Applied Mathematics & Information Sciences
An International Journal

http://dx.doi.org/10.18576/amis/150402

Numerical and Asymptotic Study of Non-Stationary Mass Transport of Binary Salt Ions in the Diffusion Layer near the Cation Exchange Membrane at Prelimiting Currents

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Received: 21 Feb. 2021, Revised: 22 Mar. 2021, Accepted: 7 May. 2021
Published online: 1 Jul. 2021.

Abstract: In this paper, we consider a depleted stationary diffusion layer adjacent to the ion-exchange membrane. The main goal is to study the structure of the diffusion layer over time. A one-dimensional non-stationary mathematical model of the transport of a binary electrolyte in a diffusion layer in a potentiostatic mode is investigated using the Nernst-Planck and Poisson equations. For the first time, it is shown that the left boundary of the space charge region is established quickly, approaching a certain straight line $x_c = const$ asymptotically. Using this fact, a new asymptotic solution is constructed. The original feature of the proposed asymptotic method is that it is based not only on asymptotic simplifications in the equations, but also on replacing the exact description of the structure of the diffusion layer with an approximate one.

Keywords: Mathematical modeling, Diffusion layer, Ion-exchange membrane, Nernst-Planck-Poisson equations, Asymptotic solution.

1 Introduction

In 1947, Levich determined that when a prelimiting current fluxes through the electrode/solution system, the entire solution region can be divided into two regions: the electroneutrality region and the space charge region. The next step was taken by Rubinstein and Shtilman in [1], in which they theoretically described the process of transporting binary electrolyte ions through a diffusion layer near the ion exchange membrane using the Nernst-Planck equations, and the Poisson equation (NPP), which sets the ratio between the local electric potential and the ion concentration. This work became the basis for further researches [2-7], developing the idea of the role of the space charge in the formation of «overlimiting current». The boundary value problems associated with the NPP equations are difficult to solve numerically, because a small parameter is present in the Poisson equation in dimensionless form (with natural normalization) [8]. Articles [9-10] are devoted to the study of non-stationary problems. In these works, the main attention is paid to the overlimiting potentiodynamic mode and the analysis of the time of establishing a stationary mode depending on the parameters of the problems. In studies [11-13], the authors obtained asymptotic solutions to the problem when using prelimiting currents in the stationary case. In this paper, a new asymptotic solution of the non-stationary problem is obtained. It is based on a simplified representation of the structure of the boundary layer of the cation-exchange membrane (CEM). This approach for solving this problem allows you to significantly reduce the computational complexity of the solution, and for an arbitrarily small parameter value.

In study [14], the mechanism of transport of NaCl ions in the boundary layer of the ion-exchange membrane is studied, considering the reaction of water dissociation and the effects of concentration polarization. Articles [15-19] addresses the main mechanism of excessive transport of salt ions in ion-exchange membrane systems in dilute solutions. Scientific investigation [20] is devoted to the mathematical description of the transport of salt ions and ions H^+(OH^-) using the Nernst-Planck and Poisson model, which considers the deviation from local electroneutrality in a depleted diffusion boundary layer.

With increasing current density, energy costs increase. However, in the mode of overlimiting current, there are phenomena that do not occur at low current densities. The main phenomena that occur when using currents exceeding

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the limiting currents ($I \geq I_{\lim}$) are electro convection [21-25] and water splitting [26-29]. The study [30] generalizes various phenomena that can occur during the transport of multivalent ions through cation-exchange membranes under conditions of intense concentration polarization and identifies the main factors that affect these phenomena.

Scientific articles [31-35] are devoted to the development of mathematical models for the potentiostatic mode, where the electric mode is set via a potential difference between two equipotential planes covering the electrode/membrane.

The development of the diffusion layer theory and the determination of its parameters are of great interest for understanding transport processes in heterogeneous systems and for engineering calculations [36].

2 Problem Statements

A non-stationary one-dimensional mathematical model of binary electrolyte mass transport is described by the following equations in dimensional form [37, 38]:

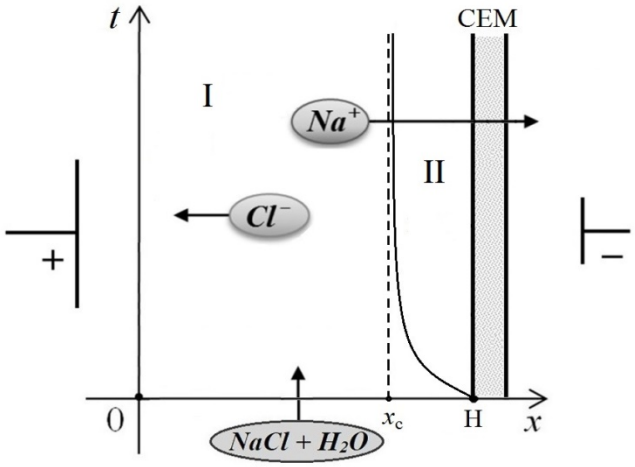
$$j_i = -\frac{F}{RT} z_i D_i C_i \frac{\partial \varphi}{\partial x} - D_i \frac{\partial C_i}{\partial x}, \qquad i = 1,2 \tag{1}$$

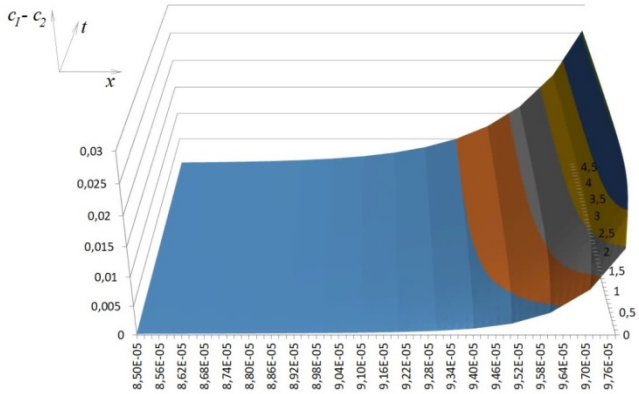
$$\frac{\partial^2 \varphi}{\partial x^2} = -\frac{F}{\varepsilon_r}(z_1 C_1 + z_2 C_2) \tag{2}$$

$$\frac{\partial C_i}{\partial t} = -\frac{\partial j_i}{\partial x}, \qquad i = 1,2 \tag{3}$$

Equation (2) – Poisson equation for electric field potential, equations (1) and (3) are Nernst-Planck equations: (1) – material balance equations, (3) – equation of fluxes of sodium ions Na^+ at $i = 1$ and chlorine Cl^- at $i = 2$, charge numbers of cations $z_1 = 1$ and anions $z_2 = -1, \varepsilon_r$ – permittivity of the solution, F – Faraday number, R – universal gas constant, T – solution temperature, $\varphi(x,t)$ – potential, $E = -\frac{\partial \varphi}{\partial x}$ – electric field strength, $C_i(x,t), j_i(x,t), D_i$ – concentration, flux, diffusion coefficient of the i-th ion.

Let's assume that x – a space variable, and $x = 0$ – corresponds to the core of the flux (the depth of the solution), and $x = H$ – the conditional interphase boundary "solution/CEM ", t – time (Fig.1a):





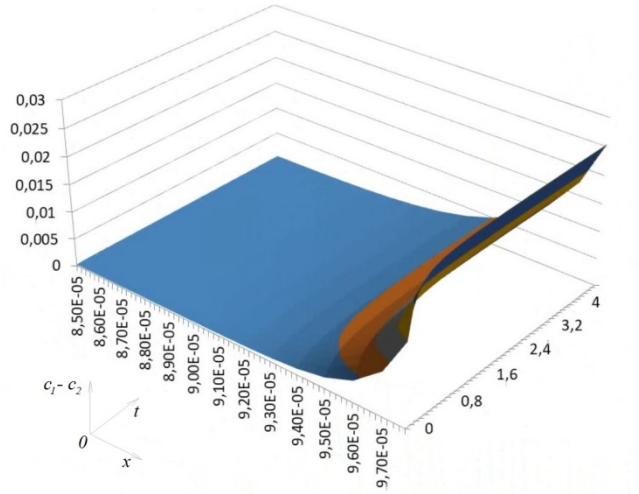


Fig.1: a) scheme of the diffusion layer (scale may vary), b) and c) plots of the function $C_1(t,x) - C_2(t,x)$.

In Figure 1, region I is the electroneutrality region, region II is the space charge region (the boundary layer near CEM).

The width of region II at $t=0$ is 0 and increases over time to a value $H-x_c$, where $x_c = H + H\sqrt{\varepsilon}\ln\varepsilon$. The curvilinear boundary of the region between regions I and II for the construction of an asymptotic solution is further approximated by a straight line $x = x_c$, which is shown as a dotted line in Figure 1. Figures 1b and 1c show graphs $C_1 - C_2$ near the diffusion layer that confirm the scheme of Figure 1a.

For certainty, we will consider the membrane to be ideally selective cation-exchange. The concentration of ions in the depth of the solution is considered constant. For the right border ($x = H$), a constant value is set for cations, determined by the exchange capacity of the CEM, and for anions, the condition of impermeability (ideal selectivity) is set. The potential jump $\varphi(H,t)-\varphi(0,t)=\Delta_r\varphi$ is considered constant, independent of time (potentiostatic mode). In the depth of the solution ($x=0$), the electroneutrality condition is considered fulfilled, and the potential value is assumed to be zero. Let's take the initial conditions as coinciding with the conditions on the left border ($x=0$). Thus, the boundary conditions have the form:

For $x=0$:

$$C_1(0,t)=C_0,\quad C_2(0,t)=C_0,\quad \varphi(0,t)=0 \tag{4}$$

For $x=H$:

$$C_1(H,t)=C_{1m},\quad \left(\frac{\partial C_2}{\partial x}-\frac{F}{RT_0}z_2C_2E\right)(H,t)=0,\quad \varphi(H,t)=\Delta_r\varphi \tag{5}$$

For $t=0$:

$$C_1(x,0)=C_0(x),\quad C_2(x,0)=C_0(x),\quad \varphi(x,0)=0, \tag{6}$$

where C_{1m} is the concentration of sodium ions on the membrane.

3 Method and Algorithm of Solution

3.1 Results of Numerical Analysis

The numerical solution of problem (1-6) was carried out by the finite element method in the COMSOL Multiphysics 5.5 environment using the Chemical Species Transport, Classical PDEs (from Mathematics) modules and their submodules Transport of Diluted Species, Poisson's Equation. During the study, many calculations were carried out with various parameter values. Below, for certainty, are the results of calculations for typical values of the potential $\varphi(H,t)=\Delta_r\varphi=-0.1V$, concentration of sodium ions at $x=0$ and $C_{10}=0.1\,mol/m^3$, at $0\le t\le 10$ seconds in increments of 0.1 seconds. The other parameters are well-known and taken from the reference list.

Figure 2a show that CEM has an area of rapid change in concentration, and there is a border layer near the border $x=H$. Thickness of the border layer increases and stabilizes over time, which is associated with the release of the cation transport process to a stationary mode. Time to enter stationary mode with an error of 1% is 4 seconds for the selected parameters. The maximum thickness of the border layer is approximately $5\cdot10^{-6}\ m$. The concentration distribution outside the border layer becomes linear fairly quickly (4 seconds). The distribution of anion concentrations (Fig. 2b) also becomes linear over time and constantly remains equal to the concentration of cations with great accuracy everywhere ($C_1(t,x)=C_2(t,x)$) except in the border layer, where $C_1(t,x)>>C_2(t,x)$. Therefore, the boundary layer is a space charge region, and outside the boundary layer, the local electroneutrality condition is fulfilled with great accuracy.

Plots of the electric field strength and cation flux are shown in Figure 3.

The plot of the electric field strength (Fig. 3a) is convex and the values of the strength increase t slowly in the region of electroneutrality from the values of the order $10^2\ V/m^2$ and then sharply in the region of space charge, reaching values of the order $10^5\ V/m^2$. The flux j_1 (Fig. 3b) is an increasing function that gradually approaches a constant value. As time increases, the flux values j_2 gradually become zero.

3.2 The Construction of Asymptotic Solutions. Transition to a Dimensionless Form

To switch to a dimensionless form, use the following characteristic values: H – channel width, which can vary from $0.5\cdot10^{-3}\ m$ to $5\cdot10^{-3}\ m$, $\varphi_0=\frac{RT}{F}$ – thermal potential, C_0 – concentration, which can vary from $10^{-3}\ mol/m^3$ to $10\ mol/m^3$, $I_{\lim}=\frac{2D_0C_0F}{H}$ – limiting diffusion current, l_D – Debay length.

Using the following transition formulas to a dimensionless view [38]:

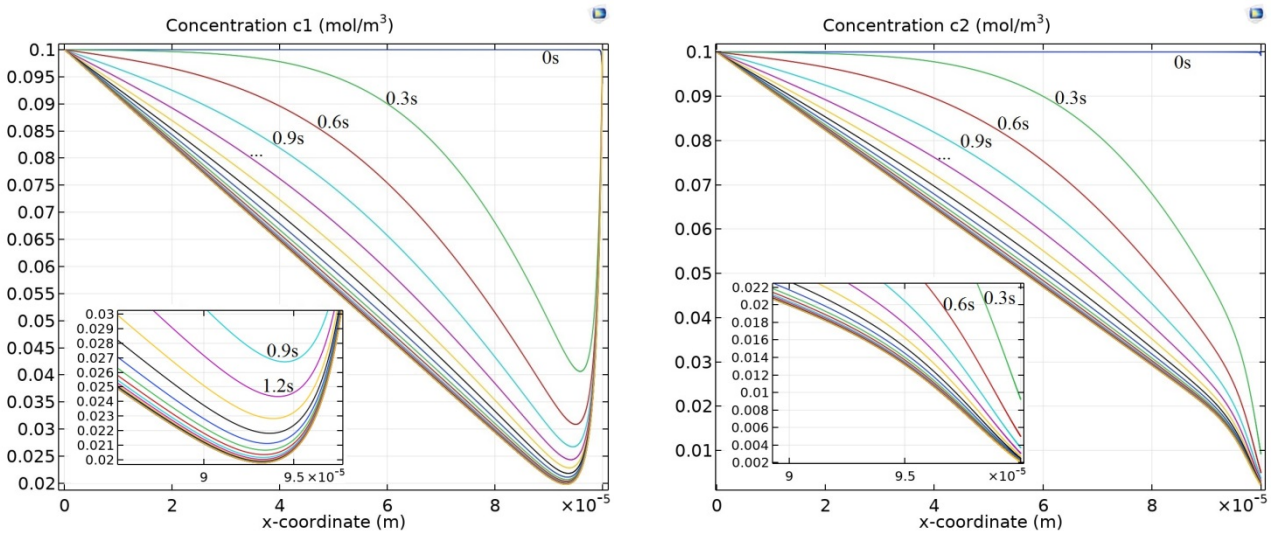


Fig. 2: Concentration profiles: a) cations, b) anions.

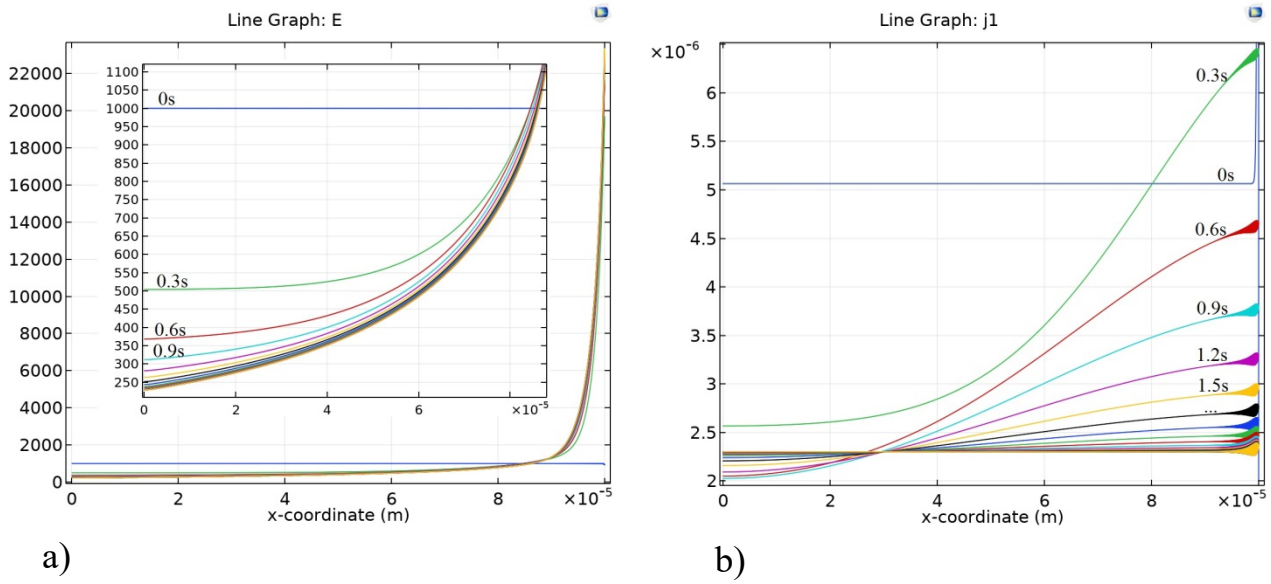


Fig. 3: a) electric field strength E, b) j_1 flux graph.

$$x^{(u)} = \frac{x}{H},\ E^{(u)} = \frac{HF}{RT}E,\ C_i^{(u)} = \frac{C_i}{C_0},\ t^{(u)} = \frac{t}{t_0},$$

$$t_0^{(u)} = \frac{D_0}{H^2},\ j_i^{(u)} = \frac{j_i H}{D_i C_0},$$

$$D_0 = \frac{2D_1D_2}{D_1+D_2},\ \varepsilon^{(u)} = \frac{RT\varepsilon_0}{C_0(F)^2H^2} = \left[\frac{l_D}{H}\right]^2$$

we obtain a system of one-dimensional non-stationary Nernst-Planck and Poisson equations in dimensionless form (the index "u" is omitted for simplicity of writing):

$$\frac{\partial C_i}{\partial x} = -z_i C_i \frac{\partial \varphi}{\partial x} - j_i,\quad i = 1,2 \qquad (7)$$

$$\varepsilon \frac{\partial^2 \varphi}{\partial x^2} = C_1 - C_2, \quad x \in (0,1) \tag{8}$$

$$\frac{\partial C_i}{\partial t} = -D_i \frac{\partial j_i}{\partial x}, \qquad i = 1,2 \tag{9}$$

Boundary conditions in dimensionless form:

For $x = 0$:

$$C_1(0,t) = 1, \; C_2(0,t) = 1, \; \varphi(0,t) = 0$$

For $x = 1$:

$$C_1(1,t) = C_{1m}, \qquad \left(\frac{\partial C_2}{\partial x} - z_2 C_2 E\right)(1,t) = 0,$$

$$\varphi(1,t) = \Delta_r \varphi$$

The initial conditions for $t = 0$:

$$C_1(x,0) = 1, \; C_2(x,0) = 1, \; \varphi(x,0) = 0$$

3.3 The Application of the Method of Boundary Layer Functions

The structure of the diffusion layer (region II) is shown in Figure 1. This drawing shows that the entire left boundary of the space charge region is curved. It must be determined during the splicing of asymptotic solutions. However, Figures 2a and 3a show that this boundary can be approximated with great accuracy by a vertical asymptote. In this regard, the vertical asymptote can be taken as the left boundary of the quasi-equilibrium region with high accuracy $x = x_c$. Thus, for an asymptotic solution, we assume that the region $\Pi = \{(x,t) \in [0,1] \times [0,+\infty]\}$ in the prelimiting case is approximately divided into two rectangular subdomains after the transition to the dimensionless form. From the numerical solution, it follows that in the region of the boundary layer, the solution does not depend on the current density, so this region can be considered a quasi-equilibrium region. In region I, the electroneutrality condition is met with great accuracy, so this region can be considered an electroneutrality region.

From the numerical results obtained, it follows that an approximate analytical solution can be found by the method of boundary-layer functions [39]. Obviously, this method will give a poor approximation to the solution in the vicinity of the curved boundary. At the same time, as will be shown below, it will give a fairly accurate approximation in the rest of the area.

We will look for a solution in the form of the sum of the regular and border layer parts. Moreover, $0 \le x \le 1$, $0 \le t < \infty$, $\xi = \frac{1-x}{\sqrt{\varepsilon}}$:

$$\begin{aligned} C_i(t,x,\varepsilon) &= \overline{C}_i(t,x) + \Pi C_i(t,\xi) + O(\sqrt{\varepsilon}) \\ j_i(t,x,\varepsilon) &= \bar{j}_i(t,x) + \Pi j_i(t,\xi) + O(\sqrt{\varepsilon}) \\ \varphi(t,x,\varepsilon) &= \overline{\varphi}(t,x) + \Pi\varphi(t,\xi) + O(\sqrt{\varepsilon}) \end{aligned} \tag{10}$$

where $\overline{C}_i(t,x)$, $\bar{j}_i(t,x)$, $\overline{\varphi}(t,x)$ is the regular part, and $\Pi C_i(t,\xi)$, $\Pi j_i(t,\xi)$, $\Pi\varphi(t,\xi)$ are border-layer functions [39].

In the future, we will substitute the representation (10) in equations (7)-(9) and perform transformations according to the method of border-layer functions

a) Transformation of equation (9) according to the method of boundary layer functions:

$$\frac{\partial(\overline{C}_i(t,x) + \Pi C_i(t,\xi))}{\partial t} + O(\sqrt{\varepsilon}) = \qquad , \quad i = 1,2$$
$$= -D_i \frac{\partial(\bar{j}_i(t,x) + \Pi j_i(t,\xi))}{\partial x} + O(\sqrt{\varepsilon})$$

or

$$\frac{\partial \overline{C}_i(t,x)}{\partial t} + \frac{\partial \Pi C_i(t,\xi)}{\partial t} + O(\sqrt{\varepsilon}) =$$
$$= -D_i \frac{\partial(\bar{j}_i(t,x))}{\partial x} - D_i \frac{1}{\sqrt{\varepsilon}} \frac{\partial \Pi j_i(t,\xi)}{\partial \xi} + O(\sqrt{\varepsilon}), \quad i = 1,2$$

We equate the regular and border layer functions separately on the left and right with the same degrees of small parameter:

$$\frac{\partial \overline{C}_i(t,x)}{\partial t} = -D_i \frac{\partial(\bar{j}_i(t,x))}{\partial x}, \quad i = 1,2$$

$$\frac{\partial \Pi j_i(t,\xi)}{\partial \xi} = 0, \quad i = 1,2$$

Where, given $\Pi j_i(t,\infty) = 0$, we get $\Pi j_i(t,\xi) \equiv 0$

b) Transformation of equation (4) according to the method of boundary layer functions:

$$\frac{\partial \overline{C}_i(t,x)}{\partial x} = -z_i \overline{C}_i(t,x) \frac{\partial(\overline{\varphi}(t,x)}{\partial x} - \bar{j}_i(t,x), \; i = 1,2$$

$$\frac{\partial \Pi C_i(t,\xi)}{\partial \xi} = -z_i \overline{C}_i(t,1) \frac{\partial \Pi\varphi(t,\xi)}{\partial \xi} - z_i \Pi C_i(t,\xi) \frac{\partial \Pi\varphi(t,\xi)}{\partial \xi}, \quad i = 1,2$$

c) Transformation Poisson equation (5) according to the method of boundary layer functions:

$$\overline{C}_1(t,x)-\overline{C}_2(t,x)=0$$

$$\frac{\partial^2 \Pi\varphi(t,\xi)}{\partial\xi^2}=\Pi C_1(t,\xi)-\Pi C_2(t,\xi)$$

After the completed transformations, we write the equations for regular functions:

$$\frac{\partial\overline{C}_i(t,x)}{\partial x}=-z_i\overline{C}_i(t,x)\frac{\partial(\overline{\varphi}(t,x)}{\partial x}-\bar{j}_i(t,x),\ \ i=1,2 \tag{11}$$

$$\overline{C}_1(t,x)-\overline{C}_2(t,x)=0 \tag{12}$$

$$\frac{\partial\overline{C}_i(t,x)}{\partial t}=-D_i\frac{\partial(\bar{j}_i(t,x))}{\partial x},\ \ i=1,2 \tag{13}$$

and for border-layer functions:

$$\Pi j_i(t,\xi)\equiv 0,\ i=1,2$$

$$\frac{\partial^2 \Pi\varphi(t,\xi)}{\partial\xi^2}=\Pi C_1(t,\xi)-\Pi C_2(t,\xi) \tag{14}$$

$$\frac{\partial\Pi C_i(t,\xi)}{\partial\xi}=-(z_i\Pi C_i(t,\xi)+z_i\overline{C}_i(t,1))\frac{\partial\Pi\varphi(t,\xi)}{\partial\xi},\ \ i=1,2 \tag{15}$$

3.4 Solving a System of Equations for Regular Functions

To solve the system of equations (11-13), we express the flux from (11) and substitute it in (13). Then we get:

$$\frac{\partial\overline{C}_i(t,x)}{\partial t}=D_i\frac{\partial^2\overline{C}_i}{\partial x^2}+D_iz_i\frac{\partial}{\partial x}\left(\overline{C}_i\frac{\partial\overline{\varphi}}{\partial x}\right)i=1,2 \tag{16}$$

Furthermore, we divide the first equation (16) for $i=1$, by D_1, and the second, for $i=2$, by D_2 and add them. Then, considering (12), we obtain for $C=C_1=C_2$ the well-known convective diffusion equation [4]:

$$\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial x^2} \tag{17}$$

where $D=\dfrac{2D_1D_2}{D_1+D_2}$ is the diffusion coefficient of the electrolyte.

For further calculations, we will introduce a new function $\alpha(t)=\overline{C}_1(t,1)+\overline{C}_2(t,1)=2C(t,1)$.

To get an equation for the electric field strength, multiply the first equation (8) by z_1, and the second by z_2, and sum them. Then considering (12), we get the transport equation for the electric field strength. Integrating this equation by x, we get:

$$\frac{\partial\overline{\varphi}}{\partial x}=-\frac{D_1-D_2}{D_1+D_2}\frac{\partial}{\partial x}(\ln C)+\frac{1}{C}\frac{\partial\overline{\varphi}(t,0)}{\partial x}$$

We integrate the resulting equation again from 0 to an arbitrary point x. Then, considering the boundary conditions for $x=0$, we obtain:

$$\overline{\varphi}(t,x)=-\frac{D_1-D_2}{D_1+D_2}\ln C(t,x)+\frac{\partial\overline{\varphi}(t,0)}{\partial x}\int_0^x\frac{dx}{C(t,x)}$$

Similarly, we get

$$\bar{j}_1(t,x)=-\frac{2D_2}{D_1+D_2}\frac{\partial C}{\partial x}+\sigma_1(t)$$

$$\bar{j}_2(t,x)=-\frac{2D_2}{D_1+D_2}\frac{\partial C}{\partial x}+\sigma_2(t)$$

Where $\sigma_i(t)$, $i=1,2$ are functions arising from integration over a variable x. Using boundary conditions for j_2, it is easy to find $\sigma_2(t)$.

3.5 Solving a System of Equations for Boundary Layer Functions

Put

$$u_i(t,\xi)=\Pi C_i(t,\xi)+\overline{C}_i(t,1)\quad i=1,2$$

$$y(t,\xi)=\Pi\varphi(t,\xi)$$

Then, from (14-15), we get a system of equations:

$$\frac{\partial u_i}{\partial\xi}=-z_iu_i\frac{\partial y}{\partial\xi} \tag{18}$$

$$\frac{\partial^2 y}{\partial\xi^2}=u_1-u_2$$

Then, after a series of transformations, we get:

$$u_1=\frac{1}{2}\frac{\partial z}{\partial\xi}-\frac{1}{4}z^2-\frac{1}{2}\alpha$$

$$u_2=-\frac{1}{2}\frac{\partial z}{\partial\xi}-\frac{1}{4}z^2-\frac{1}{2}\alpha$$

$$\frac{\partial^3 y}{\partial^3\xi}=(\frac{1}{2}(\frac{\partial y}{\partial\xi})^2-\alpha)\frac{\partial y}{\partial\xi}$$

Suppose $z(\xi)=\frac{\partial y}{\partial \xi}$, then we get:

$$\frac{\partial^2 z}{\partial^2 \xi}=(\frac{1}{2}z^2-\alpha)z$$

Integrating this equation, we find

$$z(\xi)=-\frac{\sqrt{2\alpha}}{sh(\sqrt{\alpha}\frac{1-x}{\sqrt{\varepsilon}}+d)}$$

where the constant d is defined from the boundary condition. Find the function y by integrating this equation:

$$y(\xi)=\frac{1}{2}\ln\left|\frac{1+e^{\sqrt{\alpha}(\xi+d)}}{1-e^{\sqrt{\alpha}(\xi+d)}}\right|$$

Then we find u_1 and u_2:

$$u_1=\frac{\alpha\sqrt{2}ch(\sqrt{\alpha}\xi+d)-\alpha}{2sh^2(\sqrt{\alpha}\xi+d)}-\frac{1}{2}\alpha$$

$$u_2=-\frac{1}{2}\frac{\alpha\sqrt{2}ch(\sqrt{\alpha}\xi+d)-\alpha}{sh^2(\sqrt{\alpha}\xi+d)}-\frac{1}{2}\alpha$$

3.6 The Representation of the Solution as a Sum of Regular and Boundary Layer Parts

Summing up the results described in paragraphs 3.3 and 3.4, we get a general view of the asymptotic solution:

$$C_1(t,x,\varepsilon)=C(t,x)+\frac{\alpha\sqrt{2}ch(\sqrt{\alpha}\frac{1-x}{\sqrt{\varepsilon}}+d)-\alpha}{2sh^2(\sqrt{\alpha}\frac{1-x}{\sqrt{\varepsilon}}+d)}+O(\sqrt{\varepsilon})$$

$$C_2(t,x,\varepsilon)=C(t,x)-\frac{\alpha\sqrt{2}ch(\sqrt{\alpha}\frac{1-x}{\sqrt{\varepsilon}}+d)+\alpha}{2sh^2(\sqrt{\alpha}\frac{1-x}{\sqrt{\varepsilon}}+d)}+O(\sqrt{\varepsilon})$$

$$\varphi(t,x,\varepsilon)=-\frac{D_1-D_2}{D_1+D_2}\ln C(t,x)+\frac{\partial\overline{\varphi}(t,0)}{\partial x}\int_0^x\frac{dx}{C(t,x)}+$$

$$+\frac{1}{2}\ln\left|\frac{1+e^{\sqrt{\alpha}(\frac{1-x}{\sqrt{\varepsilon}}+d)}}{1-e^{\sqrt{\alpha}(\frac{1-x}{\sqrt{\varepsilon}}+d)}}\right|+O(\sqrt{\varepsilon})$$

$$j_1(t,x,\varepsilon)=-\frac{2D_2}{D_1+D_2}\frac{\partial C}{\partial x}+\sigma_1(t)+O(\sqrt{\varepsilon})$$

$$j_2(t,x,\varepsilon)=-\frac{2D_2}{D_1+D_2}(\frac{\partial C(t,x)}{\partial x}-\frac{\partial C(t,1)}{\partial x})+O(\sqrt{\varepsilon})$$

The resulting representations are unknown d, σ_1 and the boundary value is unknown: $C(t,1)$. To find them, it is enough to solve the boundary value problem for $C(t,x)$ and then determine d and σ_1. To determine the constants d and σ_1, we will use the boundary conditions. Then, after a series of transformations, we get:

$$C(t,1)\frac{ch^2d+\sqrt{2}chd-2}{sh^2d}=C_{1m} \quad (19)$$

$$-\frac{D_1-D_2}{D_1+D_2}\ln C(t,1)+\frac{\partial\overline{\varphi}(t,0)}{\partial x}\int_0^1\frac{dx}{C(t,x)}+\frac{1}{2}\ln\left|\frac{1+e^{\sqrt{\alpha}d}}{1-e^{\sqrt{\alpha}d}}\right|=\Delta_r\varphi \quad (20)$$

It follows from these equations that if C_{1m} and $\Delta_r\varphi$ do not depend on t, then $C(t,1)$ does not depend on t. Paragraph 3.6 describes the algorithm for searching for unknowns $C(t,x)$, d and σ_1.

3.7 Algorithm for Numerical Implementation of an Asymptotic Solution

To find an asymptotic solution, it is substantial to solve the system of equations (19-20) with respect to $C(t,1)$ and d. This system of equations does not have an exact analytical solution, so it is necessary to use approximate methods that are stable with respect to rounding errors. As such, a combination of the method of dividing a segment in half and successive approximations is proposed, similar to the method [31].

The numerical solution algorithm can be divided into the following stages:

1) select a segment $[a_1;b_1]$ so that $d \in [a_1;b_1]$.

2) define $d^{(0)} = \frac{a_1 + b_1}{2}$

3) from equation (16), we define $C(t,1)$:

$$C^{(0)}(t,1) = k_c C_{1m}$$

where $k_c = \frac{sh^2 d^{(0)}}{ch^2 d^{(0)} + \sqrt{2} chd^{(0)} - 2}$ is the coefficient of relative reduction of the boundary concentration taking into account the space charge to the boundary concentration with the condition of electroneutrality

4) solve the boundary value problem:

$$\frac{\partial C^{(0)}}{\partial t} = D \frac{\partial^2 C^{(0)}}{\partial x^2} \quad (21)$$

$$C^{(0)}(t,0) = 1 \quad (22)$$

$$C^{(0)}(t,1) = k_c C_{1m} \quad (23)$$

$$C^{(0)}(0,x) = 1 \quad (24)$$

This problem can be solved by the Fourier method or numerically, for example, by the finite difference method. At this stage, the initial approximation is being searched for $C^{(0)}(t,x)$, so it is sufficient to calculate the first approximation, or at least the first two approximations.

5) calculate all functions of the current approximation $\overline{\varphi}^{(0)}(t,x)$, $j_i^{(0)}(t,x)\ldots$

6) calculate the potential jump for the resulting concentration $C^{(0)}(t,x)$ and number $d^{(0)}$ using the formula (17):

$$\Delta_r \varphi^{(0)} = -\frac{D_1 - D_2}{D_1 + D_2} \ln C^{(0)}(t,1) + \frac{\partial \overline{\varphi}^{(0)}(t,0)}{\partial x} \int_0^1 \frac{dx}{C^{(0)}(t,x)} + \frac{1}{2} \ln \left| \frac{1 + e^{\sqrt{\alpha} d^{(0)}}}{1 - e^{\sqrt{\alpha} d^{(0)}}} \right|$$

7) compare the calculated value $\Delta_r \varphi^{(0)}$ with the specified one $\Delta_r \varphi$. If they match the specified accuracy, we assume that we have received a solution. Otherwise, go to paragraph 8.

8) determine which of the intervals $[a_1; d^{(0)})$ or $(d^{(0)}; b_1]$ is the solution, then denote the segment with the solution as $[a_1; b_1]$ and go to paragraph 2.

As an example, let us consider one step of the method at $C_{1m} = 1$ and compare the numerical and asymptotic solutions for the cation concentration. Let $d^{(0)} = 0.35$, then from $C^{(0)}(t,1) = k_c C_{1m}$ get $k_c \approx 0.2$ Therefore, $C^{(0)}(t,1) = 0.2$. We get the initial approximation $C^{(0)}(t,x)$ by solving the boundary value problem (21-24) using the Fourier method, leaving the first two terms of the series in the resulting solution:

$$C^{(0)}(t,x) \approx 1 - 0{,}8x + \frac{1{,}6}{\pi} e^{-\pi^2 Dt} \sin(\pi x) - \frac{0{,}8}{\pi} e^{-4\pi^2 Dt} \sin(2\pi x)$$

Thus,

$$C_1(t,x,\varepsilon) = 1 - 0{,}8x + \frac{1{,}6}{\pi} e^{-\pi^2 Dt} \sin(\pi x) + \frac{0{,}2\sqrt{2} ch(\sqrt{0{,}2}\frac{1-x}{\sqrt{\varepsilon}} + 0{,}35) - 0{,}2}{2sh^2(\sqrt{0{,}2}\frac{1-x}{\sqrt{\varepsilon}} + 0{,}35)}.$$

Similarly, $C_1(t,x,\varepsilon)$, you can find and compare other functions you are looking for.

3.8 Comparison of Numerical and Asymptotic Solutions

To evaluate the accuracy of the constructed asymptotic solution and estimate the limits of its applicability, the relative error of the obtained solution was analyzed. The relative error was calculated for the function $C_1(t,x,\varepsilon)$ according to the formula $\delta = \frac{|C_1' - C_1''|}{C_1'}$, where C_1' and C_1'' the results of the numerical (described in paragraph 2) and asymptotic solutions.

Table 1 show that there is a fairly good consistency between the numerical and asymptotic solutions everywhere except in the vicinity of the left boundary of the quasi-equilibrium region of the space charge (in the Table, it is highlighted in bold). This is due to the approximation of the curved border (in Figure 1a – a solid line separating regions I and II) by the linear border (in Figure 1a – a dotted line). The relative error of the asymptotic solution also stabilizes over time because of the

transport process entering the stationary mode (Fig. 2a). It decreases and does not exceed 6%.

4 Discussion and Examples

In this paper, the non-stationary 1:1 transport of the electrolyte in the depleted layer of the cation-exchange membrane in the potentiostatic prelimiting mode is investigated. A mathematical model is presented and the basic laws of 1:1 salt ion transport are investigated. Calculations have confirmed that the diffusion layer consists of an electroneutrality region and a small boundary layer near the cation exchange membrane, where a space charge region occurs. It is shown for the first time that the left boundary of the space charge region is established quickly, approaching a certain straight line asymptotically $x_c = const$. An asymptotic solution is constructed using this fact. The original feature of the proposed asymptotic method is that it is based not only on asymptotic simplifications in the equations, but also on replacing the exact structure of the diffusion layer with an approximate one. The problem can be solved asymptotically and without the assumption of simplifying the boundary of the region of electroneutrality and space charge, but this requires finding this boundary analytically and, by entering local coordinates on this boundary, coordinate the solution from the region of electroneutrality with the solution in the region of space charge. However, this results in a rather cumbersome solution that is inconvenient for practical use.

Thus, a fairly simple analytical solution is found that has good accuracy everywhere except, as expected, for the left boundary of the quasi-equilibrium region of the space charge.

It is shown for the first time that the left boundary of the space charge region is established quickly, approaching a certain straight line asymptotically $x_c = const$. An asymptotic solution is constructed using this fact. The original feature of the proposed asymptotic method is that it is based not only on asymptotic simplifications in the equations, but also on replacing the exact structure of the diffusion layer with an approximate one.

A comparison of the numerical and asymptotic solutions shows that they coincide with good accuracy, with the exception of a small neighborhood of the curved boundary of the quasi-equilibrium region of the space charge.

6 Conclusions

In this paper, the non-stationary transport of 1:1 of the electrolyte in the depleted layer of the cation exchange membrane in the potentiostatic prelimiting mode was investigated. A mathematical model is presented and the main patterns of 1:1 salt ion transport are investigated. Calculations have confirmed that the diffusion layer consists of an electroneutrality region and a small boundary layer at the cation-exchange membrane, where the space occurs. It is shown for the first time that the left boundary of the space charge region is established quickly, approaching a certain straight line asymptotically $x_c = const$. An asymptotic solution is constructed using this fact. The original feature of the proposed asymptotic method is that it is based not only on asymptotic simplifications in the equations, but also on replacing the exact structure of the diffusion layer with an approximate one. The problem can be solved asymptotically and without

Table 1: The relative error of the numerical and asymptotic solutions $C_1(t, x, \varepsilon)$.

x \ t	0	0.1	1	2	4	6	7	8	10
0.1	0.072	0.024	0.080	0.07	0.061	0,049	0.031	0.022	0.01
0.2	0.102	0.053	0.159	0.151	0.125	0,081	0.066	0.053	0.023
0.3	0,07	0,091	0,232	0,232	0,182	0,142	0,095	0,062	0.037
0.4	0,014	0,142	0,296	0,293	0,235	0,182	0,116	0,067	0.055
0.5	0,109	0,21	**0,393**	**0,583**	**0,363**	0,298	0,277	0,153	0.062
0.6	0.154	0.296	**0.474**	**0.422**	**0.306**	0,243	0.147	0,096	0.054
0.7	0,094	**0,401**	**0,546**	**0,456**	**0,312**	0,229	0,137	0,082	0.022
0.8	0,098	**0,523**	**0,599**	**0,470**	0,294	0,125	0,076	0,056	0,028
0.9	**0.412**	**0.658**	**0.626**	**0.428**	0.222	0,107	0.001	0,012	0.012

the assumption of simplifying the boundary of the region of electroneutrality and space charge, but this requires finding this boundary analytically and, by entering local coordinates on this boundary, coordinate the solution from the region of electroneutrality with the solution in the space charge region. However, this results in a rather cumbersome solution that is inconvenient for practical use.

Thus, a simple analytical solution that has good accuracy everywhere is found except, as expected, for the left boundary of the quasi-equilibrium region of the space charge.

It was shown for the first time that the left boundary of the space charge region was established quickly, approaching a certain straight line $x_c = const$ asymptotically. An asymptotic solution was constructed using this fact. The original feature of the proposed asymptotic method is that it is based not only on asymptotic simplifications in the equations, but also on replacing the exact structure of the diffusion layer with an approximate one.

Comparison of the numerical and asymptotic solutions showed that they coincide except for a small neighborhood of the curved boundary of the quasi-equilibrium region of the space charge.

Acknowledgments: The present paper was funded by RFBR, project number 19-38-90314 Aspiranty.

Conflict of Interest:
The authors declare that they have no conflict of interest.

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