JOURNAL OF COMPUTATIONAL PHYSICS 75, 1–14 (1988)

# A Numerical Approach to Ionic Transport Through Charged Membranes

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Received November 25, 1986; revised February 13, 1987

The ionic transport through charged membranes has been often described in terms of Nernst–Planck and Poisson equations. The intrinsic nonlinearity of the mentioned equation system poses certain problems not always satisfactorily solved. We propose here a finite-difference numerical method for the solution of the steady state transport across charged membranes when an electric current density and a convective flux are involved. The method is capable of dealing with an arbitrary number of ionic species of any charge number. The numerical stability and the ease and flexibility for introducing the boundary conditions in the equation system, are some of the main features of the algorithm. © 1988 Academic Press, Inc.

## INTRODUCTION

When studying the ionic transport processes across liquid junctions and membranes, the macroscopic model based on Nernst–Planck flux equations and the electrostatic Poisson's equation is one of the most widely used [1, 2]. It was Planck [3, 4] who first suggested that the transport of charged matter could be described by an equation system containing so many Nernst–Planck (NP) flux equations as ionic species involved, in addition to another equation relating the local differences in the concentration of ions with the electric potential common to all NP equations. The latter expression is the Poisson equation of electrostatics. The NP equations were originally worked out from a given kinetic model of diffusion, though they may be regarded as an approximation to the (exact) nonequilibrium thermodynamics equations [5].

Despite the fact that NP equations account for the essential physical membrane phenomena, it is rather surprising how such a simple equation has such great propularity in different fields as the transport in semiconductors and electrolyte solutions, the metal-electrolyte interfacial kinetics, etc. [6].

Since its formulation, NP equations have generated large amounts of literature concerning the problem of its solution. While in their original formulation [3, 4], NP equations included a small number of parameters, further extensions of the equations to cover ionic transport through membranes have demanded the introduction of certain refinements [2]. According to this, the early proposed

0021-9991/88 $3.00

equations for the description of nonconvective transport through solution layers have turned out to be a complex equation system.

In order to solve NP equations, two hypotheses have been often used, namely the "electroneutrality" and the "constant electric field" assumptions. The mentioned approximations permit us to reach a closed solution of the problem in some (simple) cases (not allowing for a nonzero convective flux, or with restrictive conditions in the number of ions considered, for example). The need of an exact general solution for ionic transport problems and the study of the significance and applicability limits of the abovementioned assumptions may be, perhaps, some of the reasons why several authors have tackled with this problem numerically [6–10]. In addition, there are some situations that demand an exact integration of NP equations. The study of the space charge density over the diffusion zone [7], is one of these problems.

When solving the NP and Poisson equation system in the context of a given membrane system, there are four problems stating the need for a numerical method. These are as follows:

(1) The intrinsic nonlinearity of the problem. This fact comes from Poisson's equation as well as from the second term of the NP equation.

(2) The need of dealing with multiionic systems without introducing restrictive approximations on the charge numbers.

(3) The problem of considering simultaneously three mechanisms of transport: diffusion, convection, and electric conduction.

(4) The complexity that arises from considering a "membrane" composed of a charged membrane and two unstirred layers of finite thicknesses adhered to both membrane surfaces (these layers exert some effects on the process of transport [1]).

Bearing in mind (1)–(4), it seems clear that even introducing the electroneutrality assumption, a general solution of the problem dealt with here calls for numerical procedures. The numerical algorithm employed is a "finite-difference" method including refinements in distance scaling. The finite-difference scheme previously worked out by French [11] paved the way for the numerical treatment to come.

## FORMULATION OF THE PROBLEM

The steady state electrodiffusion equations ruling the ionic transport across a membrane are four. First, we have the NP equation (in diluted solution form)

$$\bar{J}_i = -\bar{D}_i\left(\frac{d\bar{c}_i}{d\bar{x}} + \bar{c}_i z_i \frac{F}{RT}\frac{d\bar{\phi}}{d\bar{x}}\right) + \bar{v}\bar{c}_i, \qquad i = 1, 2, \ldots, n, \tag{1}$$

where $\bar{J}_i$, $\bar{D}_i$, $\bar{c}_i$, and $z_i$ stand for the flux, the diffusion coefficient, the molar concentration, and the charge number of ion $i$, respectively; $\bar{x}$ is the position along the diffusion zone ($\bar{x}$ runs from $\bar{x}=0$ to $\bar{x}=d$, being $d$ the diffusion zone thickness). $\bar{\phi}$ denotes the electric potential, $\bar{v}$ is the convection, and $n$ is the number of ions. Constants $F$, $R$, $T$ have their usual meaning.

Equations (1) are restricted by the so-called continuity equations

$$\frac{d\bar{J}_i}{d\bar{x}}=0, \qquad i=1, 2,..., n-1. \tag{2}$$

On the other hand, Poisson's equation connects $\bar{\phi}$ with ionic concentrations $\bar{c}_i$. It reads

$$\frac{d^2\bar{\phi}}{d\bar{x}^2}=-\frac{F}{\varepsilon}\left(\sum_i^n z_i\bar{c}_i+\omega\bar{X}\right), \tag{3}$$

$\varepsilon$ being the dielectric constant of the medium. $\bar{X}$ is the fixed charge concentration in the membrane phase, $\omega$ being the sign of this charge. In addition, ionic fluxes are coupled by means of the equation for the electric current density $\bar{I}$,

$$\bar{I}=F\sum_i^n z_i\bar{J}_i. \tag{4}$$

Equations (1)–(4) assume an unidimensional transport problem. These equations may be written down in dimensionless form using the following transformations

$$x=\bar{x}/\bar{l}_0 \tag{5}$$

$$c_i=\bar{c}_i/\bar{c}_0, \qquad i=1, 2, ..., n \tag{6}$$

$$D_i=\bar{D}_i/\bar{D}_0, \qquad i=1, 2, ..., n \tag{7}$$

$$J_i=\bar{J}_i\bar{l}_0/\bar{c}_0\bar{D}_0, \qquad i=1, 2, ..., n \tag{8}$$

$$v=\bar{v}\bar{l}_0/\bar{D}_0 \tag{9}$$

$$\phi=\bar{\phi}F/RT \tag{10}$$

$$I=\bar{I}\bar{l}_0/F\bar{c}_0\bar{D}_0 \tag{11}$$

$$X=\bar{X}/\bar{c}_0, \tag{12}$$

where $\bar{c}_0$, $\bar{D}_0$, and $\bar{l}_0$ are suitable scaling factors for the concentration, the diffusion coefficient and the distance, respectively. With the new dimensionless parameters, Eqs. (1)–(4) can be rewritten as

$$J_i=-D_i\left(\frac{dc_i}{dx}+c_iz_i\frac{d\phi}{dx}\right)+c_iv, \qquad i=1, 2, ..., n \tag{13}$$

$$\frac{dJ_i}{dx}=0, \qquad i=1, 2, ..., n-1 \tag{14}$$

$$\frac{d^2\phi}{dx^2} = -\alpha\left(\sum_i^n z_i c_i + \omega X\right) \tag{15}$$

$$I = \sum_i^n z_i J_i, \tag{16}$$

where $\alpha$ is a dimensionless constant, given by the expression

$$\alpha = \frac{F^2 l_0^2 \bar{c}_0}{\varepsilon RT}. \tag{17}$$

Consider a simple membrane system conceptually similar to that of a constrained diffusion junction [1] of thickness $d$ (see Fig. 1). The membrane is regarded to be porous and free from fixed charge. In addition, the membrane is flanked by two electrolyte solutions at different concentration. Both solutions are artificially maintained homogeneous by means of a suitable experimental setup.

Our aim is solving Eqs. (13)–(16) in this experimental arrangement. The results obtained will be the (constant) ionic fluxes as well as the concentrations and electric potential gradient profiles along the system. The membrane potential is readily computed by integrating the latter profile through the diffusion zone. According to this, we have an equation system with $2n$ equations and $2n$ variables.

As is shown later, the algorithm allows for different choices of boundary conditions. The experimental situation here described suggests considering these conditions to be

$$\begin{aligned} c_i(0) &= c_{i\mathrm{L}}, \qquad i = 1, 2, \ldots, n \\ c_i(d) &= c_{i\mathrm{R}}, \qquad i = 1, 2, \ldots, n. \end{aligned} \tag{18}$$

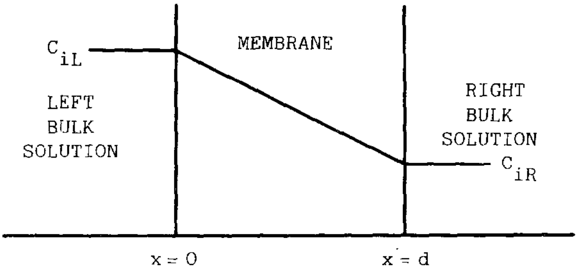

FIG. 1. Schematic representation of a constrained diffusion junction. $c_{\mathrm{L,R}}$ denote the concentrations on the left of $x=0$ and on the right of $x=d$, respectively.

## NUMERICAL PROCEDURE

In the case of multiionic systems, the number of variables to be handled demands a matrix notation. This choice simplifies the algebra to come. So, let us define a column matrix (vector) $Y$ whose elements $y_i$ are the variables of the problem

$$\begin{aligned} y_i &= c_i(x) \qquad && i = 1, 2, \ldots, n, \\ y_{n+1} &= \frac{d\phi}{dx}(x) && \\ y_{n+1+k} &= J_k && k = 1, 2, \ldots, n-1. \end{aligned} \tag{19}$$

Note that as follows from Eq. (16), there are only $n-1$ independent ionic fluxes. Equations (13)–(16) can be rewritten in terms of the $y_i$'s. Denote $y_i' = dy_i/dx$. Then, a set of equations $y_i' = f(y_1, y_2, \ldots, y_{2n})$ is readily achieved. We thus obtain—in matrix form—the equation

$$Y' = \begin{bmatrix} y_1' \\ \vdots \\ y_{n-1}' \\ y_n' \\ y_{n+1}' \\ y_{n+2}' \\ \vdots \\ y_{2n}' \end{bmatrix} = \begin{bmatrix} -z_1 y_1 y_{n+1} - y_{n+1+1}/D_1 + y_1 v/D_1 \\ \vdots \\ -z_{n-1} y_{n-1} y_{n+1} - y_{2n}/D_{n-1} + y_{n-1} v/D_{n-1} \\ -z_n y_n y_{n+1} + \sum\limits_{k=1}^{n-1} E_k y_{n+1+k} - I/z_n D_n + y_n v/D_n \\ -\alpha \sum\limits_{k=1}^{n} y_k z_k \\ 0 \\ \vdots \\ 0 \end{bmatrix}, \tag{20}$$

where $E_k = z_k/z_n D_n$. Our goal is to solve the differential equation $Y' = F(Y)$, substituting its elements by finite-difference expressions. According to this, we divide the diffusion zone (membrane) into $M$ equal subintervals so that a grid of space points $x_1, x_2, \ldots, x_{M+1}$ may then be defined. If we take the distance scaling factor to be $\bar{l}_0 = d$, then $x_1 = 0$ and $x_{M+1} = 1$ (in reduced units), being $h = 1/M$ the thickness of each interval (see Fig. 2).

The iterative procedure starts from a set of guessed values for variables $y_i$. So, an approximate profile of each variable along the diffusion zone is required. As a first approximation, a linear relationship between $y_i$ and $x$ may be assumed, though in some physical problems this assumption bears no resemblance with the final solution. However, the stability of the method permits us to reach the desired convergence after several iterations.

Once the initial guess $Y^{(0)}$ is made, the iterative relationship

$$Y'^{(m+1)} = Y'^{(m)} + \mathscr{J}^{(m)}(Y^{(m+1)} - Y^{(m)}) \tag{21}$$

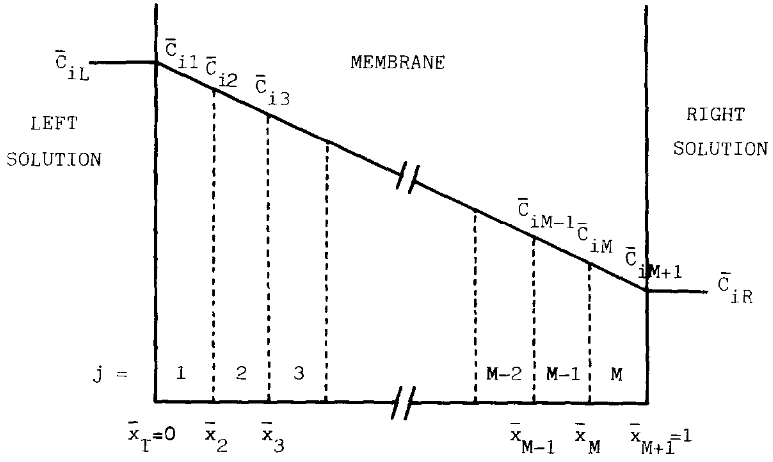

FIG. 2. Typical space grid. The grid spacing $h$ is constant, being $h = 1/M$. The refinements in the space grid are not represented.

applies, where superscripts denote the level of iteration. $\mathscr{J}$ stands for the jacobian matrix whose $ij$th element is given by

$$\mathscr{J}_{ij} \equiv \frac{\partial Y'_i}{\partial Y_j} \qquad i, j = 1, 2, ..., 2n. \tag{22}$$

Let us write Eq. (21) for the values vector $Y$ takes in the middle points of the space grid. Then

$$\tilde{Y}_j'^{(m+1)} = F(\tilde{Y}_j)^{(m)} + \tilde{\mathscr{J}}_j^{(m)}(\tilde{Y}_j^{(m+1)} - \tilde{Y}_j^{(m)}), \qquad j = 1, 2, ..., n, \tag{23}$$

where

$$\tilde{Y}_j^{(m)} = (Y_{j+1}^{(m)} + Y_j^{(m)})/2. \tag{24}$$

By substituting for $\tilde{Y}_j'^{(m)}$ (in finite-difference form) into Eq. (23), we obtain

$$\frac{I}{h}(Y_{j+1}^{(m+1)} - Y_j^{(m+1)}) = F(\tilde{Y}_j)^{(m)} + \tilde{\mathscr{J}}_j^{(m)}(\tilde{Y}_j^{(m+1)} - \tilde{Y}_j^{(m)}), \tag{25}$$

where $I$ is the identity matrix ($2n \times 2n$). Bearing in mind Eq. (24) and rearranging Eq. (25) so that the calculated matrices at $m+1$ iteration are placed in the first term of the latter equation, Eq. (25) yields

$$\left(\frac{I}{h} - \frac{1}{2}\tilde{\mathscr{J}}_j^{(m)}\right) Y_{j+1}^{(m+1)} - \left(\frac{I}{h} + \frac{1}{2}\tilde{\mathscr{J}}_j^{(m)}\right) Y_j^{(m+1)} = F(\tilde{Y}_j)^{(m)} - \tilde{\mathscr{J}}_j^{(m)}\tilde{Y}_j^{(m)}. \tag{26}$$

Let us define matrices $P_j$ and $Q_j$ and vector $R_j$ as

$$\begin{aligned} P_j &= \frac{I}{h} - \frac{1}{2}\tilde{\mathscr{J}}_j^{(m)} \\ Q_j &= \frac{I}{h} + \frac{1}{2}\tilde{\mathscr{J}}_j^{(m)} \\ R_j &= F(\tilde{Y}_j)^{(m)} - \tilde{\mathscr{J}}_j^{(m)}\tilde{Y}_j^{(m)}. \end{aligned} \tag{27}$$

Then, Eq. (26) reads

$$P_j Y_{j+1}^{(m+1)} - Q_j Y_j^{(m+1)} = R_j. \tag{28}$$

Multiplying Eq. (28) by $-Q_j^{-1}$, and defining

$$\begin{aligned} V_j &= -Q_j^{-1}P_j \\ U_j &= -Q_j^{-1}R_j \end{aligned} \tag{29}$$

we reach

$$Y_j^{(m+1)} + V_j Y_{j+1}^{(m+1)} = U_j. \tag{30}$$

Equation (30) is written for each $j$-interval ($j = 1, 2, ..., M$). Equations (18) constitute the set of boundary conditions most widely used in this sort of problem. However, in some cases other boundary conditions fit better. Then our algorithm is not restricted to conditions (18). Usually, boundary conditions are taken to be a given set of physical parameters which are defined in the limits of the membrane phase (an experimental determination of any physical magnitude inside the membrane is hardly possible). So, in general, boundary conditions will be written in terms of $Y_{j=1}$ and $Y_{j=M+1}$ (these vectors contain the values the $2n$ variables take at both extremes of the diffusion zone). In matrix form, boundary conditions are added by means of equation

$$K_0 Y_1^{(m+1)} + K_d Y_{M+1}^{(m+1)} = G, \tag{31}$$

where $K_0$ and $K_d$ are $(2n \times 2n)$-matrices in agreement with the set of boundary conditions chosen. Vector $G$ contains just the values these variables take at the diffusion zone extremes. In the present case and bearing in mind Eq. (18), Eq. (31) would be written

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \bar{c}_1(0) \\ \bar{c}_2(0) \\ \bar{\phi}'(0) \\ \bar{J}_1(0) \end{bmatrix} + \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \bar{c}_1(d) \\ \bar{c}_2(d) \\ \bar{\phi}'(d) \\ \bar{J}_1(d) \end{bmatrix} = \begin{bmatrix} \bar{c}_{1L} \\ \bar{c}_{2L} \\ \bar{c}_{1R} \\ \bar{c}_{2R} \end{bmatrix}, \tag{32}$$

where $n = 2$ (binary system) has been considered. Obviously, Eq. (32) and Eq. (18) contain the same information. However, the great flexibility achieved by means of Eq. (31) is clear. In fact, a set of $2n$ different boundary conditions can be obtained just by appropriately modifying matrices $K_0$ and $K_d$ and vector $G$.

It is possible to rewrite the $M$ Eqs. (30) and Eq. (31) as a unique matrix equation whose elements are also matrices. This leads to the equation

$$\begin{bmatrix} I & V_1 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & I & V_2 & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & \cdot & \cdot & \cdot & I & V_{M-1} & 0 \\ 0 & \cdot & \cdot & \cdot & 0 & I & V_M \\ K_0 & 0 & \cdot & \cdot & \cdot & 0 & K_d \end{bmatrix} \begin{bmatrix} Y_1^{(m+1)} \\ Y_2^{(m+1)} \\ \cdot \\ Y_{M-1}^{(m+1)} \\ Y_M^{(m+1)} \\ Y_{M+1}^{(m+1)} \end{bmatrix} = \begin{bmatrix} U_1 \\ U_2 \\ \cdot \\ U_{M-1} \\ U_M \\ G \end{bmatrix} \tag{33}$$

Here, 0 represents a $(2n \times 2n)$ matrix with all elements zero.

Among the different available methods for solving Eq. (33), we have chosen that of Cholesky [12]. This procedure works by factoring the coefficient matrix into a unitary upper triangular matrix and a lower triangular matrix.

After a little algebra, the following iterative relationships for $Y_j$ $(j = 1, 2, ..., M)$ and an expression for $Y_M$ can be reached

$$Y_j = U_j - V_j Y_{j+1}, \qquad j = 1, 2, ..., M, \tag{34}$$

$$Y_{M+1} = \left[K_d + (-1)^M K_0 \left(\prod_{k=1}^{M} V_k\right)\right]^{-1} \left[G - K_0 U_1 + \sum_{j=2}^{M} (-1)^j K_0 \left(\prod_{k=1}^{j-1} V_k\right) U_j\right]. \tag{35}$$

First, we compute $Y_{M+1}$. From $Y_{M+1}$, the $Y_j$'s $(j = M, M-1, ..., 1)$ can be readily calculated by using Eq. (34).

Vector $Y$ contains the solution of the problem (the $2n$ variables defined at each one of the $M+1$ space grid points). Once we have calculated the $Y_j^{(1)}$ $(j = 1, 2, ..., M+1)$, this result is taken to be the initial value for the following iteration and the procedure is repeated until a previously fixed convergence is reached.

In order to improve the accuracy of the computation, a refinement in the distance scaling is included at both extremes of the diffusion zone. Concentration and electric potential profiles may vary sharply in the vicinity of the boundaries. The procedure here employed envisages the two first intervals and the two last ones as a "new" diffusion zone where electrodiffusion equations should be solved according to boundary conditions slightly different from those originally considered (this is achieved by modifying appropriately matrices $K_0$ and $K_d$ and vector $G$, for each refinement). The refinement procedure may be used several times in order to reach a satisfactory convergence.

## IONIC TRANSPORT ACROSS A MEMBRANE SYSTEM

So far, we have described a numerical algorithm for the solution of Eqs. (13)–(16) in the case of a simple membrane [17]. While the procedure permits a general solution of NP and Poisson equations, the most usual synthetic membranes exhibit some additional features. For instance, a nonzero charge density fixed to the membrane matrix should be considered. Equation (15) accounts for this charge density. On the other hand, allowance should be also made for the unstirred layers flanking the membrane. As a first (but excellent [9]) approximation, a Donnan equilibrium may be assumed at the membrane–solution interfaces (this implies the existence of concentration and electric potential "discontinuities" at these interfaces; see Fig. 3).

Most of the procedures used to solve the problem of ionic transport are finite-difference methods or "shooting" methods. We can say that, in general terms, the former ones allow for a rougher initial estimate of the variables since "shooting" methods need a good initial guess of the variables to achieve convergence.

The interest of the procedure here described is due to its wide applicability to different membrane–solution systems, in contrast with other methods specially designed for particular membrane transport problems [9, 14–16] or liquid junction problems [17].

The main advantage of the present method is the great flexibility for introducing the boundary conditions. Actually, in other numerical methods [6, 9, 16] there can be no choice for the variables whose boundary values are given (usually, the ionic concentrations).

On the other hand, though there exist other algorithms capable of solving the transport problem in simple membranes, to our knowledge there is no numerical

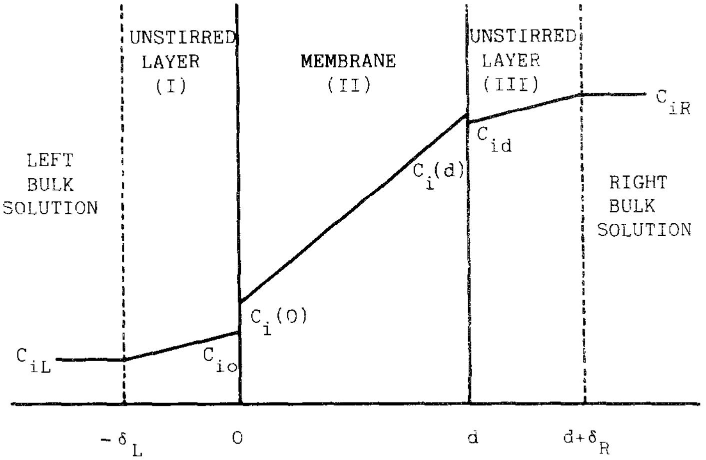

FIG. 3. Schematic diagram of the membrane system. A steady-state concentration profile for one of the counter-ions is shown. Discontinuities are due to the Donnan equilibria [1].

procedure devoted to the description of ionic transport through both the membrane and the unstirred layers, for multiionic systems and under the general conditions stated here.

In order to solve Eqs. (13)–(16) in regions (I)–(III), we need a number of boundary conditions. Bulk concentrations $c_{i\mathrm{L,R}}$ are assumed to be fixed, but external surface concentrations $c_{i0,d}$ and internal surface concentrations $c_i(0)$, $c_i(d)$ are unknown quantities. This problem shows one of the most interesting features of the algorithm, i.e., the flexibility in the choice of the boundary conditions. The latter ones may be introduced as "floating" boundary conditions, so that they can be improved even while the iterative procedure is working.

Concentrations $c_i(0)$, $c_i(d)$ are computed from concentrations $c_{i0,d}$, respectively, by solving Donnan equations at each interface. Assuming an ideal behavior for the membrane, Donnan relationships reduce to the following $n+1$ equations

$$c_i(0)=c_{i0}\left[\frac{c_{i+1}(0)}{c_{i+1,0}}\right]^{z_i/z_{i+1}}, \qquad i=1, 2, ..., n \tag{36}$$

$$\sum_{i=1}^{n} z_i c_i(0)+\omega X=0 \tag{37}$$

$$\sum_{i=1}^{n} z_i c_{i0}=0. \tag{38}$$

Equations (13)–(16) should be solved taking into account the different values of the ionic diffusion coefficiens inside and outside the membrane. The thickness of the unstirred laters and the fixed-charge density are experimental parameters (obviously, $\bar{X}=0$ in the unstirred layers). The $2n$ boundary conditions employed in regions (I)–(III) are

*left unstirred layer*:

$$\begin{aligned} &c_i(-\delta_\mathrm{L})=c_{i\mathrm{L}}, && i=1, 2, ..., n \\ &\frac{d\phi}{dx}(-\delta_\mathrm{L})=0 && \\ &J_i(-\delta_\mathrm{L})=J_i(0), && i=1, 2, ..., n-1; \end{aligned} \tag{39}$$

*right unstirred layer*:

$$\begin{aligned} &c_i(d+\delta_\mathrm{R})=c_{i\mathrm{R}}, && i=1, 2, ..., n \\ &\frac{d\phi}{dx}(d+\delta_\mathrm{R})=0 && \\ &J_i(d+\delta_\mathrm{R})=J_i(d), && i=1, 2, ..., n-1; \end{aligned} \tag{40}$$

*membrane* (results obtained from Eqs. (36)–(38)):

$$c_i(0),\ c_i(d), \qquad i=1, 2, ..., n. \tag{41}$$

The computing procedure is the following. First, we introduce the approximate values $c_{i0}=c_{i\mathrm{L}}$, $c_{id}=c_{i\mathrm{R}}$, $i=1, 2, ..., n$, in Eqs. (36)–(38). This leads to concentrations $c_i(0)$, $c_i(d)$. Then, Eqs. (13)–(16) are solved in the membrane phase. The resulting values are improved in the surroundings of each interface by using the distance scale refinement. From the ionic fluxes across the membrane $J_i^{(0)}$, a first estimate for the ionic fluxes through the membrane system as a whole $J_i^{(1)}$ is

$$J_i^{(1)}=J_i^{(0)}\frac{(D_i^*/D_i)d}{(D_i^*/D_i)d+\delta_\mathrm{L}+\delta_\mathrm{R}}, \tag{42}$$

where $D_i^*$ is the diffusion coefficient of ion $i$ in the unstirred layers. Equation (42) corrects the $J_i^{(0)}$ by introducing the thickness of the unstirred layers as well as the diffusion coefficients inside and outside the membrane. The corrected fluxes are taken as boundary conditions for the solution of (13)–(16) in the unstirred layers (see Eqs. (39)). Then, we get some new $c_{i0,d}$ (these values are no longer equal to $c_{i\mathrm{L,R}}$). From the new $c_{i0,d}$, Eqs. (36)–(38) can be solved again. The resulting $c_i(0)$, $c_i(d)$ are employed in order to solve (13)–(16) in the membrane, and a new estimate for the fluxes is obtained. By taking these new $J_i$'s as boundary conditions, the transport problem across the unstirred layers is solved again. The iterative procedure ends when a previously fixed convergence is reached.

We first attempted to solve the Donnan relationships (see Eqs. (36)–(38)) by means of an iterative procedure but some difficulties arose in the convergence and we resorted to an analytical solution in the most common cases (binary and ternary systems).

The reason for introducing expression (42) was some unstability in the computing procedure due to a "very poor" guess of the ionic fluxes that made "negative concentrations" appear.

When $D_i^*/D_i$, $\delta_\mathrm{L}/d$, and $\delta_\mathrm{R}/d$ take large values (a highly improbable situation in common experimental situations), care must be taken in appropriately selecting the initial guess of the variables.

Five different sets of boundary conditions are employed in order to solve Eqs. (13)–(16) in the unstirred layes, the membrane, and the two interfacial zones where a distance scale refinement is considered. The final results are the concentrations and electric potential gradient profiles across the three regions of the system.

## RESULTS

The reliability of the proposed method has been shown in two well-known experimental problems, namely the study of ionic transport through a concen-

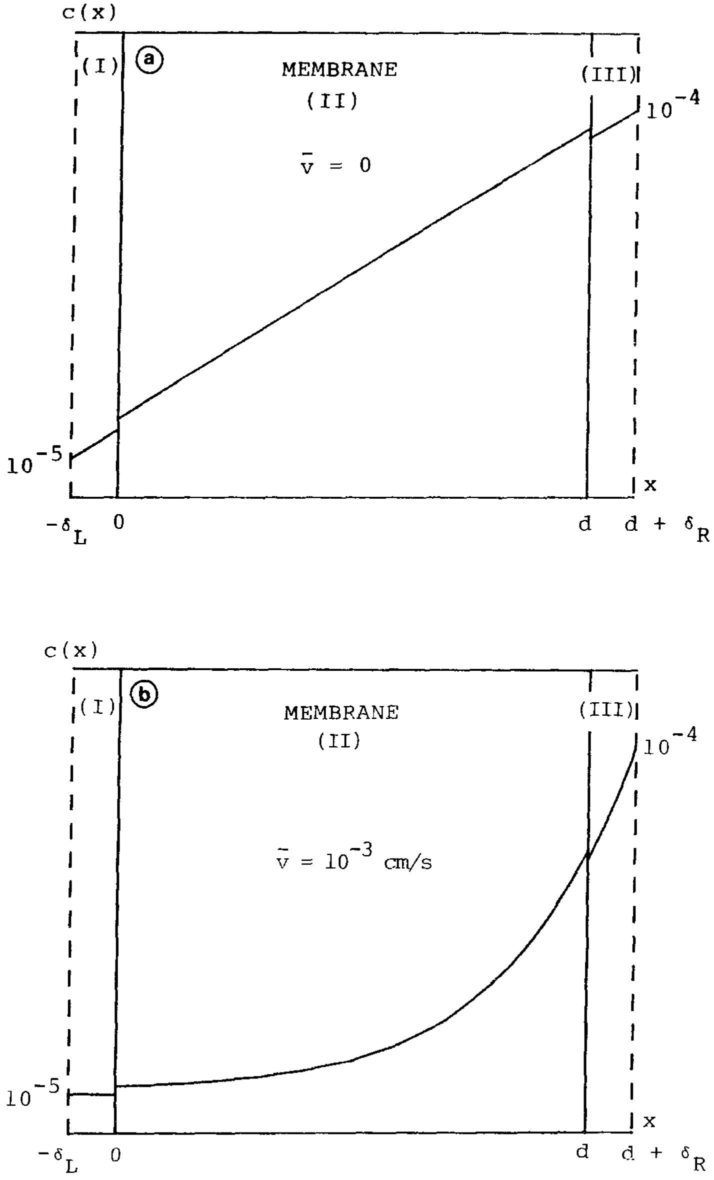

FIG. 4. Concentration profiles of $H^+$ ($Na^+$) ion through a weakly charged cation-exchange membrane. Two unstirred layers are flanking the membrane. Bulk concentrations are taken to be $c_L = 10^{-5}$ mol/cm$^3$ and $c_R = 10^{-4}$ mol/cm$^3$, for both electrolytes. As a first approximation, we consider the ionic diffusion coefficients at infinite dilution. Other parameters are $d = 5 \times 10^{-2}$ cm, $\delta_L = \delta_R = 5 \times 10^{-3}$ cm and $\bar{X} = 10^{-5}$ mol/cm$^3$: (a) convection $\bar{v} = 0$; (b) $\bar{v} = 10^{-3}$ cm/s.

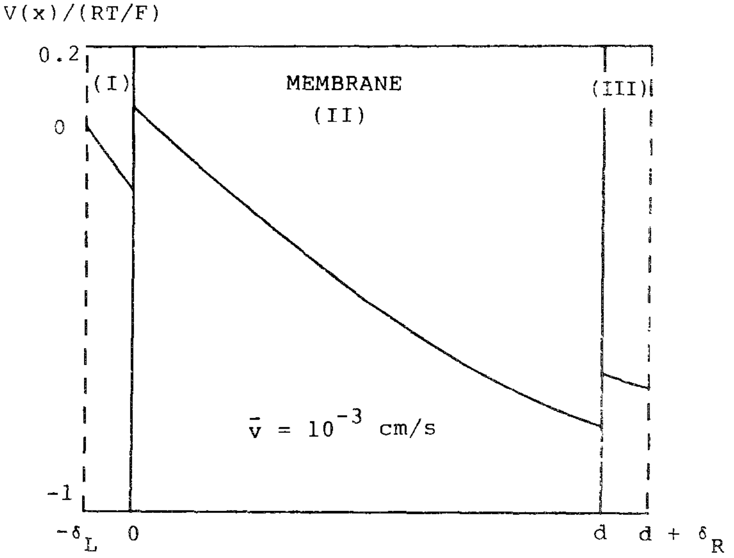

FIG. 5. Electric potential profiles across a cation-exchange membrane under the same conditions stated in Figs. 4. The potential origin is taken to be $\phi(-\delta_L) = 0$. The discontinuities at both interfaces are the so-called "Donnan potentials" [1]. Note the remarkable deviations from the classical assumption of "constant electric field" through the membrane.

tration cell, and through an ion-exchange membrane under bi-ionic conditions [18]. As an example, we consider a problem here which poses a certain complexity due to the coexistence of a concentration gradient and a convective flux opposing the former one. In addition, we assume a charged membrane with two unstirred layers flanking it, so that these layers exert some control on the transport processes.

Two electrolyte solutions at different concentrations are flanking this weakly charged membrane. The electrolyte system is NaCl–HCl–$H_2O$. In Figs. 4a–b) the calculated counterion ($Na^+$ or $H^+$) concentrations across the membrane are plotted. In the case (a), there is no convective flux, while in case (b) a nonzero convection is assumed. Other parameters like concentration gradients, ionic diffusion coefficients, etc. are taken to be the same in both cases. The changes in the concentration profiles are important, especially those appearing in both unstirred layers. This fact plays a remarkable role [18], and it had not previously been considered, mainly due to the difficulties that an exact solution of the problem involves.

Electric potential profiles are shown in Fig. 5. Discontinuities appearing at both interfaces are due to the Donnan potentials (a detailed description of the double layer at the interfaces has been omitted; it is well known [1, 19] that such a way of proceeding constitutes an approximation very close to reality in ion-exchange membranes). The situation plotted is that of a nonzero convective flux.

All calculations were performed from a numerical code first developed in HPL language. The computer used was a Hewlett Packard 89825A. New versions coded in Fortran 77 (for a HP-9000/300) are also available. A space grid of 21 points on each one of the regions (I)–(III) was considered (61 points within the membrane when the refinement is taking place).

A typical problem requires 4–5 iterations (on each one of regions (I)–(III)) in order to achieve the fixed convergence. In our problem, a relative change in any variable from one iteration to the next was required to be less than 0.01%. An average computation took 2–3 min. To evaluate the truncation error for the nonlinear system seems to be beyond the scope of this treatment. Anyway, the accuracy of the grid system was tested by doubling the number of space grid points.

## ACKNOWLEDGMENTS

Financial support from the CAICYT (Ministry of Education and Science) Project No. PB85-0202, is gratefully acknowledged. One of us (S.M.) thanks a doctoral grant from the Generalitat Valenciana.

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