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Steady-state Ion Transport through a Three-Layered Membrane System: A Mathematical Model Allowing for Violation of the Electroneutrality Condition

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Abstract—A relatively simple mathematical model based on the Poisson equation is considered. The model is intended for modeling transport through multilayered ion-exchange membranes operating at overlimiting currents. The boundary-value problem is solved by a numerical method of parallel shooting and by an approximate method based on the assumption that the charge density is distributed quasi-uniformly. Concentration profiles in diffusion layers and membranes, current–voltage curves, and dependences of effective transport numbers on the current density are examined.

INTRODUCTION

Use of intensive current modes in electrodialysis ($i > i_{lim}$) [1, 2] makes for a better process efficiency, which is especially important when desalinating dilute solutions. In the general case, when mathematically modeling electrical mass transfer at overlimiting currents, it is necessary to allow for three new factors affecting mass transfer, which are absent in sublimiting modes ($i \le i_{lim}$). First, the emergence of a macroscopic space-charge region (SCR) near the surface of an ion-exchange membrane (IEM) on the side of the diffusion layer, which gives up counterions [1–3]. Second, the effect of the water dissociation products on the mass transfer (exaltation effect) [2, 4]. And third, the action of secondary volume forces, which give rise to conjugated microconvective flows partly destroying the diffusion layer of the solution undergoing desalination [1–3, 5].

Here we investigate the emergence of SCR in a three-layered system diffusion layer–membrane–diffusion layer. We examine how SCR affects the concentration profiles of ions in the system while ignoring the exaltation effects and the decrease in the diffusion layer thickness under the action of conjugated convection. We also model the dependence of the counterion transport selectivity on the current density, including $i > i_{lim}$.

Boundary-value problems for studying the SCR effect were formulated earlier. However, the problem was considered only in an individual diffusion layer ($0 \le x \le \delta$) [1–10]. The transport was described by the Nernst–Planck equations and the Poisson equation was used instead of the traditional electroneutrality condition. A variety of solution techniques were used. In [7] and elsewhere, an asymptotic solution was used at $i \le i_{lim}$; in [1, 3], a small-parameter method at $i \ge i_{lim}$; in [8–10], analytical solutions were obtained. Approximate analytical formulas for strength $E(x)$ derived in [10] were valid at $0 \le x \le \delta$, with the exception of a narrow range near $x = \delta$. Numerical solutions obtained in [3, 6, 11] by a finite-difference method were true at any positive currents. An approximate technique for solving problems with the aid of the condition of a quasi-uniform charge density distribution (QCD) was proposed in [12]. The authors of [13, 14], using the LSODI integrator, solved a non-steady-state problem with Poisson equations in all three layers and with conditions of continuity of concentrations and potential at interfaces. A stationary solution was a limiting one at $t \longrightarrow \infty$. However, the authors of [13, 14] ignored the SCR effect on the selectivity of the membrane systems and solved the problem under a substantial restriction, specifically, they assumed that diffusion coefficients in the membrane and solution were identical.

In this work, we consider a stationary mathematical model in three layers. However, in contradistinction to [13], we examine a model with a Poisson equation only in the first diffusion layer. In the membrane and in the second diffusion layer we employ the electroneutrality condition. We analyze and compare two solutions for a model with one Poisson equation. One solution is found by a numerical method of parallel shooting [15], while the other, by using the QCD condition [6, 12]. The solutions are compared with those found by the authors of [13, 14]. Here we also extend the results obtained in [16, 17] to the case $i > i_{lim}$. The study of selectivity of three-layered membrane systems was conducted in [16, 17] in mild current modes ($i \le i_{lim}$), with the electroneutrality condition used in all three layers.

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FORMULATION OF THE PROBLEM

Initial Equations and Assumptions

Consider the transport of ions of a strong electrolyte of type NaCl through a membrane system comprising an IEM ($\delta < x < \delta + d$, $m = 2$) and two diffusion layers adjacent to IEM ($0 \le x \le \delta$, $m = 1$), ($\delta + d \le x \le d + 2\delta$, $m = 3$). The Nernst–Planck equations

$$j_j = -D_j\left(\frac{dc_j}{dx} + \frac{z_j F}{RT}c_j\frac{d\varphi}{dx}\right) \quad m = 1, 2, 3, \qquad (1)$$

are valid in all the three layers. In (1), subscript "j" refers to the sort of ions ($j = 1$ for counterions, $j = $ A for co-ions), and index "m" denotes a layer ($m = 1, 3$ for diffusion layers; $m = 2$ for membrane). In the first diffusion layer, the Poisson equation

$$z_1 c_1 + z_A c_A = -\frac{\tilde{\varepsilon}}{F}\frac{d^2\varphi}{dx^2} \quad m = 1 \qquad (2)$$

is used to take into account the space charge. In the membrane and the second diffusion layer, the electroneutrality condition

$$\begin{aligned} z_1 c_1 + z_A c_A &= Q \quad m = 2, \\ z_1 c_1 + z_A c_A &= 0 \quad m = 3 \end{aligned} \qquad (3a, 3b)$$

is used. An electric current of density i passes through the system

$$z_1 j_1 + z_A j_A = \frac{i}{F}. \qquad (4)$$

As we consider a steady-state process, by virtue of the continuity condition fluxes j_j are invariant (to be determined). At the interface between the first diffusion layer and the membrane ($x = \delta$), boundary concentrations c_j and electric potential φ are continuous in different phases ($m = 1, 2$):

$$c_j|_{m=1} = c_j|_{m=2}, \quad \varphi|_{m=1} = \varphi|_{m=2}. \qquad (5a, 5b)$$

At the other interface membrane/diffusion layer, Donnan equations link concentrations $\bar{c}_j^s$ and c_j^s in different phases ($m = 2, 3$)

$$\left.\frac{(\bar{c}_1^{s_1})^{1/z_1}}{(\bar{c}_A^s)^{1/z_A}}\right|_{m=2} = k_{1A}\left.\frac{(c_1^s)^{1/z_1}}{(c_A^s)^{1/z_A}}\right|_{m=3}. \qquad (6)$$

Boundary conditions at external boundaries of the system are specified in the form of fixed concentrations

$$c_j(0) = c_j^{II}, \quad c_j(\delta + d + \delta) = c_j^{II}. \qquad (7)$$

Here, j_j are ion flux densities, c_j are mole concentrations of ions, φ is potential, $E = -d\varphi/dx$ is the electric field strength, D_j are diffusion coefficients for ions, $\tilde{\varepsilon} = \varepsilon'\varepsilon_0$ is the permittivity of water, ε' is the dielectric constant of water, ε_0 is permittivity of empty space, Q is the exchange capacity of the membrane, z_j are charges of ions, i is the density of the passing current, k_{1A} is a Donnan constant, δ denotes thicknesses of diffusion layers, d is the membrane thickness, R is the gas constant, F is Faraday's number, and T is the absolute temperature.

The electroneutrality condition adopted for the membrane (3a) means, in particular, that the model ignores the presence of a thin charged layer of thickness $\bar{\lambda}$ inside the membrane, at its boundary with the solution undergoing desalination. This layer is the "membrane" part of EDL at the interface. In view of a high concentration of fixed ions, the value of $\bar{\lambda}$ must be considerably smaller than similar quantity λ in the first diffusion layer, as they have order of the Debye shielding length D_ρ, which is inversely proportional to $\sqrt{c^s}$, where the quantity c^s is the concentration of ions at a relevant external boundary of EDL. For the solution, the boundary concentration c^s equals approximately $\sqrt{\varepsilon}\,c_0$ at currents that are approximately equal to the limiting current [2, 6, 8]. For the membrane, $c_s = Q \approx 1$ M. Thus, the thickness $\bar{\lambda}$ is equal to a few Å, whereas λ equals a few hundred to a few thousand Å. The smallness of $\bar{\lambda}$ implies that, generally speaking, the transport through this layer must be described by some discrete models, rather than a continuous Nernst–Planck equation. On the other hand, it makes sense to employ a discrete approach only if the resistance of the layer under consideration is commensurate with that of the entire system. As will be shown below, in our case nearly 80% of the potential (a few fractions of a volt to a few volts) drop across the first diffusion layer, the contribution of the potential drop across the membrane itself is small, and the more so we can neglect the potential drop across the thin, well conducting EDL in the membrane.

Formulation of a Boundary-Value Problem in a Dimensionless Form

The mathematical model we formulated in the foregoing is a nonlinear boundary-value problem in a three-layered region. The problem is physically meaningful at any positive currents. To solve it, the set of equations (1)–(7) was reduced to a dimensionless form with the aid of parameters

$$X = x/\delta; \quad \bar{X} = \bar{x}/d; \quad C_0 = |z_j|c_j^I; \quad z = z_1/|z_A|;$$

$$C_j = c_j/C_0; \quad C_1^I = c_1^I/C_0; \quad C_A^I = c_A^I/C_0;$$

$$i_{lim}^0 = \frac{F}{\delta}[D_1 C_0(1 + z)]; \quad J_j = \frac{j_j F}{i_{lim}^0} = \frac{j_j \delta}{D_1 C_0(1 + z)};$$

$$I = \frac{i}{i_{lim}^0}; \quad I_{lim} = \frac{i_{lim}}{i_{lim}^0}; \quad I/I_{lim} = \frac{i}{i_{lim}};$$

$$d_j = D_j/D_1/(1+z); \quad \bar{d}_j = \bar{D}_j/[D_1(1+z)];$$

$$\bar{C}_j = \bar{c}_j/Q; \quad K_{1A} = k_{1A}\left(\frac{C_0}{Q}\right)^{1\backslash z_1 - 1/z_A};$$

$$r = \frac{D_1 dC_0}{\bar{D}_1 \delta Q}; \quad e = Q/C_0; \quad \psi = \frac{F}{RT}\varphi;$$

$$E = -\frac{d\psi}{dX}; \quad \varepsilon = \frac{\tilde{\varepsilon}RT}{F^2\delta^2 C_0} = \left(\frac{D_\rho^0}{\delta}\right)^2;$$

$$\rho = z_1 C_1 + z_A C_A, \quad D_\rho^0 = \sqrt{\frac{\tilde{\varepsilon}RT}{F^2 C_0}},$$

the bar over which means that this particular parameter refers to the membrane. In each diffusion layer and in the membrane we introduce a space coordinate $0 \le X \le 1$ and in the entire system, a global coordinate $0 \le Y \le 3$. In new variables, the initial set of equations looks as follows. For the diffusion layer that gives up counterions ($m = 1$; $0 \le Y \le 1$),

$$\frac{dC_j}{dX} = z_j C_j E - \frac{J_j}{d_j}, \quad j = 1, A, \tag{8}$$

$$\varepsilon\frac{dE}{dX} = z_1 C_1 + z_A C_A, \tag{9}$$

for the membrane ($m = 2$; $1 \le Y \le 2$),

$$\frac{d\bar{C}_j}{dX} = z_j \bar{C}_j E - r\frac{J_j}{\bar{d}_j}, \quad j = 1, A, \tag{10}$$

$$z_1\bar{C}_1 + z_A\bar{C}_A = 1, \tag{11}$$

for the diffusion layer that accepts counterions ($m = 3$; $2 \le Y \le 3$),

$$\frac{d\bar{C}_j}{dX} = z_j C_j E - r\frac{J_j}{d_j}, \quad j = 1, A, \tag{12}$$

$$z_1 C_1 + z_A C_A = 0. \tag{13}$$

Equations (8)–(13) are complemented by the condition of the passing of an electric current and the condition of steady-stateness

$$z_1 J_1 + z_A J_A = I, \quad \frac{dJ_j}{dX} = 0, \tag{14a, 14b}$$

conditions on the first ($Y = 1$) and second ($Y = 2$) interfaces

$$C_j = e\bar{C}_j, \text{ where } e = Q/C_0, \tag{15a}$$

$$\frac{(\bar{c}_1^s)^{1/z_1}}{(\bar{c}_A^s)^{1/z_A}} = K_{1A}\frac{(c_1^s)^{1/z_1}}{(c_A^s)^{1/z_A}}, \tag{15b}$$

conditions at the external boundaries of the system

$$C_j(0) = C_j^{\mathrm{I}}, \quad C_j(3) = C_j^{\mathrm{II}}, \tag{16}$$

and it is also assumed that the electroneutrality condition

$$z_1 C_1^{\mathrm{I}} + z_A C_A^{\mathrm{I}} = 0 \tag{17}$$

is met at the left-hand external side of the system. As to the right-hand side of a three-layered system, the electroneutrality condition is obeyed in view of (13). By the limiting current $I_{\lim} = i/i_{\lim}^0$ we understand the current at which a limiting state arises in the model for a membrane system [16], i.e. when the electroneutrality condition replaces the Poisson equation in the first diffusion layer.

A Method of Solution

The boundary-value problem (8)–(17), which contains small parameter ε at a derivative, is solved by two methods. One solution is found by a numerical method of parallel shooting [15], while the other, by a method based on using the QCD condition [6, 12].

The first method is applicable at not-too-small values of small parameter ε. The problem under consideration is solved effectively only at $\varepsilon > 10^{-5}$. The integration segment $0 \le X \le 1$ ($0 \le Y \le 1$) in the first diffusion layer was divided into 20 subsegments $[X_{k,k+1}]$ $k = 1, \ldots, 20$. The integration of the Nernst–Planck equations, the Poisson equation, and equations (14b) for the fluxes was performed at each subsegment independently. The integration in the membrane and in the second diffusion layer was also done independently. The target function was formed with the aid of equations for matching solutions [15]. The integration was performed using Runge–Kutta methods of fourth order of accuracy and each subsegment $[X_{k,k+1}]$ was divided into five parts, which means that the integration step τ was equal to $1/(5 \times 20) = 10^{-2}$. As there are merely twenty sugsegments, and the matching of solutions was performed by five functions $C_1(X)$, $C_A(X)$, $J_1(X)$, $J_A(X)$, and $E(X)$, at each iteration step we had to invert a matrix of dimensionality of order 100×100. For even smaller values of the small parameter ($\varepsilon < 10^{-5}$), each segment must be divided into a still greater number of parts, which increases the system's dimensionality, compromises the convergence of the method, and raises the computation time. The method is described in detail elsewhere [15].

The methods underlying the LSODI integrator used in [13, 14] are α-stable implicit Gear methods of fifth order of accuracy. That is why solutions obtained by either method are rather accurate and practically coincide at $\varepsilon \ge 10^{-5}$ throughout the entire integration range $0 \le X \le 1$. When modeling a real electrodialysis, parameter ε may be much smaller than 10^{-5}: its values vary from 10^{-12} to 10^{-4}. At $\varepsilon < 10^{-5}$ one has to use approximate solutions in the first diffusion layer, for example, the QCD method [6, 12]. The QCD condition assumes a slow change in the charge density along a coordinate,

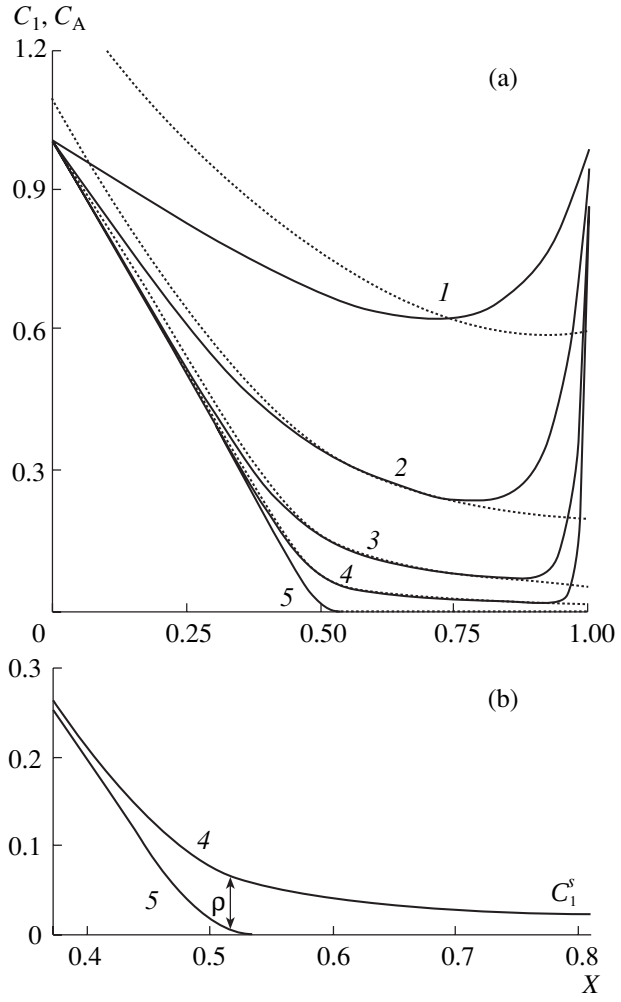

Fig. 1. (a) Distributions of concentration of counterions (j = 1) in first diffusion layer at $I = 2I_{lim}$ and ε of (*1*) 0.1, (*2*) 0.01, (*3*) 0.001, and (*4*) 0.0001; curve *5* shows distribution of co-ions (j = A) at ε = 0.0001; dashed lines represent QCD calculations; initial data: $d_1 = 0.5$, $d_A = 0.71$, $J_A = 0$, $C_1(0) = C_1(1) = 1$; and (b) distributions of (*4*) counterions and (*5*) co-ions at ε = 0.0001 and $X \in [0.4–0.8]$.

i.e. $\frac{d\rho}{dX} \approx 0$, rather than assuming a small charge density, i.e. $\rho \approx 0$, as in the local electroneutrality condition. The QCD condition is a more accurate approximation to the Poisson equation than traditional electroneutrality condition. The QCD condition is met throughout the entire volume of the diffusion layer, including SCR, with the exception of a microscopic quasi-equilibrium EDL at the boundary with the membrane [12].

The authors of [13] used the condition of continuity of dimensional concentrations and potential (5) at the interfaces between the membrane and diffusion layers. In calculations that use the QCD condition, the condition of continuity of concentrations at the interface the first diffusion layer/membrane cannot be used (Fig. 1) and must be replaced by some other relationship. Seeing in Fig. 1 that the concentration gradient at $X \approx 1$ is very great, specifically, $dC/dX \geq 10^3$ at any $\varepsilon \leq 10^{-3}$ and ion fluxes J_j are no greater than 10 for currents $I/I_{lim} <$ 2–10, we can write the dimensional equality

$$\frac{1}{c_j}\frac{dc_j}{dx} \cong -z_j\frac{F}{RT}\frac{d\varphi}{dx}, \qquad (18)$$

which is practically exact in the region $1 - \lambda \leq X \leq 1$. This condition, which follows from the Nernst–Planck equations, is more accurate at smaller ε. Integrating (18) in the limits $1 - \lambda \leq X \leq 1 + \bar{\lambda}$, we obtain [2, 12]

$$\ln\left[\frac{c_j(X = 1 + \bar{\lambda})}{c_j(X = 1 - \lambda)}\right] = \ln\frac{\bar{c}_j^s}{c_j^s} = -z_j\frac{F}{RT}\Delta\varphi. \qquad (19)$$

Assuming that $c_j(X = 1 - \lambda) = c_j^s$ is the boundary concentration in the left-hand diffusion layer and $c_j(X = 1 + \bar{\lambda}) = \bar{c}^s$ is the boundary concentration in the membrane, equation (19) leads to the Donnan equation with $k_{1A} = 1$:

$$\left.\frac{(\bar{c}_1^s)^{1/z_1}}{(\bar{c}_A^s)^{1/z_A}}\right|_{m=1} = \left.\frac{(c_1^s)^{1/z_1}}{(c_A^s)^{1/z_A}}\right|_{m=2}. \qquad (20)$$

If condition (20) with $k_{1A} = 1$ is applied to the second interface membrane/diffusion layer, then, as follows from the above, the stationary solutions within the model used by the authors of [13], who assumed that concentrations were continuous at interface, and calculations with (8)–(17) will be consistent.

The application of the QCD condition eliminates the integration of equations of transport in a very thin EDL [13]. The application of the QCD condition for a multilayered boundary-value problem allows one to employ the same interfacial boundary conditions that are employed in the case of the electroneutrality condition. If the electroneutrality condition is violated, the application of the QCD condition simplifies the solution and analysis of transport problems. The QCD method was designed in [6, 12] specifically for simplifying a complex singularly-perturbed problem. The QCD method can, hypothetically, be effectively applied to solving precisely the multilayered boundary-value problems [6, 12]. Solutions obtained with both methods ([6] and [15]) are compared below.

Thus, if one desires to employ the QCD condition, equations (5a) and (5b) must be replaced with equations (20) and (19). As in the first diffusion layer we employed the QCD condition, the boundary-value problem reduced to independent integration in the membrane and in the diffusion layers without dividing the integration region in the membrane and in the diffusion layers into subsegments $[X_{k,k+1}]$ and to a subsequent search for the roots of a set of nonlinear equations with two unknowns. For the unknowns we selected J_1 and the right-hand boundary concentration in the mem-

brane $\bar{c}_j\,(Y = 2)$. For the target functions we selected functions obtained from equations (15b) and (20) as reported in [15]. In this case one has to invert a small matrix of size (2×2).

With the QCD condition employed, the solution of problem (8), (9) reduces to the solution of a simple cubic equation for strength E, which has the following form at $z_1 = -z_A = 1$ [6, 10]:

$$\frac{\varepsilon}{2}E^3 - (G_0X - \alpha)E - G_1 = 0. \qquad (21)$$

Here, $G_0 = J_1/d_1 + J_A/d_A$, $\alpha = C_I^1 + C_A^1$, and $G_1 = J_1/d_1 - J_A/d_A$. Having found the distribution $E(x)$ at given I and J_1, we can find relevant concentrations $C_1(x)$ and $C_A(x)$ by integrating the Nernst–Planck equations. The method's justification is most comprehensively rendered in [6].

RESULTS AND DISCUSSION

Concentration Distribution in the First Diffusion Layer

Figure 1a compares concentration distributions calculated at different values of ε by two methods. One solution is found by a numerical method of parallel shooting with use made of the Poisson equation, while the other, by solving cubic equation (18) derived using the QCD condition. We clearly see in the figure that the solutions obtained with use made of the QCD condition practically coincide with the numerical solution virtually throughout the entire range of X even at $\varepsilon = 10^{-3}$. The only exception is the narrow segment $1 - \lambda \le X \le 1$, where λ has an asymptotic estimate of $\sqrt{\varepsilon}$. At large values of small parameter ε ($\varepsilon > 10^{-2}$), the deviation becomes noticeable. At $\varepsilon \ge 10^{-1}$, the method based on the QCD condition becomes useless. Thus, method [15] is applicable at $\varepsilon > 10^{-5}$, while method [6], at $\varepsilon < 10^{-2}$. At $10^{-5} < \varepsilon < 10^{-2}$, both methods yield results that coincide to within their errors.

Figure 1b shows the region where variations in the concentrations of counterions $\frac{dc_1}{dx}$ and co-ions $\frac{dc_A}{dx}$ have substantially different rates. This difference is responsible for the emergence of a maximum of the density of charge ρ (Fig. 2), whose position is dependent on the magnitude of the current (for details, see [6, 10, 13]). Figure 1b ($I = 2I_{lim}$) also shows that at large values of small parameter ε the space charge occupies the entire diffusion layer and steadily increases along the X coordinate. With decreasing ε, a quasi-electroneutral region starts forming to the right of $X = 0$ (approximately in the interval $0 \le X \le 0.4$ at $I = 2I_{lim}$). At $0.6 \le X \le 1 - \lambda$, an electromigration region forms in the space-charge region. The diffusion makes virtually no contribution to the mass transfer in the electromigration region (Fig. 1 for $\varepsilon \ge 10^{-4}$). The electric field strength in the electromigration region becomes considerable, ensuring constancy of fluxes of counterions despite their small concentration. Between the quasi-electroneutral regions and the electromigration region, the density of a volume charge reaches a maximum. The consequences of importance from a practical side, to which the formation of the maximum leads, were discussed in [1, 2]. In the fourth region ($1 - \lambda \le X \le 1$), the electromigration and the diffusion are nearly identical by their absolute values but are oriented in opposite directions and reach maximum values (region of a quasi-equilibrium EDL [2, 10, 12]). One should bear in mind that the quantity ρ in Fig. 2. is a dimensionless quantity and with increasing external concentration C_0 dimensionless parameter ε diminishes while dimensional density $\tilde{\rho} = \rho C_0$ rises. Dimensional values of $\tilde{\rho}$ for curves *1* and *4* will differ by four orders of magnitude at the same δ and $I = 2I_{lim}$.

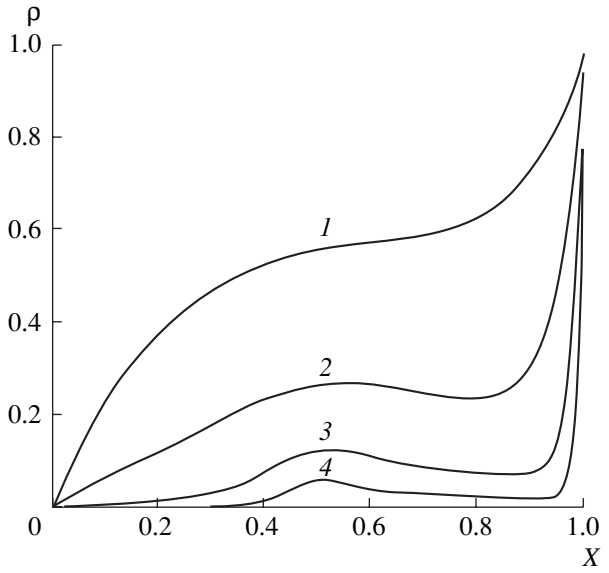

Fig. 2. Distributions of charge density $\rho = C_1(X) - C_A(X)$ in first diffusion layer at values of ε and initial parameters as in Fig. 1.

The Current–Voltage Curves

The curves in Fig. 3 illustrate how concentrations are distributed in three layers in two cases, specifically, at $i/i_{lim} = 0.5$ and $i/i_{lim} = 2$. From the figure we see and calculations show that in overlimiting modes the left-hand boundary concentration of co-ions in the membrane $\bar{C}_A^s$ is close to zero ($<10^{-6}$). This also follows from formulas (11) and (20), provided one takes into account that the product $C_1^s C_A^s$ in an overlimiting mode is also less than 10^{-6}. At $i > i_{lim}$, the concentration $\bar{C}_A^s\big|_{Y=1} \approx 0$; therefore, the boundary-value problem

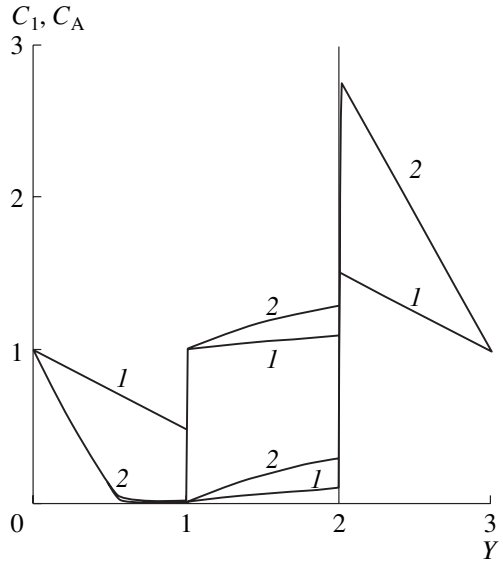

Fig. 3. Concentration distributions in a membrane system at (*1*) $I = 0.5I_{lim}$ and (*2*) $I = 2I_{lim}$; initial data: $\varepsilon = 6.82 \times 10^{-6}$; $d_1 = 0.5$; $d_A = 0.71$; $\bar{d}_1 = 0.5$; $\bar{d}_A = 0.71$; $r = 1$; $K_{1A} = 0.05$.

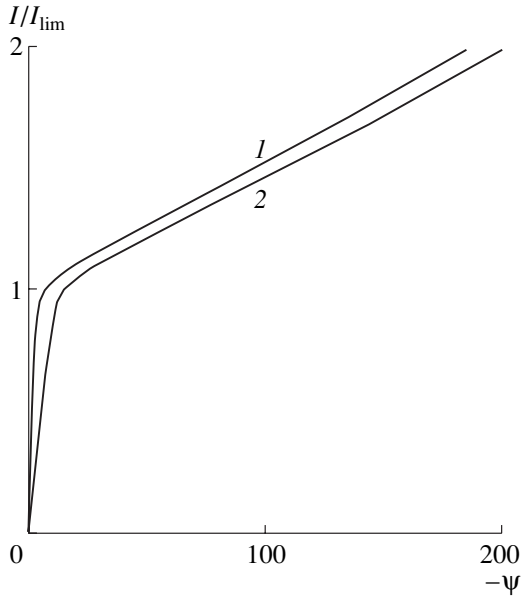

Fig. 4. Current–voltage curves for the data given in Fig. 3: (*1*) potential drop across first diffusion layer and (*2*) potential drop across the entire system.

(8)–(17) splits into two mathematically independent problems. At first one solves a two-layered boundary-value problem (membrane and second diffusion layer) and determines $T_j = \dfrac{z_j F j_j}{i}$ at a given I and, consequently, $J_j = \dfrac{j_j F}{i^0_{lim}} = \dfrac{j_j \delta}{D_1 C_0 (1+z)}$. Then one solves the second problem using the QCD condition and determines the concentration distribution in the first diffusion layer. The concentration distributions thus obtained allow one to construct current–voltage curves in the entire system. The current–voltage curves for one layer are analyzed in [2, 6]. A similar analysis for a three-layered system was done by the authors of [13]. Here we will estimate the contribution made by the membrane, the second diffusion layer, and the voltage drops across the interfaces to the voltage drops in a membrane system. Figure 4 shows that in the first diffusion layer this contribution ΔU_1 is no less than 80%. Hence, in an overlimiting mode, no more than 20% of the overall potential drop in the system occur across the membrane, the second diffusion layer, and the interfaces.

The Selectivity of a Membrane System

It is well known that in dilute solutions, when it is of interest to investigate overlimiting current modes, the selectivity of the transport of counterions is close to 100%. Nonetheless, mathematical models have also relative independence, and we will consider in the framework of the model presented in the foregoing the mechanism of the dependence of effective transport numbers $T_j = \dfrac{z_j j_j F}{i}$ on the current density and other parameters of the model. Such a consideration may come handy when considering more complex membrane systems containing several competing counterions, when a knowledge of the T_j vs. i dependence is of importance from a practical viewpoint.

The boundary-value problem for the entire system splits into two independent problems and effective transport numbers $T_j = z_j j_j F/i$ are found by solving the first problem. From this, in the framework of the model presented, follows an interesting in theoretical respect conclusion: in an overlimiting mode, the selectivity of a membrane system, i.e. T_j, is defined only by properties of the membrane and the second diffusion layer. The first diffusion layer exerts only an implicit influence through the magnitude of the limiting current.

In a special case where $D_j = \bar{D}_j$, $c_j^{I} = c_j^{II}$, and $z_1 = |z_A| = 1$ this conclusion gains an analytical confirmation. In the framework of the model proposed by the authors of [13] an exact formula was derived, which was valid at any currents $i \geq 0$. As the approximation (18), (19) is quite good, the model will be exact also in the framework of the above model with the constant $k_{1A} = 1$

$$\eta = -\frac{J_1}{J_A} = \frac{D_1}{D_A}\frac{\delta\langle c_1\rangle_1 + d\langle \bar{c}_1\rangle + \delta\langle c_1\rangle_2}{\delta\langle c_A\rangle_1 + d\langle \bar{c}_A\rangle + d\langle c_A\rangle_2}$$
$$= \frac{D_1}{D_A}\left\{\frac{\dfrac{\delta C_0}{dQ}[\langle C_1\rangle_1 + \langle C_1\rangle_2] + \langle \bar{C}_1\rangle}{\dfrac{\delta C_0}{dQ}[\langle C_A\rangle_1 + \langle C_A\rangle_2] + \langle \bar{C}_A\rangle}\right\}. \qquad (22)$$

Here, $\eta = T_1/T_A$ characterizes the selectivity of the transport; $\langle c_j\rangle_1 = (\int_0^\delta c_j(x)dx)/\delta$ is the dimensional average integral concentration of ions of the jth sort in the first diffusion layer $\langle c_j\rangle^2 = (\int_{d+\delta}^{d+2\delta} c_j(x)dx)/\delta)$; $\langle \bar{c}_j\rangle = (\int_\delta^{d+\delta} \bar{c}_j(x)dx)/d$ is the same for ions in the membrane; $\langle C_j\rangle_{1,2}$ and $\langle \bar{C}_j\rangle$ are similar designations in a dimensionless form; and $C_0 = c_1^I$ is the external concentration of electrolyte.

One can readily infer from Figs. 1 and 3 that, with increasing current, concentrations $\langle C_j\rangle_1$ in the first diffusion layer diminish, while concentrations $\langle C_j\rangle_2$ in the second diffusion layer rise. Therefore, values of η are formed chiefly by the sum of the concentration $\langle \bar{C}_j\rangle$ in the membrane and the concentration $\langle C_j\rangle_2$ in the second diffusion layer.

In view of the validity of the equalities

$$\Omega = \langle C_j\rangle_1 + \langle C_j\rangle_2 \approx \begin{cases} 2, & \text{if } i \le i_{\lim} \\ 1 + 0.5\left(\dfrac{I}{I_{\lim}} + \dfrac{I_{\lim}}{I}\right), & \text{if } i > i_{\lim}, \end{cases}$$

$$C_1^s\big|_{Y=2} \approx 1 + \frac{I}{I_{\lim}},$$

$$\bar{C}_1^s\big|_{Y=2} = \frac{1}{2} + \sqrt{\frac{1}{4} + K_{1A}(C_1^s\big|_{Y=2})^2}, \qquad (23)$$

$$\bar{C}_A^s\big|_{Y=2} = \bar{C}_1^s\big|_{Y=2} - 1, \quad \langle \bar{C}_j\rangle,$$

$$\eta = \frac{D_1}{D_A}\frac{\frac{C_0\delta}{Qd}\Omega + \bar{C}_1^s\big|_{Y=2}}{\frac{C_0\delta}{Qd}\Omega + \bar{C}_A^s\big|_{Y=2}}, \quad T_1 = \frac{\eta}{1+\eta},$$

one can use them for an approximate estimation of effective transport numbers at any currents mentioned in the above special case. The relative error of formulas (23), when performing calculations with the same constant $K_{1A} = 0.05$ (Fig. 5) as in the model (8)–(17), reaches 15% in some cases of a considerable backward diffusion, largely because of the approximation $\langle \bar{C}_j\rangle \approx \bar{C}_j^s\big|_{Y=2}$. That is why, when calculating curves in Fig. 5 (dashed lines) with approximate formula (23), we selected $K_{1A} = 0.027$. The selection was made from the condition of best coincidence with numerical calculations (solid lines) for any modes specified by parameter $\frac{\delta C_0}{dQ} = \frac{K_{1A}}{r}$, ($k_{1A} = 1$, $D_j = \bar{D}_j$, $c_j^I = c_j^{II}$, $z_1 = |z_A|$). As

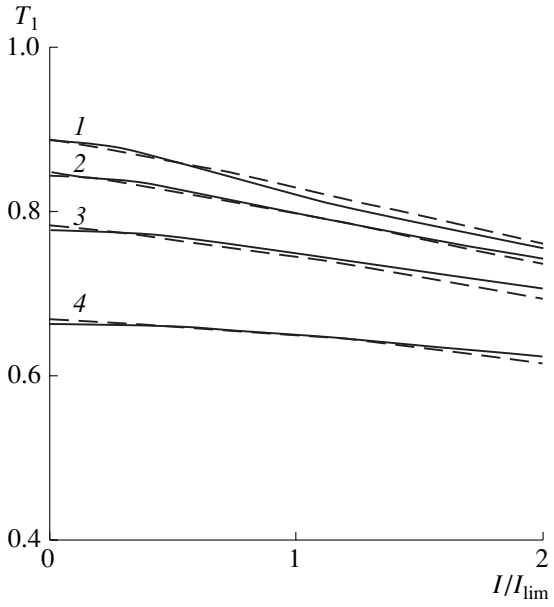

Fig. 5. Dependences of effective transport numbers (solid lines) on current density at initial data given in Fig. 3 in different kinetic modes r: (*1*) 2, (*2*) 1, (*3*) 0.5, and (*4*) 0.2; dashed lines represent calculations with approximate formula (22) at $K_{1A} = 0.027$ and $\frac{C_0\delta}{Qd}$ of (*1*) 0.035, (*2*) 0.060, (*3*) 0.110, and (*4*) 0.270.

we see from this formula, with decreasing ratio $\frac{C_0\delta}{Qd}$, the selectivity of a membrane system is defined by the membrane properties, and the estimate

$$-\frac{J_1}{J_A} \approx \frac{\bar{D}_1\langle \bar{c}_1\rangle}{\bar{D}_A\langle \bar{c}_A\rangle} = \frac{\bar{t}_1}{\bar{t}_A} \quad (\text{because } D_j = \bar{D}_j) \qquad (24)$$

is valid. At large values of the ratio $\frac{C_0\delta}{Qd}$ the selectivity is defined by the solution properties

$$-\frac{J_1}{J_A} \approx \frac{D_1}{D_A} = \frac{t_1}{t_A}. \qquad (25)$$

Let us now consider the effect the initial parameters of the model have on the selectivity of a membrane system in a more general case, i.e. in the absence of any limitations ($k_{1A} = 1$, $D_j = \bar{D}_j$, $c_j^I = c_j^{II}$, $z_1 = z_A$). As it is impossible to derive an analytical formula in a more general case, we will restrict our consideration to qualitative evaluations.

The behavior of T_j in sublimiting modes as a function of the current density i at various values of initial parameters was thoroughly explored in [17]. The dependence of T_j on i, obtained numerically with the aid of QCD using model (8)–(17) at both sublimiting and overlimiting currents, appears in Fig. 5 at a fixed

K_{1A} and various values of the relative electrodiffusion resistance r of the membrane.

It is known (and clearly seen in Fig. 3) that the concentration $\bar{c}_A^s\big|_{Y=1}$ at the interface the first diffusion layer/membrane diminishes with increasing current density, whereas the concentration $\bar{c}_A^s\big|_{Y=2}$ at the interface the second diffusion layer/membrane increases. At the same time, the gradient of concentration of co-ions and the backward diffusion in the membrane increase. Moreover, on the whole, the concentration of co-ions increases, which leads to an increase in their electromigration transport number $\bar{t}_A$. The contribution made by the backward diffusion and the electromigration transport to the transport of co-ions depends on dimensionless relative penetrability $p = P\dfrac{\delta}{D_1 d}$ [2, p. 286], where P is the diffusion penetrability of a membrane for the salt under consideration. In the case we consider, it is more convenient to represent p in the form $p = K_{1A}/r = \left(k_{1A}\dfrac{\bar{D}_1 z_1 c_1^{II}}{Q}\right)\left(\dfrac{\delta}{D_1 d}\right) = P\dfrac{\delta}{D_1 d}$, where parameter r is normalized to $C_0^{II} = z_1 c_1^{II}$ in view of the principal influence exerted by the second diffusion layer on the system's selectivity in an overlimiting mode.

At $p \ll 1$, the electrodiffusion resistance of the membrane is large as compared with the second diffusion layer. In this case, the major contribution to the transport of co-ions is made by electromigration, $T_1 \approx \bar{t}_1$, and estimate (24) is valid. At $p \gg 1$, on the other hand, the principal contribution to the co-ion transport comes from the backward diffusion. Then, as shown in [2, p. 288], the effective transport number $T_1 \approx t_1$ approaches the value of the electromigration transport number in solution (estimate (25) and Fig. 5).

The deliberations we aired in the foregoing are confirmed by numerical calculations. At large values of the relative electrodiffusion resistance of the membrane ($r \geq 2$–5), the selectivity of a membrane system is defined by the membrane (Fig. 5), while at small values ($r \leq 0.2$), by the second diffusion layer. Once a limiting state is reached, the behavior of a membrane system with regard to the transport selectivity does not change, in principle. At $i > i_{lim}$, concentrations $\bar{c}_j^s\big|_{Y=2}$ continue increasing, whereas concentrations $\bar{c}_j^s\big|_{Y=1} \approx 0$ stop varying (Fig. 3). With increasing boundary concentrations $\bar{c}_j^s\big|_{Y=2}$, the backward diffusion and the electromigration of co-ions intensify still further. As a result, the effective transport number of the co-ions continues increasing.

The rate of decrease in T_1 (or increase in T_A) in an overlimiting state somewhat diminishes. There is a simple explanation for this phenomenon: a change in the current i by Δi in a sublimiting state makes boundary concentrations at the left, $\bar{C}_1^s\big|_{Y=1}$, and the right, $\bar{C}_1^s\big|_{Y=2}$, sides of the membrane alter by ΔC, i.e. an estimate of a change in the concentration gradient amounts to $2\Delta C/d$. In overlimiting states, increasing the current by the same quantity raises only the right-hand boundary concentration $\bar{C}_1^s\big|_{Y=2}$ while leaving the left-hand concentration $\bar{C}_1^s\big|_{Y=1}$ practically unchanged. That is why the increase in the diffusion gradient in this case is estimated by a halved quantity, specifically, $\Delta C/d$. Consequently, the decrease in T_1 will be not that obvious (Fig. 5, curve *1*). At $r < 0.2$–0.5, the selectivity of a membrane system is defined by selective properties of the solution $T_j \approx t_j$ in both sublimiting and overlimiting modes (curves *3*, *4*). At $0.5 < r < 2$, the selectivity is affected by both the membrane and the solution.

CONCLUSIONS

A mathematical model describing the passing of an overlimiting current in a membrane system is examined. The violation of local electroneutrality in a depleted diffusion layer is accounted for by employing the Poisson equation. A comparison with a more complex model is made. The distinguishing feature of the model in question, which was put forth by the authors of [13], is that the Poisson equation is applied in all three regions (membrane and two diffusion layers). There is a complete coincidence of calculated concentration distributions (with the exception of the region of a quasi-equilibrium EDL) and current–voltage curves at any currents, provided parameters were selected in a proper manner. This testifies that one can ignore phenomena of violation of electroneutrality in the membrane and in the second diffusion layer, provided there is no need for detailed information about EDL in these layers.

A boundary-value problem is solved by two methods. One is a numerical method of parallel shooting [15], which effectively operates at $\varepsilon > 10^{-5}$. The other employs an approximate QCD condition and ensures sufficient enough accuracy at $\varepsilon < 10^{-2}$ (ε is a small parameter in the Poisson equation written in a dimensionless form). It is shown that at $10^{-5} < \varepsilon < 10^{-2}$ both methods yield results that coincide to within the calculation error.

The parallel-shooting method, intended mostly for solving multilayered problems, may come useful for describing electrical mass transfer in both sublimiting and overlimiting modes ($\varepsilon > 10^{-5}$). Use of the QCD condition at $\varepsilon < 10^{-2}$ radically simplifies the solution of the initial set of equations. In sublimiting modes, use of

the QCD condition is identical to the electroneutrality condition. At currents $i > i_{lim}$, the QCD condition allows one to make use of the same equilibrium condition at an interface as in the case of an electroneutral model that employs the condition of continuity of electrochemical potential.

A comparison of three different methods of solution of the problem of electrical mass transfer of ions in a membrane system with use made of the Poisson equation (a third method of solution, with the aid of an LSODI integrator, was employed by the authors of [13]) testifies that the obtained results are reliable. If there is no need to obtain accurate information about the distribution of concentrations in a quasi-equilibrium EDL, we recommend the QCD method (valid at $\varepsilon < 10^{-2}$), as the most interesting from a practical standpoint, simple, and easily applicable.

The presented model may come useful for a more complete study of the electrodiffusion phenomena in an overlimiting state, if the water dissociation and the conjugated convection are taken into account.

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