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Study of Self-Diffusion of Monovalent and Divalent Cations in Nafion-117 Ion-Exchange Membrane

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Received: February 9, 2001; In Final Form: May 13, 2001

The self-diffusion coefficients of monovalent (Na^+, K^+, Cs^+, and Ag^+) and divalent (Ca^{2+}, Sr^{2+}, Ba^{2+}, and Zn^{2+}) cations in Nafion-117 have been measured using the "nonstationary radiotracer diffusion method" for the first time. This method is based on the analysis of absorption/desorption of radiotracer ions in the membrane sample as a function of time using an analytical solution of Fick's second law. It has been found to be simple and faster than that of the commonly used "radiotracer permeation method". An attempt has been made to interpret the self-diffusion data based on the free-volume theory. The self-diffusion coefficients for monovalent and divalent ions, normalized with respect to their aqueous diffusion coefficients, correlate well with the polymer volume fractions. However, separate trends are observed for monovalent and divalent ions. The factors that lead to higher self-diffusion coefficients of the counterions in the membrane appear to lower their selectivity coefficients.

Introduction

Nafion is an extensively studied membrane having perfluorosulfonic cation-exchange sites. The high electrical conductivity, remarkable permselectivity, and excellent thermal and chemical stability of Nafion membranes compensate for their high cost. It is extensively used in chlor−alkali industries, solid polymer electrolyte fuel cells, and Donnan dialysis based applications.[1−3] Recent studies on Nafion and its applications have been reviewed in the literature.[4] The transport behavior of ions in Nafion is quite different from its chemical analogue, cross-linked poly(styrenesulfonic) acid membranes.[5] The unique behavior of Nafion membrane is attributed to the absence of cross-linking and the phenomenon of clustering of ion-exchange sites.[5] The lack of chemical cross-links in polymer chains generates a dynamic morphology for Nafion. Thus, the water content of the membrane would depend to a large extent on the hydration characteristics of the counterion and on the pretreatment of the membrane. On the other hand, the clustering of ion-exchange sites plays an important role in the selectivity properties of the Nafion membrane.[6] One of the parameters required to understand the transport selectivity is the diffusion coefficient of the diffusing ions across the membrane. The transport properties of the ions are dependent not only on the physical and chemical structures of the membrane but also on the nature of interactions of the ions with the membrane and the changes produced by the counterions in the membrane.[7] Therefore, the study of diffusion coefficients of different cations would be useful to model the cumulative effects of counterions and membrane structural parameters on the diffusional ion-transport process in the Nafion membrane. The precise information about the individual transport characteristics of the ions in the Nafion membrane can be obtained from the study of their self-diffusion coefficients.

The self-diffusion of ions in a homogeneous medium is due to continuous random motion of the ions which gives rise to a

definite probability of arrival of a given ion at some point within a given time.[8] Techniques such as radiotracer permeation,[9−15] ion exchange,[16,17] conductivity/impedance measurements,[15,18,19] and pulsed-field-gradient nuclear magnetic resonance spectroscopy (PFG-NMR)[20] have been used to determine self-diffusion coefficients of the ions in membranes. The permeation of radiotracer ions across a Nafion membrane has been used for measuring the self-diffusion coefficients of ions[9−15] using a relationship introduced by Helfferich.[21] To have good control over hydrodynamics near the membrane, a modification of the method based on a rotating cell has been proposed.[22] The self-diffusion coefficients of the counterions in the Nafion membrane have also been determined from the kinetic measurements of ion exchange between a polymer membrane and the electrolyte solution.[16,17] However, self-diffusion data obtained by this method are complicated due to the coupling between two ion transport fluxes.[17] In impedance or conductivity measurement technique, the self-diffusion coefficient is derived from the migrational mobility of ions in the membrane using the Nernst−Einstein equation.[15] The migrational mobility of the ions in the membrane under an applied electric field is often found to be higher than the effective diffusional mobility. Therefore, the self-diffusion coefficients are usually higher than the values obtained by the radiotracer permeation method, which is essentially based on the true diffusional mobility[15] of ion in the membrane matrix.

Another interesting possibility for measuring self-diffusion coefficients of ions is based on a "nonstationary" diffusion of the radiotracer ions in or out of the membrane.[23] This method is essentially a simple technical realization of an analytical solution of Fick's second law for a non-steady-state diffusion process. In the present work, we have measured the self-diffusion coefficients of monovalent cations (Na^+, K^+, Cs^+, and Ag^+) and divalent cations (Ca^{2+}, Sr^{2+}, Ba^{2+}, and Zn^{2+}) in Nafion-117 using the "nonstationary radiotracer diffusion method". The self-diffusion coefficients data have been analyzed based on the framework of the free-volume theory[24] to understand the diffusional ion transport process in the Nafion-

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117 membrane. An attempt has been made to understand the role of water content in governing the sequence of selectivity coefficients as well as self-diffusion coefficients of the ions in the Nafion-117 membrane.

Theoretical Section

The present method requires the analysis of the time dependent concentration profiles of radioactive tracer ions diffusing into or out of a sheet of membrane sample kept in contact with equilibrating solution to obtain self-diffusion coefficient of the ion. The method is based on the assumptions that (i) the membrane controls the diffusion process, (ii) the self-diffusion coefficient within the membrane is constant, and (iii) the diffusion process is one-dimensional. The first assumption is valid only if the concentrations of the radiotracer ions at both boundaries of the membrane are the same as in the bulk solution. This was achieved by stirring the membrane sample vigorously in the equilibrating solution. The concentration profile of radiotracer ions diffusing into or out of the membrane is a function of time and space and is governed by Fick's second law[25] given as

$$\partial c/\partial t = D\, \partial^2 c/\partial x^2 \tag{1}$$

where c is the concentration of radiotracer ion in the membrane, D is the self-diffusion coefficient of the radiotracer ion in the membrane, and x is the spatial coordinate. In the case of absorption experiment of radiotracer ions, the membrane initially free of radiotracer ions is kept in contact with an equilibrating salt solution containing radiotracer ions. With the initial conditions $t = 0$, $0 < x < L$, $c = 0$, and the boundary conditions $t > 0$, $c = c^*$, $x = 0$, and $x = L$, the solution of eq 1 is[23,26]

$$c(x,t) = c^* + \frac{2c^*}{\pi}\sum_{n=1}^{\infty}\frac{(\cos n\pi - 1)}{n}\sin\frac{n\pi x}{L}\exp(-Dn^2\pi^2 t/L^2) \tag{2}$$

where L is the thickness of the membrane. For a fixed time ($t = t_k$), the amount of the radiotracer ion in the membrane having area A is given by

$$n(t_k) = A\int_0^L c(x,t)\,\mathrm{d}x \tag{3}$$

which on integration gives

$$n(t_k) = n^*[1 - (8/\pi^2)\{\exp(-D\pi^2 t_k/L^2) + (1/9)\exp(-9D\pi^2 t_k/L^2) + ...\}] \tag{4}$$

where n^* is the total amount of the radiotracer ions in the membrane at equilibrium ($t = \infty$). In the case of diffusion of the radiotracer ions from the membrane into a solution in contact with the membrane, the symbol n^* in eq 4 now represents the total radiotracer ions in the salt solution at equilibrium ($t = \infty$). Therefore, the self-diffusion coefficient, D, in either case is obtained by measuring the time-dependent growth of radioactivity corresponding to the amount of radiotracer ions, $n(t_k)$, in the membrane or in the solution kept in contact with the membrane, as the case may be. In the present study, the value of D was deduced by a nonlinear least-squares fit of eq 4 with both n^* and D as free parameters. Since eq 4 converges rapidly, only the first three terms were used for fitting the data.

Experimental Section

Materials and Reagents. AR grade chemicals (NaCl, KCl, Na$_2$CO$_3$, K$_2$CO$_3$, ZnCO$_3$, BaCl$_2$, CaCl$_2$, CsCl, AgNO$_3$, and SrCl$_2$) and double-distilled water were used in the present work. Nafion-117 ion-exchange membrane with an equivalent weight of 1100 corresponding to a nominal exchange capacity of 0.91 mequiv/g dry H$^+$-form polymer and thickness 178 μm (Aldrich, Lot No. 08304cz) was used. The membrane samples were boiled in concentrated nitric acid for 3−4 h to remove organic impurities introduced during the manufacturing process.[27] The membrane samples were washed with an excess of boiled water and soaked for 4 h in 1 M HCl and then 4 h in 1 M NaOH to condition the membrane. This process was repeated twice, and finally the membrane samples in acid form were washed with an excess of distilled water. These conditioned membrane samples were immersed in 0.5 M salt solutions for 18 h at room temperature (27 °C) for converting the membrane into the corresponding ionic form. The resultant membrane is considered to be in unexpanded form (as-received form).

The chloride salts of ^{24}Na, ^{42}K, and ^{65}Zn radiotracers were prepared by irradiating known amounts of Na$_2$CO$_3$, K$_2$CO$_3$, and ZnCO$_3$ for appropriate times in the APSARA reactor at BARC, Mumbai, India. After irradiation, the carbonate compounds were dissolved in HCl and evaporated to dryness. Care was taken to ensure that no residual HCl was left after evaporation. Finally, the radiotracer solutions were prepared by dissolving chloride salts in deionized water. The other radiotracers, ^{45}Ca, ^{137}Cs, ^{133}Ba, ^{85,89}Sr, and ^{110m}Ag, were obtained from the Board of Radiation and Isotope Technology, Mumbai, India. All these radiotracers were in chloride form except ^{110m}Ag, which was in nitrate form. The radiotracers ^{24}Na, ^{42}K, ^{45}Ca, ^{85,89}Sr, ^{65}Zn, and ^{110m}Ag were not free from the carrier.

The radioactivities of ^{24}Na, ^{42}K, ^{137}Cs, ^{110m}Ag, ^{85,89}Sr, ^{133}Ba, and ^{65}Zn were monitored by γ counting using a well-type NaI-(Tl) detector connected to a single channel analyzer. ^{45}Ca being a pure β-emitter, its radioactivity was monitored by β counting in a liquid scintillation counter employing a Dioxane-based cocktail scintillator (PPO 0.1% w/v, TOPO 0.1% w/v, naphthalene 1% w/v, POPOP 0.0025% w/v).

Characterization of Nafion-117. The Nafion-117 membrane samples in different ionic forms were characterized for water-uptake capacity and polymer volume fraction (V_p). The water-uptake capacity, defined as the amount of water absorbed per unit dry weight of the membrane, was determined from the difference between the weight of wet membrane sample (W_m) and weight of dry membrane sample (W_d). The weight of dry membrane was obtained by drying the membrane sample in Cs form for 6−8 h at 70 °C. Drying at still higher temperature (100 °C) did not alter the weight of the membrane sample in Cs form. The weights of dry membranes in the other forms were computed from the weight of the membrane in Cs form with the knowledge of ion-exchange sites as it was difficult to dry the membrane samples in other ionic forms.[28] The weight of wet membrane sample was obtained after equilibrating the membrane sample (3 cm × 3 cm) in 0.5 M solution of relevant chloride salt for 18 h at 27 °C.

The volumes of the wet membrane samples in different ionic forms were measured by a pycnometer. The following equation[29] was used to obtain the volume of the membrane sample (V_m).

$$V_m = V_{pyc} - [(W_s - W_{pyc} - W_m)/\rho_w] \tag{5}$$

where V_{pyc} is the volume of the pycnometer, W_s is the weight of the pycnometer with membrane sample in water, W_{pyc} is the weight of the dry pycnometer, W_m is the weight of wet membrane sample, and ρ_w is the density of water. The polymer volume factions (V_p) of the membrane samples in different ionic forms were calculated from the volume of the water in the membrane and the volume of the wet membrane sample.

Measurements of Self-Diffusion Coefficients. The measurements of the tracer self-diffusion coefficients of Na^+, K^+, Cs^+, Ag^+, Zn^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions in the Nafion-117 membrane were carried out using a 3 cm × 3 cm piece of the membrane sample in appropriate ionic form. For the experiments involving diffusion of radiotracer ions from equilibrating solution into the membrane (absorption), the membrane sample in the appropriate ionic form was placed in 25 mL of salt solution containing relevant radiotracer ions at room temperature. The concentration of salt in equilibrating solution was kept at 0.02 M to maximize the absorption of radiotracer ions into the membrane. The equilibrating salt solution containing membrane sample was stirred vigorously (≈500 rpm) to ensure the boundary conditions. To monitor diffusion of radiotracer ions into the membrane as a function of time, the membrane sample was taken out at regular time intervals, washed thoroughly with deionized water to remove the traces of equilibrating solution clinging to its surface, and counted for radioactivity. The membrane sample was replaced again in the equilibrating solution after counting. The actual residence time of the membrane in the equilibrating solution was used as the time of cation absorption. The absorption experiments were carried out for K^+, Cs^+, Zn^{2+}, Sr^{2+}, and Ba^{2+} ions. For β-emitter ^{45}Ca, the absorption experiment was not carried out due to the lack of a suitable method for counting the β-activity in the membrane. For higher values of self-diffusion coefficients (fast diffusion process), a slight variation in recording the time during withdrawal of membrane sample for counting the radioactivity was found to introduce a significant error in the value of the self-diffusion coefficient. Therefore, the values of self-diffusion coefficients of Na^+ and Ag^+ could not be measured by the absorption method.

For desorption experiments, the membrane samples were loaded with radioactive tracers by equilibrating the membrane sample with relevant radiotracer salt solution. Subsequently, the membrane sample was placed in 25 mL of 0.5 M equilibrating salt solution (without radioactive tracer ions) at room temperature. The 0.5 M salt solution was used to maximize desorption of radiotracer ions from the membrane. The other experimental conditions were same as those used in the absorption experiments. The amount of radiotracer ions diffusing out of the membrane was monitored by taking out a 100 μL sample of equilibrating solution as a function of time. After each experiment, the total radioactivity was counted to ensure the mass balance. The desorption experiments were used to measure the self-diffusion coefficients of Na^+, K^+, Cs^+, Ag^+, Zn^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions in the Nafion-117 membrane.

Results and Discussion

The nonlinear least-squares fit of $n(t_k)$ as a function of time using eq 4 gives a set of values for n^* and D for a given ion. This value of n^* was used to normalize the values of $n(t_k)$. Figures 1 and 2 show the plot of $n(t_k)/n^*$ vs time (t_k) for monovalent and divalent cations, respectively. The values of $n(t_k)/n^*$ from both the absorption and desorption experiments are included in the plots. It is seen that, for a given ion, the values of $n(t_k)/n^*$ for both the absorption and desorption experiments are on the same curve, indicating a constant self-diffusion coefficient. The concentration of equilibrating salt solutions for absorption and desorption were different. This also shows that the self-diffusion coefficients of different ions do not significantly depend on the range of the concentrations of the equilibrating salt solutions (0.02−0.5 M) used in the absorption and desorption experiments. Finally, for a given metal
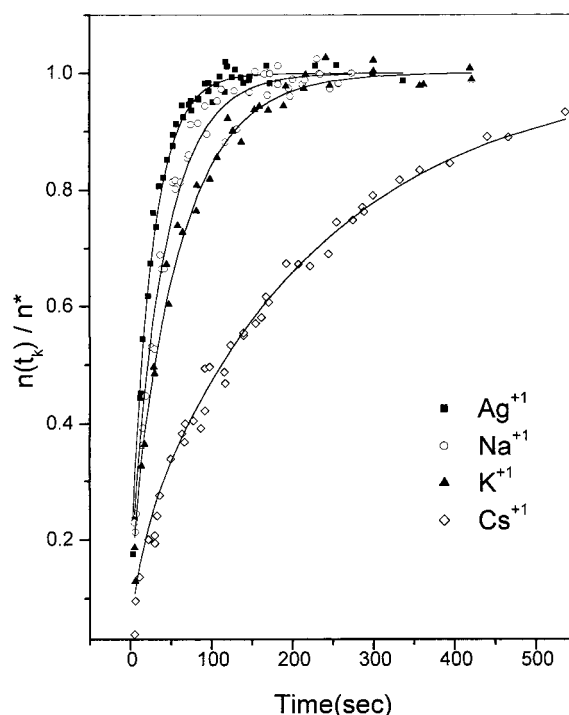

Figure 1. Variation of fractions of the radiotracer monovalent ions in the Nafion-117 membrane (absorption) or in the equilibrating salt solution (desorption) as a function of time *t*. The $n(t_k)$ represents the activity of radiotracer ions at time t_k, and n^* represents the activity of radiotracer ions at equilibrium ($t = \infty$).
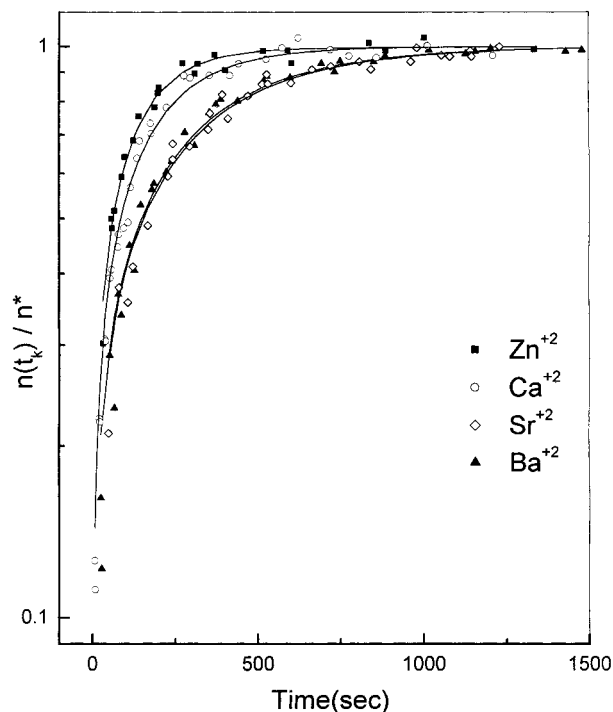

Figure 2. Variation of fractions of the radiotracer divalent ions in the Nafion-117 membrane (absorption) or in the equilibrating salt solution (desorption) as a function of time *t*. The $n(t_k)$ represents the activity of radiotracer ions at time t_k, and n^* represents the activity of radiotracer ions at equilibrium ($t = \infty$).

ion, the values of $n(t_k)/n^*$ as a function of time were subjected to a common nonlinear fit to obtain the self-diffusion coefficient of that ion. The fitted data are shown as solid lines in Figures 1 and 2. The values of the self-diffusion coefficients so obtained are given in Table 1. The overall statistical variation of self-

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

ion	$D^{\circ}{}_i{}^a$ ($\times 10^{-5}$ cm^2 s^{-1})	$D^{m}{}_i{}^b$ ($\times 10^{-6}$ cm^2 s^{-1}) present work^c	$D^{m}{}_i{}^b$ ($\times 10^{-6}$ cm^2 s^{-1}) published data	$D^{m}{}_i{}^d$ ($\times 10^{-6}$ cm^2 s^{-1})	$D^{m}{}_i{}^e$ ($\times 10^{-6}$ cm^2 s^{-1})
Ag$^+$	1.65	1.61 ± 0.05 (3)			
Na$^+$	1.33	1.03 ± 0.04 (3)	0.94−1.12[11]^f 1.8[15]^g 1.30[9]^g	0.78	1.11[18] 2.0[18]^g 1.7[15]^g
K$^+$	1.96	0.73 ± 0.03 (2)		0.71	
Cs$^+$	2.05	0.194 ± 0.007 (4)	0.170−0.188[11]^f	0.29	0.19,[18] 0.07[18]^g
Zn^{2+}	0.70	0.32 ± 0.02 (4)			
Ca^{2+}	0.79	0.25 ± 0.01 (2)	0.46[15]^g		0.34[15]^g
Sr^{2+}	0.79	0.16 ± 0.01 (3)			
Ba^{2+}	0.84	0.146 ± 0.006 (3)			

^{a} From ref 8. ^{b} Radiotracer methods. ^{c} The values given in parentheses represent the number of experiments. ^{d} Forward ion-exchange measurements.[17] ^{e} Conductivity/impedance method. ^{f} The range of the reported values at 25 °C is given in the table. The Nafion-120 membranes were used in refs 11 and 18. ^{g} Refers to expanded form of Nafion membrane.

diffusion coefficients of ions by both the absorption and desorption methods was found to be within 10%.

One of the advantages of the present method is that, unlike permeation methods, it does not require the concentration of equilibrating solution for obtaining the values of self-diffusion coefficients of ions in the membrane. The inputs required for obtaining the self-diffusion coefficients of the ions by using eq 4 are the amount of radiotracer ions either in the membrane sample or in the equilibrating solution as a function of time and the thickness of wet Nafion-117 membrane sample in the relevant ionic form (200 ± 20 μm). This eliminates the requirement of radiotracer ions in carrier-free form. However, the concentration of salt solution should be known to eliminate the ambiguity about the effects of solution concentration, kept in contact with the membrane sample, on the self-diffusion coefficient of the ions in the membrane sample. In the desorption route of the present method, the radiotracer ions diffuse from the membrane to solution and therefore the self-diffusion coefficient of the ion in the membrane can be obtained at a defined concentration of solution in contact with membrane where carrier-free radiotracers of ions are not available. Due to this reason, the self-diffusion coefficients of several monovalent and divalent cations in Nafion-117 could be measured in the present work. The variation in recording the contact time of membrane with equilibrating salt solution is expected to be of the order of ±4 s for the absorption experiment, which is significantly higher than that of the desorption route of the present method (±1 s.). The variation of self-diffusion coefficients in Nafion-117 for different radiotracer ions as a function of time for attaining of 99% equilibrium is shown in Figure 3. This gives an estimate of time required for completion of an absorption/desorption experiment for a given value of self-diffusion coefficient. Thus the advantages of this method for determining self-diffusion coefficients are the following: (i) the simplicity of the experiment—one needs only a beaker and stirrer for absorption and desorption of tracer species, as opposed to a two-compartment diffusion cell; (ii) transient experiments are faster to perform.

The reported values of self-diffusion coefficients for unexpanded (as received) and expanded forms of Nafion membrane are given in Table 1. It is seen from Table 1 that the self-diffusion coefficients of Na$^+$ and Cs$^+$ in Nafion-117 as measured in the present work are in good agreement with the data obtained by Yeager et al.[11] using a radiotracer-based permeation method and with that of Millet[18] obtained by conductivity measurements for unexpanded form of Nafion-117 membrane. As can be seen, the self-diffusion coefficients data of Pourcelly et al.[15] are in good agreement with those obtained by using an expanded form of Nafion membrane.[9,18] The self-diffusion coefficients of the ions in the Nafion-117
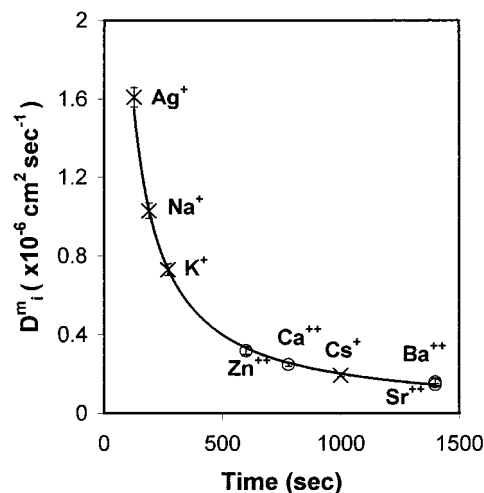

Figure 3. Self-diffusion coefficient as a function of time for 99% attainment of equilibrium by radiotracer monovalent and divalent ions in the Nafion-117 membrane.

forward ion-exchange measurement[17] are also given in Table 1. The values of self-diffusion coefficients provided by reverse ion exchange measurement are considerably lower than those obtained from the forward ion exchange method, and therefore these are not included in Table 1 for comparison. Since these values are obtained from coupled diffusion of two counterions, they may not be directly comparable to self-diffusion coefficient data.

In accordance with the free-volume approach to diffusion,[24] a change in the water content has a significant effect on diffusion coefficient of the ion in the polymer matrix. This is because of the fact that the displacements of the mobile counterions occur through a region containing water and obstructed by the polymer chains. Hence, the tortuosity effect which represents the lengthening of the path of moving ions is fundamentally related to the polymer volume fraction $f(V_p)$ in the polymer matrix. Yasuda et al.[24] showed from the free-volume theory of Cohen and Turnbull[30] that the tortuosity effect on diffusion coefficient, D, could be related to the polymer volume fraction of the matrix using the expression

$$D = D^{\circ} \exp[-b(V_p/(1 - V_p))] \tag{6}$$

where D° is the aqueous diffusion coefficient of the species, V_p is the volume fraction of polymer in the water-swollen membrane, and b is an empirical parameter to be obtained from a fit of the experimental data using eq 6. This equation provides excellent correlation between the diffusion coefficients of the ions and the degree of cross-linking and/or water contents in
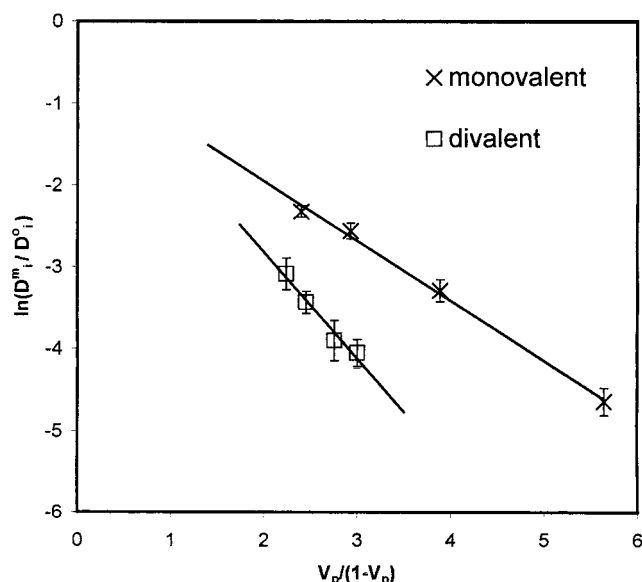
Figure 4. Logarithm of ratio of the self-diffusion coefficient of the ion in the membrane to aqueous diffusion coefficient of the ion, ln-(D^m_i/D°_i), plotted against the polymer volume fraction function $[V_p/(1 - V_p)]$ of the different ionic forms of the Nafion-117 membrane.

TABLE 2: Water Uptake and Polymer Volume Fraction in Different Ionic Forms of Nafion-117

| ion | water uptake[a] (%) | | | mol of H₂O/mol of −SO₃⁻ | | |
	present work	ref 32	ref 33	present work[a]	ref 7[b]	V_p
Ag⁺	18.8			12.7	12.2	0.706
Na⁺	17.2	18.9	18.7	10.8	11.9	0.745
K⁺	12.3	13.8	12.2	7.8	8.8	0.795
Cs⁺	8.2		8.58	5.6	6.6	0.849
Zn²⁺	21.3			13.4	14.1	0.691
Ca²⁺	19.4		18.8	12.1	12.9	0.710
Sr²⁺	17.5		17.8	11.1	12.3	0.734
Ba²⁺	15.5		15.1	10.1	11.6	0.750

[a] In Nafion-117. *[b]* In Nafion-120.

the polystyrenesulfonate ion-exchange resin.[31] The preexponential factor however is found to deviate form the diffusion coefficient of the ions in pure water, reflecting electrostatic interactions of the counterions to the fixed charge sites in the ion-exchange resin. This equation has been used by Yeager[5] to explain the variation of D (self-diffusion coefficient) with the water content in Nafion membrane for individual cations (Na⁺ and Cs⁺). The study of Samec et al.[16,17] showed that the diffusion coefficient data of several monovalent cations in the Nafion-117 membrane can be represented by the single-exponential constant b in eq 6.

To explore the dependence of measured self-diffusion coefficients on the membrane water contents, the following equation[31] has been used.

$$(D^m_i/D^\circ_i) = g \exp[-b(V_p/(1 - V_p))] \tag{7}$$

where D°_i denotes the tracer diffusion coefficient of ion i in pure water which is proportional to the absolute mobility of

the ions, and the preexponential factor g represents the deviation from eq 6 due to any specific interaction between counterions and membrane matrix. The values of $\ln(D^m_i/D^\circ_i)$ for monovalent and divalent cations are plotted in Figure 4 against $V_p/(1 - V_p)$. The values of D°_i were taken from ref 8. The V_p values for different ionic forms of Nafion-117 were obtained from the water-uptake capacities measured in the present work and are given in Table 2 along with the literature data.[32,33] As seen from the table, the water-uptake capacities measured in the present work are in good agreement with the literature values. As can be seen from Figure 4, separate straight lines for monovalent (Ag⁺, Na⁺, K⁺, and Cs⁺) and divalent (Zn²⁺, Ca²⁺, Sr²⁺, and Ba²⁺) cations are obtained. The results of this graphic analysis using eq 7 are given in Table 3. The results show the validity of the form of eq 7 and corroborate the observation of Samec et al.[17] that the different monovalent ions can be represented by a single b parameter. In Table 3, the values of b and g parameters obtained for Nafion-117 by Samec et al.[17] for monovalent metal ions are also included. It is seen that the value of b parameter obtained in the present work agrees reasonably well with the results of the unexpanded form of Nafion but differ significantly for the expanded form of Nafion. This shows that it is difficult to give a simple interpretation of the b and g parameters. This is further reflected in the fact that these parameters are entirely different for divalent ions. A difference in the membrane morphology for the expanded and unexpanded forms of Nafion and also for the different valence of the ions may be responsible for this behavior. However, clear interpretation of self-diffusion data in terms of eq 7 is still lacking.

The selectivity coefficients of the Nafion-120 (EW 1200) for monovalent-hydrogen ion and divalent-hydrogen ion exchange at 25 °C were studied by Yeager et al.[7], and the sequence of selectivity coefficients for monovelent and divalent ions was explained in terms of the difference in water-uptake capacities of the membrane associated with different counterions. The water to ion-exchange site ratio of Nafion-120 in different ionic forms does not differ significantly form those of Nafion-117 (Table 2). Therefore, it would be interesting to study the role of water content on the selectivity coefficients and the self-diffusion coefficients in Nafion. The selectivity coefficients (K^M_H) of the ions in the membrane are plotted against the self-diffusion coefficients (D^m_i) in Figure 5. It is evident from Figure 5 that K^M_H decreases systematically with increase in D^m_i for both monovalent and divalent ions. The change in selectivity coefficient of divalent ions seems to be more rapid as a function of D^m_i than that for monovalent ion. This can be qualitatively understood from the fact that absorption of a particular counterion in a membrane is related to the electrostatic interactions between fixed charge groups in the membrane and the diffusing counterions. Because of the absence of cross-linking, cations in the Nafion membrane can practically retain their hydration characteristics. Thus, the selectivity sequence of the ions having the same charge follows the sequence of decreasing radii of the hydrated ions.[7] The self-diffusion coefficients of the counterions, on the other hand, represent the mobility of ions and are governed by the free-volume fraction of the membrane. For Nafion, the free-volume fraction is decided by the water-

TABLE 3: Graphical Analysis of Self-Diffusion Coefficient Data of Monovalent and Divalent Cations in the Nafion-117 Membrane Using Eq 7

| | | b | | g | |
types of ions	correln coeff (r^2)	present work	ref 17[a]	present work	ref 17[a]
monovalent ions (Ag⁺, Na⁺, K⁺, Cs⁺)	0.99	0.73	0.77, 1.06[b]	0.62	0.23, 0.38[b]
divalent ions (Zn²⁺, Ca²⁺, Sr²⁺, Ba²⁺)	0.97	1.3		0.80	

[a] D^m_i values were obtained by ion-exchange measurements. *[b]* Expanded form of Nafion membrane.
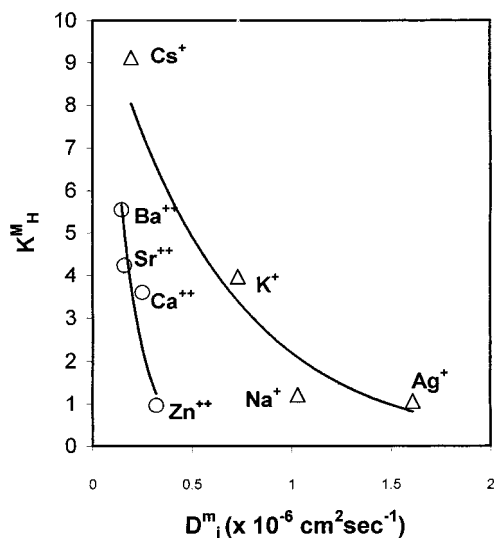
Figure 5. Selectivity coefficient[7] as a function of self-diffusion coefficient of monovalent and divalent ions in the Nafion-117 membrane.

uptake capacity of the membrane in the different ionic forms and practically follows the sequence of the degree of hydration of ions of the particular valence. Hence the mobility of the ions follows the sequence of the water-uptake capacities in different ionic forms of the membrane as reflected in the values of their self-diffusion coefficients ($Ag^+ > Na^+ > K^+ > Cs^+$; $Zn^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$). In other words, higher order morphology of Nafion governing free-volume structure is essentially dictated by the ion itself, so the parameter that enhances the selectivity of a particular ion (lower water content) essentially reduces the mobility due to reduction in the free-volume fraction. Hence, the selectivity coefficient follows the reverse trend of the self-diffusion coefficient of a particular valence ion.

Conclusion

The self-diffusion coefficients of several monovalent and divalent cations were measured in the Nafion-117 membrane using a radiotracer diffusion method based on the absorption/desorption of radiotracer ions. The self-diffusion coefficient data were found to be in good agreement with available literature values. The self-diffusion coefficients of several cations (Ag^+, K^+, Zn^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) in the Nafion-117 membrane are reported for the first time. The spread in values of the self-diffusion coefficients of monovalent ions was found to be much larger than that of divalent ions. The polymer volume fractions in different ionic forms of Nafion were also measured and used for the interpretation of the self-diffusion data based on the free-volume theory. The plot of ln $D^m_i/D°_i$ values vs polymer volume fraction function was found to follow two different straight lines corresponding to monovalent and divalent cations, indicating different membrane morphologies for them. The effect of water content on selectivity coefficients of the ions was found to be opposite that of self-diffusion coefficients in the Nafion membrane.

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