

Isotopic and Ion-Exchange Kinetics in the Nafion-117 Membrane

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The exchange kinetics of Cs⁺, Cu²⁺, and Eu³⁺ ions in Nafion-117 were measured at different H⁺ ion concentrations in equilibrating salt solutions. The exchange kinetics were found to be independent of the H⁺ ion concentration in equilibrating salt solutions over the pH range of 5–2. The exchange kinetics were therefore used to evaluate self-diffusion coefficients of the metal ions using an analytical solution of Fick's second law. The self-diffusion coefficient of Cs⁺ in Nafion-117 was found to be in agreement with the value obtained in our earlier work ($1.94 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) based on the isotopic-exchange method in the absence of H⁺ ions. This further confirmed that the exchange process in the Nafion-117 membrane represents the pure isotopic exchange in the said pH range. The self-diffusion coefficients of Cu²⁺ and Eu³⁺ were found to be 2.9×10^{-7} and $4.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively. The smaller self-diffusion coefficient of Eu³⁺ reflects its increased electrostatic interaction with the membrane matrix. The kinetics of forward ($\text{H}_{(\text{m})}^+ \rightleftharpoons \text{M}_{(\text{s})}^{n+}$) and reverse ($\text{M}_{(\text{m})}^{n+} \rightleftharpoons \text{H}_{(\text{s})}^+$) exchanges of metal ions (Cs⁺, Cu²⁺, and Eu³⁺) in the Nafion-117 membrane were also studied. The Nernst–Planck theory was examined to predict the kinetics of these exchanges. The theory was found to be reasonably accurate for predicting the kinetics of the reverse ion exchange but completely failed for the forward ion exchange. Contrary to the prediction of the theory, the kinetics of forward exchanges of Cs⁺, Cu²⁺, and Eu³⁺ with H⁺ ions in the Nafion-117 membrane were found to be independent of the metal ions. This shows that the self-diffusion coefficients of the counterions in Nafion-117 can be obtained only from the analysis of reverse exchange kinetics based on the Nernst–Planck equation.

Introduction

Studies on ionomers have been of particular interest because of their numerous electrochemical applications. One of the most intensively studied ionomers is the poly(perfluorosulfonic) acid membrane known as Nafion, which is extensively used in chloroalkali industries, water electrolysis, polymer electrolyte fuel cells, and Donnan-dialysis-based applications.¹ The absence of cross linking in the polymer chains of poly(perfluorosulfonic) acid gives rise to the clustering of ion-exchange sites on equilibrating the membrane with water.² These clusters in Nafion-117 contain water and are interconnected by narrow channels.³ The water content in these clusters, and hence in the membrane, is strongly dependent on the hydration characteristics of the counterions and on the pretreatment of the membrane.^{2,4} In contrast to the cross-linked poly(styrenesulfonic) acid membrane, the Nafion membrane shrinks if less-hydrated cations such as Cs⁺ are exchanged with H⁺ in the membrane.⁵ Thus, the physical structure of Nafion varies for different counterions. This unique behavior of Nafion-117 necessitates the measurement of diffusion coefficients for a variety of cations to understand the diffusional ion-transport process.

The self-diffusion coefficients of ions and molecules in the Nafion-117 membrane have been measured by techniques such as radiotracer permeation,^{6–10} ion exchange,^{11,12} conductivity/impedance measurements,^{13,14} and pulsed-field gradient nuclear magnetic resonance spectroscopy¹⁵ (PFG-NMR). Radiotracer

and PFG-NMR methods directly yield the well-defined self-diffusion coefficients. The radiotracer permeation method has been used to measure the self-diffusion coefficients of cations in the Nafion-117 membrane^{6–9} using a relationship introduced by Helfferich.^{16,17} However, this method requires the measurement of ion fluxes across the Nafion membrane over a wide concentration range of radioactivity-tagged counterions in the aqueous solution. To overcome this problem, we have proposed a nonstationary radiotracer diffusion method.¹⁸ This method is essentially based on the analysis of kinetics of isotopic exchange in the Nafion-117 membrane using an analytical solution of Fick's second law. This transient method is simple, does not involve stringent control over hydrodynamics near the membrane, and is faster because a single measurement can yield the self-diffusion coefficient of the ions. This method has been successfully used for the measurement of self-diffusion coefficients of monovalent (Na⁺, K⁺, Cs⁺, and Ag⁺) and divalent (Ca²⁺, Sr²⁺, Ba²⁺, and Zn²⁺) cations in the Nafion-117 membrane.¹⁸

The nonstationary radiotracer diffusion method is based on isotopic exchange kinetics and therefore cannot be used to deduce the self-diffusion coefficients of counterions when competing ions are present. Thus, this method cannot be extended to cations that undergo hydrolysis in neutral solution. Acidic pH is essential to preventing the hydrolysis of these metal ions, and the presence of H⁺ ions in the equilibrating solution would lead to competition between H⁺ ions and metal ions for the available ion-exchange sites in the membrane. In such a situation, the ideal method for obtaining self-diffusion coefficients of metal ions should be based on the analysis of ion-exchange kinetics using coupled diffusion theories.^{11,12} The

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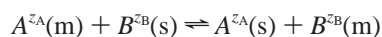
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evaluation of self-diffusion coefficients from ion-exchange kinetics is based on the assumption that the membrane retains its physical structure during the counterion-exchange process and that the mobility of the interchanging counterions depends on the coupling of their fluxes. The self-diffusion of an ion can be evaluated from ion-exchange kinetics provided that the value of the self-diffusion coefficient of the other ion is known. However, the Nafion membrane undergoes significant physical changes, as indicated by the changes in its water content when equilibrated with different counterions. This leads to complications in the evaluation of self-diffusion coefficients of counterions in the Nafion-117 membrane from the ion-exchange kinetics.¹² It has been reported that the Nafion-117 membrane has a higher affinity toward $\text{Cs}^+/\text{Rb}^+/\text{K}^+$ as compared to that toward H^+ at lower acidity in the equilibrating solution.⁵ Therefore, it is possible that the competition between H^+ ions and metal ions for available ion-exchange sites in the Nafion-117 membrane may not be significant at lower acidity in the equilibrating solution.

In this paper, we have examined the effects of H^+ ions in an equilibrating salt solution on the isotopic exchange kinetics of Cs^+ , Cu^{2+} , and Eu^{3+} ions in the Nafion-117 membrane. The choice of these ions in the present study was based on the following facts: (i) these ions have different charges and degrees of hydration, (ii) Cs^+ can be used as a reference counterion because its self-diffusion coefficient in Nafion-117 has been measured by isotopic exchange,¹⁸ (iii) Cu^{2+} and Eu^{3+} undergo hydrolysis at relatively high pH and thus the pH of the equilibrating solution can be varied to understand the role of H^+ ions in exchange kinetics, (iv) the kinetics of Cs^+ , Cu^{2+} , and Eu^{3+} counterions exchange between Nafion-117 and the equilibrating salt solution are expected to be slower and thus a slight modification in the exchange rates by H^+ ions can be clearly seen, and (v) self-diffusion coefficients and ion-exchange kinetics of Cu^{2+} and Eu^{3+} in Nafion-117 have not been reported in the literature. The exchange kinetics of these metal ions in Nafion-117 have been measured as a function of H^+ ion concentration in the equilibrating salt solution. The self-diffusion coefficients of Cs^+ , Cu^{2+} , and Eu^{3+} in Nafion-117 have been obtained from the analysis of their isotopic exchange rates, where H^+ ion competition is not significant. Because the kinetics of ion exchange have considerable importance in the electrochemical applications of the Nafion-117 membrane, the adequacy of the Nernst–Planck theory for predicting the forward and reverse ion exchanges of metal ions (Cs^+ , Cu^{2+} , and Eu^{3+}) with the H^+ ion has also been studied in the Nafion-117 membrane. The results of these analyses are presented in this paper.

Theoretical Section

We consider the process of ion exchange between an ion A initially present in the plane sheet of the membrane and an ion B initially present in the solution as



where Z_A and Z_B are the charges on ions A and B and m and s represent the membrane phase (Nafion-117) and solution phase, respectively. If the exchange kinetics are studied in a well-stirred solution, then aqueous film diffusion can be ignored. Then the interdiffusion of the two counterions species A and B will be controlled by the gradient of their chemical potential resulting from the concentration gradient of the species and the gradient of the electric potential. In the absence of any external

field, the diffusion process builds up the electric potential. The fluxes of the ionic species under such conditions are given by the Nernst–Planck equation. Because the membrane remains electrically neutral, the fluxes of the counterions are electrically coupled, and a nonlinear diffusion equation describing the time and space dependence of the ion concentration C_i in the membrane can be written as

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left[D_{AB} \frac{\partial C_i}{\partial x} \right] \quad (1)$$

where the interdiffusion coefficient D_{AB} is given by

$$D_{AB} = \frac{D_A D_B (Z_A^2 C_A + Z_B^2 C_B)}{(D_A Z_A^2 C_A + D_B Z_B^2 C_B)}$$

where C_i is the concentration of the i th species in the membrane and D_i is its self-diffusion coefficient. During the course of ion exchange, C_A , C_B , and D_{AB} change with time, and thus eq 1 becomes nonlinear.

The numerical solution of eq 1 for spherical resin beads has been described in refs 19 and 20. For a plane sheet of membrane, using the dimensionless variables

$$y_A = \frac{Z_A C_A}{C} \quad \tau = \frac{D_A t}{l^2} \quad \xi = \frac{x}{l} \quad (2)$$

where l is the half-thickness of the membrane and $C = Z_A C_A + Z_B C_B$, eq 1 can be written as

$$\begin{aligned} \frac{\partial y_A}{\partial \tau} &= \frac{\partial}{\partial \xi} \left\{ \left(\frac{1 + b y_A}{1 + a y_A} \right) \left(\frac{\partial y_A}{\partial \xi} \right) \right\} \\ \frac{\partial y_A}{\partial \tau} &= \frac{\partial}{\partial \xi} \left\{ D(y_A) \frac{\partial y_A}{\partial \xi} \right\} \end{aligned} \quad (3)$$

Parameters a and b are given by

$$a = \frac{Z_A D_A}{Z_B D_B} - 1 \quad b = \frac{Z_A}{Z_B} - 1$$

For the numerical solution of this equation, the right-hand side can be written as

$$\frac{\partial}{\partial \xi} \left\{ D(y_A) \frac{\partial y_A}{\partial \xi} \right\} = D_+ \frac{y(\xi + \Delta\xi) - y(\xi)}{(\Delta\xi)^2} - D_- \frac{y(\xi) - y(\xi - \Delta\xi)}{(\Delta\xi)^2} \quad (4)$$

where

$$D_+ = \frac{2 + b[y(\xi + \Delta\xi) + y(\xi)]}{2 + a[y(\xi + \Delta\xi) + y(\xi)]}$$

and

$$D_- = \frac{2 + b[y(\xi) + y(\xi - \Delta\xi)]}{2 + a[y(\xi) + y(\xi - \Delta\xi)]}$$

Now the solution of eq 3 can be written in finite difference form as²¹

$$y(\xi, \tau + \Delta\tau) = y(\xi, \tau) + \left(\frac{\partial y}{\partial \tau} \right) \Delta\tau \quad (5)$$

On substituting $(\partial y/\partial \tau)$ from eq 4, eq 5 takes the form

$$y(\xi, \tau + \Delta\tau) = y(\xi, \tau) + \frac{\Delta\tau}{(\Delta\xi)^2} [D_+ \{y(\xi + \Delta\xi, \tau) - y(\xi, \tau)\} - D_- \{y(\xi, \tau) - y(\xi - \Delta\xi, \tau)\}] \quad (6)$$

Although the range of ξ is -1 to $+1$, one can solve the problem in the range of $\xi = 0$ to 1 because of symmetry about the central plane of the sheet. Thus, $y(\xi, \tau + \Delta\tau)$ can be evaluated from the values of $y(\xi + \Delta\xi, \tau)$, $y(\xi, \tau)$, and $y(\xi - \Delta\xi, \tau)$ with the following initial and boundary conditions:

$$y_A(\xi, 0) = 1 \quad (0 \leq \xi < 1) \quad (7a)$$

$$y_A(1, \tau) = 0 \quad (7b)$$

$$y_A(0, \tau) = y_A(0 + \Delta\xi, \tau) \quad (7c)$$

The boundary condition in eq 7a corresponds to $C_B = 0$ at $t = 0$ and $0 \leq \xi < 1$; the boundary condition in eq 7b corresponds to $C_A = 0$ at $t > 0$ and $\xi = 1$, implying infinite solution volume or the continuous renewal of solution. The third boundary condition (eq 7c) implies that $(\partial C_A/\partial \xi) = 0$ at $\xi = 0$ (i.e., the concentration gradient vanishes at the center of the membrane). A Fortran program was used to evaluate $y(\xi, \tau)$.

The fraction $q_A(\tau)$ that is still present in the membrane at any time τ is given by

$$q_A(\tau) = \int_0^1 y_A(\xi, \tau) d\xi \quad (8)$$

This integral was numerically evaluated using Simpson's rule. Finally, the fractional attainment of equilibrium is obtained as

$$F(\tau) = 1 - q_A(\tau) \quad (9)$$

For large τ , $q_A(\tau)$ becomes zero as A^{z_A} ions in the membrane are fully replaced by B^{z_B} ions. The τ can be converted back into time (t) using eq 2. The quantity $F(t)$ is experimentally measured and can be compared with the calculated values that depend on the parameters Z_A , Z_B , and (D_A/D_B) . Because Z_A and Z_B are fixed, experimental values of $F(t)$ can be reproduced by varying (D_A/D_B) , and if one of the two diffusion coefficients is known, then the other can be obtained.

The Nernst–Planck theory predicts different rates of forward and reverse exchange in the case where interchanging ions do not have same diffusion coefficients. If ion A initially present in the membrane has a higher diffusion coefficient than ion B (initially in the solution), then the exchange of A for B is faster than the reverse process, when B is exchanged for A.

Experimental Section

AR-grade chemicals (CuSO_4 , Eu_2O_3 , CsCl ; HCl (Merck, Germany)) and deionized water (18 M Ω /cm, Gradient A-10 model, Milli-Q) were used in the present study. The Nafion-117 ion-exchange membrane with an equivalent weight of 1100 and a thickness of 178 μm (Aldrich, lot no. 08304cz) was used. As described in our earlier paper,¹⁸ the samples of Nafion-117 were treated to remove organic impurities; they were conditioned with 0.5 M HCl and 0.5 M NaOH and equilibrated with a 0.5 M relevant salt solution for 18–24 h at room temperature (27 $^\circ\text{C}$) to converting the membrane into the appropriate ionic form.

The thickness of the membrane in appropriate ionic form was measured using a digital micrometer (Mitutoyo, Japan) with an accuracy of 0.001 mm. The thickness of the wet samples was

determined using a pycnometer as described elsewhere.²² The water up-take capacity of the membrane, defined as the amount of water absorbed per unit of dry weight of the membrane, was obtained from the difference in weight of the wet membrane and dry membrane sample. The weight of the dry membrane was obtained by drying the membrane sample in Cs form for 6–8 h at 70 $^\circ\text{C}$. Drying at a still higher temperature (100 $^\circ\text{C}$) did not alter the weight of the membrane sample in Cs form. The weights of dry membranes in other forms were computed from the weight of the membrane in Cs form with the knowledge of ion-exchange sites because it was difficult to dry the membrane samples in the other ionic forms. The pH of the equilibrating salt solutions was measured using a 420A pH meter (Thermo Orion). The pH meter was calibrated using standard buffer solutions (Hamilton) having pH 4.01, 7, and 10. The pH of the equilibrating salt solution was adjusted with a dilute HCl solution.

Carrier-free radiotracer ^{137}Cs was obtained from the Board of Radiation and Isotope Technology, Mumbai, India. Radiotracers ^{64}Cu and ^{154}Eu were prepared by irradiating known amounts of CuSO_4 and Eu_2O_3 (having 99.1% enriched ^{153}Eu obtained from Euriso-top, France) for appropriate amounts of time in the Apsara and Dhruva reactors at BARC, Mumbai, India. The ^{64}Cu radiotracer solution was prepared by dissolving the irradiated CuSO_4 in a known volume of deionized water. The ^{154}Eu radiotracer solution was prepared by dissolving the irradiated Eu_2O_3 in concentrated HCl and evaporating it to near dryness. The acidity of a stock solution of ^{154}Eu was adjusted to pH 2 to prevent any hydrolysis during storage.

Measurements of isotopic exchange and ion-exchange rates were carried out using $2.0 \times 2.0 \text{ cm}^2$ pieces of a Nafion-117 membrane in the appropriate ionic form. The sorption/desorption of radiotracer counterions in the membrane samples in contact with the equilibrating solutions was monitored as a function of time to obtain exchange rates. The experimental details are given in our previous publication¹⁸ and described briefly below.

In sorption experiments, the membrane samples in the appropriate ionic form were placed in 30 mL of salt solution containing the relevant radiotracer and acidity. The solution (at 27 $^\circ\text{C}$) containing the membrane sample was stirred vigorously ($\sim 52 \text{ rad/s}$) to minimize the concentration gradient of counterions in the equilibrating solution. The number of radiotracer counterions sorbed in the membrane sample was monitored by removing the membrane sample from the equilibrating solution at regular time intervals and counting the radioactivity in the membrane. Before monitoring the radioactivity, the membrane samples were washed with deionized water to remove traces of the equilibrating solution adhering to its surface. The membrane sample was again placed in the equilibrating solution after counting. The actual residence time of the membrane in the equilibrating solution was considered to be the counterion exchange time. The radioactivity of the counterions was monitored by γ -ray counting in the fixed geometry using a well-type NaI(Tl) detector connected to a single-channel analyzer.

Desorption experiments were carried out by loading radioactivity-tagged counterions into the membrane sample. Subsequently, the membrane sample was immersed in 30 mL of vigorously stirred equilibrating solution (without radiotracer counterions) at room temperature. The number of radiotracer counterions diffusing out of the membrane sample was monitored by taking out 100- μL samples from the equilibrating solution at regular time intervals and monitoring the radioactivity by γ -ray counting. The radioactivity of the counterions having a short half-life (^{64}Cu) was corrected to account for the decay

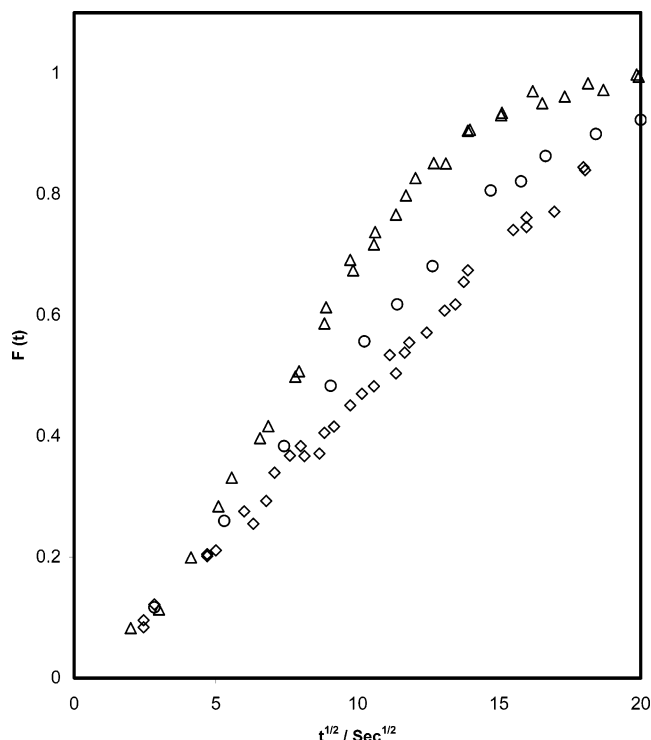


Figure 1. Fractional attainment of equilibrium $F(t)$ as a function of $t^{1/2}$ in Cs^+ -loaded samples of Nafion-117. The samples were equilibrated with aqueous solutions of (i) 0.25 M CsCl with pH 5–2 (\diamond), (ii) 0.25 M CsCl + 0.1 M HCl (\circ), and (iii) 0.25 M HCl (\triangle).

of radioactivity during the experiments. In desorption experiments, the appropriate correction has been applied to account for the volume of the equilibrating salt/acid solution taken to monitor the radioactivity.

The variation in recording the contact time of the membrane with the equilibrating solution was expected to be on the order of ± 2 s for the sorption experiments and ± 1 s for the desorption experiments. Because the forward exchange process was fast (~ 1 min), the sorption experiments were carried out by holding the membrane sample in the equilibrating solution for a specific period of time using tweezers.

Results and Discussion

The kinetics of $*M_{(m)}^{n+} \rightleftharpoons M_{(s)}^{n+}$ ($M = \text{Cs}^+$, Cu^{2+} , and Eu^{3+}) exchanges were studied as a function of time by monitoring the radiotracer diffusing out of the membrane sample into the equilibrating salt solutions having different acidities. Superscripts * and n denote the radioactivity-tagged counterion and its charge, respectively. It was shown that the fractional attainment of equilibrium $F(t)$ in the early stages of the counterion-exchange process is always proportional to $t^{1/2}$ irrespective of how the diffusion coefficient (D_{AB}) depends on concentration.²¹ Figures 1–3 show the plots of measured $F(t)$ versus $t^{1/2}$. It is evident from these figures that $F(t)$ varies linearly with $t^{1/2}$ during the initial stages of the exchange process. It is also seen from these measured exchange profiles that the kinetics of exchange do not change significantly in the Nafion-117 samples kept in contact with equilibrating solutions having fixed concentrations of M^{n+} ions (0.25 M) with the pH varying between 2 and 5. This suggests that the H^+ ions' competition with M^{n+} ions for the available ion-exchange sites in the membrane is not very significant in this pH range. Thus, the exchange profiles can be assumed to represent the pure isotopic exchange ($*M_{(m)}^{n+} \rightleftharpoons M_{(s)}^{n+}$) in this pH range and hence can be used to obtain self-

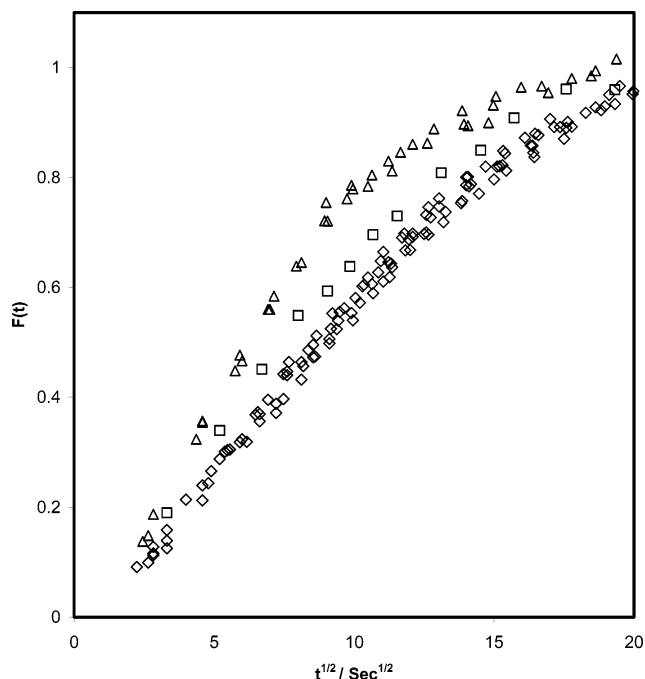


Figure 2. Fractional attainment of equilibrium $F(t)$ as a function of $t^{1/2}$ in Cu^{2+} -loaded samples of Nafion-117. The samples were equilibrated with aqueous solutions of (i) 0.25 M CuSO_4 with pH 4–2 (\diamond), (ii) 0.25 M CuSO_4 + 0.1 M HCl (\square), and (iii) 0.25 M HCl (\triangle).

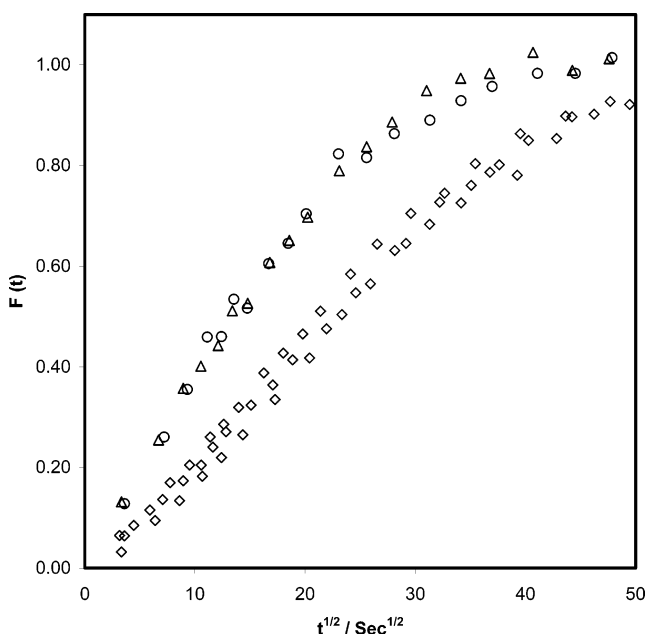


Figure 3. Fractional attainment of equilibrium $F(t)$ as a function of $t^{1/2}$ in Eu^{3+} -loaded samples of Nafion-117. The samples were equilibrated with aqueous solutions of (i) 0.25 M EuCl_3 with pH 3–1.75 (\diamond), (ii) 0.25 M EuCl_3 + 0.1 M HCl (\circ), and (iii) 0.25 M HCl (\triangle).

diffusion coefficients of counterions in the membrane. This demonstrates the possibility of obtaining the self-diffusion coefficients of the counterions for which this pH range is sufficient to prevent their hydrolysis.

As shown in Figures 1–3, the exchange kinetics of the membrane samples kept in contact with the equilibrating solution containing 0.1 M H^+ and 0.25 M of M^{n+} start deviating from the isotopic exchange curve. This indicates the onset of competition between H^+ and M^{n+} ions for available ion-exchange sites of the membrane. At this acidity, the exchange profiles involve two types of processes (mixed system): (i)

isotopic exchange ($M_{(m)}^{n+} \rightleftharpoons M_{(s)}^{n+}$) and (ii) ion exchange ($M_{(m)}^{n+} \rightleftharpoons H_{(s)}^+$). In accordance with the Nernst–Planck theory described in the Theoretical Section, the kinetics of $M_{(m)}^{n+} \rightleftharpoons H_{(s)}^+$ exchange are expected to be faster than the kinetics $M_{(m)}^{n+} \rightleftharpoons M_{(s)}^{n+}$ exchange. This prediction is based on the fact that the self-diffusion coefficient of the H^+ ion in Nafion-117 is much higher than the self-diffusion coefficients of M^{n+} ions. As expected, the exchange rates are enhanced as compared to the rate of pure isotopic exchange at the onset of H^+ competition with M^{n+} for available ion-exchange sites in the membrane. (See Figures 1–3.)

To study the contribution of H^+ ion competition in exchange rates at higher acidity, the kinetics of $M_{(m)}^{n+} \rightleftharpoons H_{(s)}^+$ exchange were also measured by immersing the membrane sample loaded with radiotracer counterions in 0.1–0.25 M HCl. The ion-exchange rates thus obtained are shown in Figures 1–3. It is evident from Figures 1 and 2 that the rates of $Cs_{(m)}^+ \rightleftharpoons H_{(s)}^+$ and $Cu_{(m)}^{2+} \rightleftharpoons H_{(s)}^+$ exchange are faster than the corresponding isotopic exchanges. The exchange profile of the mixed system (equilibrating solution having 0.25 M M^{n+} and 0.1 M H^+ ions) lies between the profiles of isotopic exchange ($M_{(m)}^{n+} \rightleftharpoons M_{(s)}^{n+}$) and ion exchange ($M_{(m)}^{n+} \rightleftharpoons H_{(s)}^+$). This seems to suggest that both isotopic and ion exchange occur in the mixed systems and that the extent of their contributions to exchange kinetics depends on the composition of the equilibrating solution. However, the profiles of $Eu_{(m)}^{3+} \rightleftharpoons H_{(s)}^+$ exchange and the mixed system (equilibrating solution containing 0.25 M Eu^{3+} and 0.1 M H^+ ions) were found to be similar, as shown in Figure 3. This seems to suggest that exchange kinetics obtained in the mixed system represent only $Eu_{(m)}^{3+} \rightleftharpoons H_{(s)}^+$ exchange and that isotopic exchange ($Eu_{(m)}^{3+} \rightleftharpoons Eu_{(s)}^{3+}$) does not contribute to exchange process under the given conditions.

Self-Diffusion Coefficients. The profiles of isotopic-exchange kinetics in the pH range of 5–2 were analyzed to obtain the self-diffusion coefficients of Cs^+ , Cu^{2+} , and Eu^{3+} ions in the membrane. The details of method used to obtain self-diffusion coefficients are described in our earlier paper.¹⁸ The number of radiotracer ions ($M_{(m)}^{n+}$) diffusing out of the membrane sample as a function of time is given by an analytical solution of Fick's second law given below:

$$n(t_k) = n^* \left[1 - \left(\frac{8}{\pi^2} \right) \left\{ \exp\left(\frac{-D\pi^2 t_k}{L^2} \right) + \frac{1}{9} \exp\left(\frac{-9D\pi^2 t_k}{L^2} \right) + \dots \right\} \right] \quad (10)$$

$n(t_k)$ and n^* are the number of radiotracer ions in the equilibrating solution at fixed times t_k and t_∞ , respectively, D is the self-diffusion coefficient of the ions in the membrane, and L is the thickness of the membrane. The value of D was obtained by a nonlinear least-squares fit of eq 10 with both n^* and D as the free parameters. The comparison of the fitted and experimental data for the isotopic exchange of Cu^{2+} and Eu^{3+} in the Nafion-117 membrane is shown in Figure 4. The values of the self-diffusion coefficients of Cs^+ , Cu^{2+} , and Eu^{3+} in the Nafion-117 membrane obtained from the analyses of isotopic exchange profiles in the pH range of 5–2 are given in Table 1. The value of the self-diffusion coefficient of Cs^+ in Nafion-117 is in close agreement with value obtained in our earlier work ($1.94 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) using the isotopic exchange method in the absence of H^+ ions.¹⁸ This confirmed that the exchange process in the Nafion-117 membrane that equilibrated with salt solution having pH 5–2 represents the pure isotopic exchange ($M_{(m)}^{n+} \rightleftharpoons M_{(s)}^{n+}$). The self-diffusion coefficient of Cu^{2+} in the Nafion-117

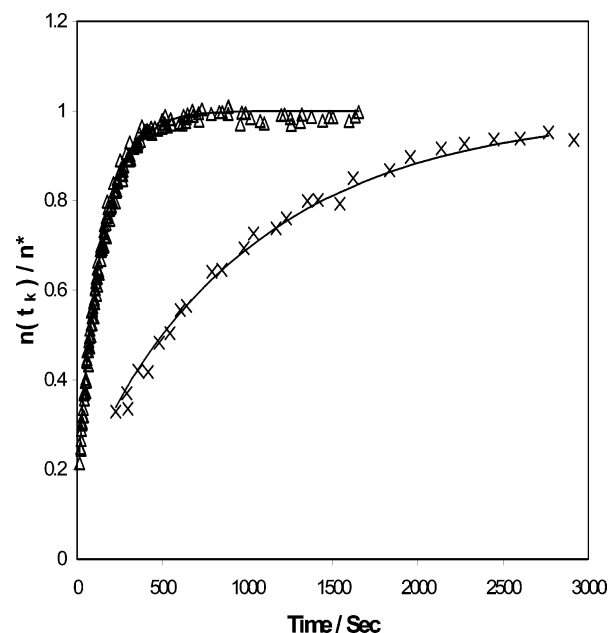


Figure 4. Variation of the fraction of radiotracer counterions in isotopic exchange between the Nafion-117 membrane and an equilibrating salt solution. Symbols Δ and \times represent $Cu_{(m)}^{2+} \rightleftharpoons Cu_{(s)}^{2+}$ and $Eu_{(m)}^{3+} \rightleftharpoons Eu_{(s)}^{3+}$ exchanges, respectively. $n(t_k)$ and n^* are the activities of radiotracer counterions at times t_k and t_∞ (at equilibrium), respectively. The solid lines are fitted data used to obtain self-diffusion coefficients from eq 10.

TABLE 1: Self-Diffusion Coefficient of Ions in the Nafion-117 Membrane

ion	water uptake (wt %)	pH range in equilibrating solution	D ($\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$)
Cs^+	7.9	5.5–2.0	2.0 ± 0.1
Cu^{2+}	17.9	3.8–2.0	2.9 ± 0.1
Eu^{3+}	13.2	3.0–1.75	0.45 ± 0.05

membrane was found to be $2.9 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is on the order of that expected from the self-diffusion coefficient of Zn^{2+} ($3.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) measured previously in the same membrane.¹⁸ The low value of the self-diffusion coefficient of Eu^{3+} as compared to those of monovalent and divalent ions in the Nafion-117 membrane can be attributed to the increase in electrostatic interactions between the Eu^{3+} counterion and the membrane matrix, which retards the mobility of the Eu^{3+} counterion. The lower water content of the Nafion-117 membrane in the Eu^{3+} form (Table 1) is also expected to reduce the mobility of the counterions because of the fact that the displacement of the mobile counterions occurs through the region containing water and is obstructed by the polymer chains.^{23–24}

Ion-Exchange Kinetics. The measured ion-exchange kinetics in the Nafion-117 membrane were used to examine the validity of the Nernst–Planck theory to describe the ion-exchange kinetics. The fractional attainment of ion-exchange equilibrium $F(t)$ was calculated as a function of time using eq 9, and the ion-exchange profile thus obtained was compared with the experimental exchange profile. As described in the Theoretical Section, the input parameters required to calculate $F(t)$ are the self-diffusion coefficients and the charges of the two interchanging ions involved in the process. The values of the self-diffusion coefficients of Cs^+ , Cu^{2+} , and Eu^{3+} obtained from isotopic exchange studies in the present work along with the value of the self-diffusion coefficient of H^+ ($2.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) used by Samec et al.¹² for the as-received form of the Nafion-117

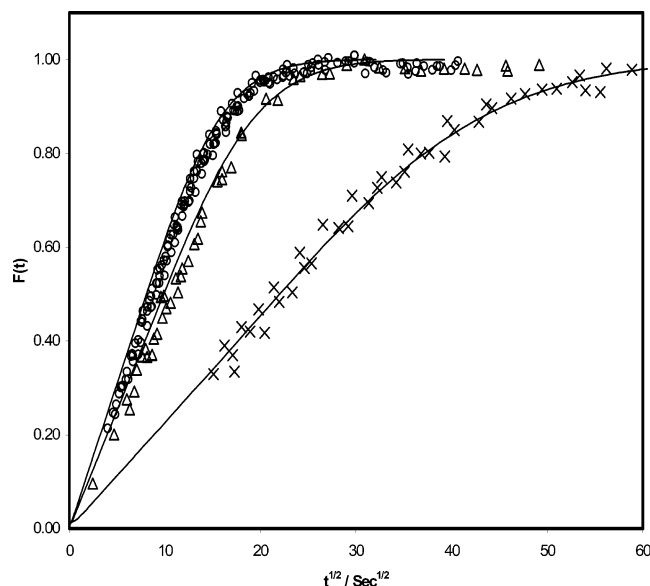


Figure 5. Comparison of experimental and calculated $F(t)$ in isotopic exchanges. Symbols O, Δ , and \times represent the experimental $F(t)$ vs $t^{1/2}$ involving Cu^{2+} , Cs^{+} , and Eu^{3+} ions, respectively. The solid lines are calculated $F(t)$ from eq 9 for these counterions.

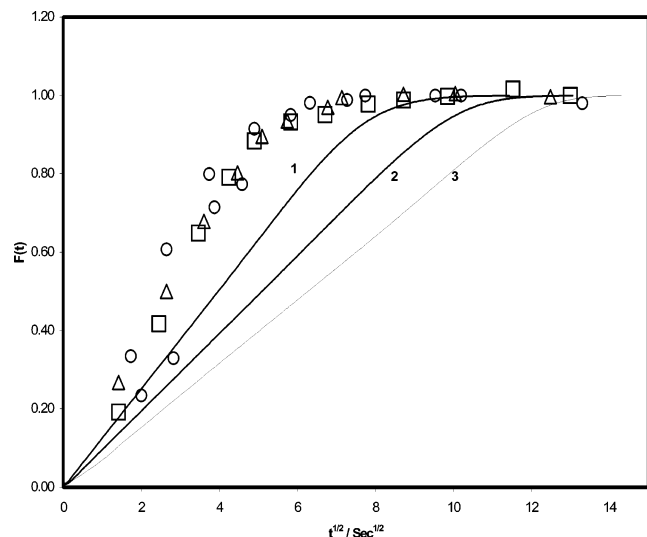


Figure 6. Calculated and experimentally measured forward ion exchanges. Symbols O, Δ , and \square represent $\text{H}_{(m)}^{+} \rightleftharpoons \text{Cu}_{(s)}^{2+}$, $\text{H}_{(m)}^{+} \rightleftharpoons \text{Eu}_{(s)}^{3+}$, and $\text{H}_{(m)}^{+} \rightleftharpoons \text{Cs}_{(s)}^{+}$ exchange processes. Solid lines 1, 2, and 3 represent calculated ion-exchange rates involving Cu^{2+} , Cs^{+} , and Eu^{3+} ions, respectively.

membrane were used to calculate $F(t)$. The validity of approach used for the analyses of ion-exchange kinetics based on the Nernst–Planck equation was tested using measured isotopic exchange. In principle, eq 9 should reproduce the kinetics of isotopic exchange under the conditions that $Z_A = Z_B$ and $D_A = D_B$. The excellent agreement of calculated $F(t)$ with that of experimentally measured $F(t)$ in the isotopic exchange kinetics, given in Figure 5, validates the approach and computer program used to predict the exchange kinetics based on the Nernst–Planck equation. The variation of calculated and experimental values of $F(t)$ as a function of time in forward exchange ($\text{H}_{(m)}^{+} \rightleftharpoons \text{M}_{(s)}^{n+}$) and reverse exchange ($\text{M}_{(m)}^{n+} \rightleftharpoons \text{H}_{(s)}^{+}$) is shown in Figures 6 and 7, respectively. It is evident from these figures that the predicted ion-exchange kinetics are close to the measured reverse-exchange kinetics but completely failed for forward exchange.

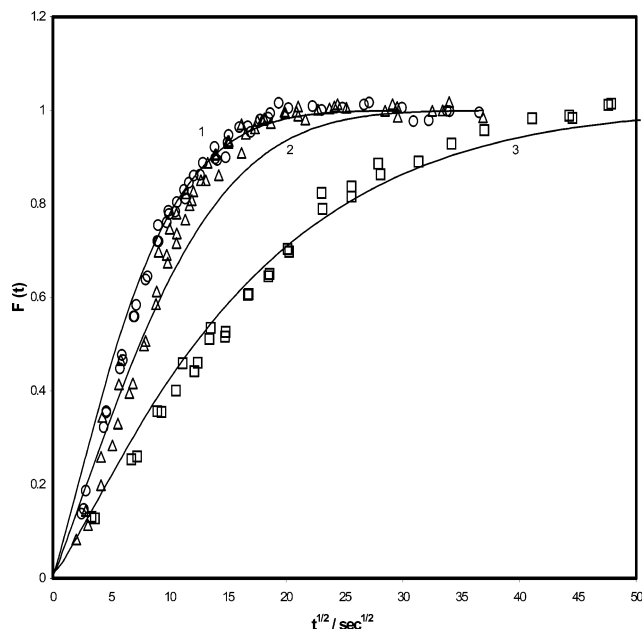


Figure 7. Calculated and experimentally measured $F(t)$ in reverse ion exchanges. Symbols O, Δ , and \square represent $\text{Cu}_{(m)}^{2+} \rightleftharpoons \text{H}_{(s)}^{+}$, $\text{Cs}_{(m)}^{+} \rightleftharpoons \text{H}_{(s)}^{+}$, and $\text{Eu}_{(m)}^{3+} \rightleftharpoons \text{H}_{(s)}^{+}$ exchange processes. Solid lines 1, 2, and 3 represent calculated ion-exchange profiles from eq 9 involving Cu^{2+} , Cs^{+} , and Eu^{3+} ions, respectively.

It is seen from Figure 7 that the calculated and experimental kinetics of reverse exchanges for Cu^{2+} and Eu^{3+} are in good agreement. However, the experimental reverse exchange rates involving Cs^{+} match fairly well with the calculated exchange rate up to 70% attainment of ion-exchange equilibrium; thereafter, the $\text{Cs}_{(m)}^{+} \rightleftharpoons \text{H}_{(s)}^{+}$ exchange process becomes faster than that predicted by the Nernst–Planck theory. The disagreement between the experimental and predicted ion-exchange profiles beyond 70% replacement of Cs^{+} ions with H^{+} ions in the membrane may be related to changes in the physical structure of the membrane. The change in the physical structure of the membrane is expected on the basis of the fact that the water content in the membrane is maximized and minimized when the membrane is in the H^{+} form and Cs^{+} form, respectively. Thus, the exchange kinetics are expected to increase with increasing water content during the exchange process. This aspect was considered by Samec et al.¹² but was not considered in the present work. As shown in Table 1, the water content in membranes with Cu^{2+} and Eu^{3+} counterions lies between the water content in the H^{+} (22 wt %) and Cs^{+} (7.9 wt %) forms, respectively. Thus, it appears from Figure 7 that the effects of the change in water content during the exchange process are not significant enough to modify the reverse exchange process involving Cu^{2+} and Eu^{3+} ions.

As can be seen from Figure 6, the kinetics involving forward exchanges of Cs^{+} , Cu^{2+} , and Eu^{3+} with H^{+} ions in the Nafion-117 membrane have the same trend. This experimental observation is contrary to the expectation from the Nernst–Planck theory. The ion-exchange rates are also much faster in forward exchange than that predicted by the Nernst–Planck theory. (See Figure 6.) Thus, it appears that the self-diffusion coefficients of ions (Cs^{+} , Cu^{2+} , and Eu^{3+} in this case) do not play any role in forward exchange processes. It is known that the water content in the H-form sample of the membrane is highest, the water transference coefficient (defined as the no. of moles of water transported per faraday) for H^{+} ions is lowest in the Nafion-117 membrane,⁵ and the H^{+} ion moves not only via ion-exchange sites but also via a proton-hopping mechanism through

water molecules inside the membrane. Because forward exchange is faster, it is probable that the membrane may not dehydrate or change its physical structure during forward exchange processes for the reasons given above. Thus, ions enter into the membrane matrix with a much higher water content than that expected in the membrane with the same counterions. Therefore, the effective diffusion coefficients of the ions would be much higher than the self-diffusion coefficients of ions in the the Nafion-117 membrane. This in turn would lead to faster exchange kinetics than those predicted by the Nernst–Planck theory using the self-diffusion coefficients of ions. However, it is very difficult to understand the same forward exchange kinetics for different ions. This seems to indicate that different ions have equal mobility in the forward exchange process in the Nafion-117 membrane. It is clear from the studies of forward and reverse exchanges that the self-diffusion coefficients of counterions can be obtained only from the analysis of measured reverse exchange kinetics based on the Nernst–Planck equation and that the evaluation of self-diffusion coefficients from forward exchanges is highly dependent on the model employed for the analysis.

Conclusions

The present work demonstrates the possibility of measuring self-diffusion coefficients of counterions in the Nafion-117 membrane from analyses of isotopic exchange even in the pH range of 5–2. Thus, the self-diffusion coefficients of those ions that undergo hydrolysis in the neutral solution can be measured. The self-diffusion coefficients of Cu^{2+} and Eu^{3+} measured in the present work indicate that the trivalent counterions have very low mobility in the Nafion-117 membrane as compared to the monovalent and divalent counterions. The reverse exchange kinetics predicted by the Nernst–Planck theory were in good agreement with experimentally measured exchange rates in the Nafion-117 membrane, but this theory completely failed in predicting the kinetics of forward exchange processes. This seems to suggest that the evaluation of self-diffusion coefficients of counterions in Nafion-117 from the analysis of forward exchange kinetics is highly dependent on the model and may not yield well-defined values.

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