Simulation of concentration polarization in electrokinetic processes by network thermodynamic methods

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ABSTRACT Simple techniques of network thermodynamics are used to study the influence of concentration polarization on the determination of electrokinetic properties of physical and biological membrane systems. A network model of the polarization phenomenon resulting from discontinuities in transport numbers between the membrane and their adjacent solutions is proposed. The concentration profiles and potential drop across the membrane in plugs of monodisperse polystyrene particles and in giant algal cells have been simulated using the electrical circuit simulation program SPICE.

INTRODUCTION

For a long time, the electrokinetic phenomena have received considerable attention, as much in the characterization of properties of various systems of industrial interest, as in explaining a variety of biological phenomena, ranging from action potentials to water transport. Two phenomena most frequently studied are those of streaming potential and electroosmosis. However, such electrokinetic effects are often obscured by concentration polarization phenomenon resulting from discontinuities in transport numbers between the membrane and their adjacent solutions. This peculiar phenomenon may in some simple systems be reduced, but never completely eliminated, by very vigorous stirring. Since in most biological systems, stirring is either absent or not very effective, polarization effects may often be of considerable importance (Barry and Hope, 1969). Concentration polarization would also manifest itself for coarse porous systems at relatively low ionic strengths where the effect of negative adsorption becomes important (Brun and Vaula, 1967; Van der Put and Bijsterbosch, 1981). Thus, liquid and/or current flow through selective membrane systems gives rise to diffusion–convection or diffusion–convection–electromigration phenomena at the interfaces (Lakshminarayanaiah, 1969; Paterson and Gardner, 1971), consequently influencing the interfacial concentrations. These would, in turn, cause local transient osmotic flows and diffusion potential differences that could well obscure the determination of the electrokinetic properties (Jacazio et al., 1972; Tanny and Hoffer, 1973).

Barry and Hope (1969) and Van der Put and Bijsterbosch (1981), studied the effects of the concentration polarization in electroosmosis and streaming potential, respectively. The general procedure carried out by these authors consists of solving the differential equations that formulate the mass balances on the basis of convection and diffusion at both sides of the membrane. However, in their studies they introduce simplified assumptions. Thus, Barry and Hope rejected in the global equation the representative term of the effect of water flow on the concentration profiles established in the external solutions that correspond to the main effect of the complex feedback caused by the discontinuity in the transport number. Van der Put and Bijsterbosch consider that the regions external to the membrane are independent, when really the concentration profiles in them are interrelated through the membrane selectivity behavior. The considerations of such a circumstance complicates the problem to such an extent that it can lead to an unviable mathematical treatment.

It is here where the study of the problem by network thermodynamics (Peusner, 1970; Oster et al., 1971, 1973; Mikulecky et al., 1977) is especially useful, since it permits the avoidance of serious difficulties of the mathematical analysis (Wyatt et al., 1980; Oken et al., 1981; Thakker et al. 1982; White and Mikulecky, 1982). The network approach makes it possible to describe a thermodynamic system through a graphic representation analogous to circuit diagrams in electrical network theory. Highly developed methods of circuit analysis may then be employed to obtain the dynamic behavior of such 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 whole systems behavior.

The aim of this work is the study, using the network

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approach, of the concentration polarization phenomena in relation to streaming potential and electroosmosis, taking into account both the global feedback and the interconnection between the two external regions of the membrane. Specifically, we propose first a network model for the study of polarization phenomena in streaming potential and electroosmosis. Secondly, some aspects of the electrokinetic behavior of systems of different nature, namely, plugs of polystyrene particles and cell membranes, are simulated with this model and the computation program SPICE (Nagel, 1975; Cohen, 1976; Vladimirescu et al., 1981). In particular, the concentration profiles near the membrane–solution interface and the potential drop across the membrane have been obtained.

Mathematical description of the concentration polarization in membranes

Let us consider a membrane of thickness l (Fig. 1), fixed at the middle of a small channel of length $2d + l$, and a dilute solution of electrolyte in contact with the membrane through the open terminals of the canal. Beyond the channel the concentration may be considered as constant and equal to the initial concentration, c_0. In a system in which there is stirring, d is formally equivalent to the width of the unstirred layers.

When a current I is forced through a membrane system, or a hydrostatic pressure difference Δp is applied across it, differences in transport numbers between the membrane and the adjacent solutions will, in general, result in enhancement and depletion of concentrations at the membrane–solution interfaces. This will cause a diffusion into external solutions, a solute back-diffusion (of opposite direction to that which is in the external solutions) through the membrane and osmosis resulting from these local concentration gradients, all of it giving rise to local transient osmotic flows and diffusion potential differences. This could well lead to a gross overestimate of the important quantities, such as streaming potential and electroosmosis.

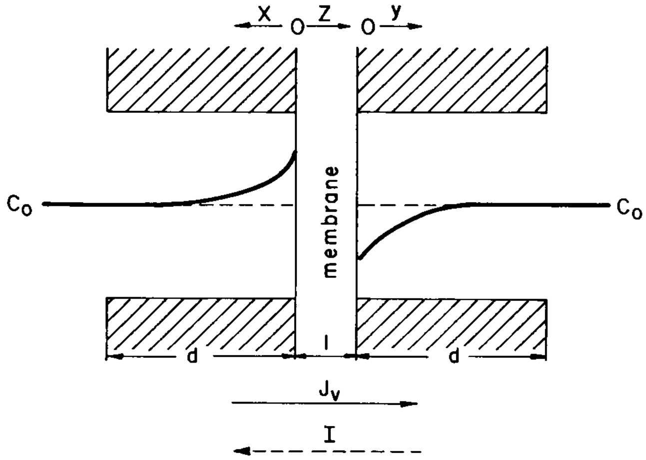

FIGURE 1 A schematic diagram of the system considered.

The mathematical description of the mass balances on the basis of convection and diffusion at both sides of the membrane can be written as (Patlak et al., 1963):

$$J_s(x,t) = -D_f\frac{\partial c(x,t)}{\partial x} - J_v \cdot c(x,t) \qquad (1)$$

$$J_s(y,t) = -D_f\frac{\partial c(y,t)}{\partial y} + J_v \cdot c(y,t). \qquad (2)$$

The minus and plus signs of the convective contribution to the net density of solute flow, J_s, depend on the direction of the selected axis x and y. D_f is the diffusion coefficient of the electrolyte in the external solution, c is its concentration and J_v is the density of the volume flow.

In the same way, coupled to the convective flow, which is conditioned by the selective properties of the membrane, a back-diffusion exists in the membrane, given by:

$$J_s(z,t) = -D_m\frac{\partial c(z,t)}{\partial z} + J_v(1 - \sigma)c(z,t), \qquad (3)$$

where D_m and σ are, respectively, the diffusion coefficient of the electrolyte in the membrane and the reflection coefficient.

The boundary conditions relative to the streaming potential process are

$$J_s(x = 0,t) = J_s(z = 0,t) \qquad (4)$$

$$J_s(z = l,t) = J_s(y = 0,t). \qquad (5)$$

In the case of electroosmosis, in which a process of diffusion–convection–electromigration exists, the boundary conditions are:

$$J_s(x = 0,t) = J_s(z = 0,t) + \Psi \qquad (4')$$

$$J_s(z = l,t) + \Psi = J_s(y = 0,t) \qquad (5')$$

with $\Psi = (\alpha/F)I$ (Barry and Hope, 1969), where I is the current, F the Faraday constant, and α the transport number difference across the membrane–solution interface.

Likewise, the volume flow has two contributions: the hydrodynamic term, $J_0 = L_p\Delta p$, where L_p is the hydraulic conductivity of the membrane and Δp the hydrostatic pressure difference (or electroosmotic component in the case $J_0 = \lambda I$, where λ is the practical electroosmotic coefficient and I the current) and the term corresponding to the osmotic flow of volume, J_1, caused by the gradient of concentration that is established in the membrane. If the liquid is incompressible ($\partial J_v/\partial_x = 0$), J_v is given by (Kedem and Katchalsky, 1958):

$$J_v = J_0 + J_1 = J_0 - \sigma L_p \nu RT\Delta c, \tag{6}$$

with $\Delta c = c(x = 0) - c(y = 0)$, and ν being the dissociation number of the electrolyte, R the gas constant, and T the absolute temperature.

Eq. 6 causes the convective term of Eqs. 1–3 to depend not only on the local concentration, but also on the concentrations in $x = 0$ and $y = 0$, which probably prevents the analytical solution of Eqs. 1–3, unless simplifying assumptions are introduced. On the other hand, the network thermodynamic approach allows us to attack the problem directly, without any simplifying assumption. For this reason, our first objective is to obtain the network model corresponding to the phenomena described by the Eqs. 1–3 and with the complete set of boundary conditions mentioned (Eqs. 4–6).

Network model for concentration polarization phenomena

The general procedure for obtaining the network model representative of any transport process consists in dividing the physical region of interest (which we consider of unit area) into volume elements or compartments of thickness Δx. Logically, the precision of quantitative modeling is greatly improved as the degree of subdivision increases because the larger the number of compartments, the closer we come to continuum behavior (Wyatt et al., 1980). If c_1 represents the concentration of the chemical species on the side through which the flow enters into the compartment and c_2 the concentration on the side through which it leaves, the diffusive contribution (J_d) to the flow of solute (Eqs. 1–3) can be given by:

$$J_d = D_i \frac{c_1 - c_2}{\Delta x}, \tag{7}$$

where D_i is the diffusion coefficient in the considered physical region. The analogy of the Eq. 7 with Ohm's law indicates that the dissipative effects of the diffusion process are synthesized by a resistance, of value

$$R = \frac{\Delta x}{D_i}. \tag{8}$$

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

$$-\mathrm{div} J = \gamma^* \left(\frac{\partial V}{\partial t}\right), \tag{9}$$

where J and V are the current density and the electric potential, respectively, and γ^* is the capacitance per unit volume. If we compare Eq. 9 with the equation of continuity of mass flux, then in the diffusion $\gamma^* = 1$, 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, is equal to Δx.

The elementary network model for a nonstationary diffusion process is the well-known model of Fig. 2 *a* (Oster et al., 1973). It is assumed in it that the volume element is symmetric such that the linear resistor is split into two equal parts, $R/2$, between which the capacitance γ is placed.

In accordance with Eqs. 1–3, the convective contribution (J_c) to the flow of solute is:

$$J_c = J_v(1 - \sigma)c = e \cdot c, \tag{10}$$

where c in each compartment is that in the center of such volume element. $\sigma = 0$ in the external regions of the membrane. It must be noted that in modeling the convective flow, J_c, by a nonlinear voltage-dependent current source (Fig. 2 *b*), it is necessary to consider the function e in Eq. 10 as a force-type variable, which is obtained by assuming $(1 - \sigma)$ to be a resistance-type term.

Both diffusive and convective effects can be combined, taking into account Kirchhoff's current law and connecting in parallel the two monoports. This constitutes the network model for nonstationary diffusion–convection in a volume element (Fig. 2 *c*) (Horno et al., 1988). Any number of them can be connected in series to form a network model for the entire physical region.

With the objective of obtaining the network model of the concentration polarization phenomena, it must be kept in mind that in each of the three regions that form the system (the two external and the membrane region), nonstationary diffusion–convection processes take place, which are modeled by means of the 1-port of Fig. 2 *c*. The model for the whole system is obtained, taking into account the boundary conditions (Eqs. 4 and 5), by the connection in series of the network models which make up each physical region, shown in circuit 1 of Fig. 3. In the case of electroosmosis, Eqs. 4′ and 5′ will have to be taken into account, that is to say, the effect that the discontinuity of the transport number in the interfaces causes in the solute flow will have to be incorporated. This flow, Ψ, is modeled by a constant current source of value $(\alpha/F)I$ (*broken line* in Fig. 3, circuit *1*). Of course, each region will be characterized by its own resistance, capacitance,

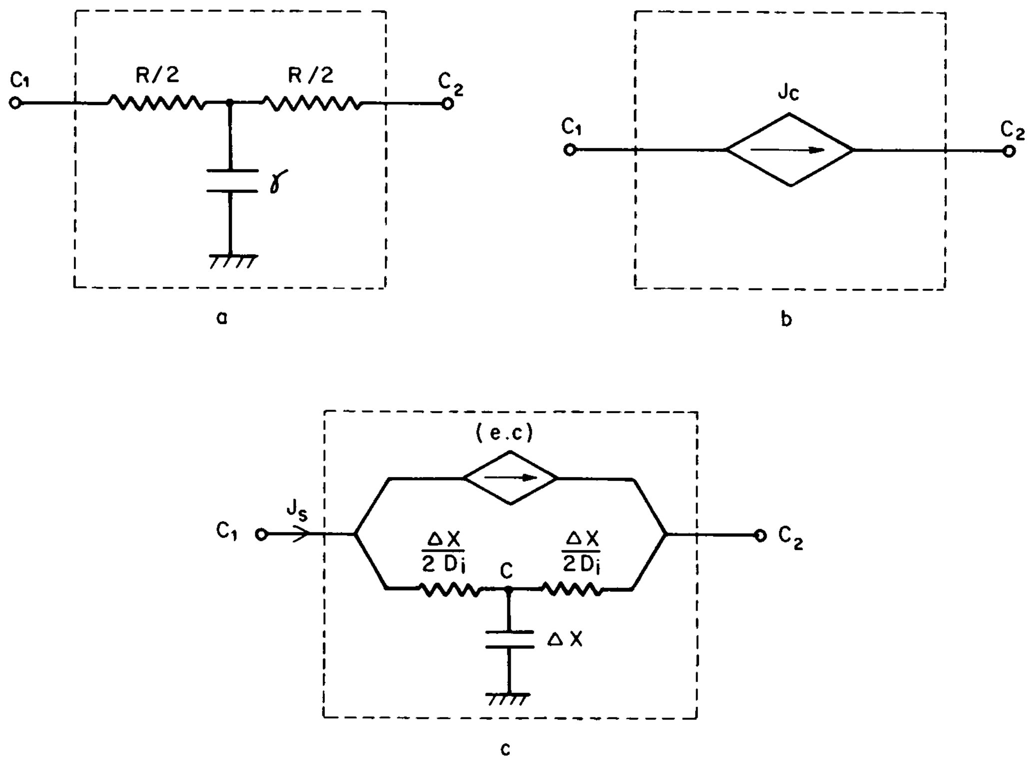

FIGURE 2 Network model for nonstationary diffusion–convection.

dependent source, and local concentrations, these being, for the external regions

$$R_i = \frac{d}{nD_f};\quad \gamma_i = \frac{d}{n};\quad J_{ci} = J_v \cdot c = e_1 c \tag{11}$$

and for the membrane

$$R_i = \frac{1}{nD_f};\quad \gamma_i = \frac{1}{n};\quad J_{ci} = J_v(1-\sigma)c = ec \tag{12}$$

with $i = 1,2,\ldots, n$.

It must be noted that modeling the convective flux, J_{ci}, by a nonlinear voltage-dependent current source requires considering functions e_1 and e as force-type variables, which are obtained by assuming 1 and $(1-\sigma)$ to be the resistance terms. This is shown in circuit 4 of Fig. 3. On the other hand, the values of e_1 and e are conditioned by those of J_0 and J_1 (Eq. 6). J_1 is represented by the resistive monoport, of value $R_1 = (\sigma L_p \nu RT)^{-1}$, shown in circuit 2 of Fig. 3. The hydrodynamic $(L_p \Delta p)$, or the electroosmotic contribution (λI), are represented, respectively, by the resistive monoport, of value $R_0 = 1/L_p$, and by a constant flow source, of value $J_0 = \lambda I$, which are represented in circuit 3 of Fig. 3.

Fig. 3, therefore, represents the global network model of the concentration polarization phenomena, both in the case of streaming potential (with $I = 0$) and in electroosmosis (with $\Delta p = 0$). Initial and boundary conditions have also been incorporated in the model, specified by

$$\text{For } t = 0,\ c(x,0) = c(z,0) = c(y,0) = c_0 \tag{13}$$

$$\text{For } t > 0 \text{ and } x,y \geq d,\ c(x,t) = c(y,t) = c_0. \tag{14}$$

Eq. 13 expresses the initial situation that the concentration is uniform throughout the system, which is equivalent to establishing a unique potential c_0 in each node of the network. Eq. 14 implies that the concentration in points at a great distance from the membrane maintains its initial value, which, for the network modeling purpose can be synthesized by a suitable constant voltage source of output c_0.

Simulation of concentration polarization phenomena in streaming potential and electroosmosis

By means of the network model of Fig. 3, with the appropriate numerical values for the parameters of the system and using the computation program SPICE, the values of the local concentration in both external solutions and membrane region can be simulated. In the first place

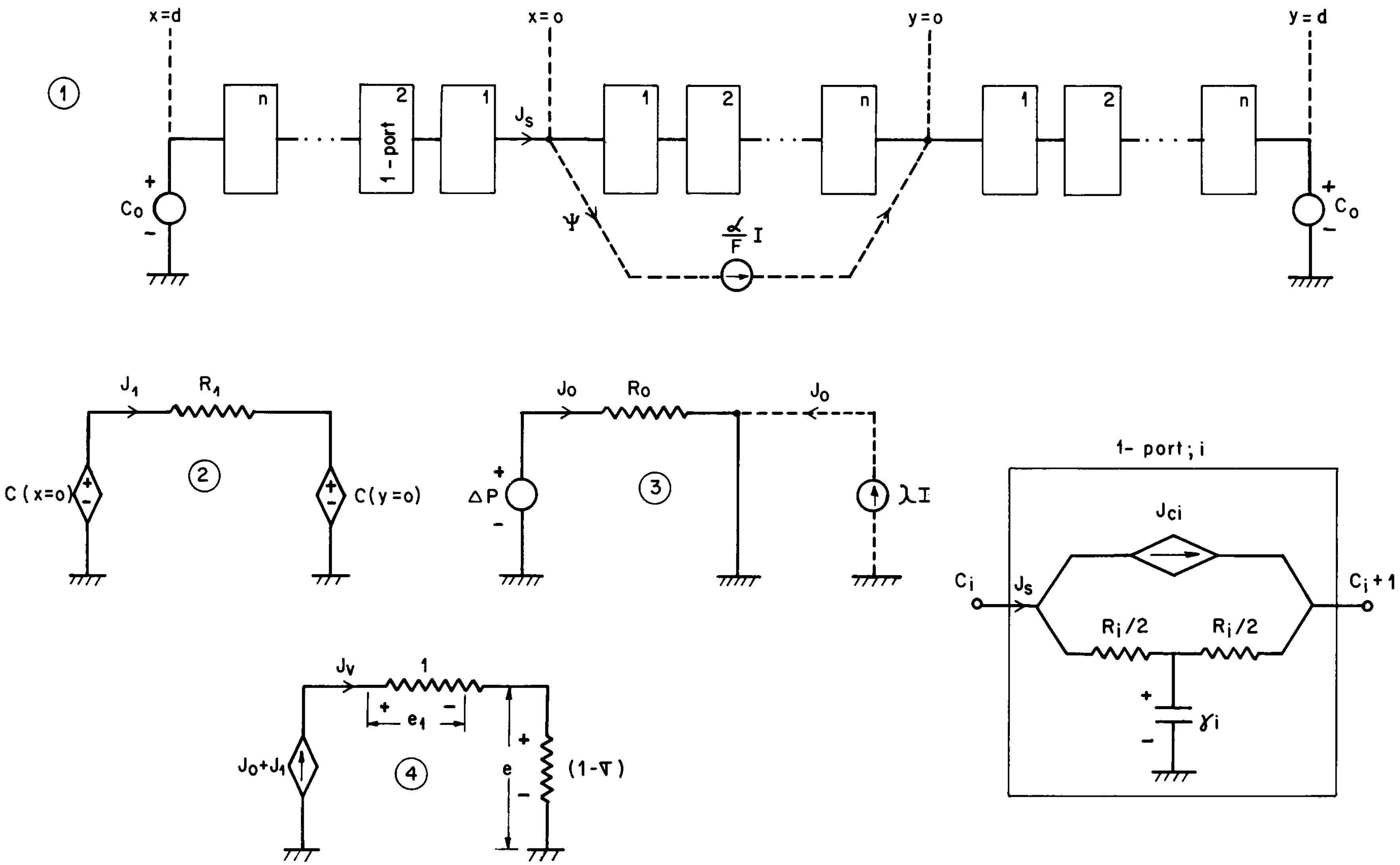

FIGURE 3 Network model for concentration polarization phenomena in streaming potential and electroosmosis effects.

TABLE 1 Parameters used in the simulation of the polarization phenomena in streaming potential effect

$c_0 = 10^{-3}$ M	$l = 1.5$ cm
$\Delta p = 30$ cm Hg	$t_+ = 0.491$
$D_f = 1.92 \cdot 10^{-5}$ cm^{2}s^{-1}	$\tilde{t}_+ = 0.655$
$D_m = 0.75 \cdot 10^{-5}$ cm^{2}s^{-1}	$\Delta\phi_s = 27.9$ mV
$L_p = 2.77 \cdot 10^{-10}$ cm^{2}dyn^{-1}s^{-1}	$T = 298$ K

Polystyrene/KCl system (from Van der Put and Bijsterbosch, 1981).

we have considered the streaming potential effect and for this we have made use of the data shown in Table 1, relative to a polystyrene/KCl system (Van der Put and Bijsterbosch, 1981). A multicompartment study has been carried out on the three regions that make up the system (external solutions and diaphragm), taking compartments 0.25 mm thick (d was taken equal to 5 mm), which permits a local estimation of the concentration without excessively lengthening the computation time (Wyatt et al., 1980).

The results obtained in a time $t = 10$ min and different reflection coefficients are shown in Fig. 4. It can be observed that the network model reproduces the experimental fact of accumulation of electrolyte on the high pressure side and decrease of concentration on the low-pressure side, an effect known as salt filtration and resulting from Donnan exclusion of electrolite at both sides. The concentration profiles are most marked for large values of the reflection coefficient. Inside the diaphragm, the concentration profiles are practically symmetrical to those of the adjacent solutions. Ignoring the effect on the limits, the concentration in the diaphragm is constant and equal to the initial concentration.

On the other hand, as is known, if a pressure difference is applied to a charged plug or membrane, a streaming potential originates. In the case of a permselective membrane or porous plug, due to an accumulation of electrolyte at the high-pressure side and a depletion at the low-pressure side, a concentration potential is superimposed on the streaming potential and a transient rise of the potential is observed. The potential difference, $\Delta\phi$, measured by electrodes in the two bulk solutions, will, however, be increased slightly by the appropriate diffusion potentials in each solution and will be given by

$$\Delta\phi(t) = \Delta\phi_s + \Delta\phi_m(t) + \Delta\phi_d(t), \qquad (15)$$

where it has been assumed that the streaming potential, $\Delta\phi_s$, is independent of time.

The time-dependent membrane potential across the plug, $\Delta\phi_m$, can be written as

$$\Delta\phi_m(t) = (2\tilde{t}_+ - 1)(RT/F)\ln\frac{c(x=0,t)}{c(y=0,t)}, \qquad (16)$$

where $\tilde{t}_+$ is the average apparent transport number of the counter ions within the plug, taking water transport into account (Staverman, 1952).

The third term of Eq. 15 represents the sum of the two diffusion potentials between the concentrations at the interfaces and in the bulk solution, and it can be formu-

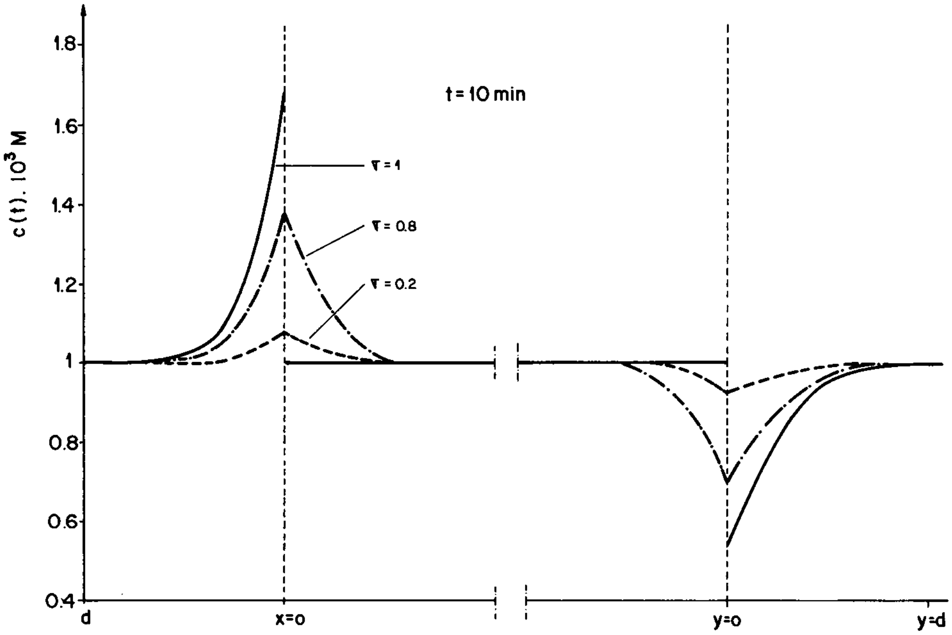

FIGURE 4 Concentration profiles at $t = 10$ min and diverse reflection coefficients.

lated as

$$\Delta\phi_d(t) = -(2t_+ - 1)(RT/F)\ln\frac{c(x = 0,t)}{c(y = 0,t)}, \qquad (17)$$

where t_+ is the transport number of the counter-ions outside the plug.

The combination of Eqs. 15, 16, and 17 leads to

$$\Delta\phi_m(t) = \Delta\phi_s + 2(\tilde{t}_+ - t_+)(RT/F)\ln\frac{c(x = 0,t)}{c(y = 0,t)}. \qquad (18)$$

From this equation, evaluating the concentrations $c(x = 0,t)$ and $c(y = 0,t)$ for different times, it is possible to obtain the evolution in time of the potential difference across the membrane. The result obtained for a pressure pulse of height 30 cm Hg and a $\sigma = 0.5$ is shown in Fig. 5, where the effect that the concentration polarization phenomenon causes on the measurement of the streaming potential can be observed. In biological systems, this effect was already pointed out by Vargas (1968) on studying streaming potentials in the squid giant axon.

In relation to electroosmosis, concentration profiles are obtained similar to those of Fig. 4, for a current passing from left to right (Fig. 1). Now, the multicompartment study has been carried out taking compartments with a thickness of $\Delta x = 0.1$ mm (d was taken equal to 2 mm). Using Eq. 18 (but now with $\Delta\phi_s = 0$) and the data of Table 2 (Barry and Hope, 1969) relative to the Characean cell wall/KCl system, we have simulated the time evolution of the potential drop across the cell membrane. Current densities, I, of 10, 100, and 500 μA·cm^{-2} have been considered. The results are shown in Fig. 6. For I = 10 μA·cm^{-2}, $\Delta\phi$ rises to a value of 8.6 mV for t = 1,000 s. However, for higher current densities, 100 and 500 μA·cm^{-2}, $\Delta\phi$ may become infinite at times near 129 and 6 s, respectively. This behavior at high current densities has been discussed by Barry and Hope (1969) as due to the nonconstancy of the transport parameters in these conditions.

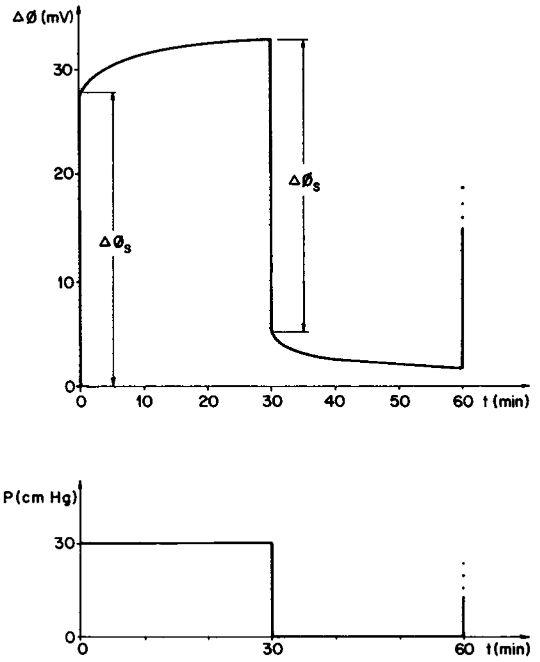

FIGURE 5 Temporal variation of the potential difference for a pressure pulse.

TABLE 2 Parameters used in the simulation of the polarization phenomena in electroosmosis effect

$c_0 = 10^{-3}$ M	$\lambda = 10\ \mu l \cdot C^{-1}$
$D_f = 1.92 \cdot 10^{-5}$ cm^{2}s^{-1}	$t_+ = 0.51$
$P_m = D_m/l = 0.9 \cdot 10^{-4}$ cm · s^{-1}	$\tilde{t}_+ = 0.98$
$L_p = 3.6 \cdot 10^{-5}$ cm · atm^{-1}s^{-1}	$T = 293$ K
$\alpha = 0.5$	$\sigma = 1$

Characean cell wall/KCl system (from Barry and Hope, 1969).

Finally, to illustrate another of the diverse possibilities that can be obtained from the proposed network model, in Fig. 7 is shown the decay of the concentration change (local concentration minus initial concentration, c_0), in the accumulation region behind the cell membrane, and at different distances from the membrane: x = 0, 0.5, 1, and 2 mm. The profiles correspond to the relaxation phenomenon after the current is turned off, having initially maintained a current of 10 μA·cm^{-2} for 200 s in the system. The results show a rapid decrease of concentration at x = 0, and a slower fall or rise of concentration at points far from the membrane. The time taken for the

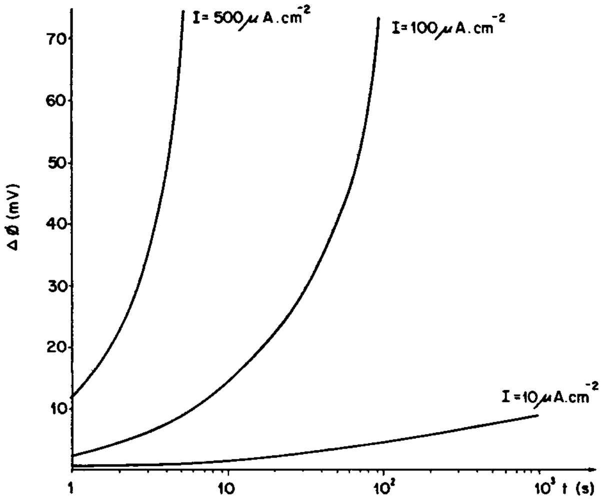

FIGURE 6 Temporal evolution of the potential drop across the membrane.

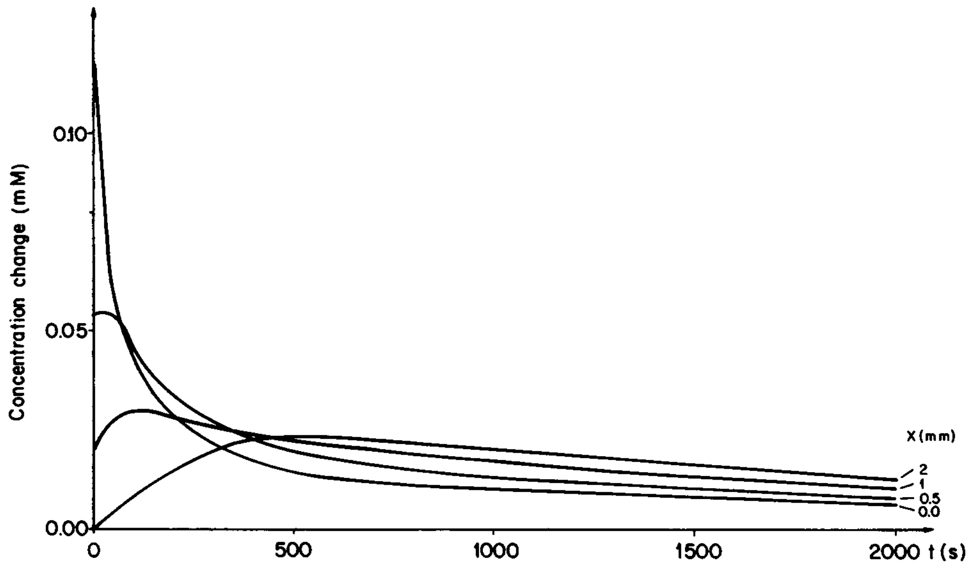

FIGURE 7 Concentration changes as a function of time after a current pulse at different distances from the membrane.

concentration at accumulation region to reach a maximum after the current pulse increased for large values of x.

To sum up, the proposed network model allows us to easily simulate the concentration polarization effects in streaming potentials and electroosmosis. The concentration profiles and the time evolution of the potential differences across the membrane are obtained without mathematical complexities, providing a useful tool in the analysis and prediction of this polarization phenomenon, owing to discontinuities in transport numbers between the membrane and the solutions on either side of it, which may often be of considerable importance.

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