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Modeling and numerical analysis of the effect of dissociation/recombination of water molecules on the transport of salt ions in diffusion layer*

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Моделирование и численный анализ влияния реакции диссоциации (рекомбинации) молекул воды на перенос ионов соли в диффузионном слое***

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Introduction. The paper presents a theoretical study on binary salt ion transport considering the water dissociation/recombination reaction. The work objectives are as follows: to build a mathematical model; to develop an algorithm for the numerical solution to the boundary value problem corresponding to the mathematical model; to work out the similarity theory including the transition to a dimensionless form using characteristic quantities; to determine a physical meaning of trivial similarity criteria; to find nontrivial similarity criteria; to build and analyze the volt-ampere characteristic (VAC).

Materials and Methods. The theoretical study and numerical analysis of the transport of binary salt ions consider the dissociation/recombination reaction of water. In this case, the heat transfer equation and the mathematical model of electrodiffusion of four types of ions simultaneously (two salt ions, as well as H^+ and OH^- ions) in the diffusion layer of electromembrane systems with a perfectly selective membrane are used. For the first-order differential equations, a singularly perturbed boundary-value problem is set. In the equation for the electric field, the right side is independent of the intensity. In the numerical solution to the digitized system of equations by the Newton-Kantorovich method, this causes the stability of the method. In this regard, the boundary-value problem is reduced for numerical solution: a transition to a system of the second-order equations is provided, and the missing boundary

Введение. Статья посвящена теоретическому изучению переноса ионов бинарной соли с учетом реакции диссоциации (рекомбинации) воды. Цели исследования: построение математической модели; разработка алгоритма численного решения краевой задачи, соответствующей математической модели; развитие теории подобия, включая переход к безразмерному виду с использованием характерных величин; определение физического смысла тривиальных критериев подобия; нахождение нетривиальных критериев подобия; построение и анализ вольтамперной характеристики (ВАХ).

Материалы и методы. При теоретическом исследовании и численном анализе переноса ионов бинарной соли учитывается реакция диссоциации (рекомбинации) воды. При этом используются уравнение теплопроводности и математическая модель электродиффузии одновременно четырех видов ионов (двух ионов соли, а также ионов H^+ и OH^-) в диффузионном слое электромембранных систем с идеально селективной мембраной.

Для дифференциальных уравнений первого порядка ставится сингулярно возмущенная краевая задача. В уравнении для напряженности электрического поля правая часть не зависит от напряженности. При численном решении дискретизированной системы уравнений методом Ньютона — Канторовича это обуславливает проблемы устойчивости метода. В связи с этим краевая задача приводится к виду, удобному для численного решения: обеспечивается переход к системе уравнений второго порядка, рассчитыв-



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conditions for the electric field strength are calculated.

Research Results. A new mathematical model, a numerical algorithm to solve a boundary value problem, and software are developed. A numerical analysis is carried out, and fundamental laws of the transport of salt ions are determined considering the dissociation/recombination reaction of water molecules, temperature effects, and Joule heating. The VAC is built and analyzed.

Discussion and Conclusions. The transport of binary salt ions through a diffusion layer near a cation exchange membrane is considered. A mathematical model of this process is proposed. It takes into account the temperature effects due to dissociation/recombination reactions of water molecules and Joule heating in a solution. The basic laws of the transport of salt ions are established considering the dissociation/recombination reaction of water molecules and temperature effects. The temperature effects of the dissociation/recombination reaction and the Joule heating in the electroneutrality region (ENR) are almost imperceptible (with the exception of the recombination region, RR). The Joule heating in the space-charge region (SCR) is by two orders of magnitude larger than the cooling effect of the water dissociation reaction. Upon recombination, approximately the same heat is released in the RR as during Joule heating in the expanded SCR. However, due to the small size of the RR, the effect of this heat is imperceptible. Therefore, we can assume that there is only one heat source at the interface in the SCR, which, due to its noticeable size, causes a significant increase in temperature in the entire diffusion layer. It follows that the emergence and development of gravitational convection is possible. General conclusions, following from the results obtained, open up the possibility of intensifying the process of transport of salt ions in the electrodialysis machines.

Keywords: membrane system, ion exchange membrane, space charge, extended space-charge region, dissociation-recombination reaction of water molecules.

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Introduction. Intensive current mode involves using currents several times higher than the limited electrodiffusion. In this case, secondary (or conjugated) phenomena of concentration polarization occur in the membrane systems:

- spatial electric charge occupies a macroscopic region comparable to the thickness of the diffusion layer;
- the solution *pH* changes [1-3], which is explained by the water splitting;
- microconvective flows are formed, etc.

Considering impact of the dissociation (recombination) reaction of water molecules is essential to understanding the transport processes in the electromembrane systems, as some authors believe that the occurrence of new charge carriers H^+ and OH^- can cause a decrease or even disappearance of the space charge, which is the basis for other transfer mechanisms (e.g. electroconvection). The dissociation reaction of water molecules is endothermic, and the recombination reaction is exothermic. Centers of the reaction sites are separated in space. This causes an uneven temperature

ваются недостающие краевые условия для напряженности электрического поля.

Результаты исследования. Разработаны новая математическая модель, алгоритм численного решения краевой задачи, программное обеспечение. Проведен численный анализ и определены фундаментальные закономерности переноса ионов соли с учетом реакции диссоциации (рекомбинации) молекул воды, температурных эффектов и Джоулева разогрева. Построена и проанализирована ВАХ. **Обсуждение и заключение.** Рассмотрен перенос ионов бинарной соли через диффузионный слой у катионообменной мембраны. Предложена математическая модель названного процесса, которая учитывает температурные эффекты, обусловленные реакциями диссоциации (рекомбинации) молекул воды и Джоулевым нагревом в растворе. Установлены основные закономерности переноса ионов соли с учетом реакции диссоциации (рекомбинации) молекул воды и температурных эффектов. Температурные эффекты от реакции диссоциации (рекомбинации) и Джоулева разогрева в ОЭН практически незаметны (исключение — область рекомбинации, ОР). Джоулев нагрев в области пространственного заряда (ОПЗ) на два порядка больше охлаждающего эффекта реакции диссоциации воды. При рекомбинации в ОР выделяется примерно столько же тепла, сколько при Джоулевом нагреве в расширенной ОПЗ. Однако из-за малых размеров ОР влияние этого тепла незаметно. Значит, можно считать, что есть только один источник тепла на межфазной границе в ОПЗ, который благодаря своему заметному размеру обуславливает значительное повышение температуры во всем диффузионном слое. Отсюда следует, что возможно возникновение и развитие гравитационной конвекции. Общие выводы, следующие из полученных результатов, открывают возможность интенсификации процесса переноса ионов соли в электродиализных аппаратах.

Ключевые слова: мембранные системы, ионообменная мембрана, пространственный заряд, расширенная область пространственного заряда, диссоциация (рекомбинация) молекул воды.

Образец для цитирования: Моделирование и численный анализ влияния реакции диссоциации (рекомбинации) молекул воды на перенос ионов соли в диффузионном слое / Н. О. Чубырь [и др.] // Вестник Дон. гос. техн. ун-та. — 2019. — Т. 19, № 3. — С. 268–280. <https://doi.org/10.23947/1992-5980-2019-19-3-268-280>

distribution and, therefore, affects all the physical properties of water: dissociation coefficient, heat capacity, etc. In addition, an uneven temperature distribution can cause gravitational convection. Thus, the study of temperature effects associated with the reactions of dissociation and recombination of water molecules is an urgent task [4]. In this paper, we confine ourselves to considering the effect of the uneven temperature distribution on the dissociation coefficient of water molecules.

Materials and Methods

1. Mathematical model

1.1. Simultaneous equations

Consider a one-dimensional stationary transport process for single-charged salt ions in the Nernst diffusion layer. We take into account the dissociation (recombination) reactions of water and the temperature effects associated with the Joule heating of the solution. Such a case is described through a system of equations [5]:

$$j_1 = \frac{-F}{RT_0} D_1 C_1 \frac{d\varphi}{dx} - D_1 \frac{dC_1}{dx}, \quad (1)$$

$$j_2 = \frac{F}{RT_0} D_2 C_2 \frac{d\varphi}{dx} - D_2 \frac{dC_2}{dx}, \quad (2)$$

$$j_3 = \frac{-F}{RT_0} D_3 C_3 \frac{d\varphi}{dx} - D_3 \frac{dC_3}{dx}, \quad (3)$$

$$j_4 = \frac{F}{RT_0} D_4 C_4 \frac{d\varphi}{dx} - D_4 \frac{dC_4}{dx}, \quad (4)$$

$$\frac{d^2\varphi}{dx^2} = \frac{-F}{\varepsilon_r} (C_1 - C_2 + C_3 - C_4), \quad (5)$$

$$0 = \frac{-dj_i}{dx} + R_i, \quad i = 1, \dots, 4, \quad (6)$$

$$k \frac{d^2T}{dx^2} + E \cdot I + \beta(C_3 C_4 - k_w(T)) = 0. \quad (7)$$

Here, $R_1 = R_2 = 0, R_3 = R_4 = k_d C_{H_2O} - k_r C_3 C_4 = k_r(k_w - C_3 C_4)$, $k_w(T) = \dot{k}_w e^{b(T-T_0)}$, $i = 1, 2$ are salt ion indices; $i = 3$ and $i = 4$ are, respectively, the indices of hydrogen ions H^+ and hydroxyl OH^- ; $E = \frac{-d\varphi}{dx}$ is the electric field strength; C_i, j_i, D_i are, respectively, concentration, flux, diffusion coefficient of the i -th ion; $k_d(T)$ is the constant of water dissociation rate; k_r is the constant of the recombination rate of hydrogen ions H^+ and hydroxyl OH^- ; \dot{k}_w is the equilibrium constant; ε_r is the dielectric capacitivity; F is the Faraday number; I is the total current density; k is the coefficient of thermal conductivity; ρ_0 is the density of the solution; c_p is specific heat of the solution; $G = E \cdot I$ is the density of heat sources associated with the passage of electric current through the solution (Joule heating of the solution); $\beta = qk_r$, $Q = \beta \left(C_3 C_4 - \frac{k_d C_{H_2O}}{k_r} \right) = qk_r (C_3 C_4 - k_w(T))$ is the density of heat sources and sinks associated with the recombination and dissociation of water molecules.

The total current density I is equal to: $I = I_s + I_w$.

Here, I_s is partial current density by salt ions; I_w is partial current density by water ions.

From (6)–(8), it follows: $j_1 = \text{const}$, $j_2 = \text{const}$, $I_s = F \cdot (j_1 - j_2) = \text{const}$, $I_w = \text{const}$, but $j_3 \neq \text{const}$, $j_4 \neq \text{const}$, $\alpha^2 = \frac{k}{\rho_0 c_p}$ is thermal diffusivity of the solution.

1.2. Boundary conditions

Assume that $x = 0$ corresponds to the depth of the solution, where the electroneutrality condition $C_1 - C_2 + C_3 - C_4 = 0$ is fulfilled, and $x = \delta$ corresponds to the conventional “solution – membrane” interface. Thus, $\delta^{(u)}$ is the thickness of the Nernst diffusion layer.

In this paper, for definiteness, a cation-selective membrane (CSM) is considered, which for simplicity will be assumed to be ideally selective ($j_2^{(u)} = 0$).

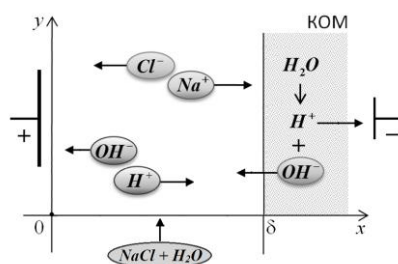


Fig. 1. Diagram of diffusion layer near cation-selective membrane

1) Boundary conditions in the depth of the solution ($x = 0$)

Assume, $C_1(0) = C_{10}$, $C_2(0) = C_{20}$, $C_3(0) = C_{30}$, $C_4(0) = \frac{\dot{k}_w}{C_{30}}$, while $C_{10} + C_{30} = C_{20}$, $T(\delta) = T_0$.

2) Boundary data at the “solution – membrane” interface ($x = \delta$)

Suppose that $C_1(\delta) = C_{1m}$, $C_3(\delta) = C_{3m}$. At this, the sum $C_{1m} + C_{3m}$ is comparable to the tabular value of the exchange capacity of the cation-selective membrane. The flux density $j_4(\delta) = j_{4m}$ of ions OH^- is determined by the catalytic reaction of dissociation of water molecules in a thin surface layer of a cation exchange membrane.

For temperature, the condition of flow balance is used at the point $x = \delta$ [1]:

$$-k \frac{dT(\delta)}{dx} = G(\delta)\delta + Q(\delta)\delta + q \frac{dj_4(\delta)}{dx}.$$

2. Transition to dimensionless form

2.1. Characteristic quantities and formulas for the transition to a dimensionless form

As a characteristic concentration of C_0 we take the concentration of salt cations C_{10} . Actual values of C_{10} are within the range of $10^{-5}M - 1M$. As a characteristic temperature, we take the room temperature $T_0 = 298K$. As a characteristic length, we consider the thickness of the diffusion layer δ , which is of the order of $10^{-4}m$. Denote $D_0 = \frac{2D_1D_2}{D_1+D_2}$

as the electrolyte ($NaCl$) diffusion coefficient $\varphi_0 = \frac{RT_0}{F}$ — as the thermal potential [5].

We pass to dimensionless quantities:

$$x^{(u)} = \frac{x}{\delta}, \varphi^{(u)} = \frac{\varphi}{\varphi_0}, E^{(u)} = \frac{-\delta}{\varphi_0} \frac{d\varphi}{dx}, I^{(u)} = \frac{I}{I_{np}}, D_i^{(u)} = \frac{D_i}{D_0}, I_s^{(u)} = \frac{I_s}{I_{np}}, I_w^{(u)} = \frac{I_w}{I_{np}}, C_i^{(u)} = \frac{C_i}{C_{10}}, j_i^{(u)} = \frac{j_i \delta}{D_i C_{10}} = \frac{j_i F}{D_i^{(u)} I_{np}}, i = 1, 2, 3, 4, T^{(u)} = \frac{T}{T_0}, I_{np} = \frac{D_0 C_{10} F}{\delta}.$$

Then, $k_w^{(u)}(T) = \frac{k_w(T)}{(C_{10})^2} = \gamma^{(u)} e^{b^{(u)}(T^{(u)}-1)}$, where $\gamma^{(u)} = \frac{k_w}{(C_{10})^2}$, $b^{(u)} = bT_0$.

Assume that $\varepsilon^{(u)} = \frac{RT_0 \varepsilon_r}{C_{10} F^2 \delta^2}$, $a^{(u)} = \frac{RT_0 \varepsilon_r}{F^2} \frac{k_r}{D_0}$.

2.2. Transition to dimensionless form in equations

Focusing on [6], we pass to the dimensionless form in the system of equations (1) - (6):

$$\frac{dC_1^{(u)}}{dx} = C_1^{(u)} E^{(u)} - j_1^{(u)}, \quad (9)$$

$$\frac{dC_2^{(u)}}{dx} = -C_2^{(u)} E^{(u)} - j_2^{(u)}, \quad (10)$$

$$\frac{dC_3^{(u)}}{dx} = C_3^{(u)} E^{(u)} - j_3^{(u)}, \quad (11)$$

$$\varepsilon^{(u)} D_3^{(u)} \frac{d}{dx} j_3^{(u)} = a^{(u)} \left(k_w^{(u)} e^{b^{(u)}(T^{(u)}-1)} - C_3^{(u)} C_4^{(u)} \right), \quad (12)$$

$$\frac{dC_4^{(u)}}{dx} = -C_4^{(u)} E^{(u)} - j_4^{(u)}, \quad (13)$$

$$\varepsilon^{(u)} D_4^{(u)} \frac{d}{dx} j_4^{(u)} = a^{(u)} \left(k_w^{(u)} e^{b^{(u)}(T^{(u)}-1)} - C_3^{(u)} C_4^{(u)} \right), \quad (14)$$

$$\varepsilon^{(u)} \frac{dE^{(u)}}{dx} = C_1^{(u)} - C_2^{(u)} + C_3^{(u)} - C_4^{(u)}. \quad (15)$$

We write the total current density in the form of $I_s^{(u)} + I_w^{(u)} = I^{(u)}$.

Here,

$$I_s^{(u)} = D_1^{(u)} j_1^{(u)} - D_2^{(u)} j_2^{(u)}, I_w^{(u)} = D_3^{(u)} j_3^{(u)} - D_4^{(u)} j_4^{(u)},$$

moreover, for a perfectly selective membrane $j_2^{(u)} = 0$ and, consequently,

$$I_s^{(u)} = D_1^{(u)} j_1^{(u)}.$$

Under the transition to a dimensionless form, the heat equation (7) takes the form:

$$k^{(u)} \frac{d^2 T^{(u)}}{(dx^{(u)})^2} + E^{(u)} \cdot I^{(u)} + \beta^{(u)} \left(C_3^{(u)} C_4^{(u)} - \gamma^{(u)} e^{b^{(u)}(T^{(u)}-1)} \right) = 0. \quad (16)$$

Here, $k^{(u)} = \frac{k}{D_0 C_{10} R}$ and $\beta^{(u)} = \frac{q K_r \delta^2 C_{10}}{D_0 R T_0}$.

2.3. Physical meaning and evaluation of the trivial similarity criteria

The parameters $\varepsilon^{(u)}$, $D_3^{(u)}$, $D_4^{(u)}$, $a^{(u)}$, $k^{(u)}$, $k_w^{(u)}$, $\beta^{(u)}$, $b^{(u)}$ are trivial similarity criteria. Let us determine their physical meaning and values at the characteristic input parameters of the problem.

1. $b^{(u)} \approx 15$.

2. The parameter $\gamma^{(u)}$ is the square of the ratio of the concentration H^+ or OH^- ions in a neutral solution ($pH = 7$) to the electrolyte concentration. Its values vary from 10^{-10} to 10^{-18} , and it can be considered a small parameter.

3. $\varepsilon^{(u)} = \frac{RT_0 \varepsilon_r}{C_{10} F^2 \delta^2} = 2 \left(\frac{l_d}{\delta} \right)^2$, where $l_d = \sqrt{\frac{RT \varepsilon_0}{2 C_{10} F^2}}$ is Debye length. Thus, the parameter $\varepsilon^{(u)}$ is the doubled

square of the Debye length ratio l_d to the diffusion layer width δ . The values of $\varepsilon^{(u)}$ vary from 10^{-11} to 10^{-7} , and this parameter can be considered small.

4. $a^{(u)} = \frac{RT_0 \varepsilon_r}{F^2} \frac{k_r}{D_0} = \frac{RT_0 \varepsilon_r}{2C_{10} F^2} \frac{2k_r C_{10}}{D_0} = \left(\frac{l_d}{l_r}\right)^2$. Here, $l_r = \sqrt{\frac{D_0}{2k_r C_{10}}}$. This value is proportional to the width of the recombination region (RR). Thus, the parameter $a^{(u)}$ is the square of the ratio of the Debye length to the width OP l_r . The parameter $a^{(u)} = 14$ and in the framework of this problem, it is a universal constant since it does not depend on the input parameters of the problem. So: $\frac{l_d}{l_r} = \sqrt{a^{(u)}} \approx 3.74$, i.e., the width of the OP is approximately 37 % of the width of the quasi-equilibrium region of the space charge (SCR, Debye length).

2.4. Nontrivial similarity criteria, physical meaning and evaluation of quantities

In the equation (16), the dimensionless coefficients $k^{(u)}$ and $\beta^{(u)}$ are trivial similarity criteria. Any relation between trivial criteria is called a nontrivial similarity criterion. Below, we express $k^{(u)}$ and $\beta^{(u)}$ through other known similarity criteria.

1) Consider $k^{(u)} = \frac{k}{D_0 C_{10} R} = \frac{\alpha^2 \rho_0 c_p}{D_0 C_{10} R} = \frac{\alpha^2}{D_0} \cdot \frac{\rho_0 c_p}{C_{10} R} = \frac{\rho_0 c_p}{C_{10} R}$. Here, $\frac{\alpha^2}{D_0}$ is the Lewis - Semenov number. We introduce the dimensionless number $\mu = \frac{C_{10} R}{\rho_0 c_p}$. Then, $k^{(u)} = \frac{1}{\mu}$. The number μ indicates the relative specific volumetric heat capacity, varies from indicates the relative specific volumetric heat capacity, it varies from 10^{-8} to 10^{-4} , and it can be considered as a small parameter.

2) Consider the parameter $\beta^{(u)} = \frac{q k_r \delta^2 C_{10}}{D_0 R T_0} = \frac{q \delta^2}{2 R T_0} \frac{2 k_r C_{10}}{D_0} = \frac{q}{2 R T_0} \frac{\delta^2}{\frac{D_0}{2 k_r C_{10}}} = Arn \frac{\delta^2}{2 l_r^2}$. Here, $Arn = \frac{q}{R T_0} = 22.8$ is the dimensionless quantity which is a thermal analogue of the Arrhenius criterion. It characterizes the sensitivity of the heat amount of a chemical reaction to temperature changes. As $\frac{1}{2} \left(\frac{\delta}{l_r}\right)^2 = \frac{1}{2} \left(\frac{l_d}{l_r}\right)^2 \left(\frac{\delta}{l_d}\right)^2 = \frac{a}{\varepsilon}$, and $\varepsilon = 2 \left(\frac{l_d}{\delta}\right)^2$, $a = 2 \left(\frac{l_d}{l_r}\right)^2$, then $\beta^{(u)} = Arn \cdot \frac{a}{\varepsilon}$. Thus, the heat equation (16) has the following dimensionless form:

$$\varepsilon Le \frac{d^2 T^{(u)}}{dx^2}.$$

3) The calculations show that

$$\gamma \mu = \frac{k_w}{C_{10}} \frac{R}{\rho_0 c_p} = \frac{k_w \varepsilon F^2 \delta^2}{R T_0 \varepsilon_r} \frac{R}{\rho_0 c_p} = \frac{k_w F^2 \delta^2}{\rho_0 c_p T_0 \varepsilon_r} \varepsilon.$$

Since $\varepsilon^{(u)} = 2 \left(\frac{l_d}{\delta}\right)^2$, then $N_a = \sqrt{\frac{k_w F^2 \delta^2}{\rho_0 c_p T_0 \varepsilon_r}} \approx 2,5 \cdot 10^{-3}$. Therefore, we obtain a nontrivial similarity criterion, which shows the relation

$$\gamma \mu = n_a^2 \varepsilon.$$

Likewise,

$$\varepsilon \mu = n_{a,1}.$$

Here,

$$n_{a,1} = \frac{R^2 T_0 \varepsilon_r}{\rho_0 c_p F^2 \delta^2} \approx 3,5 \cdot 10^{-14}, \quad (17)$$

$$\gamma = N_{a,2} \varepsilon^2, \quad (18)$$

$$N_{a,2} = \frac{F^4 \delta^4 k_w}{R^2 T_0^2 \varepsilon_r^2}.$$

Note that $n_a^2 = n_{a,1} N_{a,2}$.

2.5. Dimensionless form of a system of equations

Thus, a dimensionless system of equations describing the model has the form (index u is omitted for simplicity):

$$\begin{aligned} \frac{dC_1}{dx} &= C_1 E - j_1, \quad \frac{dC_2}{dx} = -C_2 E - j_2, \quad \frac{dC_3}{dx} = C_3 E - j_3, \\ \varepsilon D_3 \frac{d}{dx} j_3 &= a(\gamma e^{b(T-1)} - C_3 C_4), \quad \frac{dC_4}{dx} = -C_4 E - j_4, \\ \varepsilon D_4 \frac{d}{dx} j_4 &= a(\gamma e^{b(T-1)} - C_3 C_4), \quad \varepsilon \frac{dT}{dx} = C_1 - C_2 + C_3 - C_4, \\ \varepsilon Le \frac{d^2 T}{dx^2} &+ \varepsilon \mu EI + \mu a Arn (C_3 C_4 - \gamma e^{b(T-1)}) = 0. \end{aligned}$$

The system of equations contains three small parameters ε , μ and γ , connected by relations (17) and (18). The parameter ε enters the equations singularly, i.e., as a coefficient in the derivatives, and the parameter γ is regular, so the system of equations is simultaneously singularly and regularly perturbed.

2.6. Transition to dimensionless form under boundary conditions

The dimensionless boundary conditions have the form:

$$\begin{aligned} C_1|_{x=0} = 1, C_2|_{x=0} = 1 + C_{30}, C_3|_{x=0} = C_{30}, C_4|_{x=0} = C_{40} = \frac{\gamma}{C_{30}}, T(0) = 1, \\ C_1|_{x=1} = C_{1m}, C_3|_{x=1} = C_{3m}, j_4|_{x=1} = j_{4m}, \\ -k \frac{d}{dx} T(1) = \mu D_4 b_q \frac{d}{dx} j_4(1). \end{aligned}$$

Remark 1. Owing to continuity, the following is valid:

$$I_W = D_3 j_{3m} - D_4 j_{4m} = D_3 j_{30} - D_4 j_{40}.$$

3. Numerical solution algorithm

3.1. Transition to a boundary value problem for a system of second-order equations

Due to the small parameter ε in the equations (12), (14) and (15), the boundary-value problem (9) - (16) is singularly perturbed; therefore, the system is inconvenient for a numerical solution [7]. In addition, differential equations are of the first order, and a boundary-value problem is set for them. In the equation (15), for the electric field strength, the right-hand side is independent from E . This causes stability problems in the numerical solution to the discrete system of equations by the Newton – Kantorovich method [8]. Therefore, the boundary value problem (9) - (16) should be reduced to a form convenient for a numerical solution. To do this, we pass to the system of second-order equations:

$$\begin{aligned} \frac{d^2 C_1}{dx^2} = \frac{d}{dx} (C_1 E), \frac{d^2 C_2}{dx^2} = \frac{d}{dx} (C_2 E), \frac{d^2 C_3}{dx^2} = \frac{d}{dx} (C_3 E) - \frac{a(\gamma e^{b(T-1)} - C_3 C_4)}{\varepsilon D_3}, \\ \frac{d^2 C_4}{dx^2} = \frac{d}{dx} (C_4 E) - \frac{a(\gamma e^{b(T-1)} - C_3 C_4)}{\varepsilon D_4}, \varepsilon \frac{d^2 E}{dx^2} = E(C_1 + C_2) - j_1 + j_2 + \frac{dC_3}{dx} - \frac{dC_4}{dx}, \\ \varepsilon L e \frac{d^2 T}{dx^2} + \varepsilon \mu E I + \mu a A r n (C_3 C_4 - \gamma e^{b(T-1)}) = 0. \end{aligned} \quad (19)$$

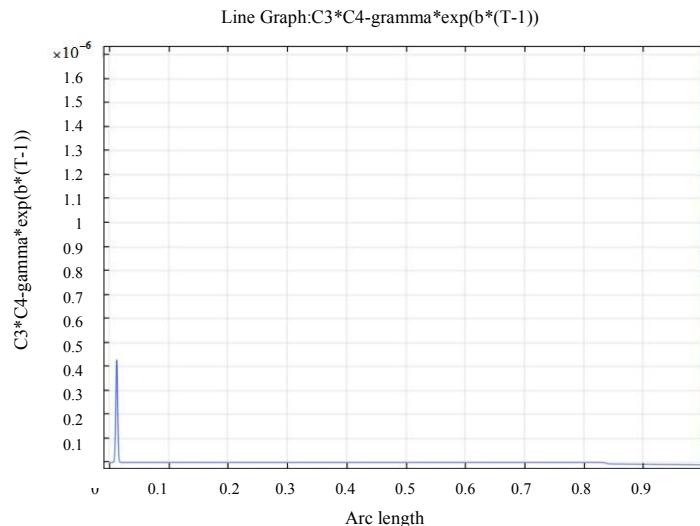
In connection with the transition to systems of the second-order equation, it is necessary to supplement the initial boundary conditions with the missing boundary conditions for the function E . From the boundary conditions, it follows that at the point $x = 0$, the electroneutrality condition $C_1 - C_2 + C_3 - C_4 \approx 0$ is satisfied. Due to the continuity, with some accuracy, in the vicinity of the point $x = 0$, $C_1 - C_2 + C_3 - C_4 \approx 0$ is fulfilled, therefore E_0 can be calculated from the electroneutrality condition. Adding the equations for C_i , $i = 1, \dots, 4$ and using the electroneutrality condition $C_{10} - C_{20} + C_{30} - C_{40} = 0$, we can obtain the relation $E|_{x=0} = \frac{I_s}{1+C_{20}} + \frac{d}{dx} (C_1(0) - C_2(0))$.

From the equation for E at $x = 1$, we have: $\varepsilon \frac{dE}{dx}|_{x=1} = (C_1 - C_2 + C_3 - C_4)|_{x=1}$.

Research Results

3.2. Numerical Results

To analyze the results of the numerical solution, along with the graphs of the desired functions C_i, E, j_3, j_4, T , we consider the graphs of the functions $\rho(x) = C_1 - C_2 + C_3 - C_4$, $p(x) = C_3 C_4 - \gamma e^{b(T-1)}$. The function $\rho(x)$ characterizes the distribution of charge density, and $p(x)$ is the deviation from the equilibrium of the dissociation (recombination) reaction.



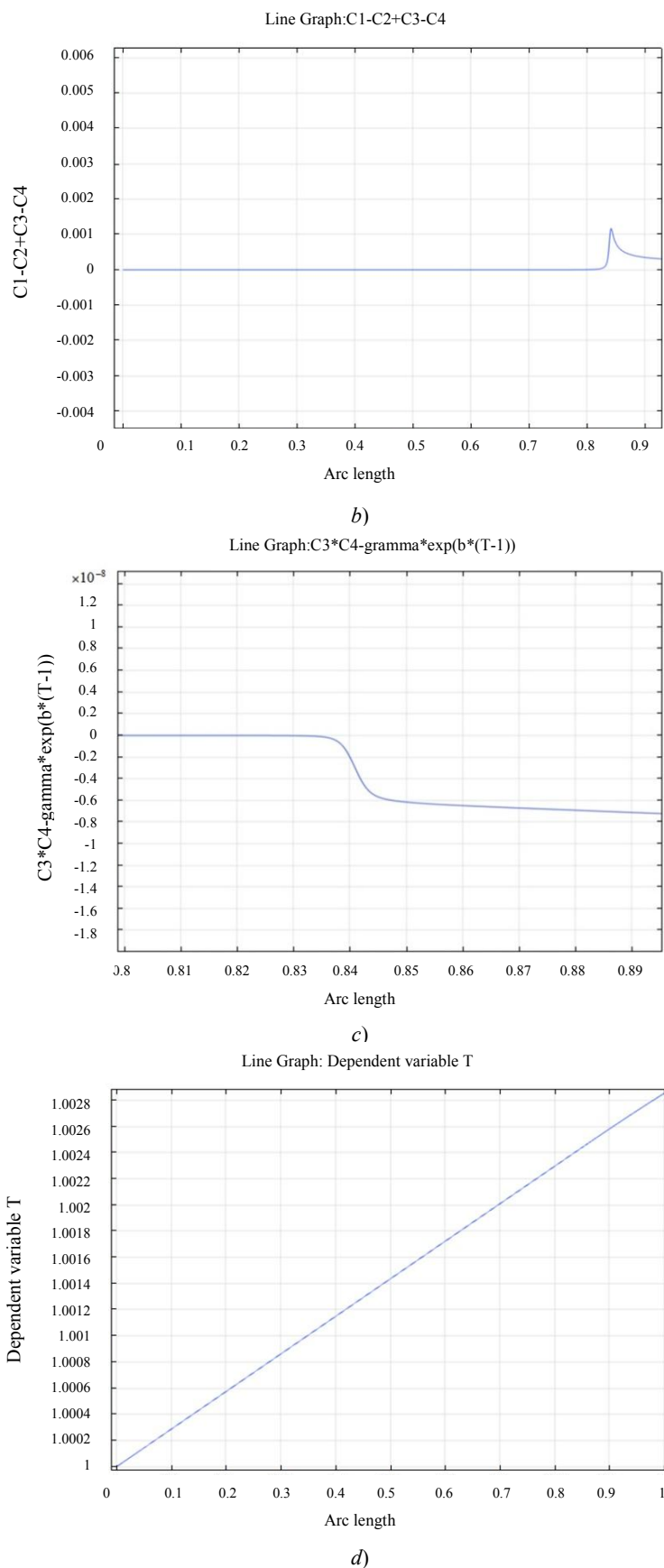


Fig. 2. Graph of function $\rho(x) = C_1 - C_2 + C_3 - C_4$ ([0; 0.93]) (a); graph of function $p(x) = C_3C_4 - \gamma e^{b(T-1)}$ (b); graph of function $p(x) = C_3C_4 - \gamma e^{b(T-1)}$ in SCR (c); temperature graph (d)

From Fig. 2(a), it follows that the diffusion layer is divided into three regions. The first is the region of electro-neutrality (ENR), where $\rho(x) = 0$. The second is the space charge region ($\rho(x) > 0$). The third is an intermediate layer

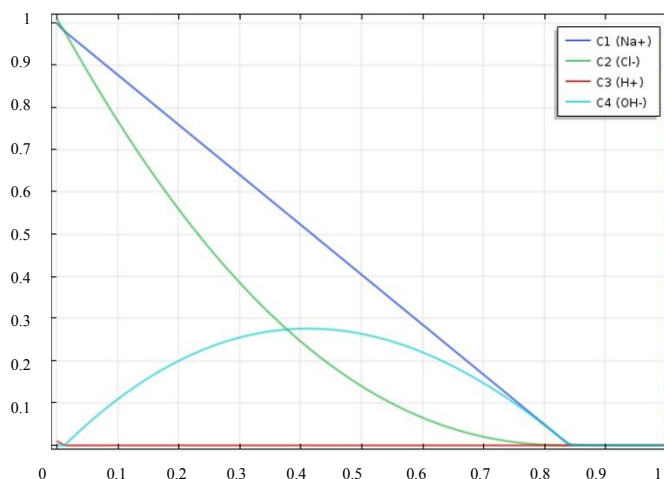
between them where the charge distribution density has a pronounced local maximum. The SCR itself is divided into two parts: extended and quasi-equilibrium (it is very small and adjacent to the interface). In the quasi-equilibrium part of the SCR, the charge density distribution obeys the exponential law (not shown in Fig. 2).

A general view of the graph of the function $p(x)$ (Fig. 2, b) shows that the deviation from equilibrium occurs:

- in the recombination region which is located inside the ENR;
- in the space charge region (Fig. 2, c).

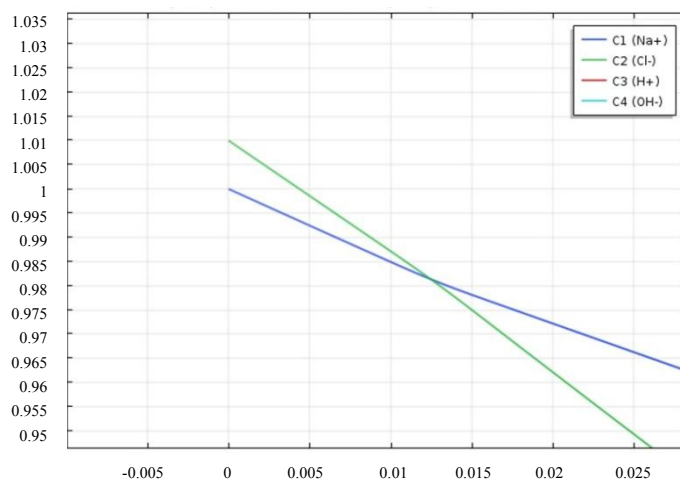
In the first case, $p(x) > 0$, .e., recombination prevails over the dissociation $C_3C_4 \gg \gamma e^{b(T-1)}$. In the second case, on the contrary, $p(x) < 0$, and dissociation prevails over recombination in the SCR, as well as in the intermediate layer. The temperature (Fig. 2, d) increases linearly by 0.0028 in a dimensionless form (or $0,0028 \cdot 298 = 0.83$ degrees). The increase depends on the total current density or potential jump in the diffusion layer and can be up to tens of degrees. Obviously, all terms of the equation (19) are small compared to the first one, that is, the second derivative is $\frac{d^2T}{dx^2} \approx 0$. From this, it follows that the temperature is linear and is determined by the boundary conditions.

Line Graph: Dependent variable C1 Line Graph: Dependent variable C2
 Line Graph: Dependent variable C3 Line Graph: Dependent variable C4



a)

Line Graph: Dependent variable C1 Line Graph: Dependent variable C2
 Line Graph: Dependent variable C3 Line Graph: Dependent variable C4



b)

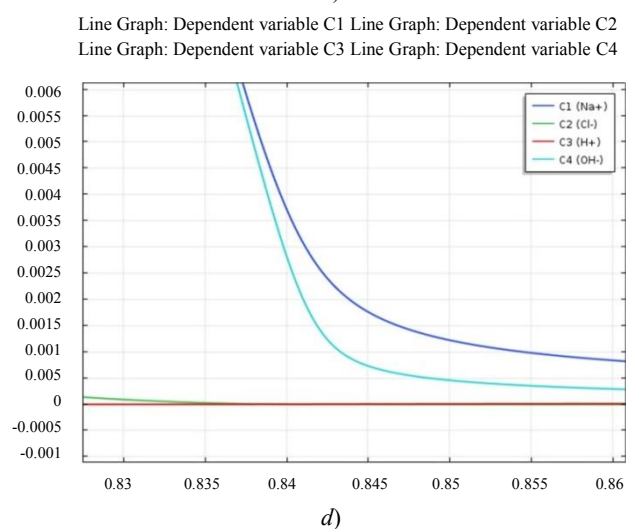
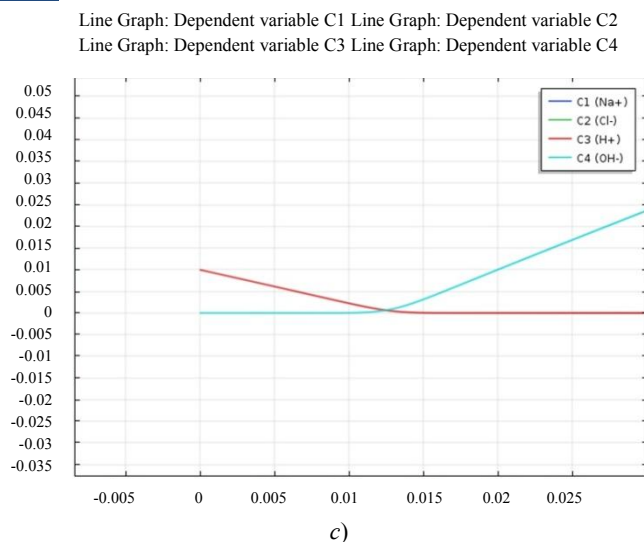
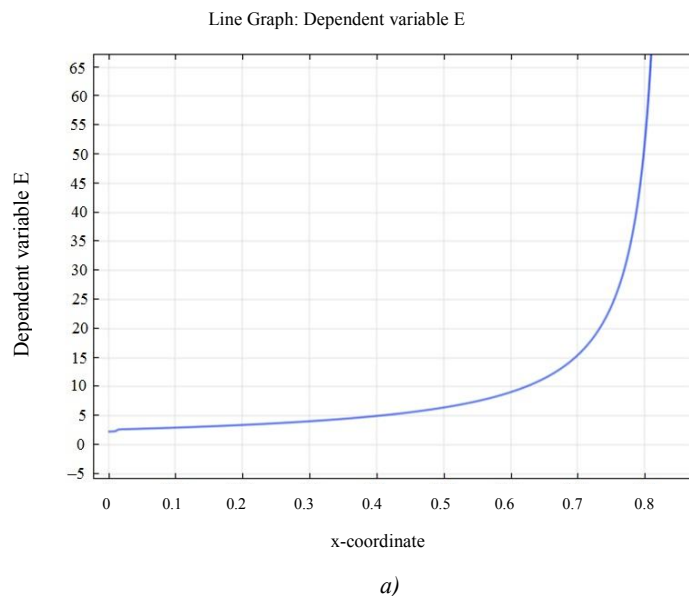
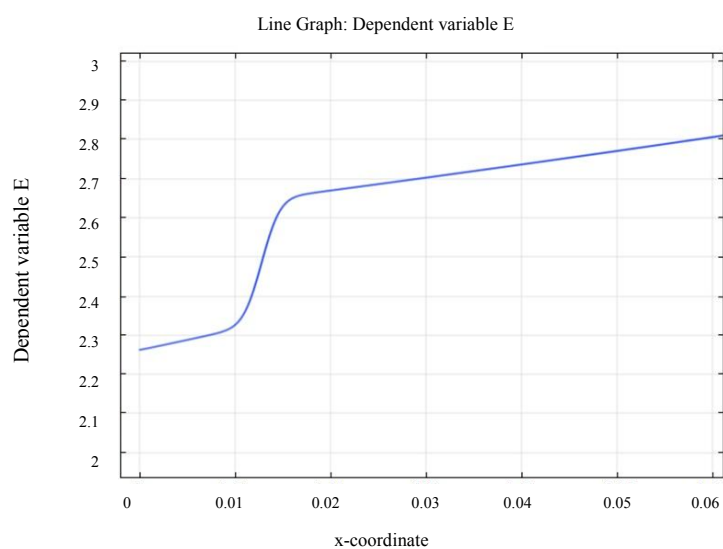


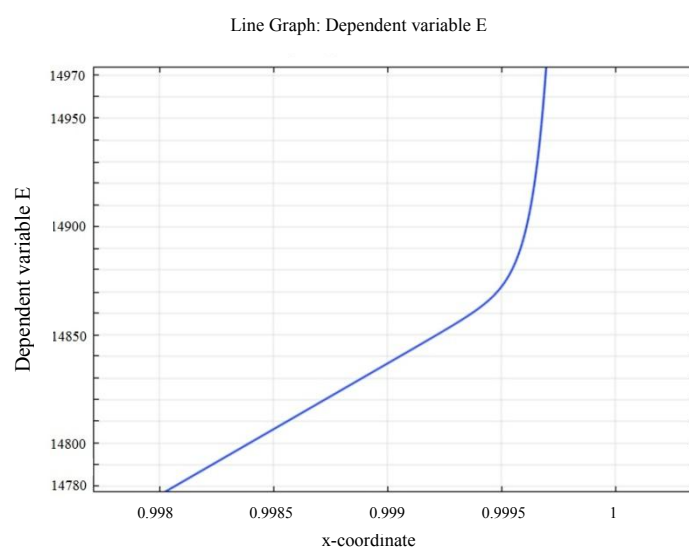
Fig. 3. General view of graphs of functions C_1 , C_2 , C_3 , C_4 (a); function graphs C_1 , C_2 near zero (b); function graphs C_3 , C_4 near zero (c); function graph C_1 , C_2 , C_3 , C_4 in space charge region (d)

As follows from Fig. 3 a, the sodium concentration decreases linearly in the ENR and becomes small in the SCR, but it is higher than the concentration of the remaining ions (Fig. 3 d). The center of the RR is the intersection point of the graphs of concentration of Na^+ и Cl^- and, respectively, of OH^- and H^+ . To the right of the center, the concentration of Cl^- decreases faster than the concentration of Na^+ . The deficit of negatively charged ions resulting from this is compensated by the rapid growth of hydroxyl ions, and the condition of electroneutrality is preserved (Fig. 3a).

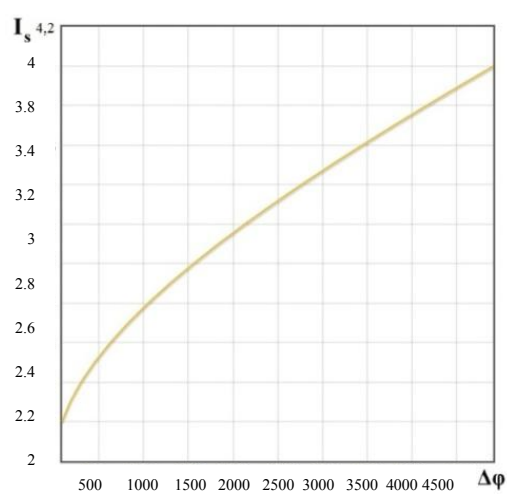




b)



c)



d)

Fig. 4. General view of graph of E function with exception of phase boundary (a); graph of E function near RR (b); graph of E function near phase boundary (c), volt-ampere characteristic (d)

From the data in Fig. 4, it follows that in ENR, the electric field strength increases rapidly tens of times (Fig. 4, *a*). A particularly high rate of the electric field strength is observed in the SCR upon reaching values of the order of $\frac{1}{\sqrt{\varepsilon}}$. In the RR there is an internal boundary layer of E electric field strength (Fig. 4, *b*). This is due to the fact that charge carriers change: before RR, the charge is determined by Na^+ , Cl^- , H^+ ions, and after — by Na^+ , Cl^- , OH^- ions. The appearance of a “step” owes to the fact that the diffusion coefficient of hydrogen is approximately two times greater than the diffusion coefficient of hydroxyl. The VAC increases without limit with a growth of the potential jump in the over-extreme mode $I_s > 2$ (Fig. 4, *d*). This growth tends to be much slower than the experimentally observed one, which means that along with the dissociation (recombination) reaction of water, there is another mechanism of super-limit transfer. It is generally accepted that electroconvection is such a mechanism [9–11]. In this regard, a problem of evaluation and interaction of the dissociation (recombination) reaction and electroconvection occurs.

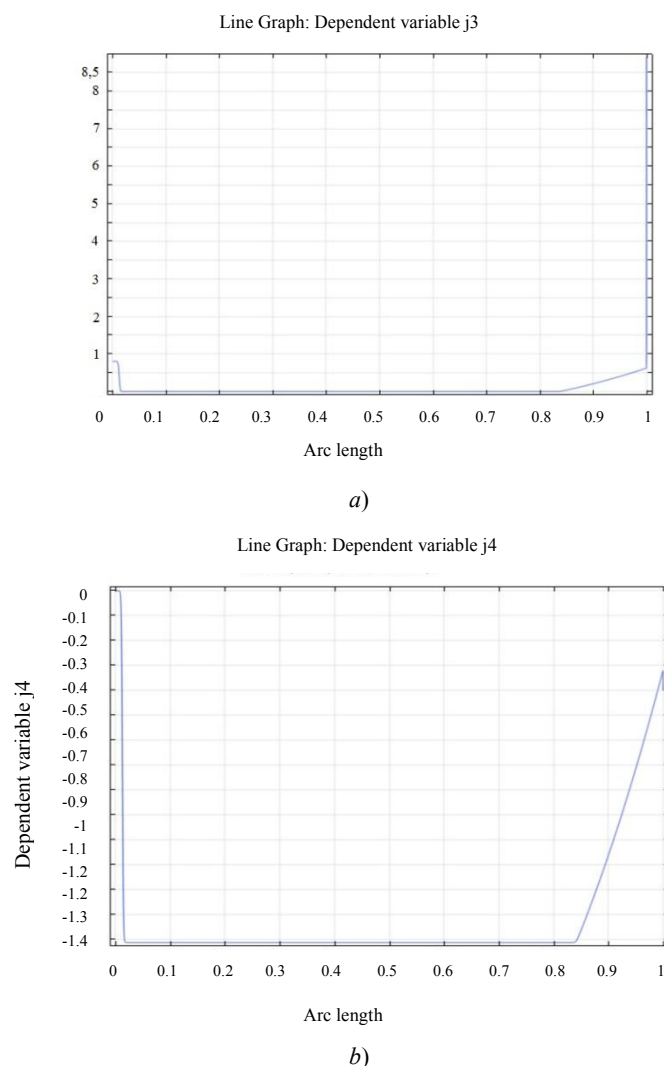


Fig. 5. Flux plot of hydrogen j_3 (*a*) and hydroxyl j_4 (*b*) ions

Fig. 5 shows that the flow of hydrogen ions is positive. It is constant to the left of the RR and is practically equal to zero to the right of the RR till the SCR. In the SCR, the flow of hydrogen ions increases linearly due to the intense dissociation of water. The flow of hydroxyl ions to the left of the RR is practically zero, and to the right, it is negative and constant until the SCR. In the SCR, the flow of hydroxyl ions, as well as the flow of hydrogen ions, increases linearly. In a quasi-equilibrium SCR, the hydroxyl ion flux changes sharply and satisfies the boundary condition $j_4(1) = j_4(m)$. The recombination region is an internal boundary layer for the flows of hydrogen and hydroxyl – they change sharply here.

Discussion and Conclusions. In this paper, the transport of binary salt ions through a diffusion layer near a cation exchange membrane is considered. A mathematical model of the process is proposed, which takes into account the temperature effects caused by the dissociation (recombination) of water molecules and the Joule heating in solution. This model consists of 9 ordinary differential equations with corresponding boundary conditions. An algorithm for the numerical solution to a boundary value problem is developed, and its computational investigation is presented. The

basic laws of the transfer of salt ions are defined considering the dissociation (recombination) reaction of water molecules and temperature effects.

It is shown that the VAC grows without limit with a growth of the potential jump in the over-extreme mode, and is much slower than in experiments. Therefore, along with the dissociation (recombination) reaction of water, there are other mechanisms of super-limit transfer (for example, electroconvection and gravitational convection). Thus, a challenge arises of assessing the interaction of dissociation (recombination) reactions, electroconvection, and gravitational convection.

Temperature effects from the dissociation (recombination) reaction and the Joule heating in the ENR are almost imperceptible (with the exception of RR). The Joule heating in the SCR is two orders of magnitude higher than the cooling effect of the water dissociation reaction. Upon the recombination, approximately the same heat is released in the RR as during the Joule heating in the expanded SCR. However, due to a small size of the RR, the effect of this heat is imperceptible. Thus, we can assume that there is only one source of heat at the interface in the SCR, which, due to its noticeable size, causes a significant increase in temperature throughout the diffusion layer. It follows that the emergence and development of gravitational convection is possible.

In the paper, a solution of sodium chloride is considered; however, the study is valid for a solution of any binary salt.

General conclusions following from the results obtained enable to intensify the process of salt ion transport in the electrodialysis machines.

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