

A network thermodynamic method for numerical solution of the Nernst-Planck and Poisson equation system with application to ionic transport through membranes

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Abstract. Simple techniques of network thermodynamics are used to obtain the numerical solution of the Nernst-Planck and Poisson equation system. A network model for a particular physical situation, namely ionic transport through a thin membrane with simultaneous diffusion, convection and electric current, is proposed. Concentration and electric field profiles across the membrane, as well as diffusion potential, have been simulated using the electric circuit simulation program, SPICE. The method is quite general and extremely efficient, permitting treatments of multi-ion systems whatever the boundary and experimental conditions may be.

Key words: Network thermodynamics, ionic transport

Introduction

When studying ionic transport processes across membranes, the theoretical model based on the Nernst-Planck flux equations and the electrostatic Poisson equation is one of the most widely used (Buck 1984). The integration of Nernst-Planck transport equations is of considerable interest in biology, since it enables evaluation of fluxes of particular species through biological membranes whose intracellular and extracellular environments are composed of different ion species. Nevertheless, the electrodiffusion equations are non-linear and their analytical solution is nearly impossible in a great number of interesting physical situations (Goldman 1943; Teorell 1953). The need for an exact general solution for ionic transport problems is the reason why several authors have tackled this problem numerically (Cohen and Cooley 1965; French 1974; Stover and Buck 1976; Brumleve and Buck 1978).

We present in this paper a novel network method which can be used with advantage in the study of such problems. The techniques derive from the theories of Peusner (1987) and Oster et al. (1971, 1973), which

permit coupled flows and driving forces to be analyzed in terms of graphs. Highly developed methods of circuit analysis may then be employed to obtain the dynamic behaviour of the system, directly from the graph, without having to deal with the differential equations explicitly, providing a very powerful tool and a rigorous basis for understanding the behaviour of the whole system.

We begin by proposing a network model which is an appropriate discrete approximation to the Nernst-Planck and Poisson equations. The problem of using a network to approximate a continuum has been discussed quite extensively in the literature (Oster et al. 1973; Thomas and Mikulecky 1978; White 1979; Mikulecky and Thomas 1979; Mikulecky et al. 1979; González-Caballero et al. 1988). We will show in detail how it is done for a problem of obvious theoretical and experimental complexity: electrodiffusion through thin membranes when convective flux and electric current are involved. The method is quite general and permits, in an efficient manner, treatment of multi-ion systems without introducing restrictive approximations on the charge numbers.

The second step is the numerical solution of the resulting network model. In the particular case of the ternary system $\text{NaCl}-\text{HCl}-\text{H}_2\text{O}$, the diffusion potential as well as concentration and electric potential gradient profiles across the membrane have been obtained using the electric circuit simulation routine SPICE (Nagel and Pederson 1977). We also study two special situations of the system, namely when the total ionic concentrations on the two sides of the membrane are not equal, and when they are equal. The last system is of special interest for biological applications (Hodgkin and Kaz 1949).

The electrodiffusion equations

The equations determining the behaviour of the system are the Nernst-Planck flux equations (in dilute

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solution form) including convection flux, (1), the continuity equation, (2), and Poisson's equation, (3):

$$\bar{J}_i(\bar{x}, \bar{t}) = -\bar{D}_i \{ (\partial \bar{c}_i(\bar{x}, \bar{t}) / \partial \bar{x}) - z_i (F/RT) \bar{c}_i(\bar{x}, \bar{t}) \bar{E}(\bar{x}, \bar{t}) \} + \bar{c}_i(\bar{x}, \bar{t}) \bar{v} \quad i=1, 2, \dots, n \quad (1)$$

$$\partial \bar{c}_i(\bar{x}, \bar{t}) / \partial \bar{t} = -\partial \bar{J}_i(\bar{x}, \bar{t}) / \partial \bar{x} \quad (2)$$

$$\partial \bar{E}(\bar{x}, \bar{t}) / \partial \bar{x} = (F/\epsilon) \sum_i z_i \bar{c}_i(\bar{x}, \bar{t}) \quad (3)$$

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{E} denotes the electric field; \bar{v} and ϵ are, respectively, the convection velocity and the dielectric permittivity. The letter \bar{t} denotes the time and \bar{x} the position along the membrane. The latter is regarded as a discontinuity from $\bar{x}=0$ to $\bar{x}=l$ which separates two electrolytic solutions. The electric field $\bar{E} = -d\bar{\phi}/d\bar{x}$ is a common quantity for every ion.

For the purpose of simulation it is convenient to replace Poisson's equation (3) by the totally equivalent displacement current equation, as described by Cohen and Cooley (1965):

$$\bar{I} = F \sum_{i=1}^n z_i \bar{J}_i(\bar{x}, \bar{t}) + \epsilon (\partial \bar{E} / \partial \bar{t}) \quad (4)$$

This conveniently introduces the total current density \bar{I} as one of the independent variables of the problem.

Equations (1)–(4) may be written in dimensionless form using the following transformations: $c_i(x, t) = \bar{c}_i(\bar{x}, \bar{t}) / \bar{c}_0$; $x = \bar{x}/l$; $t = \bar{t} \bar{D}_i / l^2$; $K_m = \epsilon R T l_i / F^2 l^2 \bar{c}_0 l_n$; $v_i = \bar{v} l / \bar{D}_i = \bar{v} l / l_i R T = l_n v_n / l_i$; $J_i = \bar{J}_i l / \bar{D}_i \bar{c}_0$; $I = \bar{I} l / F \bar{c}_0 \bar{D}_n$ and $E = (F l / R T) \bar{E}$, where \bar{c}_0 is the scaling concentration, l_i is the ionic mobility of ionic i ($l_i = \lambda_i / z_i^2 F^2$ and λ_i is the molar conductivity of ion i), l is the thickness of the membrane and K_m is the reduced dielectric permittivity. With these dimensionless parameters, (1), (2) and (4) can be written in the following reduced form:

$$J_i(x, t) = -\partial c_i(x, t) / \partial x + z_i c_i(x, t) E(x, t) + c_i(x, t) v_i \quad i=1, 2, \dots, n \quad (5)$$

$$\partial c_i(x, t) / \partial t = -\partial J_i(x, t) / \partial x \quad (6)$$

$$I = \sum_{i=1}^n z_i l_i J_i / l_n + K_m (\partial E / \partial t). \quad (7)$$

Dimensionless variables are written without bars to distinguish them from the dimensioned ones.

At any time t , the reduced membrane potential ϕ_m can be obtained by the integration of the electric field across the diffusion zone

$$\phi_m = \phi(l) - \phi(0) = - \int_0^l E \cdot dx \quad (8)$$

We assume that there is no potential drop through the geometrical interfacial planes.

Network model for the electrodiffusion

The general procedure for obtaining the network model representative of the process consists in dividing the physical region of interest (which we consider of unit area) into volume elements or compartment sufficiently small so that spatial variations within each subregion can be ignored. Logically, the precision of quantitative modelling is greatly improved as the degree of subdivision increases because the larger the number of compartments, the closer we come to continuum behaviour (Wyatt et al. 1980).

The diffusive contribution to the flux of ion i (J_{di}) in (1), and the concentration, play the same role, respectively, as the current and potential in an electric circuit. Thus, a comparison of Fick's law and Ohm's law allows us to represent the dissipative effect of the diffusion by means of a resistance R_i , given by (Horno et al. 1989 a):

$$R_i = \delta / \bar{D}_i \quad (9)$$

where δ is the thickness of the volume element in the direction of the transport process. Using the above dimensionless quantities, this R_i is reduced to

$$R_i = \delta \quad (10)$$

In order to include non-stationary effects, the model must take into account the fact that the compartment can store or release a certain number of ions, i.e. a difference between the flows entering and leaving the volume element is produced. This source of divergence is represented in the network model by a capacitor, in such a way that Kirchhoff's current law is fulfilled; thus,

$$-\text{div } I = \gamma^* (\partial \psi / \partial t) \quad (11)$$

where I and ψ are the current density and the electric potential, respectively, and γ^* is the capacitance per unit volume. If we compare (11) with the continuity equations (2), then $\gamma^* = 1$, which means that the value of the capacitance, γ , must equal the volume of each compartment and that in our case, on considering compartments of unit area, γ is equal to δ . We assume that the compartment is symmetric so that the linear resistor can be split into equal parts, $R_i/2$, between which the capacitance γ is placed.

According to (5), the electric contribution to ionic fluxes, J_{ei} , is

$$J_{ei} = z_i c_i E \quad (12)$$

where c_i in each compartment is that in the center of such a volume element. This relation, in which a "current" J_{ei} appears as a function of two "voltages" c_i and E , can be modelled by a non-linear voltage-dependent current source. The network simulation is accomplished through a circuit simulation program such as

SPICE, and this program has a special format to write such non-linear elements in a straightforward way (Wyatt et al. 1980; Horno et al. 1989 b).

Similarly, the convective term in (5), $J_{ci} = v_i \cdot c_i$, can be represented by a voltage-dependent current source. Adequate connection of several elements modelling the above contributions to J_i : diffusion (J_{di}), convection (J_{ci}) and electric conduction (J_{ei}) (taking into account Kirchhoff's current law), allows us to obtain the network model shown in Fig. 1 a.

Given that a dependent source is one whose flow or potential is a function of flows or potentials elsewhere in the network, it will be necessary to introduce the driving force E (12) from any node in the network. The electric field is obtained by multiplying (5) by z_i and summing:

$$E = \frac{\sum z_i (J_i - J_{di}) - \sum z_i c_i v_i}{\sum z_i^2 \cdot c_i} \quad (13)$$

One peculiarity of SPICE is that non-linear flow-force ("current-voltage") relations are expressed through the use of circuit elements which are dependent sources having the relation between controlling parameters and their output expressed in polynomial form. Equation (13) does not have a convenient polynomial representation, but its right hand side is easily seen to be a rational polynomial. As Wyatt et al. (1980) have pointed out, to solve this problem a special subcircuit which forces SPICE to compute the ratio of two polynomials will have to be designed. This subcircuit is shown in Fig. 1 b. It consists of two monoport elements connected in series. The expressions in Fig. 1 b give their constitutive relations, i.e. their currents as functions of J_i , J_{di} , c_i and E , where E is the voltage at the node connecting the two sources. Kirchhoff's current law at that node specifies that $i_1 = i_2$, and SPICE will find a network solution (more specifically, a value of E) such that this condition holds. Thus, E , must satisfy (13) obtained by substituting the dependent source characteristics into Kirchhoff's current law. The resistor R_{INF} is present solely to satisfy a requirement in SPICE that every node has a d.c. path to ground. The value of R_{INF} is so large that only negligible current passes through it. The monoport element i_1 can be modelled by two multidimensional current sources (which causes no problem in coding the network for computer simulation) connected in parallel: a current-dependent current source modelling the function $I_1 = \sum z_i (J_i - J_{di})$ and a voltage-dependent current source modelling the term $I_2 = \sum z_i c_i v_i$. Of course, all the flows J_i , J_{di} and forces c_i in the multivariable source already appear somewhere in the network.

It follows from (7) that there are only $n-1$ independent ionic fluxes, and the flux of ion n can be rewritten in terms of the fluxes J_j with $j = 1, 2, \dots, n-1$

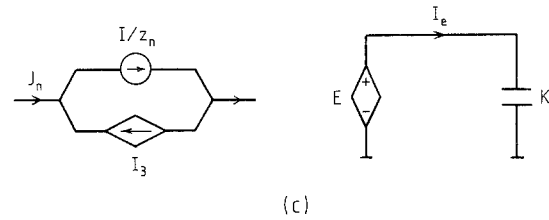
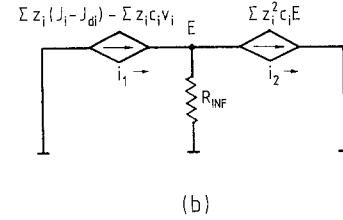
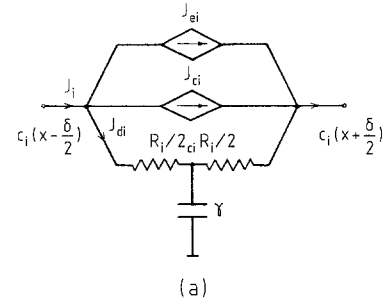


Fig. 1. **a** One way to represent diffusion-migration and convection in a single compartment. **b** Schematic for the circuit which computes E as the ratio of two polynomials. **c** Representative subcircuits for (14) and (16)

in the form

$$J_n = I/z_n - I_3 \quad (14)$$

where

$$I_3 = \sum_{j=1}^{n-1} z_j l_j J_j / z_n l_n + I_e \quad (15)$$

and

$$I_e = (K_m / z_n) (\partial E / \partial t) \quad (16)$$

Thus, the flux of ion n can be modelled by two current sources connected in parallel: a constant current source of value I/z_n and a multivariable current-dependent current source modelling the function I_3 (Fig. 1 c).

The electrical analog of (16) is a linear capacitor with capacitance equal to $K = K_m / z_n$. Thus, I_e is the current through the capacitor K in Fig. 1 c. Therefore, all the flows in the multivariable source modelling the term I_3 already appear somewhere in the network.

We could capture all effects by putting the several subcircuits together as in Fig. 2 a. The voltage-dependent voltage source, $\Delta\phi = E \cdot \delta$, computes the voltage drop across the compartment (8). The multiport which results constitutes the network model for electrodiffusion in a volume element, including a convective flux.

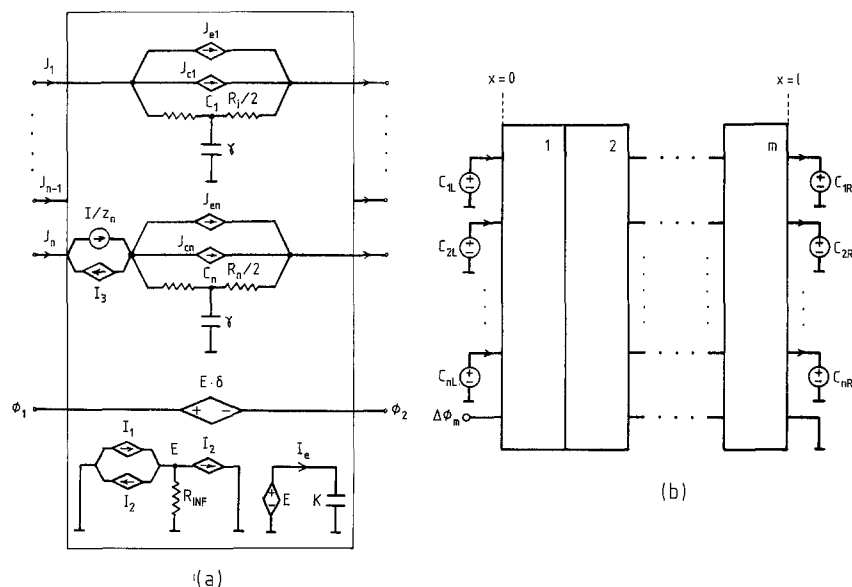


Fig. 2. **a** Model for electrodiffusion in a single compartment, including a convective flux. **b** Global network model for diffusion-migration-convection through thin membranes. Details of the structures in boxes 1-m are shown in **a**

To investigate the stationary behaviour we simply replace the capacitors (γ) by resistors R_{INF} in the network model.

For network modelling purposes, any number of the above multiports must be connected in series to form the network model for the entire physical region undergoing a diffusion-migration-convection process. The model now becomes that shown in Fig. 2b. The ideal voltage sources represent the boundary conditions, which are chosen as follows:

$$c_i(0) = c_{iL} \quad \text{and} \quad c_i(l) = c_{iR} \quad i = 1, 2, \dots, n$$

where c_{iL} and c_{iR} are the constant concentrations of the i th species in left and right bulk solution, respectively. Obviously, determination of the membrane potential will require an additional boundary condition. It will be assumed that $\phi(l) = 0$. This entails considering the position $x = l$ in the diffusion zone as the origin of the electric potential.

Network simulation and discussion

By means of the network model of Fig. 2, with the appropriate numerical values for the system parameters, the solution of the Nernst-Planck and Poisson equations can be easily obtained using the computer program SPICE. Various parameters can be varied singly or in combinations to explore their effect on model behaviour. The result is the ability to perform a series of simulations in one computer run. Without attempting to present a complete catalog of results for every choice of input parameter, we will illustrate the versatility and generality of the procedure by presenting some typical results for a well-known experimental

problem, namely the study of ionic transport through a thin membrane in the case of a ternary electrolyte system (NaCl-HCl-H₂O) with a simultaneous convection and an electric current. Bulk concentrations, current density and concentration are the same as those used by Taskinen et al. (1980). The procedure is capable of providing concentration and electric field profiles as well as fluxes and voltage drop across the diffusive zone. The results obtained are in good agreement with those of Taskinen et al. (1980), despite the use of different methods.

In our simulation, we take $\varepsilon = 0$ to force electroneutrality throughout the membrane. This condition also eliminates from the simulation any short time electrical properties of the membrane due to interfacial charging and leaves for the current density (7) expression only

$$I = \sum z_i l_i J_i / l_n \quad (17)$$

It is clear from the form of the reduced Poisson equation

$$K_m(dE/dx) = \sum z_i c_i = 0 \quad (18)$$

that this procedure places no special restrictions on the term dE/dx and that Poisson's equation remains coupled to diffusion. For network modelling purposes, the effect of setting $K_m = 0$ is the elimination of subcircuit I_e ($I_e = 0$). Likewise, as the concentration of ions is subject to the condition of electroneutrality, the contribution of the term diffusive to the electric field (13) is equal to zero ($\sum z_i J_{di} = -\sum z_i \cdot dc_i/dx = -\sum z_i c_i d(\ln c_i)/dx = 0$).

As pointed out in the above section, the accuracy goes up rapidly as the number of compartments is increased. Nevertheless, the computation time is also

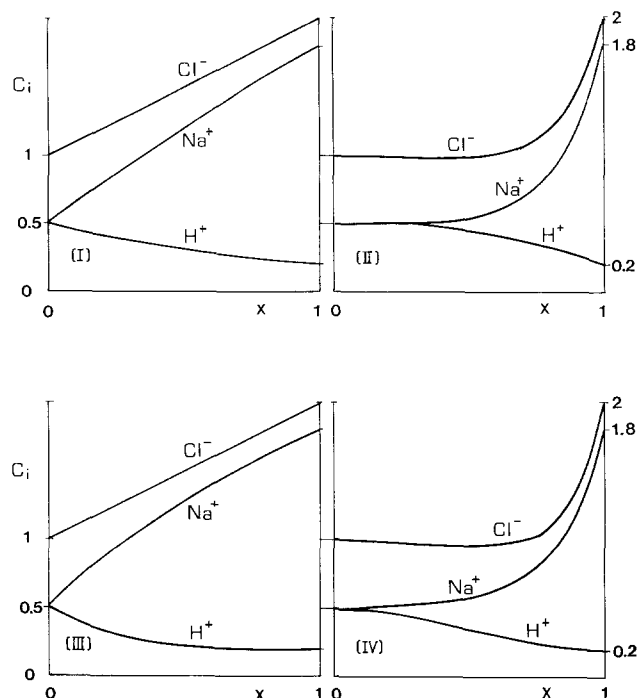


Fig. 3. Simulated concentration profiles across the membrane for the ternary system NaCl-HCl-H₂O when the concentrations on the two sides of the membrane are not equal, in the cases: $I=0$, $v=0$ (I); $I=0$, $v=6$ (II); $I=-8$, $v=0$ (III) and $I=-8$, $v=6$ (IV). Dimensionless equivalent concentrations are $c_1(X=0)=0.5$, $c_2(X=0)=0.5$ and $c_1(X=1)=1.8$, $c_2(X=1)=0.2$, where subscript 1 denotes the first cation and subscript 2 the second. The molar conductivities of ions are $\lambda(\text{Na}^+)=50.10$, $\lambda(\text{H}^+)=349.81$, $\lambda(\text{Cl}^-)=76.35$ and the unit of the molar conductivity is $\text{cm}^2 \text{S mol}^{-1}$.

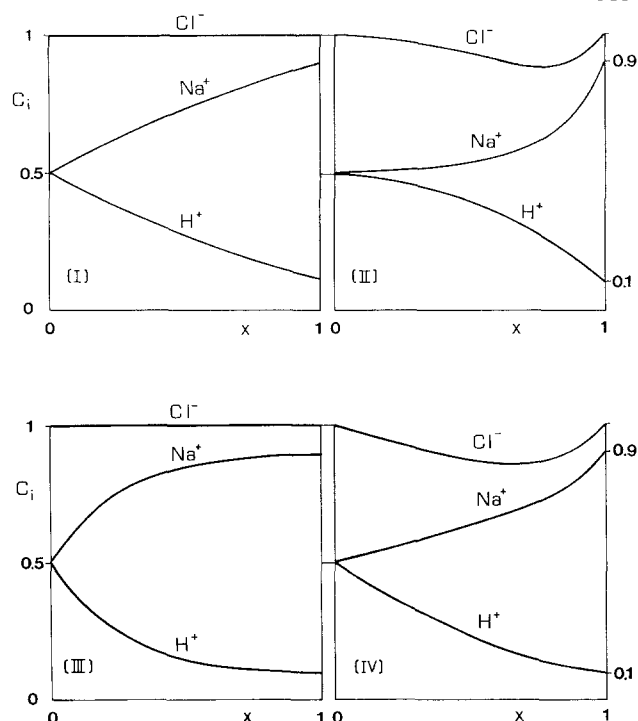


Fig. 4. Simulated concentration profiles across the membrane for the ternary system NaCl-HCl-H₂O when the concentrations on the two sides of the membrane are equal, in the cases: $I=0$, $v=0$ (I); $I=0$, $v=6$ (II); $I=-8$, $v=0$ (III) and $I=-8$, $v=6$ (IV). Dimensionless equivalent concentrations are $c_1(X=0)=0.5$, $c_2(X=0)=0.5$ and $c_1(X=1)=0.9$, $c_2(X=1)=0.1$, where subscripts are the same as in Fig. 3.

proportional to the number of volume elements. Therefore, we need to know the number of compartments needed to obtain reasonable numerical accuracy at a low cost in computer time. An excellent detailed study on this matter for reaction-diffusion systems has already been carried out by Wyatt et al. (1980). In that work, the authors observed that fair accuracy was obtained with as few as five compartments. For that reason, in this paper a ten-compartment-network model has been used.

Concentration and electric potential gradient profiles across the diffusion zone for four different cases, namely *I*) zero current density and convection; *II*) zero current density and non-zero convection; *III*) non-zero current density and zero convection and *IV*) non-zero current density and convection, are simulated from d.c. analysis of a 10-compartment model (Fig. 2) with SPICE. The concentration profiles resulting both when the total ionic concentrations on the two sides of the membrane are not equal and when they are equal, are shown in Figs. 3 and 4, respectively. In both situations we can observe an absence of linearity in the concentration profile when an external elec-

trical current is involved and particularly when a convective flux is presented.

Since the electric field is related to ionic concentration via Poisson's equation, the strong influence of current density and convection on concentration profiles makes us assume that I and v will also affect the electric field. Electric potential gradient profiles for the two situations mentioned above are plotted in Fig. 5. The differences between concentration profiles due to different values of I and v correspond with those observed in the potential gradient.

Finally, in Fig 6 the set of current-voltage curves for different concentrations of NaCl obtained from simulation of network model of Fig. 2, are plotted. As system parameters, we have now used those corresponding to the cellulose membrane/NaCl-HCl-H₂O from Ekman et al. (1982). The convection velocity through the membrane is assumed constant (volume flux $0.45 \text{ mm}^3 \text{ s}^{-1}$) and the current takes values between 1 and 3 mA. The results show that the voltage drop across the membrane increases as a function of the concentration of NaCl and this increase starts from a characteristic value of the electric current. Dif-

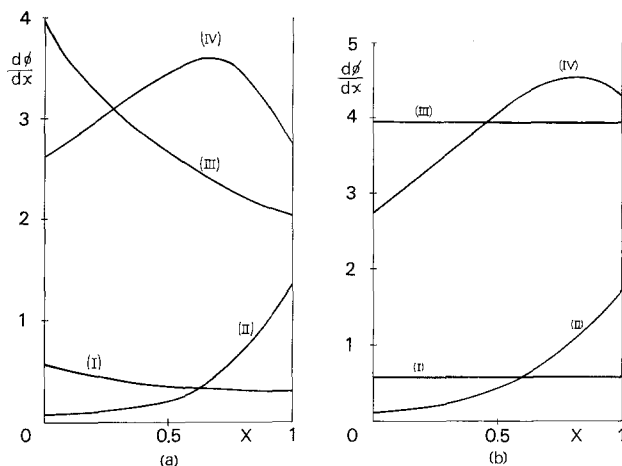


Fig. 5a and b. Potential gradient profiles across the membrane when total concentrations on the two sides of the membrane are not equal (a) and when they are equal (b) under the four different conditions described in Figs. 3 and 4, respectively. The units on the y-axis are equivalent to 25.68 mV m^{-1}

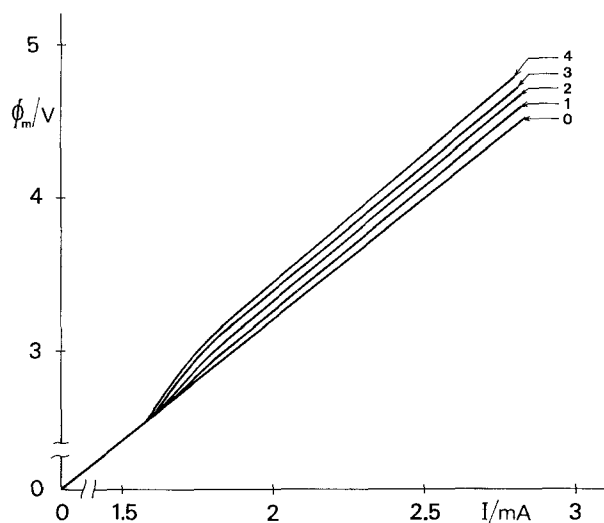


Fig. 6. Simulated current-voltage curves for different concentrations of NaCl at $x=0$: $C_{\text{NaCl}} = (0, 1, 2, 3, 4) \cdot 10^{-4} \text{ mol dm}^{-3}$. At $x=1$: $C_{\text{NaCl}}=0$; $C_{\text{HCl}}=5 \cdot 10^{-3} \text{ mol dm}^{-3}$ on both sides of the membrane

ferences between simulated results and experimental data are similar to those found by other authors (French 1974; Brumleve and Buck 1978; Ekman et al. 1982; Garrido et al. 1985).

To sum up, the proposed network model together with an electric circuit simulation program such as SPICE, allow us to easily simulate ionic transport across membranes when an electric current density and a convective flux are involved. The concentration and electric field profiles across the membrane as well as diffusion potential are obtained without mathematical complexities. Reasonable numerical accuracy can

be obtained this way at a very low cost in human effort and a moderate cost in computer time.

One particular advantage of the method used here is that the investigator need not be familiar with computer programming; rather, the investigator need only learn a few rules for providing information to SPICE, which uses a simple and concise language for representing circuit diagrams. This is generally not the case if classical numerical methods are to be used.

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