of the dielectric. At small values φ_0, the difference in ion concentrations in the dielectric volume tends to zero, and the profiles have a linear dependence on the coordinate (Fig. 2, *a*).

Due to the reduction of ions on the electrodes and their recombination in volume, the concentration profiles of ion pairs have a more complex nonmonotonic shape (Fig. 2, *b*). A consequence of the conditions at the boundaries (10), (11) is a strong increase in ion concentration as it approaches the electrodes. From the concentration profiles obtained in Fig. 2, it can be concluded that the selected value $\overline{n}_0$ corresponds to the dissociation of almost all ion pairs, i.e., after establishment, the dimensionless ion

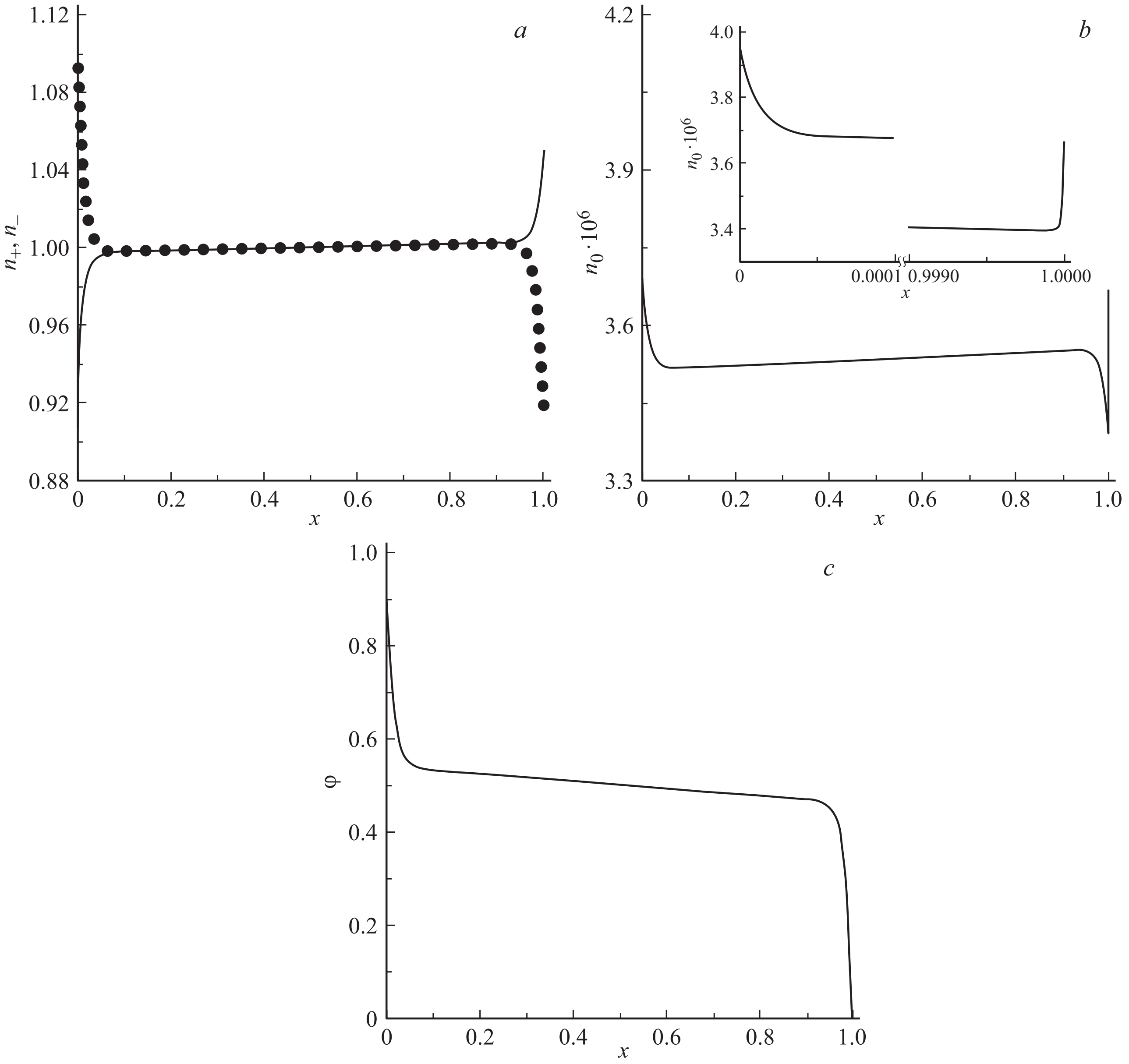

Figure 2. Concentration profiles of positive (solid line) and negative (dots) ions (*a*), ion pairs (*b*) and electric potential (*c*) at $h = 0.001$ m, $\varphi_0 = 0.01$ V, $\overline{n}_0 = 10^{17}\,\mathrm{m}^{-3}$.

concentration is close to unity, and the concentration of ion pairs tends to zero, which demonstrates a high degree of ionization of the mixture.

A characteristic view of the electric potential profile is shown in Fig. 2, *c*. It follows that the intensity vector of the field formed in the dielectric is directed along the axis x. While maintaining a relatively small potential difference at the electrodes, these monotonic profiles also follow a linear law in the center of the computational domain. In the vicinity of the electrodes, the slope of the profiles always increases. The specific distribution of the electric potential at the selected parameter values in Fig. 2 shows that the electric field is homogeneous in the volume of the dielectric, but the absolute value of the field strength increases as the concentration difference increases as it approaches the electrodes.

Varying the values of the initial concentration of ion pairs makes it possible to simulate the case of an even lower degree of ionization. Thus, with an increase in $\overline{n}_0$ (Fig. 3), the number of ion pairs remaining in the space between the electrodes at the time of installation becomes larger compared to the profiles in Fig. 2. At the same time, there is a noticeable decrease in ion concentrations relative to the concentration of ion pairs. The distributions in Fig. 2 and 3 are qualitatively similar. And it is precisely the thin near-electrode regions in which the concentration increases that persist even at large $\overline{n}_0$ for both ions and ion pairs. However, the scale of these areas in Fig. 3 is significantly smaller than

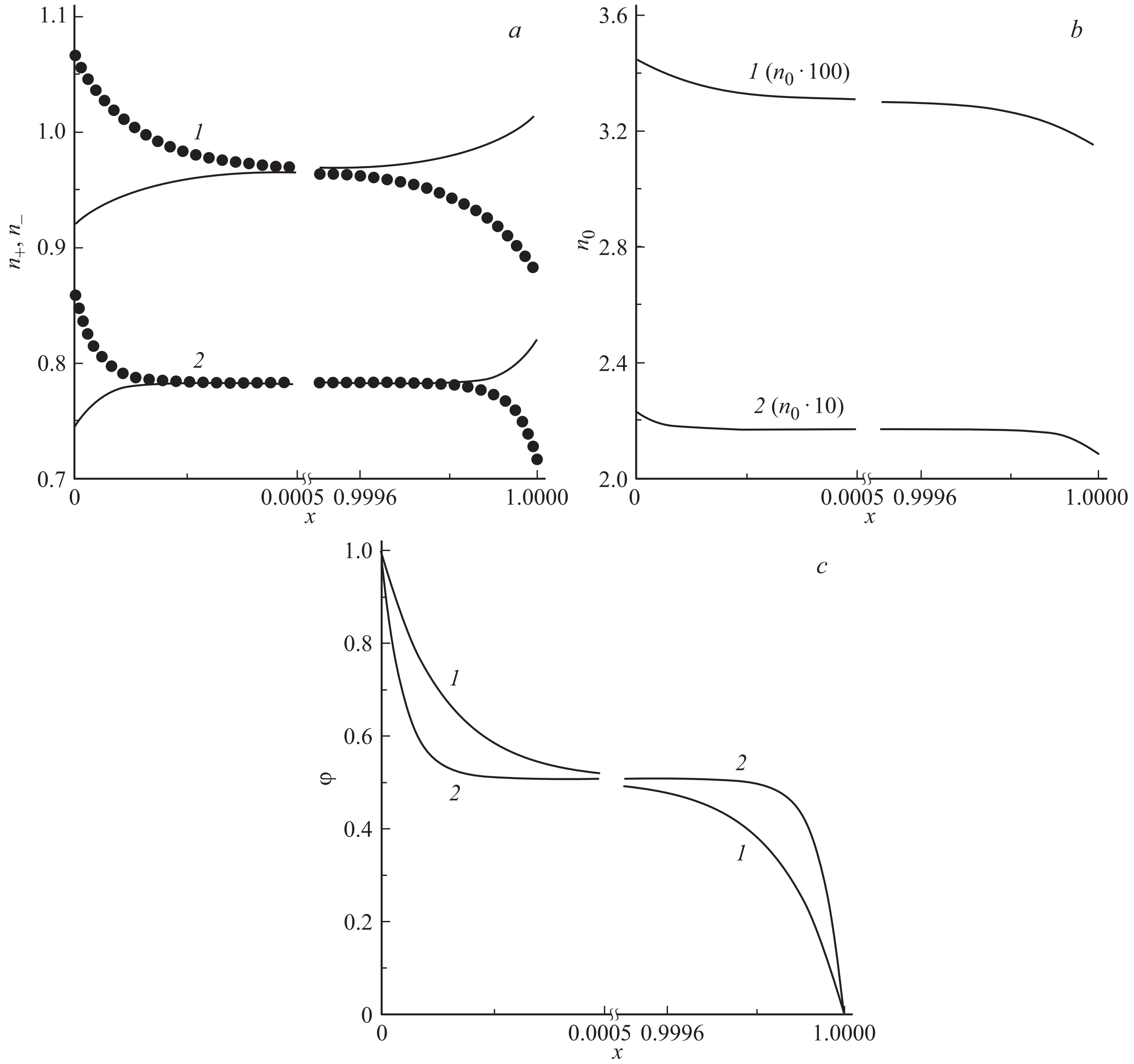

Figure 3. Concentration profiles of positive (solid line) and negative (dots) ions (*a*), ion pairs (curves *1* and *2* have concentration values multiplied by 100 and 10, respectively) (*b*) and electric potential (*c*) for $h = 0.001\,\mathrm{m}$, $\varphi_0 = 0.01\,\mathrm{V}$: *1* — $\overline{n}_0 = 10^{21}\,\mathrm{m}^{-3}$, *2* — $\overline{n}_0 = 10^{22}\,\mathrm{m}^{-3}$.

in Fig. 2. Thus, the growth of $\overline{n}_0$ leads to an intensification of migration and diffusion fluxes near the electrodes due to the growth of electric potential and concentration gradients in these regions. When φ_0 is selected, the linear sections in the center of the calculated area are saved for all profiles.

On the contrary, as $\overline{n}_0$ decreases, the size of the border sections increases. In the case when the mixture is almost completely ionized, the concentration distributions tend to be linear [2]. If we exclude the effects of dielectric breakdown, then the system reaches the maximum currents in this situation.

Depending on the values of the potential difference maintained on the electrodes, several modes of electrical conductivity can be distinguished. In the region of small φ_0, an increase in this parameter leads to a sharp increase in the ion concentration in the near-electrode regions (Fig. 4). At the same time, the remaining space between the electrodes is depleted. So, in the case of $h = 0.001\,\mathrm{m}$, $\overline{n}_0 = 10^{17}\,\mathrm{m}^{-3}$ and $\varphi_0 = 3\,\mathrm{V}$, the ion concentration in the center of the calculated area will be two times less than at $\varphi_0 = 0.01\,\mathrm{V}$. In this case, electrical conductivity is provided by active dissociation and recombination of ions in the electrode boundary layers. The growth of φ_0 increases the intensity of ion reduction and, accordingly, the current strength. One of the key characteristics of this mode is the area in the volume of the dielectric in which the concentrations of positive and

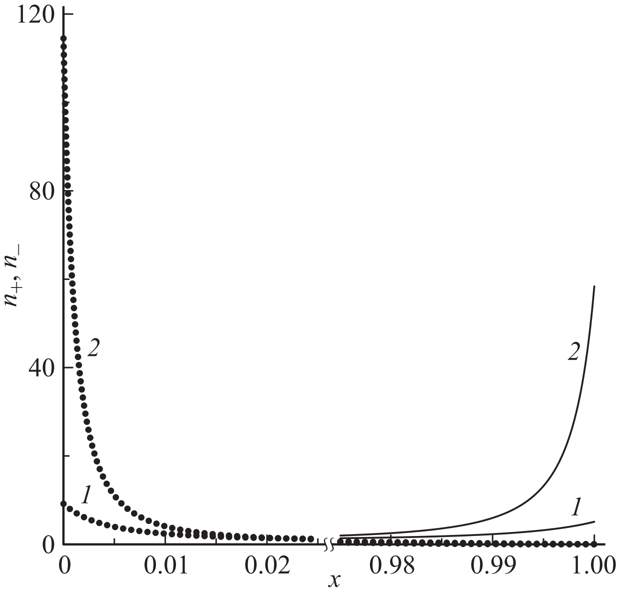

Figure 4. Concentration profiles of positive (solid line) and negative (dots) ions at $h = 0.001$ m, $\overline{n}_0 = 10^{17}$ m^{-3}: *1* — $\varphi_0 = 0.3$ V, *2* — $\varphi_0 = 0.8$ V.

negative ions are equal (curves *1* and *2*, Fig. 5,*a*). With moderate potential differences, the width of this area is comparable to the distance between the electrodes.

Further increase of φ_0 strongly deforms all profiles. The slope of the linear section in the profiles of ion concentrations increases. At the same time, the size of the boundary layer near the anode is also growing. Gradually, this leads to the fact that the area where the ion concentrations are equal narrows.

In the end, the width of this region takes on extremely small values, and the equality of ion concentrations occurs only at one point (curves *3* and *4*, Fig. 5,*a*). A significant part of the liquid becomes depleted by this point. A decrease in ion concentrations in the volume of the dielectric inevitably leads to a decrease in the intensity of recombination, which is why the concentration of ion pairs also gradually decreases (Fig. 5,*b*). Nevertheless, it can be seen from the presented profiles that there is no complete purification of the bulk part of the carrier liquid from ion vapors.

An increase in φ_0 also leads to strong changes in the electric field. An analysis of the profiles of electrical potential and voltage (Fig. 6) allows explaining the change in the nature of conductivity. So, for small φ_0, i.e., in the case when electrical conductivity is provided mainly by electrodiffusion processes in the boundary layers, the generated electric field, leading to the appearance of a through-current between the electrodes, has a relatively low voltage. The width of the region in which the ion concentrations are equal coincides with the width of the characteristic well in the electric field strength profile. This region can be called the stagnation region, since it is in it that the rate of ion electromigration is low compared to the same rate in the boundary layers of the electrodes. The probability of recombination of ions trapped in the stagnation region is high, which is why they do not have time to approach the electrodes.

An increase in the potential difference maintained at the electrodes leads to a qualitative change in the profiles. The area of equal concentrations is reduced, and now ions are less likely to recombine during migration from one electrode to another. In other words, a through-current appears in

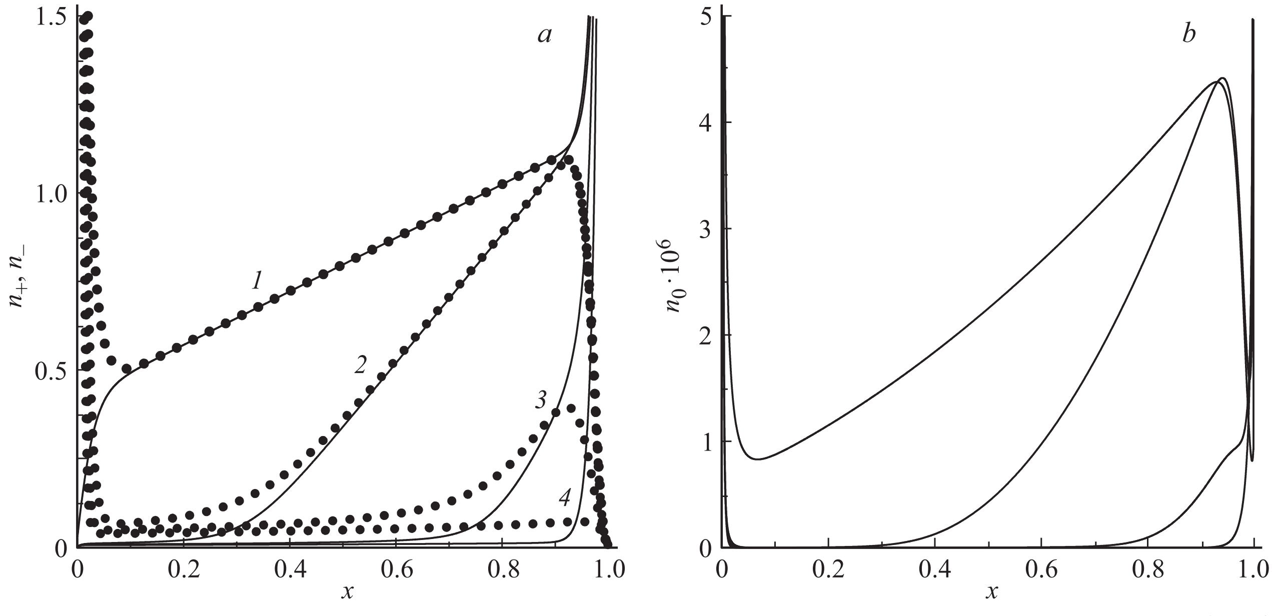

Figure 5. Concentration profiles of positive (solid line), negative (dots) ions (*a*) and ion pairs (*b*) at $h = 0.001$ m, $\overline{n}_0 = 10^{17}$ m^{-3}. φ_0: *1* — 0.8, *2* — 2.5, *3* — 7, *4* — 12 V.

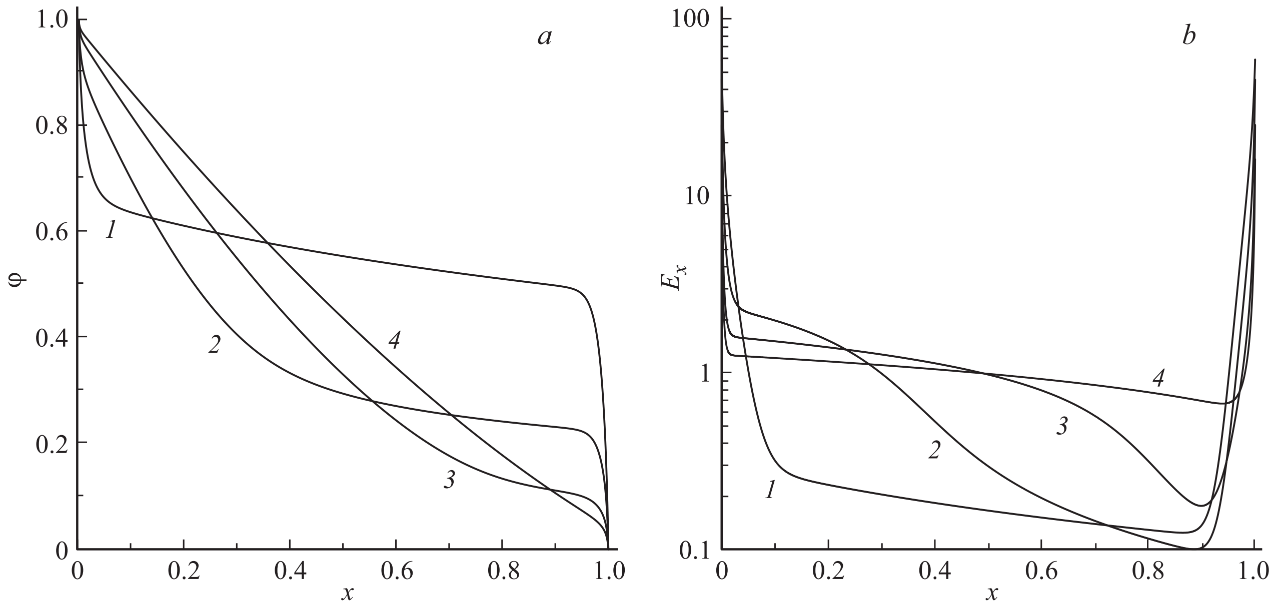

Figure 6. The electric potential profiles (*a*) and x are the components of the electric field strength (*b*) at $h = 0.001\,\mathrm{m}$, $\overline{n}_0 = 10^{17}\,\mathrm{m}^{-3}$. φ_0: *1* — 0.8, *2* — 2.5, *3* — 7, *4* — 12 V.

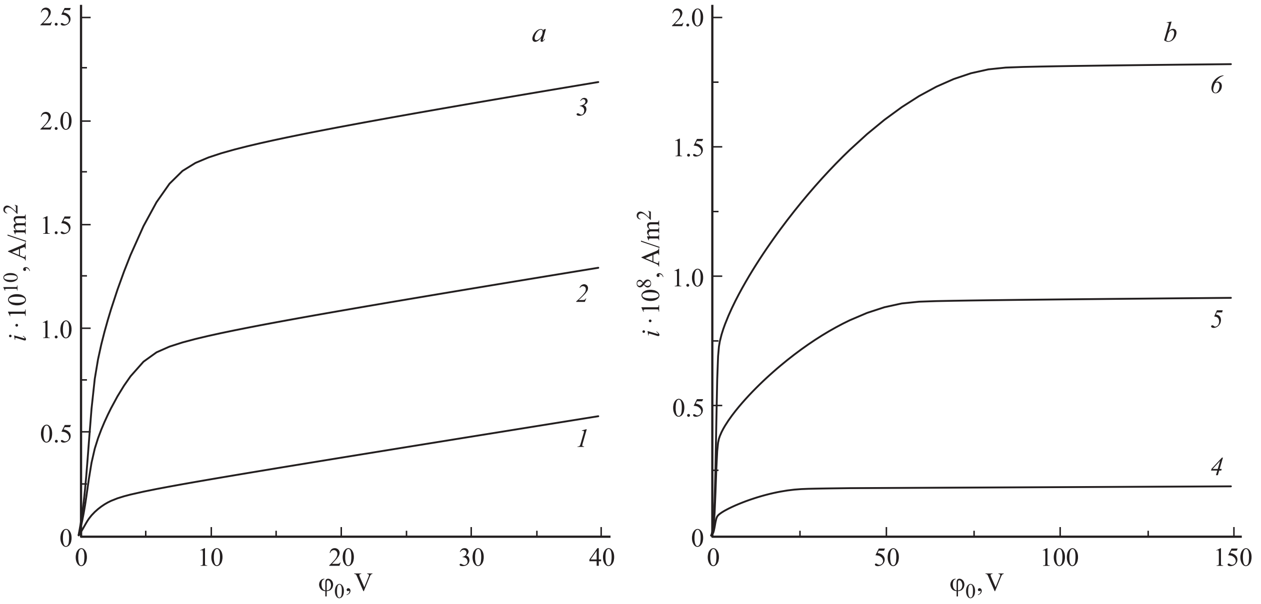

Figure 7. Dimensional VAC at $h = 0.001\,\mathrm{m}$. $\overline{n}_0$: *1* — 10^{16}, *2* — $5 \cdot 10^{16}$, *3* — 10^{17}, *4* — 10^{18}, *5* — $5 \cdot 10^{18}$, *6* — $10^{19}\,\mathrm{m}^{-3}$.

the dielectric in question. It should be noted that in such a situation, the electric field strength in the thin electrode regions reaches sufficiently large values. However, this effect is local in nature and is not able to integrally change the electrical conductivity of the entire array. Thus, the Wien effect is not the „main“ for the system in question, and taking it into account will only slightly adjust the results obtained.

A change in the electrical conductivity regime can also be traced in the VAC, which always leave the origin and demonstrate a linear increase in current strength from voltage in the initial sections (Fig. 7). In the case of $h = 0.001\,\mathrm{m}$, $\overline{n}_0 = 10^{17}\,\mathrm{m}^{-3}$, starting approximately from $\varphi_0 = 1.5\,\mathrm{V}$, non-linearities appear on the VAC. The profile transformations described earlier lead to a more intense increase in current strength than in the linear section with an increase in φ_0. This continues until there is a through current of ions between the electrodes. Its appearance can be traced by the bending of the VAC and the appearance of a new linear section in it, but for large φ_0. It is interesting to note that the angle of inclination of this section coincides with good accuracy with the value of the electrical conductivity σ used in boundary conditions (10), (11).

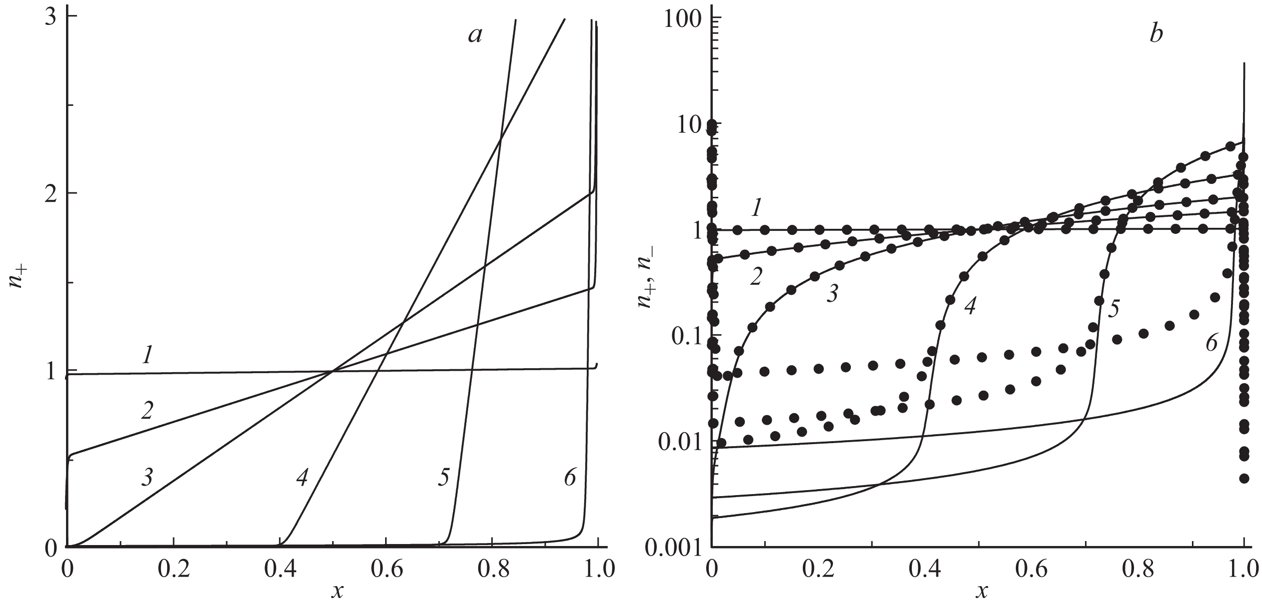

Figure 8. Concentration distributions of positive (solid lines) and negative (dots) ions at $h = 0.01$ m, $\overline{n}_0 = 10^{17}\,\mathrm{m}^{-3}$. φ_0: *1* — 0.01, *2* — 0.3, *3* — 1.25, *4* — 32, *5* — 150, *6* — 800 V.

In Fig. 7, *a*, the final linear sections have the same angle of inclination as in Fig. 7, *b*, however, in the latter case, the slope looks insignificant against the background of an increase in current strength in the initial section. There is a logical consequence of this, i.e. the higher the initial concentration of ion pairs $\overline{n}_0$, the greater the potential of the system for high-intensity current transmission.

This form of the dependence of current strength on voltage qualitatively repeats the one that was obtained in experiments [8]. As mentioned earlier, when the system is reduced, it will approach the maximum current carrying capacity. It can be seen from Fig. 7 that reducing this parameter gradually eliminates all the nonlinearities of the VAC. In the extreme case, the characteristic is transformed into a straight line.

The behavior of the system under study becomes much more complicated as the distance between the electrodes increases. Thus, an increase in h to 0.01 m (Fig. 8) leads to the fact that the linear section in the concentration profiles is much more pronounced at low φ_0. As a result, a stagnation region is formed in almost the entire volume of the dielectric. The initial stages of increasing the potential difference lead to the same effect as at $h = 0.001$ m, namely, an increase in the slope of the concentration profiles and a gradual increase in the thickness of the boundary layer. However, unlike the case discussed earlier, changes in the size of the electrode layers have little effect on the processes occurring in the volume, and linear dependencies in the profiles persist (curves *1–3*, Fig. 8, *a*). Nevertheless, the ion concentration near the anode gradually decreases, and at a certain stage a sharp bend appears in the concentration profiles (curves *4–6*, Fig. 8, *a*). This bend represents the boundary of the stagnation region, the size of which decreases with growth φ_0, and at a certain moment reaches its limit. Thus, electric fields with sufficient intensity appear in the system again to organize end-to-end ion migration.

The VAC for the case $h = 0.01$ m are shown in Fig. 9. The general trend of an initial linear increase in current strength remains, as shown in Fig. 7. However, further bending appears in the characteristic, which, unlike the previous case, slows down the increase in current strength (Fig. 9, *a*). This bend reflects the moment when ion concentrations near the positive electrode reach very small values, and initially linear concentration profiles in the volume of the dielectric become broken (curve *3*, Fig. 8). At this moment, the active diffusion of ion pairs between the electrodes stops, which is why the accumulation of ions in the electrode regions is also inhibited.

This effect is not visible in Fig. 7 due to the fact that the boundary layers have a greater impact on the system with a small scale. As the potential difference increases, the sizes of the near-electrode structures increase, and due to this, a relatively intense diffusion of ion pairs is maintained.

At first glance, after such a transformation of the concentration profiles, the VAC reaches a linear section similar to those shown in Fig. 7. However, a further increase in φ_0 leads to a slow increase in the slope angle in the characteristic (Fig. 9, *b*). In this area, the stagnation region is gradually displaced until, by analogy with Fig. 6, an electric field with sufficient strength to generate a through current is formed everywhere between the electrodes. At this moment, the last linear section appears in the characteristic, the angle of inclination of which is the same as in the case of $h = 0.01$ m, is equal to σ regardless of the values of $\overline{n}_0$.

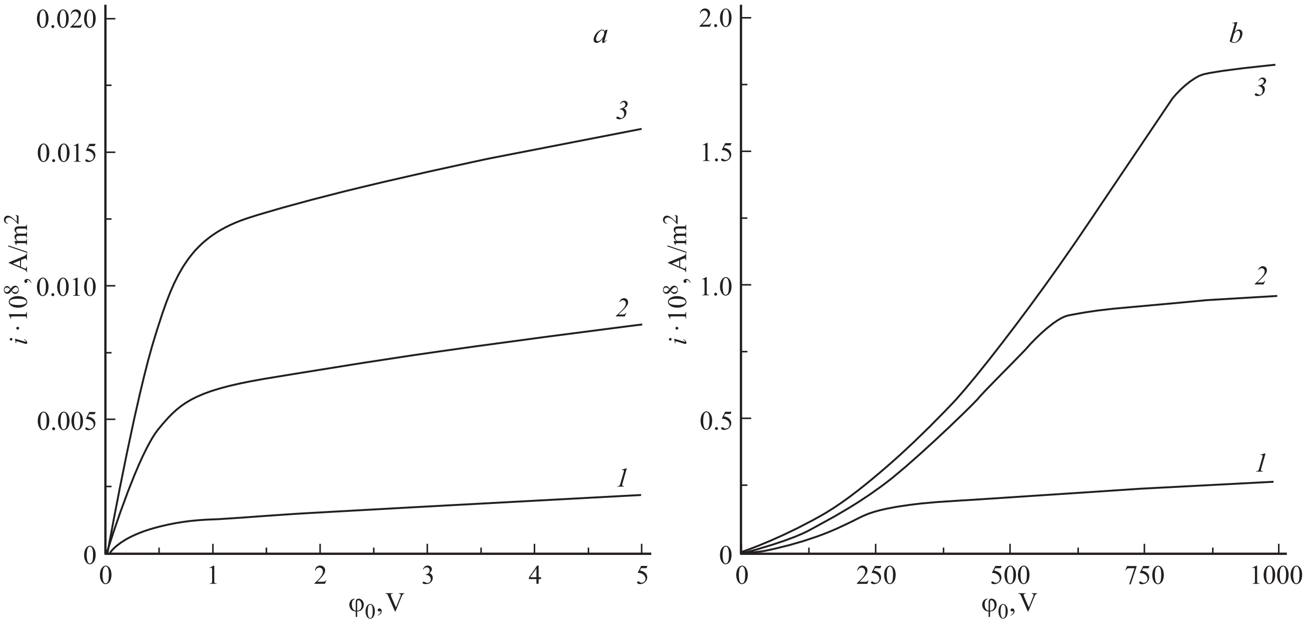

Figure 9. Dimensional VAC at $h = 0.01$ m. $\overline{n}_0$: *1* — 10^{16}, *2* — $5 \cdot 10^{16}$, *3* — 10^{17} m^{-3}.

Thus, as the scale of the problem increases, the shape of the resulting VAC becomes close to that demonstrated in the field of small potential differences in many theoretical and experimental studies of the electrical conductivity of membranes [20–23]. It should be noted that the proposed physico-mathematical model does not take into account convective mass transfer, as a result of which deviations from the linear section with the maximum electrical conductivity [25] should appear at high voltages.

The resulting VAC has many inflection points, but the complex behavior of the system is not related to the fact that there is competition of partial currents due to a complex multicomponent chemical reaction, as indicated by Ref. [9,10]. This is due to the qualitative restructuring of the current formed by a single pair of ions.

Conclusion

The physicomathematical model presented in this paper makes it possible to describe two different modes of electric current passing through a liquid dielectric enclosed between two metal electrodes. The equations used in the model, together with the boundary conditions, make it possible to study the features of diffusion and electromigration during the redox process. Depending on the potential difference maintained on the electrodes, different kinetic modes of electrical conductivity are distinguished, provided either by the development of near-electrode boundary layers due to a decrease in the concentration of ions and ion pairs in the volume of the dielectric, or by a through flow of ions between the electrodes. The VAC obtained from the calculations have a much more complex shape than those usually demonstrated in the study of weakly conductive liquids in a flat gap, which is most likely due to a more complete coverage of the physico-chemical mechanisms involved in redox processes. Based on the shape of these characteristics, a flat layer of a liquid dielectric under the conditions of the redox process resembles an ion-selective membrane to a certain extent in terms of its conductive properties.

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Conflict of interest

The authors declare that they have no conflict of interest.

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