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Ionic Transport in Electrochemical Cells Including Electrical Double-Layer Effects. A Network Thermodynamics Approach

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The network thermodynamics approach has been used to obtain the numerical solutions of the Nernst–Planck and Poisson equations governing the ionic transport in electrochemical cells, including electrical double-layer (EDL) effects. By using the electric circuit simulation program PSPICE, a model has been proposed, which permits easily the numerical solutions of those equations describing the behavior of the system under steady–state and equilibrium conditions, as well as the transient and frequency responses to electrical perturbations. Two physical problems are studied, namely, (i) the formation of the equilibrium EDL and (ii) the transient and frequency responses of the system to electric potential perturbations. Impedance–frequency responses and the time evolution of the surface charge density on the electrodes and the electric current density are given. Also, the ionic concentration, the electric potential and the electric field profiles across the cell were obtained as a function of time. The method is quite general and extremely efficient and permits dealing with multiion systems, whatever the boundary and experimental conditions may be.

Introduction

The theoretical model based on the Nernst–Planck and Poisson equations is one of the most widely used when studying ionic transport processes in electrochemical systems.[1] Nevertheless, the electrodiffusion equations are nonlinear and their analytical solution is nearly impossible in a great number of interesting physical situations. The need for an exact general solution for ionic transport problems is the reason why several authors have tackled this problem numerically.[2–7] One of the procedures most commonly employed is Brumleve and Buck's algorithm,[4] which is quite general, permits treatment of multiion systems without introducing restrictive approximations on the charge numbers, and can accommodate not only steady-state and transient responses but also impedance–frequency responses to electrical perturbations. However, the algorithm[4] considers the ionic concentration and the electric field as the independent variables, and thus the electric potential cannot be directly controlled. In a recent work, Murphy et al.[8] have proposed a procedure to solve the Nernst–Planck and Poisson transport equations in electrochemical cells, which permits the control of both the electric current and the drop of electric potential. However, this method does not contemplate the impedance–frequency responses in such systems.

Analysis of the impedance–frequency response of electrochemical cells and membranes is of great interest in electrochemistry, because it provides fundamental information about the transport processes in these systems.[1] The nature of the Nernst–Planck and Poisson equations is such that an exact analytical solution for the impedance has been given only for certain limited conditions, namely, the equilibrium flat-band condition in binary systems.[9] Analytical solutions for other general steady-state conditions and multiion systems are nearly impossible to obtain and are best solved by numerical methods.[4,10,11]

We present here an alternative method, based on the network thermodynamics approach,[12] which allows to obtain the frequency response of such systems as above, but by controlling either the electric current or the drop of electric potential through the cell. Network thermodynamics[12] allows to investigate the dynamics of interdependent flux–force relationships in terms of electrical networks. Network thermodynamics takes advantage of the similarities in the mathematical structure underlying different phenomena with balance and constitutive equations of the same type. As such equations fix the topology (the connection modes of the circuit branches) and the geometry (the circuit elements: resistors, capacitors, sources, etc.) of the network model, they allow us to establish a formal similitude between the mathematical model of the system and the electric networks. Once the model has been developed, an electrical network whose topology and geometry are identical to those of the system is obtained, the behavior of the network model being identical to that of the system. The network model is independent of the mathematics used to solve it, and its simulation can then be carried out by a suitable electric simulation program. Highly developed methods of circuit analysis can thus be used to obtain the dynamic behavior of the system directly without having to deal explicitly with the differential equations.

Another aim of this paper is to emphasize the utility of the network approach in deriving information about diffusion–migration situations involving the coupled nonlinear Nernst–Planck and Poisson equations. To accomplish this (i) a network model has been proposed for the ionic transport in electrochemical cells, including electrical double layer (EDL) effects and (ii) with this model, and the electric circuit simulation program PSPICE,[13] two problems of well-known complexity were studied, namely, (1) the formation of the equilibrium EDL at the metal electrode/electrolyte solution interface, and (2) the transient and frequency responses of an electrochemical cell to electric potential perturbations. In particular, the impedance–frequency response, the time evolution of the surface charge density on the electrodes, and the electric current density, are

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given. Also, the ionic concentration, the electric potential, and the electric field profiles across the cell were obtained as a function of time.

Mathematical Description of the Problem

Let us consider a system consisting of m ionic species and undergoing transport in an electrochemical cell. Assuming the ionic transport to be in one dimension, the equations determining the behavior of the system are the Nernst—Planck flux equations, the continuity and Poisson's equations (eqs 1—3, respectively):

$$J_i' = -D_i'\left(\frac{\partial c_i'}{\partial x} + z_i c_i'\frac{F}{RT}\frac{\partial \phi'}{\partial x}\right), \quad i = 1, ..., m \quad (1)$$

$$\frac{\partial J_i'}{\partial x} = -\frac{\partial c_i'}{\partial t} \quad (2)$$

$$\frac{\partial E'}{\partial x} = \frac{F}{\epsilon'}\sum z_i c_i' \quad (3)$$

where J_i', D_i', c_i', and z_i stand for the ionic flux, the diffusion coefficient, the molar concentration, and the charge number of ion i, respectively. R, T, and F are the gas constant, absolute temperature, and Faraday constant, respectively. ϕ', E', and ϵ' are, respectively, the electric potential, the electric field, and the dielectric permittivity. The letter t denotes the time and x the position along the electrodiffusion region, $-d \leq x \leq d$, with $2d$ being the total cell thickness. The electric field, $E' = -(\partial \phi'/\partial x)$, is a common quantity for every ion.

On the other hand, it is convenient to introduce the overall electric current density I', which takes the following form:

$$I' = F\sum z_i J_i' + \epsilon'\frac{\partial E'}{\partial t} \quad (4)$$

the last term being the displacement current.

Equations 1—4 may be written in dimensionless form using the following transformations:

$$\xi = x/l_0$$

$$\tau = D_0 t/l_0^2$$

$$c_i = \frac{c_i'}{c_0}; \quad J_i = \frac{l_0 J_i'}{D_0 c_0}; \quad D_i = \frac{D_i'}{D_0}; \quad i = 1, ..., m$$

$$\phi = \frac{F\phi'}{RT}; \quad E = \frac{l_0 F E'}{RT}; \quad \epsilon = \frac{RT\epsilon'}{F^2 c_0 l_0^2}; \quad I = \frac{l_0 I'}{FD_0 c_0}$$

where D_0, c_0, and l_0 are scaling factors having the dimensions of diffusion coefficient, concentration, and length, respectively. With these dimensionless parameters, eqs 1—4 can be written in the following reduced form:

$$J_i = -D_i\left(\frac{\partial c_i}{\partial \xi} + z_i c_i \frac{\partial \phi}{\partial \xi}\right), \quad i = 1, ..., m \quad (5)$$

$$\frac{\partial J_i}{\partial \xi} = -\frac{\partial c_i}{\partial \tau} \quad (6)$$

$$\frac{\partial D}{\partial \xi} = \sum z_i c_i = \varrho \quad (7)$$

$$I = \sum z_i J_i + \frac{\partial D}{\partial \tau} = I_f + I_d \quad (8)$$

where $\tau > 0$, and $-L \leq \xi \leq L$, with $L = d/l_0$. D, ϱ, I_f, and I_d stand for the electric displacement ($D = \epsilon E = -\epsilon(\partial \phi/\partial \xi)$), the electric charge density, the Faradaic current density, and the displacement current density in dimensionless form, respectively.

We shall now consider a particular system consisting of three ionic species ($m = 3$) having different charges (z_1, z_2, z_3). When an electric current is passed through the cell, cathodic and anodic reactions coupled with transport of the reacting species occur. The electrode process we consider here is a redox reaction involving the ionic species of charges z_1 and z_3. Thus, we agree that at the left-hand electrode ($\xi = -L$), the process is an oxidation:

$$c_1^{z_1} - ne^- \rightarrow c_3^{z_3} \quad (9)$$

and, at the right-hand electrode ($\xi = L$), the process is a reduction:

$$c_3^{z_3} + ne^- \rightarrow c_1^{z_1} \quad (10)$$

where $n = z_3 - z_1$ is the number of electrons transferred. The electrode kinetics are described by the Butler—Volmer equation, which including the structure of the double layer and the specific adsorption of ions can be written in dimensionless form as[14]

$$I_f(\pm L,\tau) = \pm nk^\circ[c_3(\pm L,\tau)e^{-\alpha n(\phi_e - \phi(\pm L,\tau) - \phi_0)} -$$
$$c_1(\pm L,\tau)e^{(1-\alpha)n(\phi_e - \phi(\pm L,\tau) - \phi_0)}] \quad (11)$$

where $\xi = \pm L$ now stand for the planes of closest approach of ions to the electrode surfaces. k° is the dimensionless standard kinetic rate constant (in FD_0/l_0 units), α the transfer coefficient, ϕ_e is the electric potential at the electrode, and ϕ_0 is the standard electrode potential. In this work, ions are assumed to be point charges, which is the basic assumption in the Gouy—Chapman model for the diffuse EDL. Therefore, the plane of closest approach of ions is just the electrode surface, and then $\phi(\pm L,\tau) = \phi_e$. Thus, from eq 11

$$I_f(\pm L,\tau) = \pm nk^\circ[c_3(\pm L,\tau)e^{\alpha n\phi_0} - c_1(\pm L,\tau)e^{-(1-\alpha)n\phi_0}] \quad (12)$$

For this system, the initial and boundary conditions can be expressed in the following way:

$\tau = 0$, $-L \leq \xi \leq L$:

$$c_1(\xi,0) = c_1^\circ(\xi), \quad c_2(\xi,0) = c_2^\circ(\xi), \quad c_3(\xi,0) = c_3^\circ(\xi) \quad (13)$$

$$\phi(\xi,0) = \phi^\circ(\xi) \quad (14)$$

$\tau > 0$, $\xi = \pm L$:

$$J_1(\pm L,\tau) = -J_3(\pm L,\tau) \quad (15)$$

$$J_2(\pm L,\tau) = 0 \quad (16)$$

$$J_3(\pm L,\tau) = (1/n)I_f(\pm L,\tau) \quad (17)$$

$$\frac{\partial D}{\partial \tau}(L,\tau) = I - I_f(L,\tau) = I_d(L,\tau) \quad (18)$$

$$\phi(-L,\tau) = 0 \quad (19)$$

The value of $I_f(\pm L,\tau)$ in eqs 17 and 18 is that given in eq 12.

Equations 15 and 17 indicate that the ions of charges z_1 and z_3 are those which react at the electrodes. Equation 18 is the boundary condition for the time evolution of D at $\xi = L$ and is obtained from eq 8. Finally, eq 19 entails considering the position $\xi = -L$ as the origin of the electric potential.

On the other hand, to consider the case in which the current I is not known a priori, it is necessary to take into account the new boundary condition eq 20, instead of eq 18:

$$\tau > 0, \quad \xi = L:$$

$$\phi(L,\tau) = f(\tau) \tag{20}$$

where $f(\tau)$ is an externally applied electric potential perturbation.

Network Model for Ionic Transport in Electrochemical Cells

The general procedure for obtaining the network model representative of the above processes consists of dividing the physical region of interest, which we consider of unit area, into N volume elements or compartments of width δ_k ($k = 1, ..., N$), sufficiently small for the spatial variations within each compartment to be negligible. By proceeding in this way, the diffusive (J_{di}) and electrical (J_{ei}) contributions to the ionic flux can be replaced by those corresponding to the discrete case:

$$J_{di}\left(\xi_k \pm \frac{\delta_k}{2}\right) = \pm D_i \frac{c_i(\xi_k) - c_i(\xi_k \pm \delta_k/2)}{\delta_k/2} \tag{21}$$

$$J_{ei}\left(\xi_k \pm \frac{\delta_k}{2}\right) = \pm D_i z_i c_i\left(\xi_k \pm \frac{\delta_k}{2}\right)\frac{\phi(\xi_k) - \phi(\xi_k \pm \delta_k/2)}{\delta_k/2} \tag{22}$$

where the minus and plus signs stand for the flux entering and leaving the compartment k, respectively. Therefore, $c_i(\xi_k)$ and $\phi(\xi_k)$ in each compartment are those in the center of such a volume element.

The diffusive flux in eq 21 and the concentration play the same role, respectively, as the current and potential in an electric circuit. Thus, a comparison of eq 21 and Ohm's law allows us to represent the dissipative effect of the diffusion in the compartment by means of a linear resistor of value:

$$R_{ik} = \delta_k/2D_i \tag{23}$$

Relation 22, in which the "current" J_{ei} is a function of the "voltages" c_i and ϕ, can be modeled by the multivariable voltage-controlled current source GJ_{ei}. The controlled sources are multiple (up to eight) input devices with a single output. The continuity equation (eq 6) can be approximated as

$$J_i\left(\xi_k - \frac{\delta_k}{2}\right) - J_i\left(\xi_k + \frac{\delta_k}{2}\right) = \delta_k\frac{dc_i(\xi_k)}{dt} \tag{24}$$

which can be viewed as the current across a capacitor of capacitance $C_k = \delta_k$.[7]

Adequate connection of two elements modeling the above contributions to J_i, diffusion (J_{di}) and electric conduction (J_{ei}), taking into account Kirchhoff's current law), allows us to obtain the network model shown in Figure 1a.

Given that a controlled source is one whose current or voltage is a function of currents or voltages elsewhere in the network, it will be necessary to introduce the driving force ϕ (eq 22) from any node in the network. The electric potential is obtained
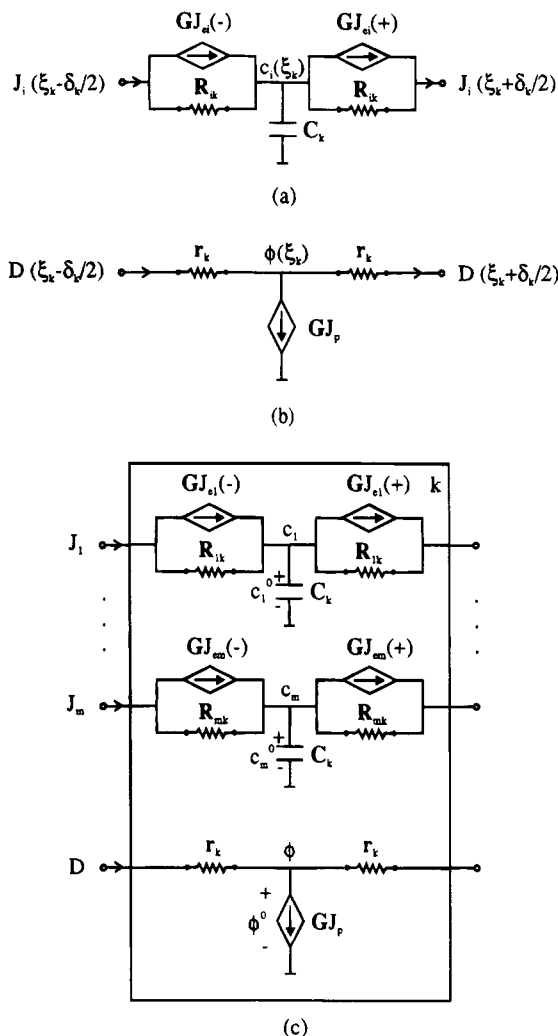

Figure 1. (a) One way to represent diffusion—migration in a single compartment. (b) Model for Poisson's equation in a volume element. (c) Network model for electrodiffusion in a single compartment.

from electric displacement, D, which is given by eq 7. To the discrete case, eq 7 can be written in the following form:

$$D\left(\xi_k - \frac{\delta_k}{2}\right) - D\left(\xi_k + \frac{\delta_k}{2}\right) = J_p(\xi_k) \tag{25}$$

where

$$D\left(\xi_k \pm \frac{\delta_k}{2}\right) = \pm\epsilon\frac{\phi(\xi_k) - \phi(\xi_k \pm \delta_k/2)}{\delta_k/2} \tag{26}$$

$$J_p(\xi_k) = -\delta_k\sum z_i c_i(\xi_k) \tag{27}$$

Relation 26 is similar to the current—voltage relation of a resistor, i.e., $i = \Delta\psi/r_k$, where i and ψ are the current and the electric potential, respectively, and r_k is the resistance. Comparison of the two expressions shows the resistance r_k to be equal to $\delta_k/2\epsilon$. Equation 27 can be represented by the multivariable voltage-controlled current source (GJ_p) modeling the function $J_p = -\delta_k\sum z_i c_i$. Equation 25 is a Kirchhoff's type current law at the node ξ_k, and we can incorporate this equation by connecting the two elements: a series resistance r_k and a shunt current source GJ_p as in Figure 1b. Therefore all the potentials in the multivariable source modeling the electric contribution to ionic fluxes (eq 22) already appear somewhere in the network.
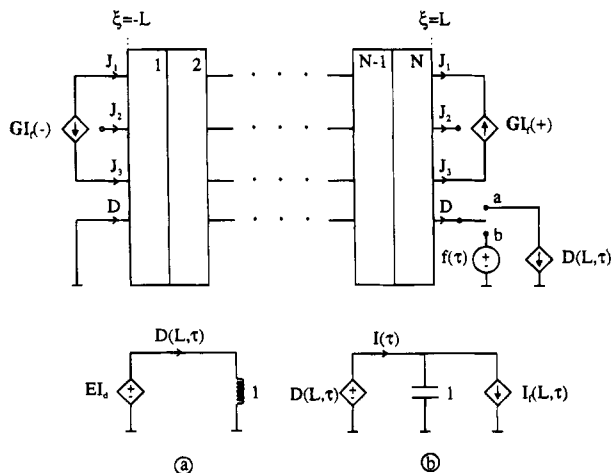
Figure 2. Global network model for a system consisting of three ions having different charges and undergoing transport in an electrochemical cell.

We could capture all effects by putting the several subcircuits together as in Figure 1c. The multiport thus resulting constitutes a model for the electrodiffusion process in a volume element. Any number of them, N, must be connected in series to form a network model for the entire physical region undergoing a diffusion−migration process, which is prescribed by the Nernst−Planck and Poisson equations.

The next step is to include the initial and boundary conditions of our particular problem into the model. The initial conditions for concentrations and electric potential (eqs 13 and 14) are included in a natural manner by means of the initial voltages at the correspondent nodes of the network (Figure 1c). The boundary conditions given by eqs 15 and 17 can be modeled by means of the voltage-controlled current sources GI_f modeling the function $I_f(\pm L, \tau)/n$ given by eq 17, as shown for $\xi = \pm L$ in Figure 2. The open circuit for J_2, at $\xi = \pm L$, represents a zero flux of ion of charge z_2 on the electrode surfaces (eq 16). Implementation of eq 18 into the model requires an additional subcircuit in the network: the electrical analog of eq 18 is an inductor with unit inductance. Thus, $D(L, \tau)$ is the current through the inductor in subcircuit a. It must be noted that in modeling the displacement current density, I_d, by a nonlinear voltage-controlled voltage source ($EI_d = I - I_f(L, \tau)$ in Figure 2), it is necessary to consider the function I_d in eq 18 as a voltage-type variable. Finally, eq 19 is introduced by short-circuiting the node ϕ at $\xi = -L$.

On the other hand, to analyze the case in which the electric potential is an independent variable, the boundary condition for the electric potential at $\xi = L$ has to be considered. For this purpose, eq 20 is modeled by an independent voltage source with a time-dependent value for transient analysis given by $f(\tau)$, as shown for $\xi = L$ in Figure 2.

Given that the total electric current density is not known in this case, it will be necessary to obtain its value from any branch in the network. Equation 8 at $\xi = L$ allows us to compute the current I through the cell. Thus, the current I can be modeled by two current elements connected in parallel: a multivariable current-dependent current source modeling the function $I_f(L, \tau)$ $= \sum z_i J_i(L, \tau)$, and the current across a capacitor of unit capacitance as in subcircuit b. It must be noted that the modeling of the displacement current density, I_d, by the current across a capacitor requires considering $D(L, \tau)$ as voltage-type variable, which is obtained by a current-controlled voltage source of output $D(L, \tau)$.

All these initial and boundary conditions have been taken into account in the network of Figure 2, which represents the

global network model for the above-mentioned electrodiffusion problem in electrochemical cells, both in the case of the electric current (switch a and subcircuit a) and the drop of electric potential (switch b and subcircuit b) are used as the independent variables.

Network Simulation

The implementation of the model of Figure 2 by an electric network simulation program allows us to simulate the ionic transport in electrochemical cells including EDL effects. We have found the PSPICE package to be very usual for this purpose. PSPICE is a sophisticated circuit simulation program for nonlinear dc, nonlinear transient, and linear ac analysis which can be run in personal computers. The format for entering a description of the network into the program is quite simple, and a complete explanation is given in the user's guide.[13] We will make use of some of the potential applications of this method by applying them to the study of the formation of the equilibrium EDL at the metal electrode/electrolyte solution interface, and the transient and frequency responses of the system to electrical perturbations.

1. Formation of the EDL at the Electrode/Solution Interface. Let us first illustrate the development of the equilibrium diffuse EDL at the electrode/solution interface under open circuit conditions ($I = 0$). The network model in this case will be the one shown in Figure 2 with switch a and $I = 0$.

By means of this model, with the appropriate numerical values for the parameters of the system, the quantitative simulation of the formation of the EDL at the metal electrode/electrolyte solution interface can be easily obtained using PSPICE. Because the variables c_i and ϕ change rapidly near the interfaces ($\xi = \pm L$), a multicompartment study has been carried out on the electrodiffusion region ($-L \leq \xi \leq L$), taking $N = 100$ compartments, which permits an excellent accuracy without excessively lengthening the computation time. The compartment thickness on this interval is given by

$$\delta_k = \frac{L}{200}, \quad k = 1, ..., 40, \quad 61, ..., 100 \quad (28)$$

$$\delta_k = 2L/25, \quad k = 41, ..., 60 \quad (29)$$

The characteristic parameters of system under study are the same as those used by Murphy et al.,[8] namely, $z_1 = 2$; $z_2 = -1$; $z_3 = 3$; $D_1 = D_2 = D_3 = 1$; $\epsilon = 1$; $L = 10$; $c_1{}^\circ(\xi) = 0.1$; $c_2{}^\circ(\xi) = 1$; $c_3{}^\circ(\xi) = 0.267$, and $\phi^\circ(\xi) = 0$.

The results obtained for $\phi_0 = 0$, $k^\circ = 1$, and $\alpha = 0.5$ are shown in Figures 3−6. Because of the symmetry of the problem an EDL identical to that considered in Figures 3−5 exists at the interface $\xi = -L$. This is not shown in the figures. Figure 3 gives the time evolution of the electric potential profile from the initial value $\phi(\xi, 0) = 0$ to the final equilibrium value (the Nernst potential), which is reached in about 100 time units. The evolution of the electric field shown in Figure 4 resembles that of the electric potential, because it is the process of charge separation between solution and electrode which gives rise to the electric potential drop. Important deviations from electroneutrality can be observed in the spatial zones adjacent to the electrodes, as expected.[15] Figure 5 shows the equilibrium profiles achieved for the ion concentrations across the cell. Negative ion accumulation and positive ion depletion in the EDL are observed, this breaking the electroneutrality in those regions. On the other hand, the surface charge density on the electrodes ($\sigma(\pm L, \tau)$) can be computed by integration of the Poisson's
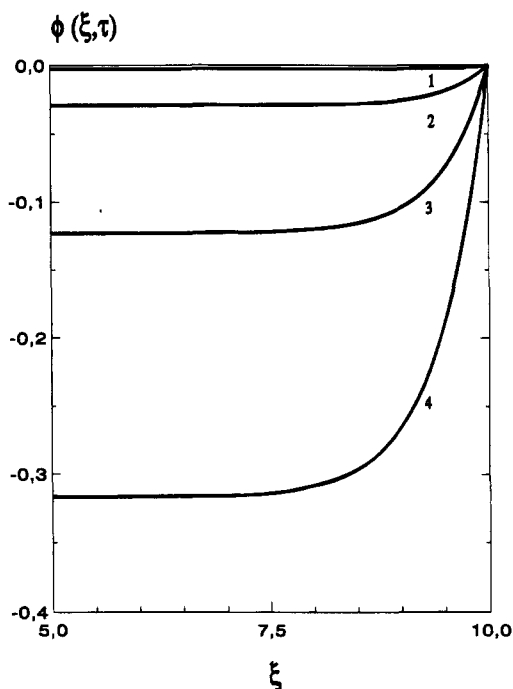
$\phi(\xi,\tau)$

Figure 3. Electric potential profiles for times: (1) $\tau = 0.1$, (2) $\tau = 1$, (3) $\tau = 10$, (4) $\tau \to \infty$. The plot corresponds to the development of the equilibrium diffuse EDL (case 1) for $\phi_0 = 0$, $k^\circ = 1$, and $\alpha = 0.5$. Note that only part of a cell of thickness $2L = 20$ is represented.
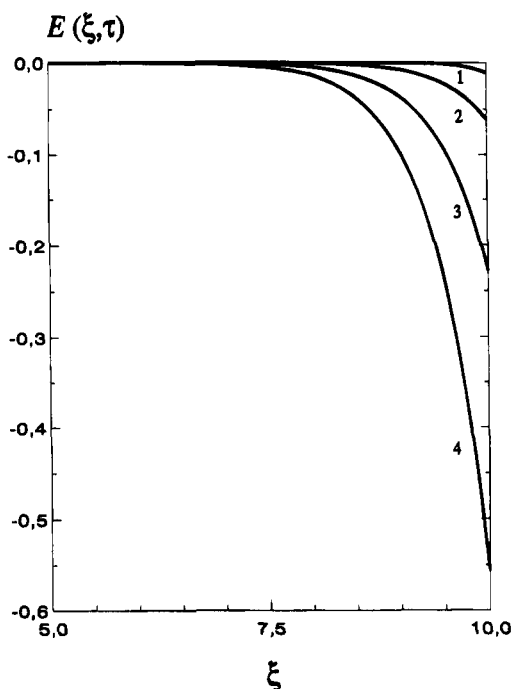
$E(\xi,\tau)$

Figure 4. Electric field profiles for times (1) $\tau = 0.1$, (2) $\tau = 1$, (3) $\tau = 10$, (4) $\tau \to \infty$, and the same conditions given in Figure 3.

equation from the midpoint of the cell, $\xi = 0$, to the position of the electrodes, $\xi = L$:

$$\sigma(\pm L, \tau) = \pm \int_0^{\pm L} \varrho(\xi,\tau) \, d\xi = \pm[D(\pm L,\tau) - D(0,\tau)] \quad (30)$$

and therefore it can be evaluated by obtaining the displacement currents $D(\xi=\pm L)$ and $D(\xi=0)$ in the network. Temporal evolution of the surface charge density on the electrode at $\xi = L$ for different values of the kinetic rate constant k° is shown in Figure 4. Note that $k^\circ = 1$ is a high value of the kinetic rate constant. With an additional order of magnitude reduction of
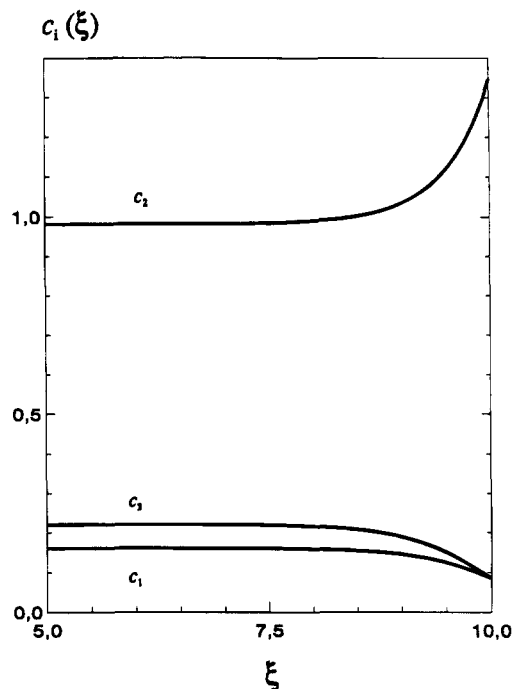
$c_i(\xi)$

Figure 5. Steady-state ion concentration profiles for the same conditions given in Figure 3.
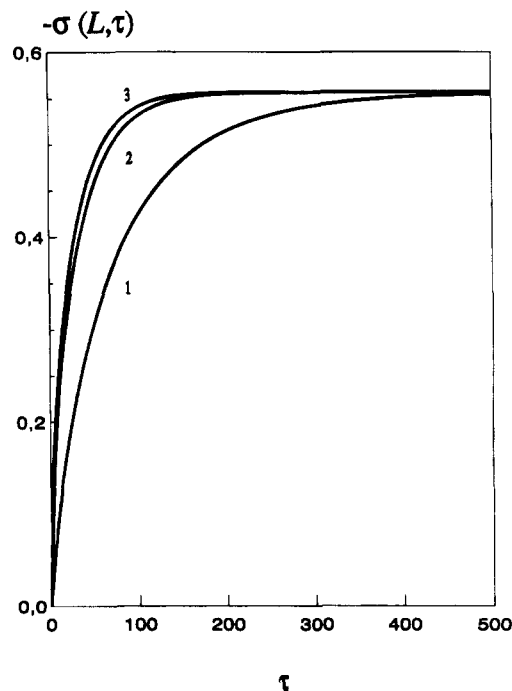
$-\sigma(L,\tau)$

Figure 6. Surface charge density on the electrode at $\xi = L$ for kinetic rate constants (1) $k^\circ = 0.1$, (2) $k^\circ = 1$, (3) $k^\circ = 10^6$, and the same conditions given in Figure 3.

k° the electrode offers resistance to the charging process, and thus the time required for the EDL to attain its equilibrium state greatly increases.

The above results are in good agreement with those of Murphy et al.,[8] despite the use of different methods.

2. Transient and Frequency Responses. We will now study the transient response of the system to an externally applied electric potential perturbation, $f(\tau)$. Our starting point will be the equilibrium EDL obtained in case 1. A transient analysis of an exponentially shaped potential perturbation (Figure 2 with switch b), as used by Murphy et al.,[8] will be performed with PSPICE. The initial conditions, $c_i^\circ(\xi)$ and ϕ°-
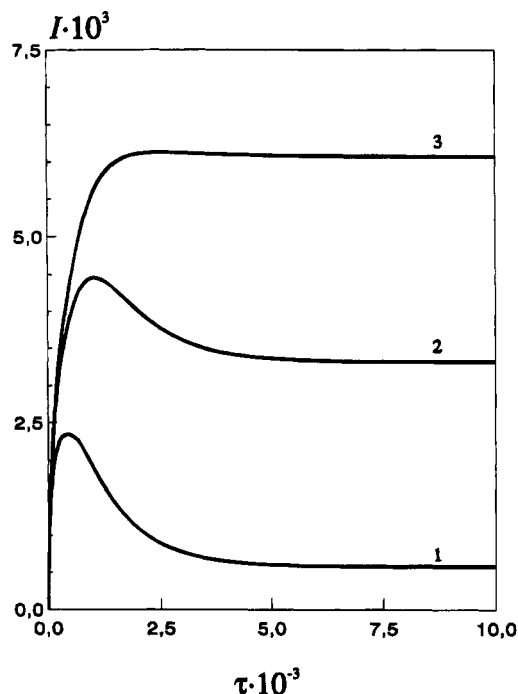
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Figure 7. Total electric current density for kinetic rate constants (1) $k° = 0.1$, (2) $k° = 1$, (3) $k° = 10^6$. The plot corresponds to the transient response of the system to the electric potential perturbation $f(\tau) = \phi(L,0) - 2(1 - \exp(-10^{-3}\tau))$ ($\phi(L,0)$ is the equilibrium electrode potential obtained in case 1) for $\phi_0 = 0$ and $\alpha = 0.5$.

Figure 8. Impedance plane plot for kinetic rate constants (1) $k° = 0.1$, (2) $k° = 1$, (3) $k° = 10^6$. The plot corresponds to a small-signal ac perturbation about the equilibrium steady-state obtained in case 1 for $\phi_0 = 0$ and $\alpha = 0.5$.

(ξ), correspond to the equilibrium values obtained in case 1 (Figures 3 and 5).

The time evolution of the total electric current density I for different values of the kinetic rate constant $k°$ is shown in Figure 7. It can be seen in this figure that the electric current density increases sharply above its steady-state value and then approaches it. Moreover, the results obtained for $\phi(\xi,\tau)$, $E(\xi,\tau)$, and $c_i(\xi,\tau)$ (not shown for brevity) closely resemble those in ref 8.

Finally, to illustrate another possibility offered by the proposed network model, we will now study the linear response of the system to a small-signal ac perturbation about the equilibrium steady-state obtained in case 1. The perturbating potential is now a small sinusoidal signal, which is superimposed on an external steady potential equal to the open-circuit voltage, i.e.

$$f(\tau) = \phi(L,0) + \Delta\phi e^{j\omega\tau} \tag{31}$$

where $\phi(L,0)$ is the equilibrium electrode potential obtained in case 1, $\Delta\phi$ the amplitude of the potential perturbation, ω its angular frequency, and $j = (-1)^{1/2}$.

In the regime of the lineal behavior of the system, each of the time-dependent quantities in eqs 5–8 can be expressed as the sum of equilibrium and sinusoidally varying components. In particular, the electric current density, which is computed from eq 8, is given by

$$I(\tau) = I(0) + \Delta I(\tau)e^{j\omega\tau} \tag{32}$$

where, in this case, $I(0) = 0$. From eqs 31 and 32 the dimensionless electrochemical impedance (in units of $l_0RT/F^2D_0c_0$) is given by the following equation:
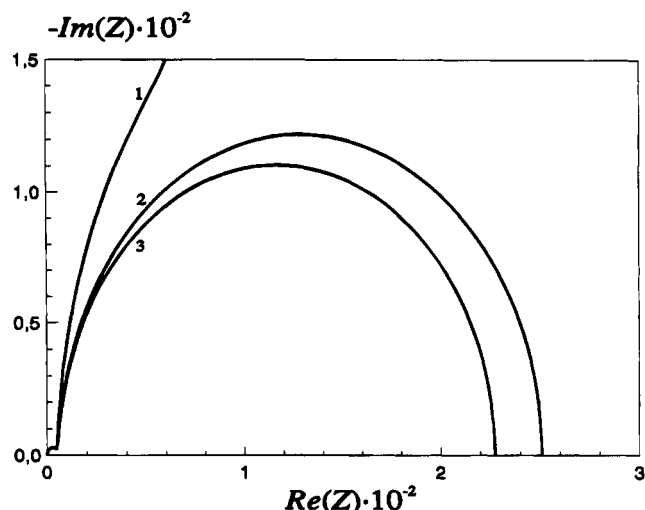
$$Z = -\Delta\phi/\Delta I \tag{33}$$

where the minus sign corrects for the electrochemical current–voltage convention. Note that $\Delta\phi$, ΔI, and Z are complex quantities.

The network thermodynamics approach can be easily accommodated to obtain the frequency response of a system. PSPICE contains special instructions to perform the ac analysis of the network model shown in Figure 2 about any steady state. This analysis is linear and thus is not necessary to impose any condition to the potential perturbation in order to ensure that the system responds linearly. Figure 8 shows the complex impedance plane plots (Nyquist plots) at the equilibrium state of case 1 for $\phi_0 = 0$, $\alpha = 0.5$, and various values of $k°$. In the case $k° = 1$, the impedance plot shows two semicircles: a bulk semicircle with peak frequency $\omega_1 = 3.1$, and an interfacial semicircle with peak frequency $\omega_2 = 0.0043$. Diffusional arc is absent because of the small cell thickness, and thus the system is in the regime of interfacial rather than diffusional control. With $k°$ an order of magnitude smaller, one begins to see a blocking behavior at low frequencies, although for any $k° > 0$ the impedance curve eventually bends back to the real axis.

Conclusions

Single techniques of network thermodynamics have been used to obtain the numerical solution for a boundary value problem involving the Nernst–Planck and Poisson equation system. A network model for a particular physical situation, namely, ionic transport in electrochemical cells including diffuse EDL effects, has been proposed. This model, together with an electric circuit simulation program such as PSPICE, allow us to easily study the equilibrium and nonequilibrium diffuse EDL at the metal electrode/electrolyte solution interface. The electric field, the electric potential, and the ionic concentration profiles across the cell are given. Also, the time evolution of the electric current density and the surface charge density on the electrodes as well as the impedance–frequency responses are obtained without mathematical complexities.

The proposed network method is quite general and extremely efficient and has found application in a large number of interesting biological processes[16] and electrochemical systems.[17] The procedure permits the imposition of conditions on both the electric current and the electric potential and can be applied to systems with multiple ions, which take different charge numbers and diffusion coefficients. Moreover, our approach can ac-

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commodate not only steady-state and transient responses but also impedance–frequency responses, providing a useful tool in deriving information about transport processes through spatial regions where large gradients in the physical variables occur.

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