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Enhancement of Membrane Transport of Ions by Spatially Nonuniform Electric Fields

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Abstract: The influence of spatially nonuniform electric fields on the transport of ions through ion-selective membranes is investigated both experimentally and theoretically. The flux of ions is determined indirectly by following the change of pH with time. The uniformity of the field is varied with a Pt wire electrode configuration by changing the relative positions of the anode and cathode. Higher fluxes are found for the nonuniform configuration than for the uniform configuration. These results were previously predicted in a theoretical investigation which revealed the importance of nonlinearity in the transport laws. The experimental observations are found to be consistent with theoretical calculations based on the Goldman flux equation.

I. Introduction

A polymer composed of units capable of forming ionic bonds is known as an ionomer.[1] Some ionomers will form spatially inhomogeneous membranes; examples include certain polyethylenes with pendant carboxylic salt groups and polymers of the Nafion type (a fluorocarbon backbone supporting side chains of perfluorosulfonic acid). The latter has been the object of a great deal of interest lately since it has an unusually high selectivity for cations over anions, leading to a much larger than normal current efficiency. Its spatially inhomogeneous morphology has been linked experimentally to this high selectivity.[2] In addition, several theoretical studies have indicated that nonuniformity can be expected to lead to enhanced transport of cations over anions in the Nafion system.[3-7]

Recently, we proposed that the enhancement of transport seen in Nafion could be explained in terms of a nonlinear effect.[8] It can be shown theoretically that transport rates will be different in a spatially nonuniform system than in an otherwise identical uniform system if the transport laws are nonlinear in the descriptive variables. Nonlinearity may be associated with a variety of physical phenomena. Examples include carrier-mediated transport, electrically facilitated transport, and Fickian diffusion with concentration-dependent diffusion coefficients.

In Nafion, nonuniformity is the result of clustering of the charged side chains, which would result in a nonuniform electrical potential throughout the membrane. The mechanism by which this nonuniformity enhances cation transport is still being debated. In this work, we show that the nonuniformity of electrical potential could enhance the flux of cations and that nonlinearity of the transport mechanism may be the cause.

We have performed experiments in which an electric field is applied to an ion-exchange membrane separating two electrolyte solutions. The uniformity of the applied field is varied by changing the electrode configuration. The flux of ions through the membrane is compared for a uniform field vs. a nonuniform field, and it is determined that the flux corresponding to the latter is consistently higher. In the following sections, we describe the experimental procedure and our observations and propose a model based on Goldman's solution of the Nernst–Planck flux equations.

II. Experimental Section

Cells were constructed as shown in Figure 1 with two reservoirs of equal dimensions, separated by a divider holding an ion-exchange membrane. The walls of the cell were acrylic plastic 0.25 cm thick, as were the divider pieces. The volume of each cell was 750 mL. A hole 1 in. in diameter was drilled in the center of the divider pieces, and the membrane was sandwiched between. The acrylic pieces were cemented together with a solvent comprised of methylene chloride, 1,1,1-trichloroethane, and ethyl acetate. All edges were then sealed with a silicone sealent.

The membranes were generously donated by Ionics, Inc. of Watertown, MA. The anion-transfer membrane (No. 103-QZL-386) is a proprietary vinyl polymer with quaternary ammonium groups as the ion-exchange site. The cation-transfer membrane (No. 61-CZL-386) is also a proprietary vinyl polymer with sulfonate groups. Both membranes are backed with a modacrylic fiber netting and are thought to be homogeneous.[9]

The cells were filled with 0.1 M KCl solutions prepared with deionized water. The field was applied via platinum wire grid electrodes, described below, connected to a B and K Precision Model 1601 regulated dc power supply from Dynscan Corporation with a Micronta digital multimeter in line as a voltage multiplier. A Corning Model 140 pH meter with a Corning combination Type X-EL electrode and an automatic temperature controller was used to follow the concentration changes in the cell. The solutions were stirred from overhead for an hour without the field to equilibrate. Vigorous stirring continued after the field was turned on and throughout the entire experiment.

The electrodes used for application of the field are shown schematically in Figure 2. They are constructed from platinum wire and attached to the acrylic divider sheets which hold the membrane with silicon sealant. The distance from each electrode to the membrane surface was approximately 0.25 cm. Silicone sealant was spread to cover the horizontal connecting wires on the electrodes in order to electrically insulate these portions of the wire from the electrolyte solution. Gershoni et al.[10] investigated the uniformity of the field applied via this electrode arrangement in a protein blotting apparatus. Electrical potential measurements made by scanning through the plane midway between the electrodes and perpendicular to the lengths of the wires showed a spatial variation when the electrodes were in the arrangement of Figure 2b but gave constant readings when they are arranged as in Figure 2a. These observations are confirmed by simple electrostatic calculations.[10]

III. Results and Discussion

Upon application of the field, the pH began to change in both compartments, increasing on the side with the negative electrode and decreasing on the side with the positive electrode. When the cation-exchange membrane was in place, the rate of change was slightly higher than when the anion-exchange membrane was in place. At the voltages used, one would expect OH^- to be produced at the cathode according to

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^0 = -0.83\ V$$

and H^+ to be produced at the anode via

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^0 = -1.23\ V$$

To retain charge neutrality in both compartments, negative charge must be transported across the anion-selective membrane from

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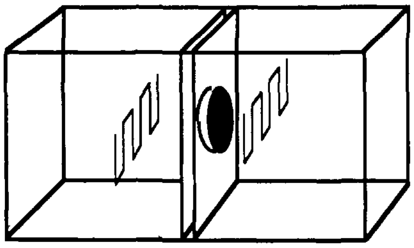

Figure 1. Sketch of membrane cell configuration showing location of Pt wire electrodes relative to opening containing membrane.

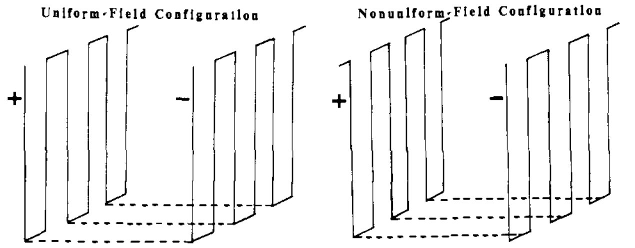

Figure 2. Arrangement of Pt wire electrodes to impose a uniform or nonuniform electric field on the membrane located in the plane midway between the two electrodes.

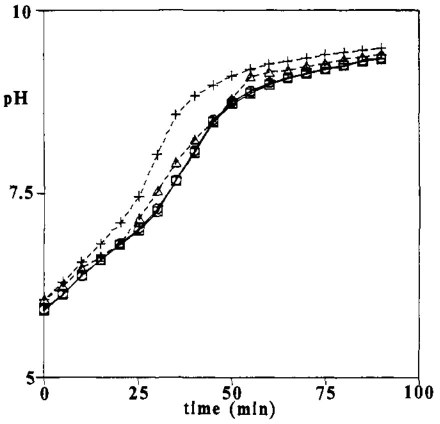

Figure 3. Typical changes in pH observed in the cathode compartment with either an anion-selective membrane in place (solid curves) or a cation-selective membrane in place (dashed curves). The electrodes are in the uniform field configuration in all cases; applied potentials are 1.90 (□), 1.93 (○), 1.90 (△), and 1.91 V (+).

the cathode compartment to the anode compartment. When the cation-selective membrane is in place, charge neutrality can be maintained by transporting cations in the opposite direction, from anode to cathode. The charge will most likely be carried by the Cl^- ions when the anion-selective membrane is in place and by the K^+ ions when the cation-selective membrane is used. H^+ and OH^- are other possible charge carriers but since their concentration in the solution is so small compared to that of K^+ or Cl^- we would not expect them to carry much of the current. The flux of Cl^- across the anion-selective membrane will, thus, occur at the same rate as the production of OH^- at the cathode.

According to the above-described scenario, the flux of transported ions can be determined indirectly by following the change of pH with time. Some typical results are shown in Figure 3 for the pH changes in the negative electrode compartment. Converting pH to $[OH^-]$ results in Figure 4 in which the $[OH^-]$ is seen to rise slowly for the first 30 min and then increase linearly with time for the remainder of the experiment. After 30 min, then, the system reaches a steady state which is defined to occur when the flux of transported ions is constant. Since the slope of the linear portion of this curve corresponds to the change in concentration of OH^- per unit time, the flux will be given by

$$J = \frac{\Delta[OH^-]}{\Delta t}\,\frac{\text{compartment volume}}{\text{membrane area}} \tag{1}$$

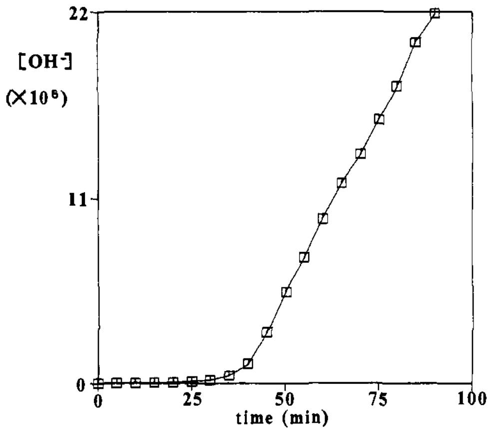

Figure 4. Concentration of OH^- vs. time for the average of the two anion-selective membrane curves of Figure 3. Qualitatively similar results are found for cation-selective membranes and when the applied field is nonuniform. The slope of the linear portion of this curve varies, however (see Table I).

Table I. Measured Flux through Anion-Selective Membrane[a]

appl. potential, V	flux, mol/(cm^2 s) uniform	flux, mol/(cm^2 s) nonuniform
1.94	1.06×10^{-9}	1.15×10^{-9}
2.13	1.15×10^{-9}	1.27×10^{-9}

[a] Each entry corresponds to an average of three identical trials.

Here, the compartment volume is 750 mL and the membrane area is 5.06 cm^2. The linear portion of the curve (e.g., the last 11 data points in Figure 4) was fit to a straight line by using the usual least-squares method. The error in the value of J calculated from the slope of this line, $\Delta[OH^-]/\Delta t$, and eq 1 will be mostly due to errors in the pH determination (±0.01 pH unit) since the membrane area is the same for all runs and the volume varies by only a few tenths of a milliliter. By use of the usual treatment for propagation of errors, the error in J is found to be approximately $\pm 1 \times 10^{-11}$ mol/(cm^2 s).

The measured fluxes for different applied voltages with the electrodes in the uniform field configuration are shown in Table I and are on the order of 10^{-9} mol/(cm^2 s). The fluxes through the anion and cation membranes are comparable, although somewhat higher for the cation membrane, and generally increase with applied voltage.

Similar results were observed when the electrodes were in the nonuniform field configuration. However, the flux was higher in these trials than it was in the uniform field trials. These results are also shown in Table I. The difference between the flux observed with the nonuniform field for a given applied voltage and that for the uniform field is greater than the experimental error associated with these trials in all cases. The only difference between the uniform field experiments and the nonuniform field experiments is the position of the Pt grid electrodes with respect to one another. Hence, it appears that the nonuniformity of the field is, indeed, enhancing the flux of ions through the ion-exchange membrane.

In a previous paper,[8] we showed that nonuniformity of a particular descriptive variable (such as applied potential) could be expected to alter the flux only if the flux depends on that variable in a nonlinear fashion. Even though we cannot determine whether the relationship between flux and applied voltage is linear in this experiment, theoretical considerations would predict that the relationship is, in fact, highly nonlinear. In the following section, we consider a model based on a solution of the Nernst–Planck flux equations due to Goldman. Calculations of the flux from this model in the presence of a nonuniform field show that the nonuniformity will increase the flux in certain situations.

IV. Model

The flux of an ionic species in the z direction in the presence of an electric field is given by the Nernst–Planck equation[12]

$$J_i = -D_i\frac{\partial c_i}{\partial z} - M_i c_i \frac{\partial V}{\partial z} \tag{2}$$

where c_i is the concentration of the ionic species, D_i its diffusion coefficient, M_i its mobility (given by the Nernst–Einstein relation $M_i = z_iD_iF/RT$ where z_i is the valence of the ion), and V the electrical potential. In the presence of a constant field, $\partial V/\partial z$ is a constant. If steady state is assumed, Fick's first law implies that the flux J_i is also constant. It is an easy manner to integrate the steady-state Nernst–Planck equation under these conditions. Rearrangement of (2) yields a single, ordinary differential equation for $c_i(z)$ subject to the boundary conditions $c_i = c_i^L$ (and $V = V^L$) at $z = 0$ and $c_i = c_i^R$ (and $V = V^R$) at $z = d$, where d is the thickness of the membrane. This was done by Goldman[11] in the 1940s and results in the following expression for the flux:

$$J_i = h_iz_iE\frac{c_i^R - c_i^Le^{z_iE}}{1 - e^{z_iE}} \tag{3}$$

where $h_i = D_i/d$ is the permeability of the ion in the membrane of thickness d. The concentrations at the right and left surfaces of the membrane are, respectively, c_i^R and c_i^L, and the constant potential across the membrane is E, defined as

$$E = V^L - V^R \tag{4}$$

where V^L and V^R are the potential at the left and right surfaces, respectively. All quantities in (2)–(4) are considered dimensionless. In Goldman's approach, no attempt is made to account for fixed charge in the membrane matrix or Donnan potentials between the membrane phase and the aqueous phase. Equation 3 may, therefore, be only qualititatively applicable to our experimental system, but it's study provides some interesting insight into the experimental results given above.

Goldman's equation (3) is highly nonlinear in the variable E. In a previous paper,[8] we considered the effect of perturbations in the uniformity of E. These calculations were restricted to small deviations away from uniformity and predicted that passive transport according to Goldman's equation would be enhanced by nonuniformity while electrically facilitated transport would not be. Passive transport occurs when the ion travels down a concentration and electrical potential gradient; electrically facilitated transport occurs when the ion travels *up* a concentration gradient but *down* an electrical potential gradient. Here we consider the effects of nonuniformities of larger magnitude than those which can be treated by a perturbation approach. As shown below, the conclusions reached via the perturbation approach are valid also for larger nonuniformities. We have investigated the influence of nonuniformities in applied potential by numerically integrating the flux equation (3). To determine if nonuniformity in E is expected to enhance the flux, we calculated the flux enhancement factor described in our previous paper.[8] The flux enhancement factor, α, is defined as

$$\alpha = \frac{\langle J_i\rangle - J_i(\langle E\rangle)}{J_i(\langle E\rangle)} \tag{5}$$

where the angle brackets indicate a spatial average. Thus,

$$\langle J_i\rangle = 1/L\int_0^L J_i(E(x))\,dx \qquad \langle E\rangle = 1/L\int_0^L E(x)\,dx \tag{6}$$

The quantity, α, is, then, the fractional increase ($\alpha > 0$) or decrease ($\alpha < 0$) in J_i due to a spatially nonuniform membrane potential $E(x)$. The direction x is perpendicular to the direction of flux, z, in Figure 1. We could also consider nonuniformities of E in both perpendicular directions, i.e., $E(x,y)$ but the one-dimensional case will illustrate our point with less computational time and yields the same conclusions. Notice that we consider the flux in the presence of a uniform field which is equal in magnitude to the spatial average of the nonuniform field. We compare this with the spatial average of the flux in the presence of the nonuniform field. Thus, we assure that the total energy available for the transport of ions is the same in the spatially nonuniform case as in the uniform case so that any differences we may calculate can be attributed solely to the nonuniformity.

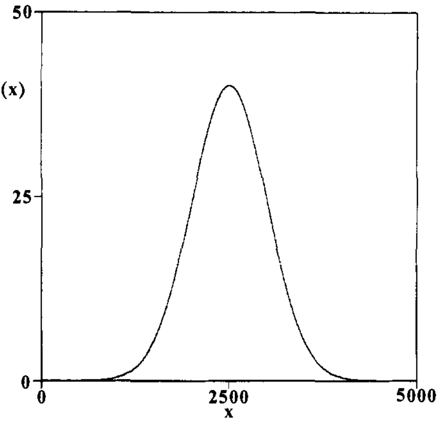

Figure 5. Typical nonuniform membrane potential used in model. Here, $N_g = 1$, $x_1 = 2500$, and $x_L = 5 \times 10^5$ in (7).

An example of the type of nonuniformity $E(x)$ we considered is

$$E(x) = \sum_{i=1}^{N_g} E_{\max}\exp(-(x - x_i)^2/x_L) \tag{7}$$

i.e., a sum of N_g Gaussians centered at the positions x_i. The maximum of each Gaussian is $E_{\max}$, and x_L is related to the width of the Gaussians. To determine numerical values for all the parameters in the equations, we chose to dedimensionalize the variables in the flux equation with

$$\mathbf{E} = \frac{\mathbf{F}}{\mathbf{RT}}E \qquad \mathbf{c}_i = c_{\text{ref}}c_i \qquad \mathbf{x} = x_{\text{ref}}x \qquad \mathbf{D}_i = D_{\text{ref}}D_i$$

$$\mathbf{J}_i = \frac{D_{\text{ref}}c_{\text{ref}}J_i}{x_{\text{ref}}}$$

Here, for example, the actual transmembrane potential is $\mathbf{E}$, whereas the dimensionless variable in the Goldman equation is E. The quantity F/RT, where F is the Faraday constant, has units of volts and is approximately 0.25 V at room temperature. The other variables are dedimensionalized with typical values of concentration, c_{ref}, distance, x_{ref}, and diffusion coefficient, D_{ref}. As an example, we consider $c_{\text{ref}} = 500$ mM (i.e., approximately the concentration of seawater), $D_{\text{ref}} = 10^{-5}$ cm^2/s (a typical ionic diffusion coefficient in water), and $x_{\text{ref}} = 10^{-3}$ cm (the distance a particle would travel in 1 s with this diffusion coefficient). These choices will not affect the qualitative nature of the results but will affect any quantitative physical interpretation we attempt to make of the results.

With the above choices of dimensions, we must take $E_{\max}$ in (6) to be approximately 40 since typical applied potentials $\mathbf{E}$ in our system are on the order of 1 V. To consider a membrane of macroscopic size, we must consider lengths on the order of $L = 5000$ which would correspond to a membrane 5 cm in width. We consider the case of univalent cations ($z = 1$) so that a positive flux ($J_i > 0$) in a positive field ($E > 0$) will be to the right. Notice that the permeability h_i drops out of the flux enhancement factor (4) so we set it to $h_i = 1$ even though this is probably not the correct order of magnitude. (By taking unity for h_i, we avoid specifying the thickness of the membrane.)

The spatial averages (5) were calculated numerically with a simple trapezoidal rule algorithm which converged rapidly. We considered the effect of several different patterns $E(x)$ on the flux enhancement factor, α, (5). The general result is in agreement with that predicted from perturbation theory, namely that passive transport (flux down a concentration gradient) is enhanced by nonuniformities in E but electrically facilitated transport (flux up a concentration gradient but down a potential gradient) is not.

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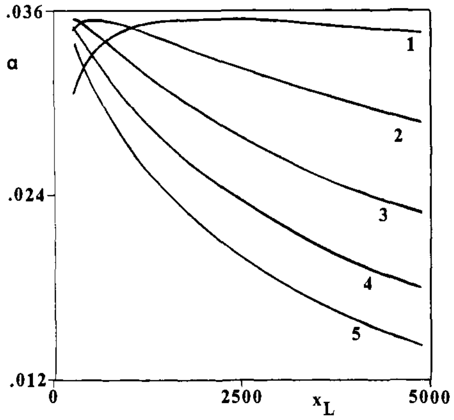

Figure 6. Calculated values of the flux enhancement factor, α, for the Goldman equation as a function of x_L, the width of the Gaussians. Each curve is labeled with N_g, the number of Gaussians. Note that even the widest Gaussians studied here are much narrower than that shown in Figure 5.

A typical nonuniformity is shown in Figure 5, in which $E(x)$ is a single Gaussian function ($N_g = 1$ in eq 7). We also considered sinusoidal functions and found qualitatively similar results.

Figure 6 shows calculated values of α for various widths of the Gaussian in Figure 5. Passive transport is always associated with positive α, whereas facilitated transport is associated with negative α. For the former case we find that α increases with x_L for the nonuniformtiy shown in Figure 5; i.e., the wider the Gaussian, the larger the enhancement. This is not necessarily the case for other nonuniformities, $E(x)$, however. For example, we also considered the effect of sums of Gaussians, i.e., for $N_g > 1$ in (7). We find that α generally decreases with x_L when more than one Gaussian is used.

The results of these calculations may not be quantitatively applicable to our experiment since they are based on the Goldman flux equation, and the assumptions made in its derivation may not be applicable to our experimental conditions. For example, one assumption is that the voltage profile across the membrane is linear; another is that the membrane contains no fixed charges, so the concentration of ions at the surface in the bulk is the same as that just inside the membrane. Both of these assumptions may not hold in our experiment. Therefore, the results of the calculations with this model cannot be quantitatively compared to our experiment. However, the model calculations do confirm that nonuniformity in an applied field can enhance the flux of ions through a membrane which is in qualitative agreemtent with our experimental observations.

A computational study by another group also confirms our experimental observations. Selvey and Reiss[7] have integrated the Nernst–Planck flux equations for a one-dimensional membrane containing nonuniformly distributed fixed charges. They find that the current efficiency (ratio of the flux of cations to the total flux of cations and anions) shows a maximum as a function of cluster size. The cluster size is a measure of the nonuniformity of the electrical potential within the membrane. The results of Selvey and Reiss, thus, also predict that transport of ions in a membrane with a nonuniform electrical potential is greater than that with a uniform electrical potential.

The results of our calculations indicate that nonlinearity in the transport laws can be a source of flux enhancement in nonuniform systems. The role of nonlinearity was not considered by Selvey and Reiss. In the model considered here, the nonlinearity enters as an exponential dependence of the flux on the membrane potential. The actual flux in our experiment may not obey the Goldman equation, but other sources of nonlinearity exist in this type of system. For instance, the fixed charges in the membrane matrix (sulfate groups in the cation-exchange membrane) may act as binding sites for the transported ions. It has been shown that fast binding in conjunction with diffusional transport is equivalent to transport with an effectively concentration-dependent diffusion coefficient.[13] This concentration dependence leads to, essentially, a nonlinear term in Fick's law and, hence, a nonlinear transport equation. This may be one source of nonlinearity in our experiment.

V. Conclusions

We have demonstrated experimentally that transport of ions through ion-exchange membranes via the application of electric field can be enhanced by about 10% if the field is spatially nonuniform. This can be understood in terms of the influence of nonuniformity in a transport system which obeys nonlinear transport laws. A model based on the Goldman flux equation was investigated and qualitative agreement with experiment observed. Previous calculations by another group are also in qualitative agreement with our observations.

The results of this research may have some impact on our understanding of the role of nonuniformity in the high selectivity of spatially inhomogeneous membranes of the Nafion type. The electrical potential within these membranes is certainly spatially nonuniform since the spatial inhomogeneity occurs by clustering of ionic groups in the membrane. Hence, the transported ions will be subjected to a spatially nonuniform electric field much like that considered here.

The conclusions of this study could also be applied to the design of more efficient membrane separation devices. A direct application would be to those which function with applied electric fields such as electrodialysis units, fuel cells, batteries, and the like. The use of nonuniform fields in these devices may lead to more efficient transport of ions and, therefore, less energy consumption.

Acknowledgment. We thank Prof. Gordon Fricke for some very helpful conversations during the course of this work.

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