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Coupled Diffusion of Multiple Ionic Species in Ion-Exchange Membranes with Fixed Ionic Groups

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ABSTRACT

The theory of coupled diffusion of multiple ionic species based on complete Donnan exclusion has been applied to a diffusion process involving an ion-exchange membrane and three counter ions. The influence of the main process parameters (e.g., diffusion coefficients and ionic charges) has been studied by numerical simulations. The results obtained underline the importance of taking into account the coupled diffusion of all counter ions in a multi-ion system to describe adequately the transport of each individual counter ion.

Key Words: Coupled diffusion; Ion transport; Ion-exchange membrane; Mathematical modeling.

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INTRODUCTION

The industrial and analytical applications of permselective ion-exchange membranes (e.g., Nafion) with fixed ionic groups have grown considerably in recent years.[1,2] The ability to describe the mass transfer of ions of opposite charge (counter ions) to fixed ionic groups of these membranes is essential for better understanding and optimization of the corresponding ion-exchange and mass-transfer processes. An equation Eq. (1) describing the coupled diffusion of two-counter ions of the same or different valences in a fixed-site ion-exchange membrane was derived by taking into account the influence of both the electrostatic potential gradient and the concentration gradients in the membrane.[3,4]

$$\mathrm{J_A} = -\left[\frac{\mathrm{D_A D_B}\left(\mathrm{z_A^2 c_A} + \mathrm{z_B^2 c_B}\right)}{\mathrm{D_A z_A^2 c_A} + \mathrm{D_B z_B^2 c_B}}\right]\mathrm{grad(c_A)} \tag{1}$$

where **J**, **D**, **z**, and **c** are the flux, the diffusion coefficient, the electronic charge, and the concentration of ionic species A and B.

Equation (1) was successfully utilized in the mathematical description of mass-transfer processes involving ion-exchange membranes.[5,6] However, ion-exchange membranes are usually exposed to solutions of complex ionic composition and the resulting mass-transfer processes are likely to involve more than two different counter ions. In the general case the flux of **M** different counter ions within an ion-exchange membrane with fixed ionic groups assuming complete Donnan exclusion can be described by the following equation[7]:

$$\mathrm{J_j} = -\mathrm{D_j grad(c_j)} - \mathrm{z_j c_j}\frac{\sum_{\mathrm{i=1}}^{\mathrm{i=M}} \mathrm{z_i D_i grad(c_i)}}{\sum_{\mathrm{i=1}}^{\mathrm{i=M}} \mathrm{z_i^2 D_i c_i}} \tag{2}$$

where $\mathbf{j} = 1, 2, \ldots, \mathrm{M} - 1$.

The flux $\mathbf{J_M}$ can be calculated by the equation expressing the zero-current condition (Eq. (3)) once all other fluxes ($\mathbf{j} = 1, 2, \ldots, \mathrm{M} - 1$) have been calculated by Eq. (2).

$$\sum_{\mathrm{j=1}}^{\mathrm{j=M}} \mathrm{z_j J_j} = 0 \tag{3}$$

The transient coupled mass-transfer of each ionic species participating in the ion-exchange process can be described by the corresponding equation of continuity

$$\frac{\partial c_j}{\partial t} = -\mathrm{div}(J_j) \tag{4}$$

where $\mathbf{j} = 1, 2, \ldots, M - 1$.

The concentration of the **M**-th species can be determined by the electroneutrality requirement Eq. (5) if the concentrations of the other ionic species ($\mathbf{c_j}, \mathbf{j} = 1, 2, \ldots, M - 1$) are known.

$$\sum_{j=1}^{j=M} z_j c_j = c_0 \tag{5}$$

The importance of taking into account the coupled diffusion of all ionic species present can be illustrated by modeling the ionic transport in a system incorporating an ion-exchange membrane and three counter ions. To clarify better the influence of the system parameters directly responsible for the coupled diffusion within the membrane (e.g., diffusion coefficients and electronic charges of the counter ions) effects resulting from boundary layers resistance and interfacial equilibria and kinetics are neglected.

COUPLED DIFFUSION IN A THREE COUNTER ION SYSTEM

Formulation of the Problem

Let's consider a flat ion-exchange membrane of thickness 2δ and concentration of fixed ionic groups c_0 immersed into an ideally mixed solution of infinite volume containing counter ions A^{z_A} and B^{z_B}. The infinite volume assumption suggests that the concentrations of ions A^{z_A} and B^{z_B} in the solution and at the membrane/solution interface can be considered as constant. The membrane is assumed to incorporate initially counter ions M^{z_M} only whose concentration in the solution and at the membrane/solution interface ($c_M(t, 0) = 0$) will be negligible as a result of the assumption regarding the solution volume. After immersing the membrane in the solution mentioned above, ions M^{z_M} in the membrane are gradually replaced by ions A^{z_A} and B^{z_B} from the solution. If the other linear dimensions of the membrane are much greater than its thickness (2δ), the mass transport within the membrane can be considered as one-dimensional and symmetrical with respect to the central plane of the membrane. This will simplify the computations as only half the membrane with thickness δ needs to be considered (Fig. 1). The equations of continuity (Eq. (4)) with c_M substituted by $(c_0 - z_A c_A - z_B c_B)/z_M$ (Eq. (5))

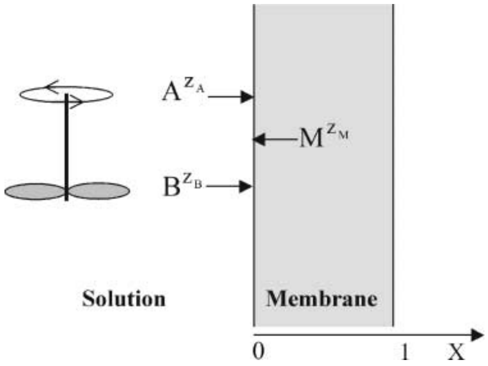

Figure 1. Schematic representation of the three-counter ion system.

and the corresponding initial and boundary conditions, all in dimensionless quantities and variables, describing the ion-exchange process between the membrane and the solution are the following:

$$\frac{\partial C_A}{\partial \tau} = \overline{D_A}\left\{\frac{\partial^2 C_A}{\partial X^2} - z_A \times \frac{\partial}{\partial X}\left[C_A \frac{(\overline{D_A}-1)C_A + (\overline{D_B}-1)C_B}{(z_A\overline{D_A}-z_M)C_A + (z_B\overline{D_B}-x_M)C_B + z_M}\right]\right\} \tag{6}$$

$$\frac{\partial C_B}{\partial \tau} = \overline{D_B}\left\{\frac{\partial^2 C_B}{\partial X^2} - z_B \times \frac{\partial}{\partial X}\left[C_B \frac{(\overline{D_A}-1)C_A + (\overline{D_B}-1)C_B}{(z_A\overline{D_A}-z_M)C_A + (z_B\overline{D_B}-x_M)C_B + z_M}\right]\right\} \tag{7}$$

$$C_A(0, X) = 0 \tag{8a}$$

$$C_B(0, X) = 0 \tag{8b}$$

$$C_A(\tau, 0) = \kappa \tag{8c}$$

$$C_B(\tau, 0) = 1 - \kappa \tag{8d}$$

$$\left(\frac{\partial C_A}{\partial \tau}\right)_{X=1} = 0 \tag{8e}$$

$$\left(\frac{\partial C_B}{\partial \tau}\right)_{X=1} = 0 \tag{8f}$$

where $\tau = D_M t/\delta^2$, $X = x/\delta$, $C_A = z_A c_A/c_0$, $C_B = z_B c_B/c_0$, $\overline{D_A} = D_A/D_M$, and $\overline{D_B} = D_B/D_M$.

Boundary condition (8d) follows from the electroneutrality requirement in dimensionless quantities and variables (Eq. (9)) and the assumption of infinite solution volume, which as mentioned earlier leads to $C_M(\tau, 0) = 0$.

$$C_A + C_B + C_M = 1 \tag{9}$$

Boundary conditions (8e) and (8f) reflect the fact that the mass transfer within the membrane is symmetrical with respect to its center at $X = 1$ (Fig. 1).

After differentiating the second term of Eqs. (6) and (7), the resulting equations with initial and boundary conditions (8a)–(8f) were numerically solved by an implicit finite difference method.[8] The tridiagonal matrices of the two sets of finite difference equations for A^{z_A} and B^{z_B} were solved by the Gaussian elimination method.[8]

The influence of B^{z_B} on the coupled diffusion of A^{z_A} was studied by inspecting the transient concentration of A^{z_A} at $X = 1$, $C_A(\tau, 1)$, (Fig. 1) for different values of the main system parameters, i.e., $\overline{D_A}$, $\overline{D_B}$, z_A, z_B, and z_M. In all simulations, it was assumed for simplicity that $\kappa = 0.5$, i.e., $C_A(\tau, 0) = C_B(\tau, 0)$.

RESULTS AND DISCUSSION

Influence of $\overline{D_A}$ and $\overline{D_B}$

Figure 2 shows the dependence of $C_A(\tau,1)$ on $\overline{D_B}$ while maintaining the remaining system parameters constant (i.e., $z_A = z_B = z_M = 1$ and $\overline{D_A} = 1.0$). A comparison is made with the case of coupled diffusion of two different counter ions only[3,4] (curve $\kappa = 1.0$, Fig. 1). The steady-state (equilibrium) concentration of A^{z_A} within the membrane irrespective of the number of counter ions present in the system is equal to $C_A(\tau, 0) = \kappa$. However, in the three counter ion systems depending on the ratio between $\overline{D_A}$ and $\overline{D_B}$, $C_A(\tau,1)$ may deviate substantially from the monotonously increasing

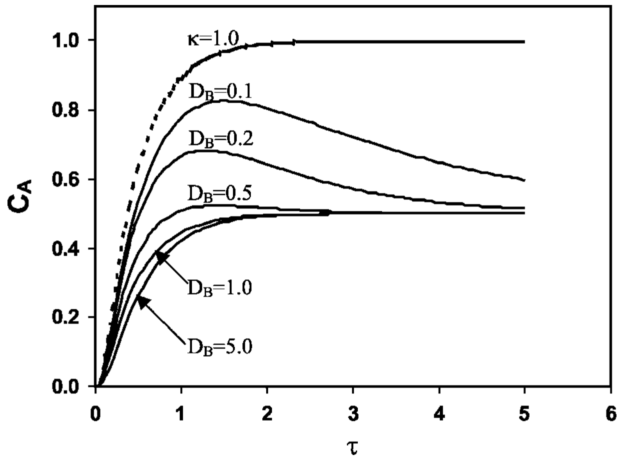

Figure 2. Influence of $\overline{D_B}$ on $C_A(\tau,1)$ ($z_A = z_B = z_M = 1$, $\overline{D_A} = 1.0$).

and asymptotically approaching κ transient concentration typical for a two-counter ion system (curve $\kappa = 1$, Fig. 2). The maxima observed for $\overline{D_B} < \overline{D_A}$ (Fig. 2) are caused by the faster diffusion of the A^{z_A} ions compared with that of the B^{z_B} ions. As a result, $C_A(\tau, X)$ and in particular $C_A(\tau,1)$ can exceed initially its equilibrium value, i.e., κ. In the cases when $\overline{D_B} > \overline{D_A}$, the diffusion of A^{z_A} within the membrane is slightly retarded by the faster moving B^{z_B} ions. Under the conditions of the simulations (i.e., $z_A = z_B = z_M = 1$ and $\overline{D_A} = 1.0$), the magnitude of this effect did not change for values of $\overline{D_B}$ greater than 5.

The strongest influence of $\overline{D_B}$ on $C_A(\tau, 1)$ was observed for $\overline{D_B}/\overline{D_A} = 0.1$ (Fig. 2) at $\overline{D_A} = 1.0$, i.e., $D_A = D_M$. Figure 3 shows that this influence is enhanced for $\overline{D_A} < 1.0$ (i.e., $D_A < D_M$) and suppressed for $\overline{D_A} > 1.0$.

Influence of z_A, z_B, and z_M

The effect of the ratio z_A/z_B on $C_A(\tau,1)$ for $z_M = 1$ and $\overline{D_A} = \overline{D_B} = 0.5$ is illustrated in Fig. 4. This result, showing an inverse dependence between the charge of a counter ion and its rate of diffusion, agrees with earlier findings for a two-counter ion system.[4] The influence of the ratio z_A/z_B resembles that of $\overline{D_B}$ (Fig. 2). Simulations performed under the same conditions, except for $z_M = 2$ or $\overline{D_A} = \overline{D_B} = 2.0$, produced similar

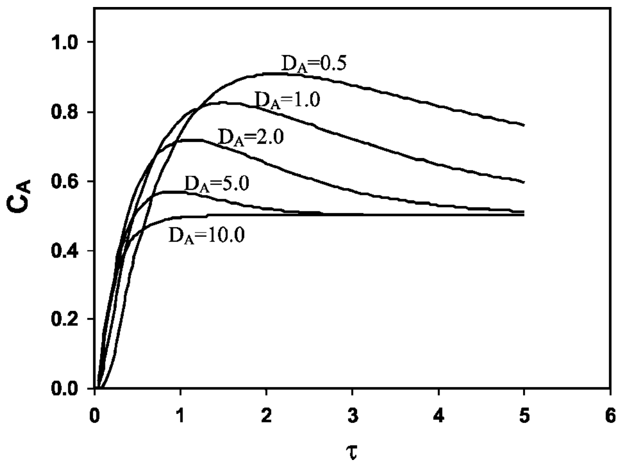

Figure 3. Influence of $\overline{D_A}$ on $C_A(\tau,1)$ ($z_A = z_B = z_M = 1$, $\overline{D_B}/\overline{D_A} = 0.1$).

results to those shown in Fig. 4 but with less pronounced effect of the z_A/z_B ratio on $C_A(\tau, 1)$.

The simulations outlined above show that the presence of B^{z_B} will influence considerably the coupled diffusion of A^{z_A}. This influence will be most pronounced when $\overline{D_A} > \overline{D_B}$ and $z_A < z_B$.

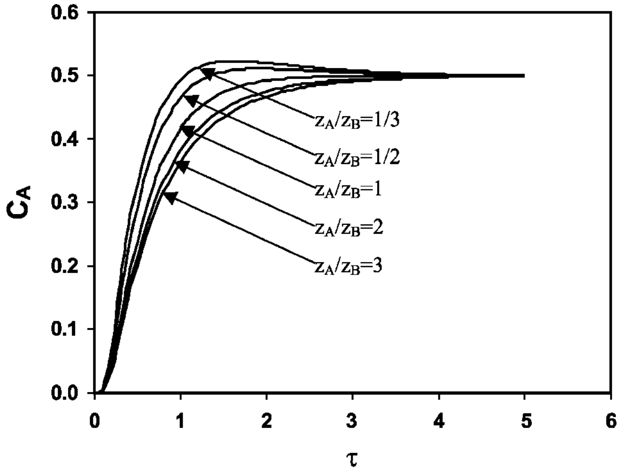

Figure 4. Influence of z_A/z_B on $C_A(\tau,1)$ ($z_M = 1$ and $\overline{D_A} = \overline{D_B} = 0.5$).

The three-counter ion system considered above can be applied in a straightforward manner to a potentiometric chemically modified electrode selective for A^{z_A} ions. In this case the sensing surface of the electrode is covered by an ion-exchange membrane of thickness δ conditioned in a solution containing M^{z_M} only. Ions B^{z_B} can be considered as interferents. The transient concentration curve $C_A(\tau, 1)$ in this example generates the response curve of the electrode. The simulations outlined above (Figs. 2–4) illustrate the importance of taking into account the coupled diffusion of all chemical species, not of the analyte ions (A^{z_A}) only, to describe adequately the sensor's response and to formulate guidelines for correct measurement procedures (e.g., selecting an appropriate duration of the contact time between the electrode and the sample solutions before a reading is taken). This is particularly important for the cases when the response curve of the electrode passes through a maximum before reaching its equilibrium value (Figs. 2–4).

CONCLUSIONS

The simulation results for a three-counter ion system emphasize the importance of taking into account the coupled diffusion of all ionic species. This may become crucial in those cases when the ions of interest have higher diffusion coefficients and lower charges compared to the other counter ions in the system.

NOMENCLATURE

c	concentration ($\mathrm{mol\,L^{-1}}$)*
c_0	equivalent concentration of fixed ionic groups in the membrane ($\mathrm{mol\,L^{-1}}$)*
C	$= zc/c_0$, dimensionless concentration*
D	diffusion coefficient ($\mathrm{m^2\,s^{-1}}$)*
$\overline{D}$	$= D/D_M$, dimensionless diffusion coefficient*
J	flux ($\mathrm{mol\,m^{-2}\,s^{-1}}$)*
M	number of ionic species diffusing within the membrane
t	time (s)
x	axial distance (m)
X	$= x/\delta$, dimensionless axial distance
z	electronic charge of ionic species*

Greek Symbols

δ	half thickness of the membrane (m)

κ = $C_A(\tau,0)$, dimensionless interfacial concentration of A
τ = Dt/δ^2, dimensionless time
*Subscripts j and i refer to the j-th and i-th ionic species while subscripts A and B refer to ionic species A^{z_A} and B^{z_B}, respectively

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