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Enhanced migration and ionic transport through membranes

Wilson Barros, Jr. and M. Engelsberg*
Departamento de Física, Universidade Federal de Pernambuco, 50670-901 Recife, Pernambuco, Brazil

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The effect of Coulomb forces upon transport enhancement of mobile ions, in the presence of slowly migrating charged polymeric chains, is investigated in a nonequilibrium regime brought about by a semipermeable membrane and a chemical reaction. By means of a numerical solution of the Nernst-Planck-Poisson equations, we predict the size of the effect, the conditions for positive or negative enhancement, and the dependence upon all relevant parameters. The limitations of the description of migration enhancement by an effective diffusion coefficient are also established.

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I. INTRODUCTION

Diffusion, transport, and chemical reaction in ionic systems under the action of Coulomb forces are subjects of great interest in many areas of knowledge. Although the physical origin of the effect has been known for a very long time [1], the change in ionic migration caused by the Coulomb interaction has not deserved sufficient attention, in spite of its importance in the interpretation of a vast variety of phenomena.

When spatially separated reacting ionic species are placed in contact, the reacting interface may act as a virtual membrane with different transit times for the various types of ions involved in the process. As a consequence, the ensuing transport across the reacted region, as well as the progress of the reaction, may be affected not only by the diffusion coefficients and chemical reaction rates, but also by induced electric fields [2]. In the case where one of the species consists of long slowly migrating charged polymeric chains, the induced electric field may modify substantially the transport of other, much more rapidly diffusing, ionic species. In spite of the long history of this problem, the conditions for positive or negative migration enhancement of the mobile ions, the size of the effect, and its dependence on various parameters have not been treated in sufficient detail.

Slightly different versions of this effect have consequences in areas such as biopolymer chemistry, electrochemistry [3], soil science [4], semiconductor physics, and microbiology. In the latter case, negatively charged microbial polysaccharides appear to play a central role in enhancing the migration of nutrient cations across the protecting gel layer enclosing the living cell [5]. In the case of semiconductors, the smaller mobility of holes, compared to electrons, gives rise to the Dember potential [6].

From an experimental point of view, the specific focus upon the dynamics of mobile ions in the presence, in one of the sides of a membrane, of charged polymeric chains has been a relatively recent ocurrence. On the other hand the conditions to achieve equilibrium in the same type of physical systems have been studied extensively following the pioneering work of Donnan [7].

Various nuclear magnetic resonance (NMR) experiments, involving transport across real membranes under the effect of concentration gradients, were able to probe the considerable changes in ionic transport when charged polysaccharide chains are present in one of the compartments limited by the membrane. Using Overhauser magnetic resonance imaging (OMRI) [2], for example, the effective diffusion coefficient of Ca^{2+}, during the gelation of sodium alginate, was found to reach unexpectedly large values. In a different experiment involving spatially resolved NMR relaxometry, the effective Mn^{2+} diffusion coefficient in the presence of negatively charged polymeric chains was larger, by a factor between 2 and 2.5, than for neutral ones [5]. Moreover, in other recent studies [8] of calcium alginate beads, vastly employed as cell immobilization traps, ionic transport was also found to be affected by electrostatic effects.

II. NERNST-PLANCK-POISSON EQUATIONS

With the aim of giving a quantitative answer to the questions raised above, we present in this paper a numerical solution of the Nernst-Planck-Poisson (NPP) equations [9] for a model system consisting of four different ionic species and a neutral reaction product in an environment of cylindrical symmetry. The model was chosen so that it permits a rather realistic comparison with calcium alginate gel profiles determined by low field OMRI [2]. It also provides a natural explanation for the size of Mn^{2+} diffusion enhancement or suppression observed by Hart *et al.* [5], as well as of several other experiments [8,10,11]. Furthermore, it permits to assess under what conditions the simplifying assumption of an effective diffusion coefficient may be applicable to describe the effect of Coulomb forces between ions with very different mobilities. Starting with the particle flux densities $F_q(R,T)$ for a cylindrically symmetric system consisting of five species, the dependences upon the concentrations $C_q(R,T)$ and the induced radial electric field $\Xi(R,T)$ have the form [9]

$$F_q = d_q\left[\frac{\partial C_q}{\partial R} - z_q C_q \Xi\right] \quad (q=1,\ldots,5). \tag{1}$$

The dimensionless quantities appearing in Eq. (1) have the following meaning: $d_q = D_q/D_1$ denotes the diffusion coef-

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*Electronic address: mario@df.ufpe.br

ficient of species q relative to that of a reference species characterized by $q=1, R=r/b$ is the ratio of the radial distance, from the center, of the cylindrical region where the charged polymeric chains are confined, to the radius of that cylinder. The dimensionless field in Eq. (1) is defined by $\Xi=(EFb)/\Theta R$, where E denotes electric field, F is Faraday's constant, R is the gas constant, and Θ denotes absolute temperature. The valences of the ionic species are denoted by z_q, and $C_q=c_q/c_2$ are dimensionless concentrations relative to the initial concentration of a reference species characterized by $q=2$.

Although the predictions of our model are rather general, it is specifically designed to describe the spatiotemporal evolution of the gelation of an aqueous solution of sodium alginate dialyzed against a $CaCl_2$ solution. The negatively charged alginate chains are confined to a cylindrical region, separated by a membrane, from a bath initially containing only the $CaCl_2$ solution. Furthermore, the membrane is assumed to be permeable to sodium, calcium, and chloride ions but not to the charged alginate polymeric chains or to the gel formed by calcium bridging of carboxyl repeating units. The following correspondence can then be established for this example: $q=1$ with $z_1=2$ corresponds to calcium ions; $q=2, z_2=-1$ to guluronic carboxyl repeating units in the alginate chains; $q=3, z_3=0$ to calcium alginate gel; $q=4, z_4=1$ to sodium ions; and $q=5, z_5=-1$ to chloride ions. Moreover, the diffusion coefficient d_3 is assumed to be zero and consequently $F_3(R,T)=0$.

The spatiotemporal evolution is assumed to obey the following set of Nernst-Planck-Poisson [9,12] nonlinear partial differential equations in mks (rationalized units):

$$\frac{\partial C_1}{\partial T}=-\frac{1}{R}\frac{\partial}{\partial R}(RF_1)-KC_1C_2^2, \tag{2}$$

$$\frac{\partial C_2}{\partial T}=-\frac{1}{R}\frac{\partial}{\partial R}(RF_2)-2KC_1C_2^2, \tag{3}$$

$$\frac{\partial C_3}{\partial T}=2KC_1C_2^2, \tag{4}$$

$$\frac{\partial C_q}{\partial T}=-\frac{1}{R}\frac{\partial}{\partial R}(RF_q) \quad (q=4,5), \tag{5}$$

$$\frac{\partial \Xi}{\partial T}=-K_d\sum_{q=1}^{5} z_qF_q, \tag{6}$$

with $T=(tD_1/b^2)$ representing dimensionless time and $K_d=(Fb)^2c_2(0)/\epsilon\Theta R$, where ϵ denotes the permissivity of the medium. Equations (2)–(4) include a chemical reaction of first order in the concentration C_1 of the bivalent cations and of second order in the concentration C_2 of the monovalent carboxylic anions [12]. The reaction rate k' (M^{-2} sec^{-1}) is represented in Eqs. (2)–(4) by the dimensionless quantity $K=k'b^2c_2(0)^2/D_1$. The following initial conditions are employed: $C_1(R,0)=0, C_2(R,0)=1, C_3(R,0)=0, C_4(R,0)=1, C_5(R,0)=0$, and $\Xi(R,0)=0$. Boundary conditions are further represented by $F_q(R,T)=0$ at the center of the cylinder, whereas at $R=1$ the following homogeneous rate equations [9,12] are assumed:

$$F_q(1,T)=K_{tq}[C_{qb}-C_q(1,T)] \quad (q=1,\ldots,5). \tag{7}$$

In Eq. (7) C_{qb} denote constant dimensionless concentrations of the external bath surrounding the cylindrical region of radius b, and the dimensionless parameters K_{tq} are defined by $K_{tq}=k_{tq}b/D_1$, where k_{tq} are homogeneous rate constants [3]. For our particular application, the bath contains a $CaCl_2$ solution of a given concentration and can be described by $C_{1b}=C_0, C_{5b}=2C_0$, with $C_{qb}=0$ for other values of q. Furthermore, the transit rate constants k_{t2} and k_{t3} are assumed to be zero.

III. RESULTS AND DISCUSSION

NMR is a powerful tool to study transport, not only in the case of self-diffusion, but also when a concentration gradient [13] is present. In the latter case, the spatiotemporal information provided by NMR imaging can serve as a stringent test for the proposed models of migration. ^{1}H OMRI at very low magnetic field has proven to be especially sensitive to small changes in local water mobility yielding quite revealing information, particularly in the case of gel systems [14].

Figure 1 shows a limited portion of the time evolution of bound calcium profiles obtained by OMRI in a magnetic field of only 16 mT [2]. The data are normalized by the constant B_c, which denotes the stoichiometric bound calcium concentration when the reaction is complete. The initial concentrations employed in the experiment were $c_2(0)=0.106$ M for the guluronic carboxyl repeating units and $C_0=0.579$ for the relative calcium concentration in the bath.

It has been proposed [12] that the complex dynamics of the gelation of alginate chains by calcium ions could be described by equations involving simply diffusion and chemical reaction. However, OMRI experiments [2] suggest that this is not the case.

Nonlinear differential equations such as Eqs. (1)–(6), involving a chemical reaction and diffusion, are inherently intriguing and have been able to predict, under special circumstances, new and quite interesting phenomena [15]. Rather than explore a vast parameter range, we here limit our dicussion to a range of values where Eqs. (1)–(6) could provide a realistic description of the experiment presented earlier. In this regime, the main shortcoming of Eq. (1) is that convection currents caused by bulk osmotic solvent flow have not been included. Although this is not an insurmountable difficulty [16], their inclusion in the present case would considerably complicate the analysis. Collective fluid motion leads to non-Fickian profiles [17], which are quite apparent in the OMRI data for the initial stages of the gelation process. However, as the gelation progresses, and macroscopic viscosity drastically increases, the effect of bulk flow is expected to become negligible.

The NPP equations contain two very different length scales. One is determined by cylinder radius b, whereas the Debye length $[\epsilon R\Theta/c_2(0)F^2]^{1/2}=b/\sqrt{K_d}$ determines the

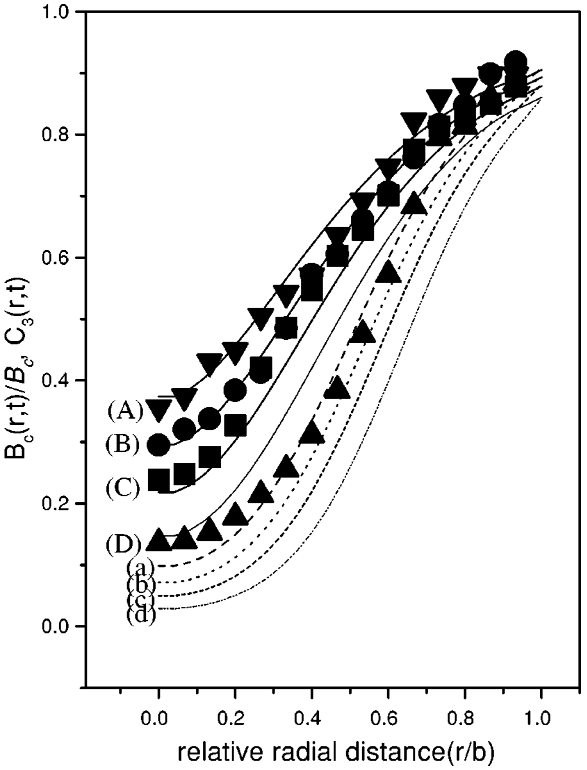

FIG. 1. Normalized bound calcium concentration profiles obtained from low-field OMRI of the gelation process of sodium alginate. Dialysis times, in minutes, against a $CaCl_2$ solution were (▼) $t=300$, (●) $t=270$, (■) $t=240$, and (▲) $t=210$. Solid lines are calculated $C_3(r,t)$ profiles with $D_1=0.43\times10^{-5}$ cm^2/sec, $k'=6\times10^{-2}$ M^{-2} sec^{-1}, $d_4=1.6, d_5=2.6$, and $k_{tq}=10^4$ cm/sec ($q=1,4,5$) for (A) $t=300$, (B) $t=270$, (C) $t=240$, (D) $t=210$. The dotted lines represent calculated profiles for the same parameters when Coulomb forces are ignored for (a) $t=300$, (b) $t=270$, (c) $t=240$, and (d) $t=210$.

other. The latter controls the evolution of the very narrow diffuse bilayer adjacent to the membrane [3], which is inacessible to OMRI. Thus, the role of several parameters involved in Eqs. (1)–(7) is rather irrelevant as far as the acessible region is concerned. The behavior of the accessible region is, for example, quite insensitive to the exact values of K_d. Thus, any possible uncertainty in the exact value of the dielectric permissivity compared to that of pure water has no appreciable consequence. Furthermore, the gelation process is assumed to be limited by diffusion rather than by the transit time through the external membrane. Since this requires $K_{tq}\gg1$, the profiles in the accessible region, for the time scale of interest, are also quite insensitive to differences in the values of K_{tq}, as long as these rates are assumed to be sufficiently large. Under these conditions, the only sensitive adjustable parameters in Eqs. (1)–(6) are the calcium diffusion D_1 coefficient, the reaction rate k', and the relative diffusion coefficients d_4 and d_5 of all other charged species. The coupled transport resulting from the Coulomb interaction, through the role of the relative diffusion coefficients d_4 and d_5, is the main ingredient of Eqs. (1)–(6).

The numerical solution of the equations was based upon the powerful procedure introduced by Brumleve and Buck [9]. This completely implicit scheme employs the Newton-Raphson method to solve iteratively the finite difference equations for a given Jacobian matrix. A single large value $k_{tq}\gtrapprox10^4$ cm/sec was assumed for all transit rates [3] except, of course, for k_{t2}, which was assumed to be negligibly small. Assuming also for the very slowly diffusing polymeric chain a value $d_2\lessapprox10^{-3}$, only the diffusion coefficients for sodium and chloride ions relative to that of calcium need to be specified. As a first, not unreasonable trial, the sodium and chloride diffusion coefficients were allowed to maintain the same ratio $d_4=1.6$ and $d_5=2.6$, as in an aqueous solution at infinite dilution. Using the same reaction rate $k'=6\times10^{-2}$ M^{-2} sec^{-1}, as in earlier simulations involving no electrostatic effects [2], the calculated gel profiles are shown in Fig. 1. It appears that, although some convective flow effect is still present at $t=210$ min, the dominant effects in the ensuing regime are caused by diffusion, chemical reaction, and Coulomb interactions. Moreover, instead of the large effective diffusion coefficient 0.81×10^{-5} cm^2/sec needed when electrostatic effects are ignored in the calculations, the theoretical profiles that best fit the data of Fig. 1 require a value $D_1=0.43\times10^{-5}$ cm^2/sec. This demonstrates that Coulomb forces are responsible for a migration enhancement by a factor 1.9. The result is already close to the range of values reported by Hart *et al.* [5], but even larger enhancements of Ca^{2+} migration could be obtained for special values d_4 and d_5. However, an enhancement of approximately the predicted size still persists for any reasonable choice of parameters.

A more vivid illustration of the enhancement can be obtained by making $z_q=0$ for all ionic charges in Eqs. (1)–(6), thereby removing electrostatic effects, but keeping $D_1=0.43\times10^{-5}$ cm^2/sec as well as the values of the other parameters. A quite substantial reduction in the calculated gel concentration results, as shown in Fig. 1.

The presence of a chemical reaction partially masks the fact that a description of the electrostatic effects, simply by an enhanced diffusion coefficient, can only be qualitatively correct. This aspect and the conditions for positive or negative enhancement can be better visualized by setting $K=0$ in Eqs. (2)–(4).

Figure 2 shows concentration profiles $C_1(R,T)$ for the bivalent cation, whose concentration in the external bath is now assumed to have the constant value $C_0=0.5$. Three different configurations are examined.

(i) $K=0$, with $z_2=-1, z_4=1, d_4=1.6$, and $d_5=2.6$, as in the previous example.

(ii) Same as (i) but with the slowly diffusing species now bearing positive charge ($z_2=1, z_4=-1$) and the following values of diffusion coefficients: $d_4=3.6$ and $d_5=1.6$. This particular choice, together with the charge inversion, leads to a change in sign of the radial electric field.

(iii) Same as (i) but with no charge ($z_q=0$).

It is apparent from Fig. 2 that for $K=0$, the migration enhancement is also quite significant. It is positive in case (i) and becomes negative in case (ii) as observed by Hart *et al.* [5]. Moreover, it also exhibits some differences with respect to the case where the chemical reaction is present. The concentration of bivalent cations near the membrane can reach

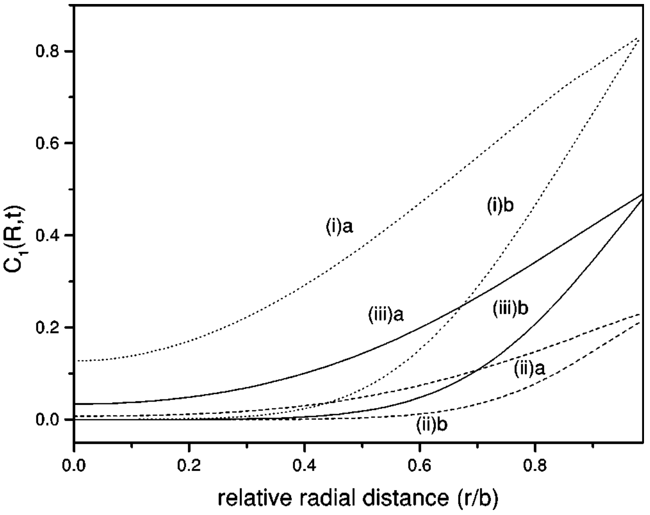

FIG. 2. Calculated concentration profiles $C_1(R,T)$ of bivalent cations in the absence of chemical reaction, and $C_0=0.5$, for times (a) $T=75\times10^{-3}$ and (b) $T=25\times10^{-3}$: (i) Negatively charges chains with $z_2=-1,z_4=1$ and $d_4=1.6,d_5=2.6$. (ii) Positively charged chains with $z_2=1,z_4=-1$ and $d_4=3.6,d_5=1.6$. (iii) All charges equal to zero.

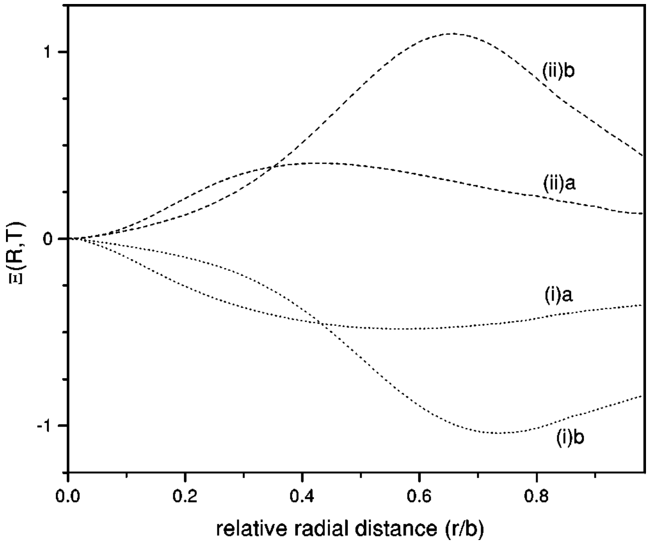

FIG. 3. Dimensionless radial electric field profiles $\Xi(R,T)$ in the absence of chemical reaction, and $C_0=0.5$, for times (a) $T=75\times10^{-3}$ and (b) $T=25\times10^{-3}$: (i) Negatively charged chains with $z_2=-1,z_4=1$ and $d_4=1.6,d_5=2.6$. (ii) Positively charged chains with $z_2=1,z_4=-1$ and $d_4=3.6,d_5=1.6$.

values that are significantly larger or smaller than those of the bath. This is expected as a consequence of the approach to Donnan's [7] equilibrium, which is implicit in Eqs. (1)–(6). Hence, the description of concentration profiles (i) and (ii) by means of an effective diffusion coefficient, with positive or negative enhancement with respect to profiles (iii), can be seen to be erroneous in the absence of the chemical reaction. In spite of this, the general trend can still be globally characterized as positively or negatively enhanced migration.

Figure 3 shows calculated radial dimensionless electric fields $\Xi(R,T)$, which for geometrical dimensions typical of our experiments correspond to electric fields of order 36Ξ mV/cm. Adopting the same three configurations considered in Fig. 2, one observes that the choice of values d_4 and d_5, as well as the charge inversion in case (ii) relative to (i), alter the delicate balance between charge and diffusivity in such a way that an almost perfect inversion of the radial electric field occurs. The results also demonstrate the correlation between the sign of the induced radial field and the migration enhancement or suppression prevailing in the profiles of Fig. 2.

We conclude that a solution of the NPP equations for a simple but rather realistic model, such as the one presented in this paper, can explain a wealth of experimental results whose interpretation has led, in some cases, to considerable controversy. A sizable enhancement or suppression of migration of mobile ions can occur, in a situation of nonequilibrium, when slowly migrating charged species are present. In some instances, as when a chemical reaction is taking place, the effect can be approximately characterized by an effective diffusion coefficient with positive or negative enhancement. For negatively charged slowly migrating polysaccharide chains, for example, a positive diffusion enhancement of Ca^{2+} ions by a factor close to 2 was found to explain Overhauser imaging gelation profiles. However, when the spatiotemporal evolution of concentration profiles in the absence of a chemical reaction is required, the concept of an effective diffusion coefficient becomes rather meaningless and could only be helpful in a qualitative characterization of global migration enhancement effects.

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