

Self-diffusion coefficient of water in Nafion-117 membrane with different monovalent counterions: a radiotracer study

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Abstract

The self-diffusion coefficient of water in Nafion-117 membrane in different cationic forms was measured by the transient radiotracer method, which is based on an analytical solution of Fick's second law. The self-diffusion coefficient of water in the membrane was obtained from the analysis of time-dependent isotopic-exchange rates of tritium tagged water between sample of Nafion-117 membrane and equilibrating water. This transient method does not require the knowledge of partition coefficient of water, which is an essential parameter in the radiotracer permeation method. In present work, self-diffusion coefficients of water in the Nafion-117 membrane with H⁺, Li⁺, Ag⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ monovalent counterions were obtained. The values of logarithm of self-diffusion coefficients were found to vary linearly as a function of polymer volume fraction except for membrane sample with H⁺ counterions. The self-diffusion coefficient of water in Nafion-117 membrane with H⁺ counterions was significantly different from the trend observed in the variation of self-diffusion coefficient of water as a function of polymer volume fraction in the membrane with other monovalent counterions. This observation seems to suggest that the physical structure of Nafion-117 membrane in H⁺ form may be quite different from the Nafion-117 membrane with other monovalent counterions. The high self-diffusion coefficient of water (1.67×10^{-6} cm²/s) in Nafion-117 membrane with Cs⁺ counterions indicates that the ionic clusters in Nafion-117 membrane are well connected even at low water content (8.2 wt.%) in the membrane.

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1. Introduction

Poly(perfluorosulphonic) acid ionomer is extensively used as a membrane (Nafion) in numerous applications like polymer electrolyte fuel cell, Donnan- and electro-dialysis-based applications, and membrane-based chemical sensors [1]. According to the cluster-channel network model of the structure of water-swollen Nafion membrane, the transport of ions/species through the membrane is restricted by narrow channels (links) between water-swollen ionic clusters [2]. However, it has been suggested that the water-swollen ionic cluster may not be spherical in shape and there may be

a local intrusion of fluorocarbon phase in hydrated ionic clusters [3]. A three phases sub-microstructure model of Nafion membrane, consisting of fluorocarbon crystallites, ionic hydrophilic clusters and an amorphous hydrophobic region (with lower ionic and water content) has been proposed by Yeager and Steck [4] and Pineri et al. [5]. The atomic force microscopic studies of hydrated Nafion membrane support the cluster model with a range of cluster size from 5 to 30 nm depending on the water content [6].

The size of ionic clusters in Nafion membrane varies due to change in water content depending on the counterions and pretreatment conditions [7–9]. In order to understand the water–polymer and ionic interactions in the Nafion membrane, the various cationic forms of Nafion membrane with water have been studied by infrared spectroscopy

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[3,10], small angle X-ray scattering [11], differential scanning calorimetry (DSC) [12] and magnetic resonance methods [13–14]. The small angle neutron scattering studies on Nafion membrane with different counterions have indicated that the change of counterions and its concentration lead to a reversible local reorganization of the ionic clusters [15]. The change in sub-microstructure of the Nafion on different degree of hydration can alter the mobility of counterions/water in the membrane significantly [9,16–17]. This is because of the fact that water in the Nafion membrane not only governs its sub-microstructure, but also provides a medium where transport of the certain species (or water itself) takes place. Zelsmann et al. [18] have studied the self-diffusion coefficients of water in Nafion membrane using far infrared spectroscopy. This study indicates that the change in water diffusion is not due to the plasticization of ionomer chains by water in Nafion membrane, but to a change in microstructure depending on the membrane water content. Therefore, the information about the diffusivity of water is required for understanding the dependence of elementary mobility of species in Nafion membrane with different counterions.

The most common methods for measurements of the self-diffusion coefficients of water in polymer matrix are pulsed-field-gradient nuclear magnetic resonance spectroscopy (PFG-NMR) [14,19–22], radiotracer permeation of tritium tagged water across the membrane [4,23–25] and change in weight of the membrane on sorption/desorption of water from the vapor phase [26,27]. The change in weight of membrane is useful for obtaining apparent diffusion coefficients for water from vapor sorption kinetics. However, the water sorption kinetic and equilibrium data of H^+ , Li^+ and Cs^+ forms of the Nafion membrane at different water contents seem to suggest that the onset of water-cluster formation depends on the water content and counterions in the membrane [27]. Thus, the method involving change in weight of membrane on water sorption/desorption may not represent the true self-diffusion coefficient of water in Nafion-117 membrane with different counterions at normal water content. The self-diffusion of water can be obtained by the radiotracer permeation method [4]. The PFG-NMR has been extensively used for measuring the self-diffusion coefficient of water and methanol in Nafion-117 membrane in acid form under different physical conditions prevailing in polymer electrolyte fuel cell [20–22].

In present work, we have used a transient radiotracer method for measuring the self-diffusion coefficient of water in Nafion-117 membrane with different counterions. This method is based on the measurement of rate of desorption of tritium tagged water from Nafion membrane into equilibrating water by monitoring the radioactivity of equilibrating water as a function of time [9]. The rates of desorption of tritium tagged water from Nafion membrane with H^+ , Li^+ , Ag^+ , Na^+ , K^+ , Rb^+ and Cs^+ monovalent counterions were analyzed using an analytical solution of Fick's second law to obtain the self-diffusion coefficients of water in Nafion membranes with different counterions. An attempt has been made

to analyze the variation of self-diffusion coefficient of water in Nafion membrane in terms of free volume theory [28]. The results of these analyses are presented in this paper.

2. Experimental

2.1. Material and apparatus

AR grade chemicals ($LiCl$, $NaCl$, KCl , $RbCl$, $CsCl$ and $AgNO_3$), deionized water (18 $M\Omega/cm$, Gradient A-10 model, Milli-Q USA) and AR grade HCl (Merck, Germany) were used in the present study. Nafion-117 ion-exchange membrane (Aldrich) with an equivalent weight of 1100, and thickness of 178 μm was used. As described in our earlier paper [9], the samples of Nafion-117 were treated to remove organic impurities, conditioned with 0.5 mol/L HCl and 0.5 mol/L $NaOH$, equilibrated with 0.5 mol/L of relevant salt solution for 18–24 h at room temperature (27 °C) for converting the membrane into the appropriate ionic form.

2.2. Membrane characterization

The water uptake capacity of the membrane, defined as the amount of water absorbed per unit dry weight of the membrane, was obtained from the difference in weight of the wet membrane and dried membrane sample. 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 the other ionic forms. 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 volume and thickness of the wet samples were determined using a pycnometer as described elsewhere [9]. The polymer volume fraction (V_p) of the membrane samples in different ionic forms was calculated from the volume of the water in the membrane and the volume of the wet membrane sample.

2.3. Measurements of isotopic-exchange rates

The transient experiment was carried out using $2.0 \times 2.0 cm^2$ pieces of Nafion-117 membrane in the appropriate ionic form. The membrane samples were equilibrated with water, containing 3 mCi radioactivity of tritiated water (HTO) for 4 h at 27 °C. The HTO-loaded Nafion membrane sample with relevant counterions was immersed in a 30 mL of well-stirred deionized water (without HTO radiotracer) at 27 °C. The amount of radiotracer HTO diffusing out of the membrane sample was monitored by taking out 50 μL samples from the equilibrating deionized water at regular time intervals, and monitoring the radioactivity of HTO

by β -scintillation counting. The β -radioactivity of tritiated water (HTO) was measured by spiking the sample in a vial, containing 5 mL of scintillation cocktail-w (2,5-diphenyl oxazole = 10 g, 1,4-di-2-(5-phenyloxazolyl) benzene = 0.25 g, and naphthalene = 100 g in 1000 mL 1,4-dioxane solvent), and counting the samples with a Packard Liquid Scintillation Analyser (model TRI-CARB 2100 TR).

2.4. Evaluation of self-diffusion coefficients of water

The experimentally measured rates of isotopic-exchange ($\text{HTO}_m \rightleftharpoons \text{H}_2\text{O}_{\text{sol}}$) were analyzed to obtain the self-diffusion coefficient of water in the membrane with different counterions. The detail procedure used for analyzing the time-dependent isotopic-exchange profiles to obtain the self-diffusion coefficients is described in our earlier paper [9]. The amounts of HTO diffusing out of the membrane sample as a function of time is given by an analytical solution of Fick's second law:

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

where $n(t_k)$ and n^* are the amounts of radiotracer (HTO) in the equilibrating solution at fixed time t_k and t_∞ , respectively, D the self-diffusion coefficient of the water in the membrane and L the thickness of the membrane. The value of D was obtained by a non-linear least-square fit of Eq. (1) with n^* and D as the free parameters. Only first three terms in Eq. (1) was used for fitting.

3. Results and discussion

The measurement of the self-diffusion coefficient of water in the Nafion-117 membrane by radiotracer (HTO) was based on the assumption that the isotopic-exchange occurs via displacement of HTO by H_2O in water-swollen membrane in contact with equilibrating water. This means that tritium transfer from a water molecule to another in pure water is negligible. The validity of this assumption is based on the fact that the values of the self-diffusion coefficients of water traced by three isotopes D, T and ^{18}O were found to be very close to each other [29]. Thus, it is expected that there would be exchange of radioactivity tagged water molecules (HTO) between water in the Nafion-117 membrane and equilibrating water.

In the case of Nafion membrane with H^+ counterions, there is a possibility of exchange of H^+ and T^+ between the sulfonic acid groups and the HTO inside the membrane [30]. However, the amount of H^+ in the Nafion-117 is small compared to the amount of water in the membrane. Hence, the possibility of existence of tritium in T^+ form in the membrane would be insignificant. Also, H^+ ion concentration in

the equilibrating water is negligible. Therefore, no direct exchange of H^+ ions in the membrane with the equilibrating water is possible. Thus, the transport of tritium via Grotthuss mechanism can be ignored, and the observed self-diffusion coefficient in ($\text{HTO}_m \rightleftharpoons \text{H}_2\text{O}_{\text{sol}}$) exchange would correspond to H_2O in the H^+ form of membrane.

There are three possible routes to measure the self-diffusion coefficient of water in the membrane using radiotracer HTO. These are: (i) time-lag method, (ii) permeation method and (iii) transient method. The self-diffusion coefficient of water in Nafion membrane was measured earlier using the methods based on time-lag [31] and permeation [4]. The measurement of self-diffusion coefficient by time-lag method is difficult as hold-up or time-lag in the steady-state permeation of HTO across Nafion-117 membrane is very short. Thus, the evaluation of self-diffusion coefficient from this method may not be very accurate. The permeation method directly yields the permeability coefficient of water, and the self-diffusion coefficient of water in the membrane can be obtained if water partition coefficient between membrane and equilibrating water is known [24,28].

The transient method proposed in the present work directly yields the self-diffusion coefficient of water in membrane from the analysis of time-dependent isotopic-exchange profile using an analytical solution of Fick's second law, and require only knowledge of thickness of the membrane as shown in Eq. (1) [9]. This method is based on the assumptions that: (i) the membrane controls the diffusion process, (ii) the self-diffusion coefficient of water 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 HTO at both boundaries of the membrane sample are same as in the bulk solution. In order to test this requirement, the HTO-loaded Nafion-117 membrane sample with counterion Na^+ was equilibrated with stirred deionized water. The equilibrating water was stirred by using the magnetic stirrer with rotation speed ranging from 100 to 900 rpm. The profile of ($\text{HTO}_m \rightleftharpoons \text{H}_2\text{O}_{\text{sol}}$) isotopic-exchange, thus obtained, is shown in Fig. 1. It is clearly seen that there is no significant effect of stirring speed on the isotopic-exchange rates. However, the isotopic-exchange profile was quite off when equilibrating water was not stirred. This suggests that the membrane control the diffusion of HTO from membrane to the well-stirred equilibrating water.

The fractional attainment of equilibrium $F(t_k)$ as a function of time was obtained from the ratio of radioactivity of HTO ($n(t_k)$) in equilibrating water at time t_k to radioactivity of HTO (n^*) in the equilibrating water at time t_∞ , $F(t_k) = n(t_k)/n^*$. The experimental value of n^* was obtained from the least square fitting of the variation of $n(t_k)$ in equilibrating water as a function of time t . The variation of the $F(t_k)$ as a function of square root of equilibration time $t^{1/2}$ for the membrane samples with the different counterions are shown in Figs. 2 and 3. It is evident from these figures that the $F(t_k)$ varies linearly with $t^{1/2}$ during initial stages of the exchange process, which is a characteristics of the Fickian

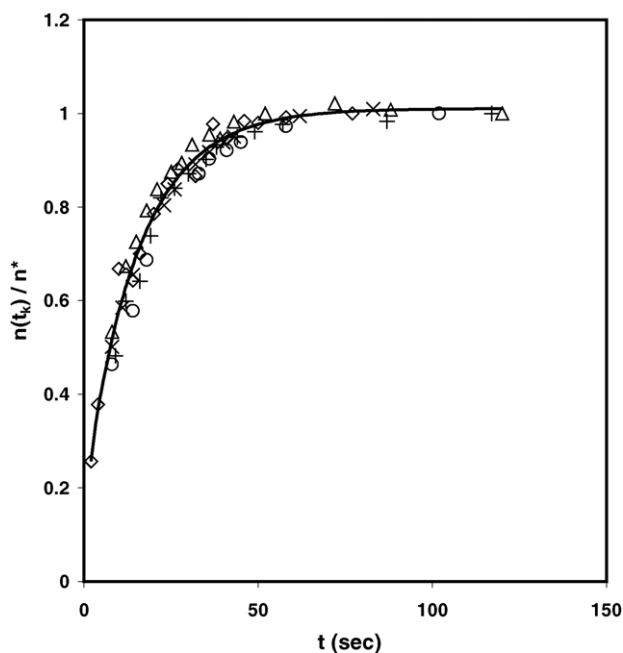


Fig. 1. Fractional attainment of isotopic-exchange equilibrium ($n(t_k)/n^*$) with time in Nafion-117 membrane with Na^+ counterions. The symbols represent the stirring speed of equilibrating deionized water at 100 (Δ), 200 (\diamond), 400 (+), 600 (\times) and 900 (\circ) rpm.

diffusion. The rates of ($\text{HTO}_m \rightleftharpoons \text{H}_2\text{O}_{\text{sol}}$) exchange in the Nafion-117 membrane with different monovalent counterions were analyzed using Eq. (1) as described in Section 2.4. The solid lines in Figs. 2 and 3 represent the least square fits of experimental data in terms of Eq. (1). The self-diffusion coefficients of water, obtained from the analyses of isotopic-exchange profiles, are given in Table 1. The literature reported

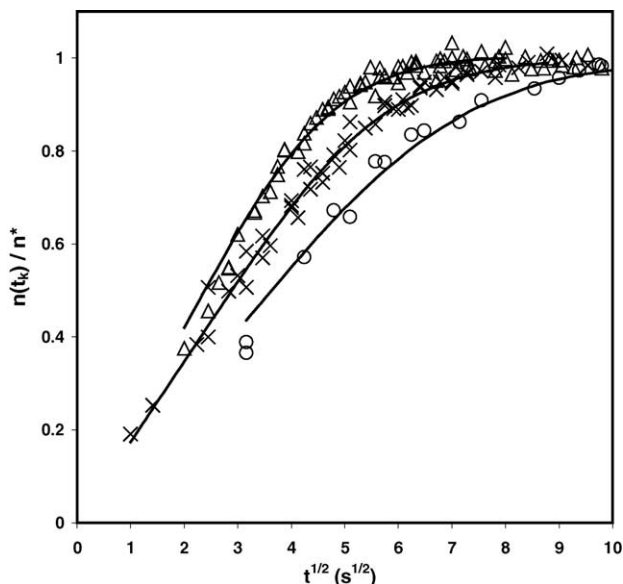


Fig. 2. Fractional attainment of isotopic-exchange equilibrium as a function of square root of time. Symbols (Δ), (\times) and (\circ) represent the Nafion-117 membrane in H^+ , K^+ and Cs^+ forms, respectively. The solid lines are fitted data used to obtain self-diffusion coefficients of water from Eq. (1).

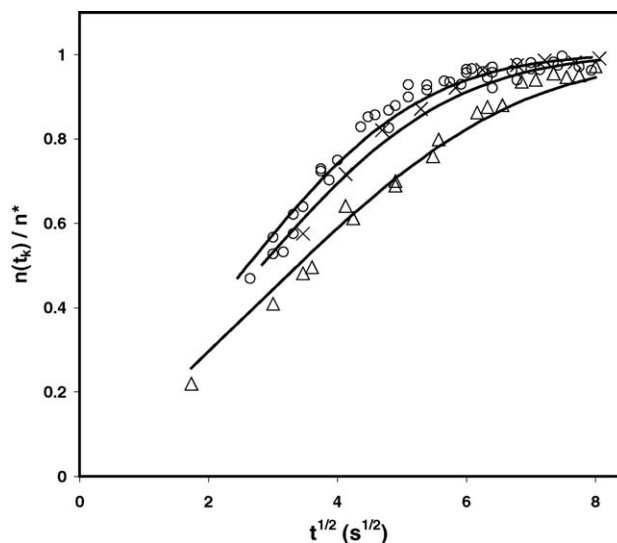


Fig. 3. Fractional attainment of isotopic-exchange equilibrium between the Nafion-117 membrane and equilibrating water. Symbols (\circ), (Δ) and (\times) represent the Nafion-117 membrane in Li^+ , Rb^+ and Ag^+ forms, respectively. The solid lines are fitted data used to obtain self-diffusion coefficients of water from Eq. (1).

values of the self-diffusion coefficient of water in Nafion-117 membrane are also given in Table 1 [4,14,17,31,32]. It is seen from Table 1 that the values of self-diffusion coefficient of water obtained in the present work with Na^+ , K^+ and Cs^+ counterions are in good agreement with the values of self-diffusion coefficient of water obtained by the permeation [4] and time-lag [31] methods using HTO radiotracer. The self-diffusion coefficients of water with other monovalent counterions are obtained for the first time by using a transient radiotracer method. The values of self-diffusion coefficient of water obtained by Okada et al. [17] in the Nafion-117 membrane with Li^+ and Rb^+ counterions are in close agreement with the values obtained in the present work, while the values for other counterions are slightly on the higher side. Okada et al. have measured water permeability under pressure gradient to obtain the values of self-diffusion coefficient

Table 1
Self-diffusion coefficients of water in Nafion-117 membrane with different counterions

Ion	Water uptake (wt.%)	V_p	$D(\text{H}_2\text{O}) (\times 10^{-6} \text{ cm}^2/\text{s})$	
			Present work	Literature
H^+	23.4	0.68	3.87 ± 0.20	$1.6^a, 3.31^b, 5.56^c$
Li^+	21.1	0.69	3.17 ± 0.11	$2.45^b, 2.83^d$
Ag^+	18.8	0.72	2.91 ± 0.14	–
Na^+	17.2	0.75	2.85 ± 0.20	$2.4^a, 2.65^e, 2.3^b, 3.6^d$
K^+	12.3	0.80	2.25 ± 0.07	$2.15^e, 1.2^b, 3.4^d$
Rb^+	9.3	0.83	1.89 ± 0.06	2.2^d
Cs^+	8.2	0.85	1.67 ± 0.06	$1.32^e, 0.74^b, 2.1^d$

^a Time-lag method [31].

^b PFG-NMR [14].

^c PFG-NMR [32].

^d Water permeability under pressure gradient [17].

^e Permeation method [4].

of water in Nafion-117 with different monovalent counterions. This method is sensitive to applied pressure and does not directly yield the value of self-diffusion coefficient of water. Also, there is a possibility that the membrane physical structure may be changed under applied pressure. As seen from Table 1, the PFG-NMR data on self-diffusion coefficient of water in Nafion-117 membrane reported by Volkov and Timashev [14] are lower than that reported in the present work and in literature [4,17,31]. The self-diffusion coefficient of water in H⁺ form of Nafion-117 membrane measured by another group [32] using PFG-NMR is also found to be higher than that reported by Volkov and Timashev [14]. Thus, the lower values of self-diffusion coefficients of water reported by Volkov and Timashev could not be explained.

The self-diffusion coefficients of water in Nafion-117 membrane are considerably less than the self-diffusion coefficient of pure water, $D(\text{H}_2\text{O}) = 2.5 \times 10^{-5} \text{ cm}^2/\text{s}$ at 25 °C [29,31]. In our previous study, it was observed that the self-diffusion coefficient of the counterions, D , could be related to the polymer volume fraction of Nafion-117 membrane using the expression [9]:

$$D = D^0 \exp \left[-b \left(\frac{V_p}{(1 - V_p)} \right) \right] \quad (2)$$

where D^0 is the aqueous diffusion coefficient of the species, V_p the volume fraction of polymer in the water-swollen membrane and b an empirical parameter. Eq. (2) is based on the free volume theory of Yasuda et al. [28]. Since water uptake in Nafion-117 membrane depends on the hydration characteristics of counterions, the V_p of the membrane also changes depending upon counterions in the membrane (Table 1). Fig. 4 shows the plot of logarithm of self-diffusion coefficients of water obtained in the membrane samples with different counterions as a function of $(V_p/(1 - V_p))$. The values obtained by PFG-NMR [14] and radiotracer permeation method [4] are also shown in Fig. 4. It is seen from Fig. 4 that the self-diffusion coefficients of water in Nafion membrane vary linearly with $(V_p/(1 - V_p))$ except for H⁺ counterions. The systematic variation of the self-diffusion coefficients of water in Nafion-117 membrane as a function of polymer volume fraction $(V_p/(1 - V_p))$ was also observed by Yeager and Steck [4]. The self-diffusion coefficients of water obtained by Okada et al. [17] were not plotted, as these values do not show any systematic trend with the polymer volume fraction.

In accordance with cluster network model of the physical structure of Nafion-117 membrane [2], the systematic decrease of self-diffusion coefficients of water as a function of the polymer volume fraction seems to suggest that the dimensions of channels connecting the water-swollen ionic clusters decreases systematically for membrane with different monovalent counterions. This is because of the fact that water contents also vary depending upon the hydration characteristics of counterions in the Nafion membrane. However, the decrease in self-diffusion coefficient of monovalent counterions in the Nafion-117 membrane is more rapid as

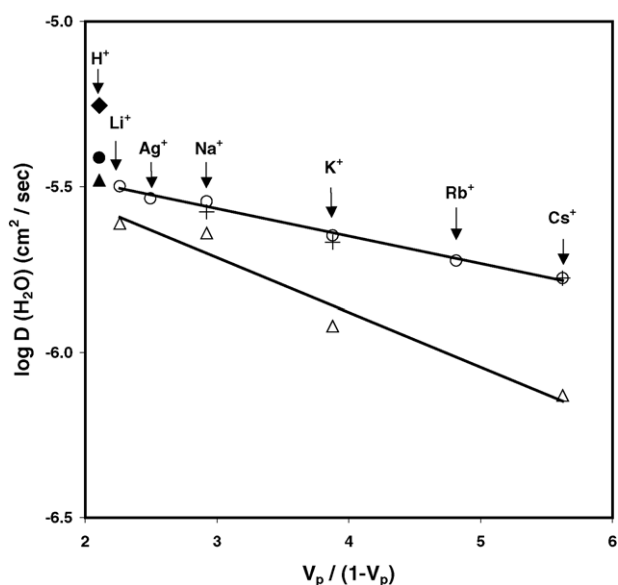


Fig. 4. Variation of logarithm of self-diffusion coefficients of water as a function of polymer volume fraction. Each point represents Nafion-117 membrane with different monovalent counterions. The symbols (○), (+), (Δ) and (◇) represent the self-diffusion coefficients data of water from this work, radiotracer permeability measurement [4], PFG-NMR [14] and PFG-NMR [32], respectively.

a function of polymer volume fraction than that in the self-diffusion coefficient of water in the corresponding cationic form [9]. For example, the self-diffusion coefficient of Cs⁺ ($2.0 \times 10^{-7} \text{ cm}^2/\text{s}$) is eight times lower than that of Ag⁺ ($1.6 \times 10^{-6} \text{ cm}^2/\text{s}$) [9]. It is seen from Table 1 that the water self-diffusion coefficient in Cs⁺ form is only two times lower than that in the membrane in Ag⁺ form. As water self-diffusion coefficient represents the extent of tortuosity factor, the steeper decrease in the self-diffusion coefficients of ions as a function of polymer volume fraction in the membrane may be attributed to the increase in electrostatic interactions on increasing the polymer volume fraction. Thus, even with 8 % water content in Cs⁺ form of Nafion-117 membrane, the water has reasonably good mobility but the narrow connecting channels considerably retard the mobility of Cs⁺ ion.

The considerably higher self-diffusion coefficient of water in the H⁺ form of Nafion-117 membrane than the observed trend with $(V_p/(1 - V_p))$ for other monovalent counterions may be related to the change in physical structure of the membrane associated with the high water content in H⁺ form of membrane. This physical change in H⁺ form of the membrane may be due to shortening of connecting channels between the water-swollen ionic clusters or overlap of some of the highly water-swollen ionic clusters. In our work, the kinetics of forward ($\text{H}_{(m)}^+ \rightleftharpoons \text{M}_{(s)}^{n+}$) and reverse ($\text{M}_{(m)}^+ \rightleftharpoons \text{H}_{(s)}^{n+}$) exchanges of metal ions (Cs⁺, Cu²⁺ and Eu³⁺) in Nafion-117 membrane were studied [33]. The Nernst-Planck theory was used to predict the kinetics of these exchanges. The theory was found to be reasonably accurate for predicting 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^+ , Cu^{2+} and Eu^{3+} with H^+ ions in the Nafion-117 membrane were found to be independent of the metal ions. Thus, it appears that Nafion-117 membrane with H^+ counterions has different behavior than same membrane with other counterions. The study of water self-diffusion coefficient in Nafion-117 membrane with multivalent counterions and expanded form may clarify the role of counterions and water contents on physical structure of the Nafion-117 membrane.

4. Conclusions

The self-diffusion coefficients of water in Nafion-117 membrane with H^+ , Li^+ , Ag^+ , Na^+ , K^+ , Rb^+ and Cs^+ monovalent counterions were measured by transient method using HTO radiotracer. This method is based on an analytical solution of Fick's second law and directly yields the value of self-diffusion coefficient of water from analyses of isotopic-exchange rates. This transient method is simple, rapid and fairly accurate for the measurement of self-diffusion coefficient of water in the membrane as indicated by the comparison of self-diffusion coefficients values reported by using radiotracer (HTO) permeation method and time-lag method.

The values of D (H_2O) obtained in the present work in Nafion-117 membrane was found to vary linearly as a function of polymer volume fraction, except for membrane sample in H^+ form. This seems to indicate that: (i) ionic clusters are well connected even in the membrane sample with low water content (Cs^+ form of membrane), (ii) the physical structure of membrane in H^+ form may be quite different than that in membrane with other monovalent counterions.

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