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ИНФОРМАТИКА, ВЫЧИСЛИТЕЛЬНАЯ ТЕХНИКА И УПРАВЛЕНИЕ INFORMATION TECHNOLOGY, COMPUTER SCIENCE, AND MANAGEMENT

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Stationary model of salt ion transfer in two-dimensional electrodialysis desalting channel in galvanostatic mode[*]

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Стационарная модель переноса ионов соли в двумерном электродиализном канале обессоливания в гальваностатическом режиме[***]

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Introduction. The theoretical description of the ion transport in membrane systems in the galvanostatic mode is presented. A desalting channel of the electrodialysis apparatus is considered as a membrane system. The work objectives are the development and verification of a two-dimensional mathematical model of the stationary transport of salt ions in the desalting channel of the electrodialysis apparatus for the galvanostatic mode.

Materials and Methods. A new model of ion transfer is proposed. It is based on the Nernst – Planck – Poisson equations for the electric potential and on the equation for the electric current stream function. A numerical solution to the boundary value model problem by the finite element method is obtained using the Comsol Multiphysics software package.

Research Results. The developed mathematical model enables to describe the stationary transfer of binary salt ions in the desalting channel of the electrodialysis apparatus. Herewith, the violation of the solution electroneutrality and the formation of the dilated domain of space charge at overlimiting currents in the galvanostatic mode are considered. A good agreement between the physicochemical characteristics of the transfer calculated by the models for the galvanostatic and potentiostatic modes implies adequacy of the constructed model.

Discussion and Conclusions. The developed model can interpret the experimental study results of ion transfer in membrane systems if this process takes place in the galvanostatic mode. Some electrokinetic processes are associated with the appearance of a dilated domain of space charge at overlimiting currents. When describing the formation of this domain, it is possible to find out how the processes dependent on it affect the ion transfer in the galvanostatic mode.

Введение. Статья посвящена теоретическому описанию процесса переноса ионов в мембранных системах в гальваностатическом режиме. В качестве мембранной системы рассматривается канал обессоливания электродиализного аппарата. Цели работы: создание и верификация двумерной математической модели стационарного переноса ионов соли в канале обессоливания электродиализного аппарата для гальваностатического режима.

Материалы и методы. Предложена новая модель переноса ионов. Она основана на системе уравнений Нернста — Планка — Пуассона для электрического потенциала и на уравнении для функции электрического тока. Получено численное решение краевой задачи модели методом конечных элементов с помощью программного пакета *Comsol Multiphysics*.

Результаты исследования. Разработанная математическая модель позволяет описать стационарный перенос ионов бинарной соли в канале обессоливания электродиализного аппарата. При этом учитываются нарушение электронейтральности раствора и формирование расширенной области пространственного заряда при сверхпредельных токах в гальваностатическом режиме. Об адекватности построенной модели свидетельствует хорошее совпадение физико-химических характеристик переноса, рассчитанных по моделям для гальваностатического и потенциостатического режимов.

Обсуждение и заключения. Разработанная модель позволяет интерпретировать результаты экспериментальных исследований переноса ионов в мембранных системах, если данный процесс протекает в гальваностатическом режиме. Некоторые электрокинетические процессы связаны с появлением расширенной области пространственного заряда при сверхпредельных токах. Описывая формирование указанной области, можно выяснить, каким образом зависящие от нее процессы влияют на перенос ионов в гальваностатическом режиме.

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Ключевые слова: перенос ионов, ионообменная мембрана, мембранная система, гальваностатический режим, математическая модель, уравнения Нернста — Планка — Пуассона, расширенная область пространственного заряда.

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Introduction. Membrane systems form the basis for electrodialysis machines, nano- and microfluidic devices, which are used in water treatment, agricultural products (milk, wine, etc.) processing, performing chemical analysis, and in other areas of activity [1-4]. In numerous mathematical models of mass transfer processes in membrane systems for potentiostatic or potentiodynamic modes, the electrical mode is defined as a potential jump between two equipotential planes parallel to the membranes. A detailed review of the papers devoted to modeling for the potentiostatic mode is presented in [5–7].

All the while, in the practice of electrodialysis, electrochemical characterization of membranes (chronopotentiometry, impedansometry, etc.), the galvanostatic mode is often used, in which a constant average current density is maintained at the interface. A huge amount of experimental data has been compiled about this mode. They must be interpreted [8–10]. Studies in the mathematical modeling of the galvanostatic mode are conducted in several directions.

The first direction is the inverse problem method. As is clear from the name, this is about solving an inverse problem: for the specified current density at the "solution – membrane" interface, the corresponding potential jump is found, and then the problem for the potentiostatic mode is considered [11]. The low efficiency of this method is due to the fact that its implementation requires multiple solutions to the problem in potentiostatic mode for one given value of current density.

The second direction is the decomposition method. In this case, the system of Nernst – Planck – Poisson equations is replaced by a system of decomposition equations [12–16]. The assumption of a quasi-uniform charge distribution enables to obtain a model for the galvanostatic mode in the approximation of Ohm's law [17–20].

The third approach can be called the direct method. In this case, the equation replacing the Poisson equation is derived for the current density in the desalination channel [21].

The galvanostatic mode can be described differently — by numerical solution to the Nernst – Planck – Poisson equations for an electric potential with a special boundary condition that allows the current density to be set as a parameter specifying the electrical mode in the system. In [22, 23] for the one-dimensional case, the time derivative of the electric potential gradient was determined as an explicit function of the current density. This distinguishes the authors' approaches from potentiostatic models in which the difference of potentials is set.

This paper presents a stationary model of the ion transfer process in membrane systems for the galvanostatic mode. It is based on the Nernst-Planck-Poisson equation system with the boundary condition that enables to establish the current density as a parameter that sets the electric mode in the system. This solution is similar to [22, 23]. The difference is that the proposed model is two-dimensional and considers the variability of the current density along the channel.

Materials and Methods. The desalting channel of the electrodialysis apparatus (EDA) formed by the anion-exchange (AEM) and cation-exchange membranes (CEM), is taken to mean a membrane system. A binary electrolyte solution is pumped through it at V_0 average rate.

In Fig. 1, x is a coordinate normal to the membrane surface varying from 0 (border with AEM) to h (border with CEM); y is a tangential coordinate to the surface of the membrane varying from 0 (channel entrance) to l (channel exit).

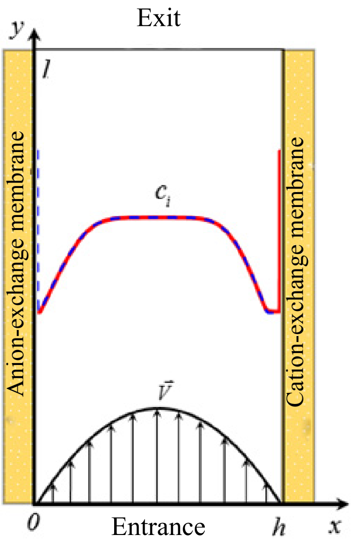


Fig. 1. Scheme of EDA desalination channel. Concentration profiles of C_1 cations (solid line) and C_2 anions (dot line), $\vec{V}$ forced flow rate are shown.

(*System of equations.* Consider a two-dimensional stationary case of the system of equations describing the transfer of a binary electrolyte with no chemical reactions [24]:

$$\vec{j}_i = -\frac{F}{RT} z_i D_i C_i \nabla\phi - D_i \nabla C_i + C_i \vec{V}, \ i = 1, 2, \tag{1}$$

$$-\operatorname{div} \vec{j}_i = 0, \quad i = 1, 2, \tag{2}$$

$$\varepsilon_0 \varepsilon_r \Delta\phi = -F(z_1 C_1 + z_2 C_2), \tag{3}$$

$$\vec{I} = F(z_1 \vec{j}_1 + z_2 \vec{j}_2). \tag{4}$$

Here, $\vec{j}_i$, D_i, z_i and C_i are, respectively, flux, diffusion coefficient, charge number, and molar concentration of the i-th ion; ϕ is electric potential; $\vec{V}$ is flow rate of the electrolyte solution; ε_0 is electric constant; ε_r is relative dielectric constant of the electrolyte solution (assumed to be constant); $\vec{I}$ is current density; F is Faraday constant; R is gas constant; T is absolute temperature; $\vec{j}_1$, $\vec{j}_2$, $\vec{I}$, ϕ, C_1, C_2 are unknown functions of x and y coordinates.

The Nernst – Planck equations (1) describe the ion flux due to electromigration, diffusion, and convection; (2) is the material balance equation in the stationary case; (3) is Poisson's equation for the electric field potential; (4) is current density in the electrolyte solution. We assume that the velocity distribution in the channel corresponds to the Poiseuille flow [24]:

$$V_x = 0, \quad V_y = 6V_0 \frac{x}{h}\left(1 - \frac{x}{h}\right). \tag{5}$$

To determine the unknown functions listed above, it is necessary to set boundary conditions for the system (1) - (3). Let us consider two electrical modes: potentiostatic, when the potential jump at the system boundaries is set constant, and galvanostatic, when the density of the current flowing through the interface is constant.

Boundary conditions for modeling potentiostatic mode. We assume that the surfaces of ion-exchange membranes are equipotential. The system (1) - (4) includes the potential of the electric field only in the form of derivatives with respect to the spatial coordinate. In this case, only $\tilde{\Delta\phi} = \phi(h, y) - \phi(0, y)$ potential jump is significant, where $\tilde{\Delta\phi}$ is a known function, so we set, for example:

$$\phi(0, y) = 0. \tag{6}$$

Then

$$\Delta\tilde{\phi} = const. \tag{7}$$

The conditions (6) and (7) determine the potentiostatic mode. Other boundary conditions are given below.

At the "AEM - solution" interface (x = 0), the concentration of coions (cations) is determined from the condition of continuity of their flow at the "membrane – solution" boundary considering the selective AEM properties [16]:.

$$\left(\frac{\partial C_1}{\partial x} + \frac{F}{RT} z_1 C_1 \frac{\partial \phi}{\partial x}\right)(0, y) = \frac{(1 - T_2) I_x(0, y)}{z_1 F D_1}, \tag{8}$$

where T_i ($i = 1, 2$) are effective numbers of transfer of counterions in the membrane (CEM and AEM, respectively); T_i are numbers close to 1, and also for $T_i = 1$ ideally selective membrane, and the condition (8) turns into the condition of membrane impermeability for coions.

The concentration of counterions (anions) depends on the exchange capacity of the CEM, which can be specified as:

$$C_2\left(0,y\right) = C_{2m} = N_a C_0 . \tag{9}$$

Here, N_a constant shows how many times this concentration differs from the concentration in the volume of the solution [25].

At the "solution - CEM" ($x = h$) interface for ion concentrations, the conditions similar to those at the "AOM - solution" ($x = 0$) border, are accepted:

$$C_1\left(h,y\right) = C_{1m} = N_c C_0 , \tag{10}$$

$$\left(\frac{\partial C_2}{\partial x} + \frac{F}{RT} z_2 C_2 \frac{\partial \phi}{\partial x}\right)\left(h,y\right) = \frac{\left(1-T_1\right) I_x(h,y)}{z_2 F D_2}. \tag{11}$$

At the channel entrance ($y = 0$) a uniform distribution of ion concentrations is assumed:

$$C_i\left(x,0\right) = C_0, \quad i = 1,2. \tag{12}$$

The condition for the potential of the electric field is obtained from the equations (1) and (4) considering the absence of current flow through I_x input (x, 0, t) = 0:

$$\frac{\partial \phi(x,0)}{\partial y} = -\frac{RT}{F(z_1^2 D_1 + z_2^2 D_2) C_0}\left(z_1 D_1 \frac{\partial C_1(x,0)}{\partial y} + z_2 D_2 \frac{\partial C_2(x,0)}{\partial y}\right). \tag{13}$$

At the channel exit ($y = l$), ions are freely carried by the solution flow:

$$(\vec{n}, \vec{j}_i) = (\vec{n}, -\frac{F}{RT} z_i D_i\, C_i \nabla\phi - D_i \nabla C_i + C_i \vec{V}) = C_i V_y , \ i = 1, 2 . \tag{14}$$

The system (14) also means that the sum of the diffusion and migration tangential components of the anions and cations flow is equal to 0:

$$\left(-\frac{\partial C_i}{\partial y} - \frac{F}{RT} z_i C_i \frac{\partial \phi}{\partial y}\right)\left(x,l\right) = 0, i = 1,2 . \tag{15}$$

A "soft" condition is accepted for the potential, meaning that there are no sharp changes in the potential at the channel exit:

$$\frac{\partial \phi}{\partial y}\left(x,l\right) = 0. \tag{16}$$

The boundary problem, which includes equations (1) - (4) and boundary conditions (6) - (16), simulates the potentiostatic mode, and its control key condition is (7).

Boundary conditions for simulating the galvanostatic mode. Under the simulation of the galvanostatic mode, the condition (6) remains, and (7) should be replaced by the condition related to the specified value of i_{av} average current density at the "solution – CEM" interface ($x = h$).

To derive such a boundary condition, we substitute the relations (1) into (4) and express the gradient of the electric field potential:

$$\nabla\phi = -\frac{RT}{F^2(z_1^2 D_1 C_1 + z_2^2 D_2 C_2)}(\vec{I} + F(z_1 D_1 \nabla C_1 + z_2 D_2 \nabla C_2) - F(z_1 C_1 + z_2 C_2)\vec{V}). \tag{17}$$

Assuming $x = h$ in (17), we obtain the relation that connects the gradient of the electric potential with the given value of the current density at the boundary, that is, the boundary condition at the "solution – CEM" interface:

$$\frac{\partial \phi}{\partial x}\left(h,y\right) = -\frac{RT}{F^2}\left(\frac{I_x + F z_1 D_1 \dfrac{\partial C_1}{\partial x} + F z_2 D_2 \dfrac{\partial C_2}{\partial x}}{z_1^2 D_1 C_1 + z_2^2 D_2 C_2}\right)\left(h,y\right). \tag{18}$$

In this case, I_x current density must satisfy the condition:

$$\frac{1}{l}\int_0^l I_x(h,y)dy = i_{av}. \tag{19}$$

The mathematical model of the galvanostatic mode consists of the system of equations (1) - (4). The boundary conditions (18) and (19) replace the condition (7). The other boundary conditions coincide with those for the potentiostatic mode.

The potential jump in the galvanostatic mode is a calculated value.

Transformation of the boundary conditions for simulating the galvanostatic mode. The condition (19) is inconvenient for a numerical solution, since it contains an integral. One of this condition conversion options is given below.

In the stationary case, the current density is a solenoidal vector. Indeed, if we multiply (2) by z_i and sum up, then $\operatorname{div}\vec{I} = 0$. Consequently, there is such η function that

$$\frac{\partial \eta}{\partial x} = I_y, \qquad \frac{\partial \eta}{\partial y} = -I_x . \tag{20}$$

Using η function, the conditions (18) and (19) are rewritten as follows:

$$\frac{\partial \varphi}{\partial x}(h,y) = -\frac{RT}{F^2}\left(\frac{-\dfrac{\partial \eta}{\partial y} + Fz_1D_1\dfrac{\partial C_1}{\partial x} + Fz_2D_2\dfrac{\partial C_2}{\partial x}}{z_1^2D_1C_1 + z_2^2D_2C_2}\right)(h,y), \tag{21}$$

$$\frac{1}{l}\int_0^l I_x(h,y)\,dy = -\frac{1}{l}\int_0^l \frac{\partial \eta}{\partial y}(h,y)\,dy = -\frac{1}{l}(\eta(h,l) - \eta(h,0)) = i_{av} . \tag{22}$$

The equation (22) can be rewritten as:

$$\eta(h,l) - \eta(h,0) = -i_{av}l . \tag{23}$$

To close the expression system, it is necessary to obtain an equation for η function. To this end, as in [15, 16], we inject a linear differential operator, which is a vortex function (rotor) in the two-dimensional case, for $\vec{W}$ arbitrary two-dimensional vector:

$$r(\vec{W}) = \left(\frac{\partial W_y}{\partial x} - \frac{\partial W_x}{\partial y}\right). \tag{24}$$

It is easy to check that:

1) $r(\nabla u) = 0$ for any u smooth function;

2) $r(u\vec{W}) = (\nabla u, \vec{W})_1 + ur(\vec{W})$ for any u smooth function and any $\vec{W}$ smooth vector.

Here, $(\nabla u, \vec{W})_1 = \frac{\partial u}{\partial x}W_y - \frac{\partial u}{\partial y}W_x$ is skew-symmetric scalar product of ∇u and $\vec{W}$ vectors, moreover, $(\vec{a}, \vec{a})_1 = 0$ is for any $\vec{a}$ vector.

Applying (24) to the equation for current density (4), we obtain:

$$r(\vec{I}) = Fz_1r(\vec{j}_1) + Fz_2r(\vec{j}_2). \tag{25}$$

Using the formula of flows (1), we obtain the ratio:

$$r(\vec{j}_i) = -\frac{F}{RT}z_iD_ir(C_i\nabla\phi) - D_ir(\nabla\, C_i) + r(C_i\vec{V}), \qquad i = 1,2 . \tag{26}$$

Hence, considering the properties of r operator:

$$r(\vec{j}_i) = -\frac{F}{RT}z_iD_i\left(\nabla C_i, \nabla\phi\right)_1 + \left(\nabla C_i, \vec{V}\right)_1 + C_ir(\vec{V}),\ i = 1,2 . \tag{27}$$

Considering (27) and $r(\vec{I}) = \frac{\partial I_y}{\partial x} - \frac{\partial I_x}{\partial y} = \Delta\eta$, the equation (25) can be written as:

$$\begin{gathered}\Delta\eta = -\frac{F^2}{RT}\cdot\left(\left(z_1^2D_1\frac{\partial c_1}{\partial x} + z_2^2D_2\frac{\partial c_2}{\partial x}\right)\frac{\partial \varphi}{\partial y} - \left(z_1^2D_1\frac{\partial c_1}{\partial y} + z_2^2D_2\frac{\partial c_2}{\partial y}\right)\frac{\partial \varphi}{\partial x}\right) + \\ + F\left(z_1\frac{\partial c_1}{\partial x} + z_2\frac{\partial c_2}{\partial x}\right)V_y - F\left(z_1\frac{\partial c_1}{\partial y} + z_2\frac{\partial c_2}{\partial y}\right)V_x + F\left(z_1c_1 + z_2c_2\right)\left(\frac{\partial V_y}{\partial x} - \frac{\partial V_x}{\partial y}\right).\end{gathered} \tag{28}$$

It follows from (28) and (20) that η function is determined up to a constant, therefore we can assume:

$$\eta(h,0) = 0 . \tag{29}$$

Then we obtain from (23)

$$\eta(h,l) = -i_{\text{av}} l\ . \tag{30}$$

The conditions (29) and (30) are boundary for η function.

Mathematical model for the galvanostatic mode in a dimensionless form. For a numerical study of boundary value problems, it is convenient to go to a dimensionless form. So we can simplify the equations and find out the actual number and set of parameters that determine the system behavior. Dimensionless variables describe a class of similar processes characterized by the same value of dimensionless numbers.

Characteristic values describing the problem. When simulating mass transfer processes in the EDA desalination chamber, a number of characteristic values are taken:

- for spatial coordinates – h intermembrane distance;
- for ion concentrations – C_0 volume concentration of the electrolyte;
- for speed – V_0 average speed of the forced flow;
- for diffusion coefficients – $D = D_1 D_2 (z_1 - z_2)/(D_1 z_1 - D_2 z_2)$ diffusion coefficient of the electrolyte;
- for electric potential – $\varphi_0 = RT/F$ thermal potential;
- for current density – $i_0 = FDC_0/h$ value (analogue of the limiting density of diffusion current);
- for ion flow – $j_0 = DC_0/h$ diffusion flow.

Transition formulas. We translate the equations into a dimensionless form through the following relations ((u) index denotes the dimensionless variants of quantities):

$$\begin{gathered} x^{(u)} = \frac{x}{h},\quad y^{(u)} = \frac{y}{h},\quad l^{(u)} = \frac{l}{h},\quad \vec{V}^{(u)} = \frac{\vec{V}}{V_0},\quad C_i^{(u)} = \frac{C_i}{C_0}, i = 1, 2, \\ \phi^{(u)} = \frac{\phi}{\phi_0},\quad \vec{I}^{(u)} = \frac{1}{i_0}\vec{I}, \eta^{(u)} = \frac{\eta}{FDC_0},\quad \vec{j}_i^{(u)} = \frac{1}{j_0}\vec{j}_i, i = 1, 2,\quad D_i^{(u)} = \frac{D_i}{D}. \end{gathered} \tag{31}$$

The system of equations in a dimensionless form has the form ((u) index is omitted for simplicity):

$$\vec{j}_i = -z_i D_i C_i \nabla\phi - D_i \nabla C_i + PeC_i\vec{V},\ i = 1, 2\ , \tag{32}$$

$$-\operatorname{div}\vec{j}_i = 0,\quad i = 1, 2\ , \tag{33}$$

$$\varepsilon\Delta\phi = -(z_1 C_1 + z_2 C_2)\ , \tag{34}$$

$$\begin{gathered} \Delta\eta = -\left(\left(z_1^2 D_1 \frac{\partial c_1}{\partial x} + z_2^2 D_2 \frac{\partial c_2}{\partial x}\right)\frac{\partial\phi}{\partial y} - \left(z_1^2 D_1 \frac{\partial c_1}{\partial y} + z_2^2 D_2 \frac{\partial c_2}{\partial y}\right)\frac{\partial\phi}{\partial x}\right) + \\ + Pe\left(z_1 \frac{\partial c_1}{\partial x} + z_2 \frac{\partial c_2}{\partial x}\right)V_y - Pe\left(z_1 \frac{\partial c_1}{\partial y} + z_2 \frac{\partial c_2}{\partial y}\right)V_x + Pe\left(z_1 c_1 + z_2 c_2\right)\left(\frac{\partial V_y}{\partial x} - \frac{\partial V_x}{\partial y}\right), \end{gathered} \tag{35}$$

$$\vec{I} = z_1\vec{j}_1 + z_2\vec{j}_2\ . \tag{36}$$

The system of equations (29) - (35) contains two dimensionless numbers: the Peclet number $Pe = V_0 h/D$ and $\varepsilon = \varepsilon_r \varepsilon_0 RT/(C_0 h^2 F^2)$. The physical meaning of ε parameter is that it is double square of dimensionless Debye length - l_D: $\varepsilon = 2\left(l_D/h\right)^2$ [5].

Estimation of the parameter values shows that under natural conditions for electrodialysis, the Peclet number has $10^2 - 10^6$ order, ε number has $10^{-13} - 10^{-7}$ order, that is, it can be considered a small parameter.

For computational convenience, we transform the system of equations through plugging the flux density (32) in the equations (33) and (36):

$$div\left(-z_i D_i C_i \nabla\varphi - D_i \nabla C_i + PeC_i\vec{V}\right) = 0,\quad i = 1, 2\ , \tag{37}$$

$$\vec{I} = \sum_{i=1}^{2} z_i\left(-z_i D_i C_i \nabla\phi - D_i \nabla C_i + PeC_i\vec{V}\right). \tag{38}$$

Thus, the system of equations contains the following unknown x, y functions: C_1, C_2, ϕ, I_x, I_y. The fields of C_1, C_2 concentrations and φ potential are determined by solution to the equations (37), (34), respectively. I_x, I_y current density components are calculated using (38). Speed distribution (5) in dimensionless form:

$$V_x = 0,\quad V_y = 6x\left(1 - x\right). \tag{39}$$

The presence of ε small parameter in the Poisson equation (34) means that the boundary problem is singularly perturbed. This significantly complicates its numerical solution, since such problems are stiff [26]. φ potential of the electric field and C_1, C_2 ion concentrations change very quickly in a narrow boundary layer whose thickness is equal to l_D Debye length [5].

To solve this problem, it is advisable to compact the computational grid in the boundary layer and use special methods for solving stiff problems [26].

Boundary conditions in dimensionless form. At the "AEM – solution" interface (x = 0):

$$\left(\frac{\partial C_1}{\partial x}+z_1 C_1\frac{\partial \phi}{\partial x}\right)(0,y)=\frac{(1-T_2)\,I_x(0,y)}{z_1 D_1}, \tag{40}$$

$$C_2(0,y)=N_{\mathrm{a}}, \tag{41}$$

$$\phi(0,y)=0, \tag{42}$$

$$\frac{\partial \eta}{\partial x}(0,y)=0. \tag{43}$$

At the "solution – CEM" interface (x = 1):

$$C_1(1,y)=N_{\mathrm{c}}, \tag{44}$$

$$\left(\frac{\partial C_2}{\partial x}+z_2 C_2\frac{\partial \phi}{\partial x}\right)(1,y)=\frac{(1-T_1)\,I_x(1,y)}{z_2 D_2}, \tag{45}$$

$$\frac{\partial \phi}{\partial x}(1,y)=-\left(\frac{-\dfrac{\partial \eta}{\partial y}+z_1 D_1\dfrac{\partial C_1}{\partial x}+z_2 D_2\dfrac{\partial C_2}{\partial x}}{z_1^2 D_1 C_1+z_2^2 D_2 C_2}\right)(1,y), \tag{46}$$

$$\frac{\partial \eta}{\partial x}(1,y)=0. \tag{47}$$

At the channel entrance (y = 0):

$$C_i(x,0)=1,\quad i=1,2, \tag{48}$$

$$\frac{\partial \phi(x,0)}{\partial y}=-\frac{1}{z_1^2 D_1+z_2^2 D_2}\left(z_1 D_1\frac{\partial C_1}{\partial y}+z_2 D_2\frac{\partial C_2}{\partial y}\right)(x,0), \tag{49}$$

$$\eta(x,0)=0. \tag{50}$$

At the channel exit ($y = l$):

$$\left(-\frac{\partial C_i}{\partial y}-z_i C_i\frac{\partial \phi}{\partial y}\right)(x,l)=0,\ i=1,2, \tag{51}$$

$$\frac{\partial \phi}{\partial y}(x,l)=0, \tag{52}$$

$$\eta(x,l)=-i_{av}l\,,\ i_{av}=const\,. \tag{53}$$

After numerical calculation of the system (34), (35), (37) - (53), $\tilde{\Delta}\varphi$ potential jump in the desalination channel is determined by the formula:

$$\tilde{\Delta}\varphi=\frac{1}{l}\int_0^l \varphi(1,y)\,dy\,. \tag{54}$$

The numerical solution is found by the finite element method using the Comsol Multiphysics package on an uneven computational grid (the density of grid elements is increased at the "solution – membrane" boundaries) [27].

Research Results. The calculations are performed for $\varepsilon=1{,}9\cdot 10^{-9}$, $Pe=2355$, which corresponds to the following values of the system parameters:

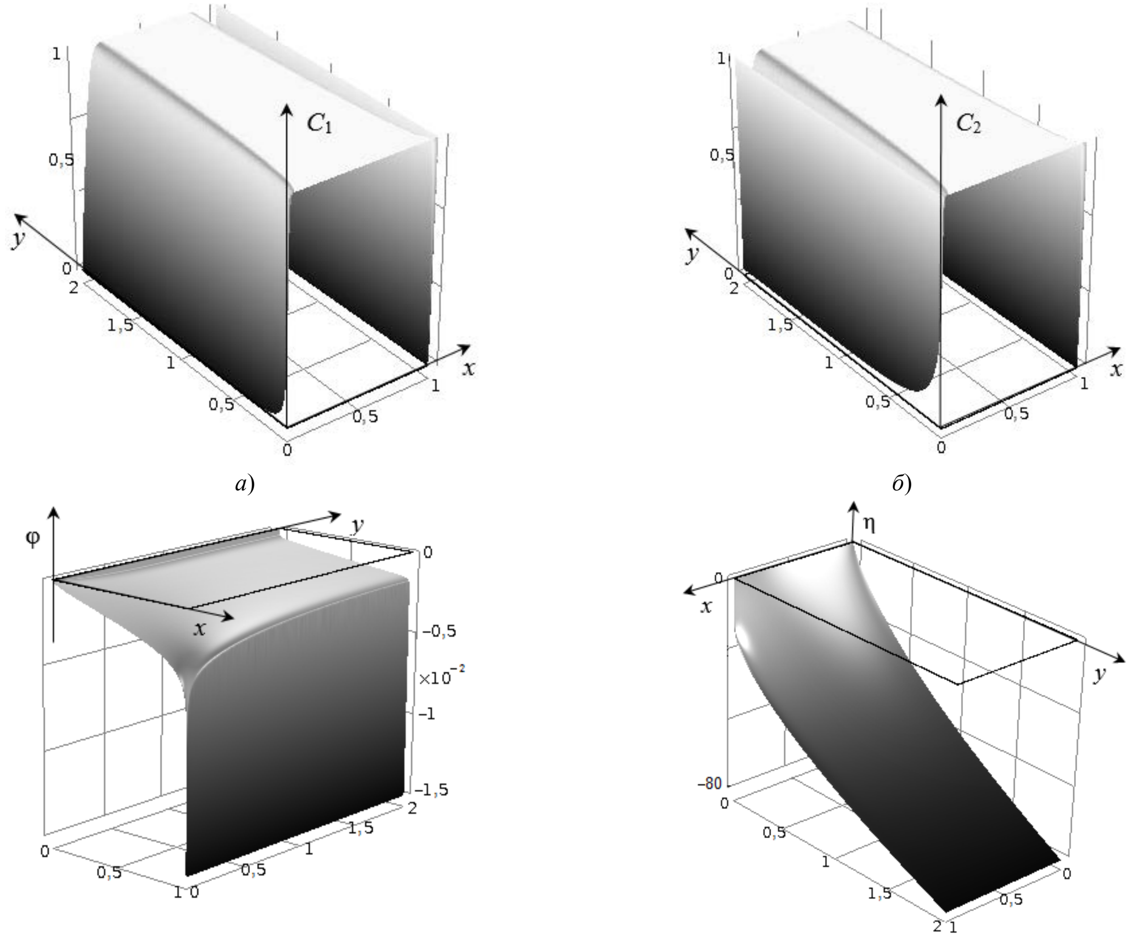
- input concentration of the electrolyte solution of NaCl: C_0 = 0.1 mol/m^3;
- temperature: T = 298 K;
- diffusion coefficients of cations and anions, respectively: D_1 = 1.33·10^{-9} m^2/s, D_2 = 2.05 · 10^{-9} m^2/s;
- numbers of counterions transfer in the membranes: T_1 = 0.972, T_2 = 1;
- ion charge numbers: z_1 = 1, z_2 = –1;
- ratio of the counterions concentration at the boundary with the membranes to its value at the channel entrance: $N_c = N_a = 1$;

- channel width: $h = 10^{-3}$ m;
- channel length: $l = 2 \cdot 10^{-3}$ m;
- rate of the solution pumping: $V_0 = 3{,}8 \cdot 10^{-3}$ m/s.

Fig. 2 shows the fields of C_1 и C_2 concentrations, φ potential and η functions calculated at $i_{av} = 1{,}5 i_{lim}$ current density, where i_{lim} is the limiting current density determined by the Leveque formula (in dimensionless form) [28]:

$$i_{\lim} = \frac{1}{T_1 - t_1}\left(1{,}47\left(\frac{h^2 V_0}{lD}\right)^{1/3} - 0{,}2\right). \tag{55}$$

Here, t_1 = 0.395 is kation transport number in the solution [9].



а)

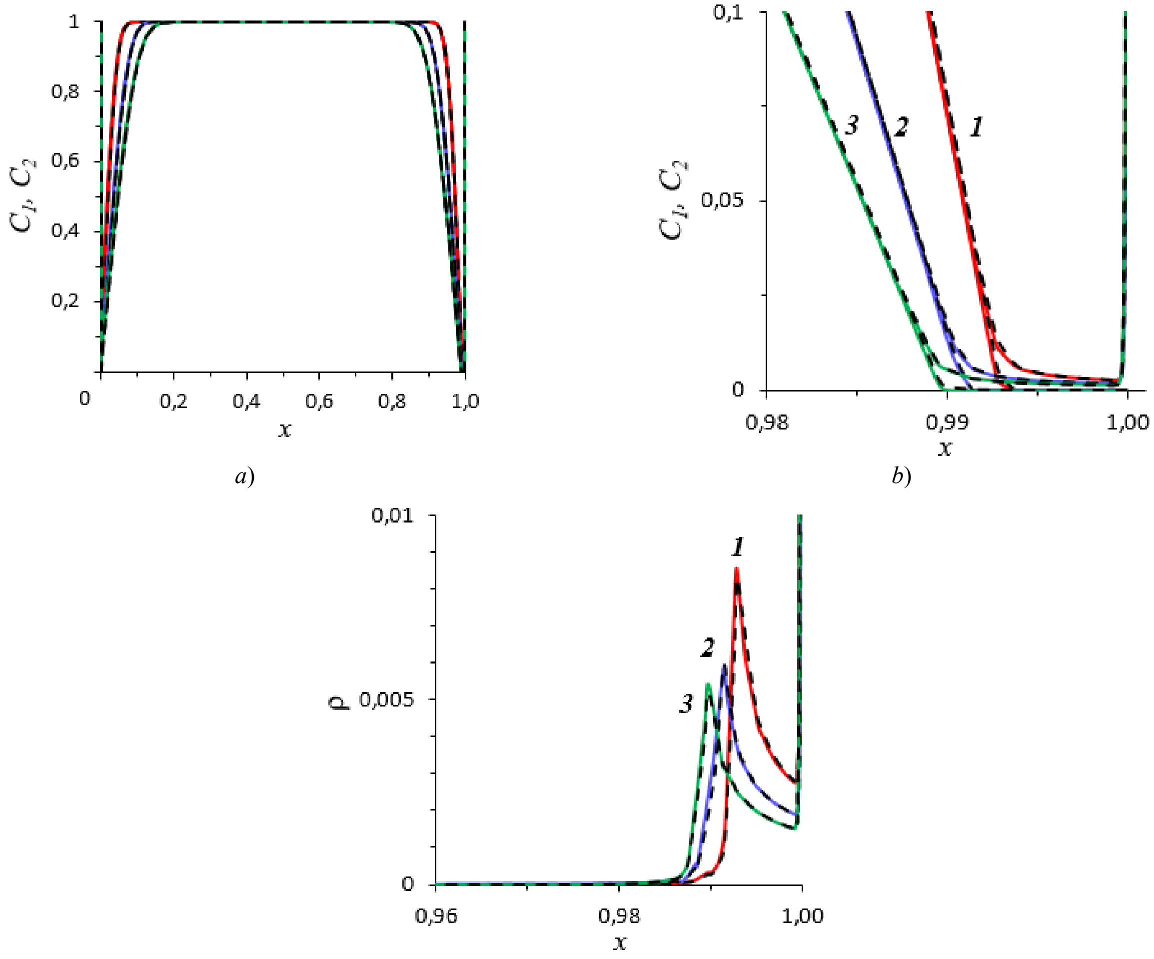
б)

в)

г)

Fig. 2. Concentration fields of cations C_1 (*a*) and anions C_2 (*b*), φ potential (*c*) and η function (*d*). Model calculation for galvanostatic mode at $i_{\text{av}} = 1.5\, i_{\lim}$ current density.

The forced flow acts in the channel, therefore in the areas near the membranes, the depletion of the ion concentration increases with distance from the channel entrance (along the direction tangential to the membrane surfaces). Accordingly, the thickness of the expanded space-charge region increases along the channel (Fig. 3).



a)

b)

c)

Fig. 3. Results of numerical calculation based on the model for galvanostatic (solid lines) and potentiostatic (dot lines) modes at $i_{av} = 1{,}5 i_{\lim}$ current density in cross sections $y = 0{,}1l$ (1), $y = 0{,}4l$ (2), $y = 0{,}9l$ (3): C_1 and C_2 concentration profiles (*a*); enlarged fragment of fig. 3, a (*b*); $\rho = z_1 C_1 + z_2 C_2$ space charge density (*c*)

The volt-ampere characteristic (VAC, curve 1 in Fig. 4) is calculated on the basis of the galvanostatic model. In this case, the specified current density changed: i_{av} = 0; 0,005i_{lim}; …; 1,5i_{lim}.

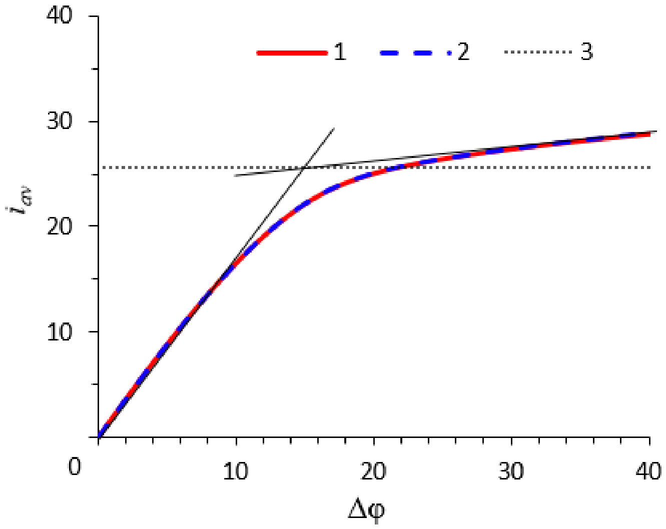


Fig. 4. VACs calculated on the models for galvanostatic (1) and potentiostatic (2) modes; $i_{\lim}$ limiting current density (3) determined by formula (55)

The limiting current density is determined by the point of intersection of the tangents to the VAC in the initial part and on the inclined plateau [5]. Here it coincides with i_{lim} value estimated using the approximate Leveque formula

(55). Besides, the VAC was calculated on the basis of the potentiostatic model under a change in the potential jump $\Delta\varphi = 0; 0.4; ...; 40$ (curve 2 in Fig. 4). As Fig. 4 shows, VAC 1 and 2 are congruent. Thus, there is a unique correspondence to each potential jump of a certain current density, and vice versa.

Fig. 3 and 4 demonstrate a fairly good agreement of various physicochemical transport characteristics calculated on the models for galvanostatic and potentiostatic modes. This proves the adequacy of the model of the transport in galvanostatic mode built by the authors.

The computational costs of the proposed model were estimated as follows. The time spent on solving boundary value problems for the galvanostatic and potentiostatic modes was recorded. Herewith, the specified accuracy values of the calculations and the system parameters were the same, and $i_{av} = 1{,}5\, i_{\lim}$. Then time indicators were compared. Thus, it has been found that the calculation on the galvanostatic model requires 1.6 times more time. This is due to the fact that:

- galvanostatic model contains an additional equation for determining the current density distribution;
- for the potential at $x = 1$boundary, the condition of the second kind (46) is established.

Complex potential of the electro-membrane system for the galvanostatic mode. In [25], a generalization of the impedance of an electrochemical system using η function introduced under the electroneutrality conditions was proposed. A similar generalization is acceptable in this case. Note that when using electrochemical impedance, an object is considered only as a “black box”, and its intrinsic properties are determined indirectly. The results obtained above enable to introduce the concept of a complex potential of the electro-membrane system: $P = \phi + i \cdot \eta$. Complex potential is a coordinate function of any point inside the object, therefore, unlike the electrochemical impedance, it allows us to explore the intrinsic properties of the object.

Discussion and Conclusions. A new technique of mathematical simulation of the stationary process of mass transfer in the galvanostatic mode for membrane systems is described. In this case, the two-dimensional case is considered with the use of a special boundary condition that enables to specify current density in the system. The equations for the current electric function are presented. The numerical solution results for potentiostatic and galvanostatic models are in good agreement. This shows the adequacy of the proposed transport model in the galvanostatic mode.

The developed model makes it possible to interpret the experimental studies results of the ion transfer in membrane systems if this process proceeds in the galvanostatic mode. Some electrokinetic processes are associated with the appearance of a dilated space-charge region under over-limiting currents. The description of the formation of this region allows us to find out how the processes dependent on it affect the ion transfer in the galvanostatic mode.

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