# Self-Diffusion of Ions in Nafion-117 Membrane Having Mixed Ionic Composition

Sanhita Chaudhury, Chhavi Agarwal, A. K. Pandey, and A. Goswami*

Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

ABSTRACT: The self-diffusion coefficients (SDCs) of Na^+, Cs^+, and Ba^{2+} have been determined in Nafion-117 membrane having mixed cationic compositions. Membranes with different proportions of Na^+-Cs^+, Cs^+-Ba^{2+}, Na^+-Ba^{2+}, and Ag^+-Ba^{2+} cations have been prepared by equilibrating with solutions containing different ratios of these cations. The SDCs of the cations (D_{Na}, D_{Cs}, D_{Ba}) and the ionic compositions of the membrane have been determined using a radiotracer method. For the Na–Cs and Cs–Ba systems, the SDCs of the cations have been found to be independent of the ionic compositions of the membrane. In the case of the Na–Ba system, D_{Na} does not change with ionic composition, while D_{Ba} has been found to be strongly dependent on the ionic composition of the membrane and decreases continuously with increasing Na^+ content in the membrane. Similar results have also been obtained for D_{Ba} in the case of the Ag–Ba system. The specific conductivities (κ_{imp}) of the membrane in mixed cationic forms have also been obtained from ac impedance measurement and compared with that (κ_{cal}) calculated from the SDC data. For the Na–Ba system, the increment of κ_{imp} with increase in the Na^+ content of the membrane has been found to be parabolic, whereas for the Na–Cs system the increment is linear. The reason behind the different behaviors for different types of ionic systems has been qualitatively explained based on different transport pathways of the cations in the membrane.
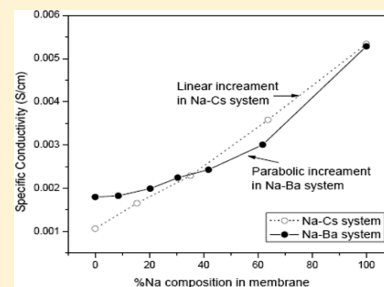
■ INTRODUCTION

Ion exchange membranes can act as a separator between two electrolyte solutions as they allow counterions to pass through while co-ions are excluded from the membrane. This property is utilized in ion exchange based separation processes such as Donnan dialysis and electrodialysis.[1] The industrial applications of ion exchange membranes include their uses as separators in the chlor-alkali industry,[2] in battery cells, and in pervaporation to dehydrate organic solvents.[3] The transport characteristics of a diffusing species across the membrane governs its permeability in the membrane.[4,5] The permeability coefficient of a species depends on its self-diffusion coefficient (SDC) in the membrane and partition coefficient between the solution and the membrane phase. The ratio of permeability coefficients of two diffusing species across the membrane determines their separation factor. Understanding the mechanism of diffusion of ions in the ion exchange membranes has been the subject of extensive research for designing membranes for specific applications. Since there is no external gradient involved in the measurement of the SDC of the ions, intrinsic diffusional-transport properties of the membrane can be understood from the study of SDCs of different valence counterions.

Nafion-117 is a poly(perfluorosulfonic acid) ion exchange membrane having a polytetrafluoroethylene (PTFE) backbone with pendant side chains containing $-SO_3H$ groups. In general, Nafion-117 membrane is known to have different microstructures and water contents depending upon the counterions and pretreatment conditions.[6,7] The SDCs of water and a variety of counterions have been measured in this membrane. However, most of the SDC measurements of the counterions have been carried out involving either isotopic exchange or counterion exchange.[8]

The SDCs thus obtained represent the diffusion mobilities of the single counterion or exchanging counterions.[9]

According to the cluster channel model of Hsu and Gierke, the ions and water in the membrane form spherical clusters connected by narrow channels[10] and the ions move through these water channels. As suggested by Yeager and Steck,[11] the diffusional properties of Nafion cannot be explained based only on the free volume theory, as there are distinct regions in which cations may exist depending upon its charged density and ionic size. Robertson and Yeager[12] showed using a fluorescence probe that Cs^+ is located on an aqueous side of the interfacial region that separates the fluorocarbon phase from the ion and water-rich phase, while other hydrated alkali metal ions prefer the water-rich phase of the membrane. The lower diffusion coefficient and higher selectivity of Cs^+ over other alkali metal cations for Nafion-117 has been attributed to this difference in the average location and the transport pathways. Pintauro et al.[13,14] studied the divalent/monovalent cation uptake selectivity in Nafion-117 and concluded that a fraction of the divalent cations exist as ion pairs with the fixed charges of the membrane backbone and this fraction varies with the extent of monovalent cation present. In our earlier studies, it was shown that the SDCs of the divalent and monovalent cations varied linearly with free volume fraction with different slopes,[15] indicating a higher interaction of the divalent cation with the fixed charges of the backbone. It can be concluded from these studies that hydrated monovalent cations such as H^+, Li^+, and

Table 1. Compositions of Equilibrating Solutions, Ionic Compositions, Water Exchange Site Mole Ratios (λ), and SDCs of Na$^+$ and Ba^{2+} Ions along with the Calculated (κ_{cal}) and Measured (κ_{imp}) Specific Conductivities in the Na−Ba System

Na$^+$:Ba^{2+} in equilibrating soln	λ ($n_{H_2O}/n_{SO_3^-}$)	ionic composition in membrane (%)		SDC ($\times 10^6$ cm^2 s^{-1})		sp conductivity ($\times 10^3$ S cm^{-1})	
		Na$^+$	Ba^{2+}	Na$^+$	Ba^{2+}	κ_{cal}	κ_{imp}
0:1	9.47	−	100	−	0.15	1.5	4.3
1:1	9.67	8.6	91.4	0.94	0.125	1.9	4.4
4:1	9.77	20.3	79.7	0.96	0.083	2.3	4.8
8:1	10.02	30.5	69.5	0.93	0.063	2.7	5.4
14:1	10.47	41.8	58.2	0.94	0.057	3.1	5.9
29:1	10.65	61.8	38.2	0.96	0.045	3.8	7.3
1:0	10.51	100	−	1.03	−	5.3	12.8

Na$^+$ would prefer to transport through the central region of the water channels, while for divalent ions a significant fraction may remain as a contact ion pair. For Cs$^+$, on the other hand, there is a third region of transport. Thus, the SDCs of cations may be modified by the ionic composition of the membrane due to their different locations and strengths of interaction in the membrane.

It is not clearly known how the self-diffusion mobility of the counterion would be modified in the presence of other counterions. Okada et al.[16] determined ionic mobility in Nafion-117 in mixed ionic composition of H$^+$ ion and alkali metal cations. They did not observe any significant dependence of counterion mobilities on the ionic composition of the membrane. Pourcelly et al.[17] observed from radiotracer studies that SDCs of Na$^+$ and Ca^{2+} were independent of ionic composition of the membrane. Karavanova and Yaroslavtsev[18] have also studied the diffusion parameters of mixed monovalent cation membranes and evaluated diffusion coefficients from ionic conductance. They have shown a parabolic variation of ionic conductance with mole fraction of KCl in the membrane MK-40.

In the present work, we report the measurement of SDCs of X and Y ions (D_X/D_Y) in a bi-ionic form of Nafion-117 membrane (X−Y system) loaded with different proportions of X and Y ions using the corresponding radiotracers. The systems studied are Na−Cs, Na−Ba, Cs−Ba, and Ag−Ba. The proportions of the cations in the membrane samples were varied by equilibrating the membrane with solutions containing different proportions of the corresponding salt solution. The ion exchange isotherms for the Na−Ba and Na−Cs systems in Nafion-117 membrane have also been generated. Further, ac impedance measurement studies using a frequency response analyzer system have been done with Nafion-117 having different mixed cationic compositions for the Na−Cs and Na−Ba systems. The specific conductivities obtained from the impedance measurements were compared with those calculated from the corresponding SDCs.

■ EXPERIMENTAL SECTION

Reagents and Chemicals. The metal salts CsCl, BaCl$_2$, and AgNO$_3$ (99.999%, ultrapure grade) were procured from Sisco Research Lab., Mumbai, India. The other reagents, such as NaCl and Ba(NO$_3$)$_2$ (99.9%, Analytical Reagent grade), were received from SD Fine Chem. Ltd., India. Deionized water (18 MΩ/cm, Gradient A-10 model, Milli-Q USA) and analytical grade HCl and HNO$_3$ (Merck, Germany) were used in the present study. Radiotracers ^{22}Na, ^{133}Ba, and ^{137}Cs used in the present study were obtained from Board of Radiation and Isotope Technology, Mumbai, India. Nafion-117 (purchased from DuPont) ion exchange membrane with an equivalent weight of 1100 g

and a thickness of 178 μm (fully dried condition) was used for the present set of experiments. The membrane samples were preconditioned to remove organic impurities following the method described elsewhere.[15] The samples were refluxed in 5 mol L^{-1} HNO$_3$ for 3 h. These were then treated with 0.5 mol L^{-1} NaOH and 0.5 mol L^{-1} HCl separately. The 0.1 N salt solutions were prepared by dissolving a known amount of the respective salt in 250 mL of deionized water.

Measurement of Self-Diffusion Coefficients and Ion Exchange Isotherm. For the Na−Ba system, five different equilibrating solutions containing different proportions (as shown in Table 1) of 0.1 N NaCl and 0.1 N BaCl$_2$ were prepared, keeping the total ionic concentration fixed at 0.1 N. For each equilibrating solution, two sets of experiments were carried out: one for the Na$^+$ ion and another for the Ba^{2+} ions. In each experiment, the conditioned membrane sample (2 cm × 2 cm) in proton form was kept in well-stirred equilibrating solution (30 mL) at 27 °C for ∼3 h. After equilibration, the membrane sample was taken out and the required (^{22}Na or ^{133}Ba) radiotracer was added to the respective solution. In order to ensure that there is no change in the ionic composition of the membrane and the external solution, the self-diffusion measurement of the respective ions (Na$^+$/Ba^{2+}) in the membrane sample was carried out with this radiolabeled equilibrating solution. The further steps involved in the measurement of SDC were the same as described in ref 15. Experiments with ^{22}Na and ^{133}Ba radiotracers were done separately since the 511 keV γ-ray of ^{22}Na could cause a significant increase in the background in the low energy γ-rays of ^{133}Ba. For the measurement of ion exchange isotherms, the total amount of radioactivity added into the equilibrating solution and the equilibrium uptake of radiotracer in the membrane were required. The amount of radiotracer in the equilibrating solution was accounted for by preparing filter paper standards following the method described elsewhere.[19] The same procedure was followed for equilibrating solutions of different ionic compositions.

For the other ionic systems (Na−Cs, Cs−Ba, and Ag−Ba), the same experimental procedure was followed to obtain the SDCs of the individual cations. It is to be mentioned that, for the Ag−Ba system, 0.1 N AgNO$_3$ and 0.1 N Ba(NO$_3$)$_2$ solutions were used to avoid precipitation of AgCl. In this system, the self-diffusion profile of only the Ba^{2+} ion was monitored. The compositions of the equilibrating solutions used for these three ionic systems are given in Tables 2, 3, and 4, respectively.

Impedance Measurement. The specific conductivities of the membrane samples in different mixed cationic compositions were obtained from electrochemical impedance measurements for the Na−Ba and Na−Cs systems. The measurements were carried out using an Autolab PGSTAT 302 voltammetric analyzer

Table 2. Compositions of Equilibrating Solutions, Ionic Compositions, Water Exchange Site Mole Ratios (λ), and SDCs of Na$^+$ and Cs$^+$ Ions along with the Calculated (κ_{cal}) and Measured (κ_{imp}) Specific Conductivities in the Na−Cs System

Na$^+$:Cs$^+$ in equilibrating soln	λ ($n_{H_2O}/n_{SO_3^-}$)	ionic composition in membrane (%)		SDC ($\times 10^6$ cm^2 s^{-1})		sp conductivity ($\times 10^3$ S cm^{-1})	
		Na$^+$	Cs$^+$	Na$^+$	Cs$^+$	κ_{cal}	κ_{imp}
0:1	5.01	−	100	−	0.19	1.1	2.5
1:1	5.37	15.4	84.6	0.93	0.192	1.8	4.0
3:1	7.54	35.1	64.9	0.90	0.188	2.5	5.5
14:1	9.18	63.7	36.3	0.92	0.184	3.9	8.7
1:0	10.51	100	−	1.03	−	5.3	12.8

Table 3. Compositions of Equilibrating Solutions, Ionic Compositions, and SDCs of Cs$^+$ and Ba^{2+} Ions in the Cs−Ba System

Cs$^+$:Ba^{2+} in equilibrating soln	ionic composition in membrane (%)		SDC ($\times 10^6$ cm^2 s^{-1})	
	Cs$^+$	Ba^{2+}	Cs$^+$	Ba^{2+}
0:1	−	100	−	0.15
1:1	46.2	53.8	0.21	0.16
4:1	70.1	29.9	0.21	0.14
1:0	100	−	0.19	−

Table 4. Compositions of Equilibrating Solutions, Ionic Compositions, and SDCs of Ba^{2+} Ions in the Ag−Ba System

Ag$^+$:Ba^{2+} in equilibrating soln	% Ag$^+$ in membrane	SDC ($\times 10^6$ cm^2 s^{-1})
0:1	0	0.154
4:1	35	0.077
8:1	41	0.059
14:1	60	0.040
29:1	71	0.029

in conjuction with the 663 VA stand multimode electrode. The FRA 2 software (developed by Eco-Chemie B.V., The Netherlands) controlled the functions of the Autolab PGSTAT 302. The conditioned Nafion-117 samples (2 cm × 2 cm) in H$^+$ form were kept for ∼3 h in different equilibrating solutions containing different proportions of NaCl and CsCl/BaCl$_2$ as given in Tables 1 and 2. After attainment of equilibrium, the membrane samples were kept in deionized water to ensure that there were no sorbed electrolytes in the membranes. Different membrane samples were used for different cationic compositions. The details of the impedance measurement are given elsewhere.[20] The thickness of the membrane before and immediately after the experiment was found to remain the same. It was assumed that there was no loss of water from the membrane during the course of the measurement. The impedance measurements were repeated thrice to verify the consistency of the data. The relative standard deviation of the specific conductivities varied from 2 to 10%.

■ CALCULATIONS

Ion Exchange Isotherm. The ion exchange isotherms for the mixed ionic systems (Na−Cs and Na−Ba) were calculated from the equilibrium uptake of radiotracer in the membrane and the amount of total radioactiy added to the equilibrating solution following the method described elsewhere.[19]

Self-Diffusion Coefficients. The SDCs of each cation for different compositions of the membrane were obtained from a fit of the experimental data with the equation obtained from the

analytical solution of Fick's second law given below.[15]

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

where n^* is the total amount of the radiotracer ions in the membrane at equilibrium ($t = \infty$), $n(t_k)$ is the amount of radiotracer at any time t_k in the membrane, D is the diffusion coefficient, and L is the thickness of the membrane in swollen condition. n^* and D were taken as free parameters, and only the first three terms in eq 1 were used for fitting.

Specific Conductivity (κ). The obtained impedance spectra were analyzed with the help of Frequency Response Analyzer software, and the resistance (R) values of the membrane samples were obtained from the intercept of the Nyquist plot with the real axis.[17,21−25] The specific conductivities (κ_{imp}, S cm^{-1}) of the membrane samples were calculated from the total resistance (R) using the following expression.

$$\kappa_{imp} = \frac{L}{RA} \tag{2}$$

where L is the membrane thickness in fully hydrated condition and A is the membrane contact area during the impedance measurement.

An attempt had been made to calculate the specific conductivities (κ_{cal}) of the membrane samples from the SDCs of the cations in the pure monocationic form of Nafion-117. For the Na−Ba system, the specific conductivities had been calculated using the equation[26]

$$\kappa_{cal} = \frac{F^2 C_4}{RT} [y_1 (D_{Na} - 2D_{Ba}) + 2D_{Ba}] \tag{3}$$

For the Na−Cs system, the following equation has been used.

$$\kappa_{cal} = \frac{F^2 C_4}{RT} [y_1 (D_{Na} - D_{Cs}) + D_{Cs}] \tag{4}$$

where

$$y_1 = \frac{C_1}{C_4} \quad \text{and} \quad C_4 = Z_1 C_1 + Z_2 C_2$$

Z_1 and Z_2 are the valences of the cations present in the membrane. F and R are the Faraday constant (C equiv^{-1}) and the ideal gas constant (J mol^{-1} K^{-1}), respectively. C_i (mol cm^{-3}) is the concentration of the ith species in the membrane.

■ RESULTS AND DISCUSSION

The isotherm shown in Figure 1 for the Na−Ba system indicates higher selectivity of the Nafion-117 membrane for Ba^{2+}
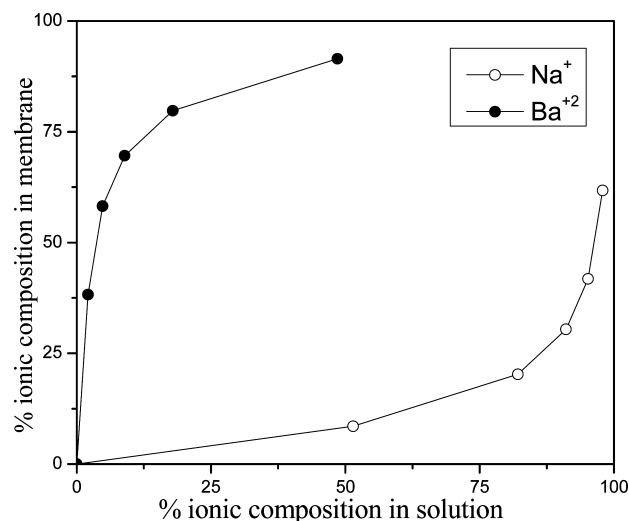

Figure 1. Ion exchange isotherm for the Na−Ba system in Nafion-117.

compared to the Na$^+$ counterion. This is also evident from the data given in Table 1. For example, 40% of the ion exchange sites in Nafion-117 membrane are occupied by Ba^{2+} when it was equilibrated with solution containing 97% Na$^+$ and 3% Ba^{2+}. For the Na−Cs system, the isotherm is in good agreement with that reported in the literature.[19]

The isotopic exchange profiles of different cations in mixed compositions of the Nafion membrane, obtained from radio-tracer measurements, are shown in Figures 2 and 3. It should be mentioned that the error bars associated with the experimental data points are the same size as the symbols. The experimental isotopic exchange rate profiles obtained for Na$^+$ and Cs$^+$ ions in the Na−Cs system are shown in parts a and b, respectively, of Figure 2. Figure 2 indicates that there is no significant change in Na$^+$/Cs$^+$ isotopic exchange profiles for membrane samples having different ionic compositions. The D_{Na} and D_{Cs} values obtained for different ionic compositions along with the

corresponding water exchange site mole ratios ($\lambda = n_{H_2O}/n_{SO_3^-}$) are given in Table 2.

The SDCs obtained for Cs$^+$ and Ba^{2+} ions in the Cs−Ba system in the Nafion membrane with different ionic compositions are given in Table 3. The data indicate that the results are similar to what has been observed in the Na−Cs system. It can be seen that for the Cs−Ba system, though there is an ∼10% increment in D_{Cs}, D_{Ba} is independent of the membrane cationic composition.

For the Na−Ba system, the self-diffusion profiles of Na$^+$ and Ba^{2+} ions are shown in parts a and b, respectively, of Figure 3. It is seen from Figure 3 that the rate of isotopic exchange for the Na$^+$ ion does not change with change in ionic composition of the membrane while that of the Ba^{2+} ion decreases significantly with increase in Na$^+$ content (Na^+_m) in the membrane. The data given in Table 1 indicate that D_{Na} is reduced by ∼7% compared to the value of 1.03×10^{-6} cm^2 s^{-1} for the pure Na$^+$ form of Nafion-117 and it is independent of the membrane composition. By contrast, D_{Ba} gradually decreases as the Na$^+$ content in the membrane increases. At 61.8% Na^+_m, the D_{Ba} is reduced by ∼70% compared to that (1.5×10^{-7} cm^2 s^{-1}) for the pure Ba^{2+} form of Nafion-117. The water exchange site mole ratios (λ) obtained for different ionic compositions in the Na−Ba system are also included in Table 1.

For the Ag−Ba system, the change in D_{Ba} with change in the membrane composition is shown in Table 4. It can be seen that, as in the case of the Na−Ba system, here also D_{Ba} decreases continuously as the amount of Ag$^+$ (Ag^+_m) increases in the membrane. The data indicate that there is an 80% reduction in D_{Ba} for 75% Ag^+_m compared with that in the pure Ba^{2+} form of the membrane.

The observed dependence of the SDCs of the different cations on the membrane cationic composition can be qualitatively explained based on the locations of the cations in different regions of the membrane and their interactions with the backbone and the fixed ionic sites. Thus Cs$^+$ with low charge density follows a transport pathway through the aqueous side of the interfacial region, while Na$^+$ moves mainly through the water-rich[11,12] microphase of the membrane. Hence the ions follow a mutually independent path and do not influence the SDCs of each other. The slight decrease (∼10%) in D_{Na} with increase in Cs$^+$ content in the membrane is due to reduction
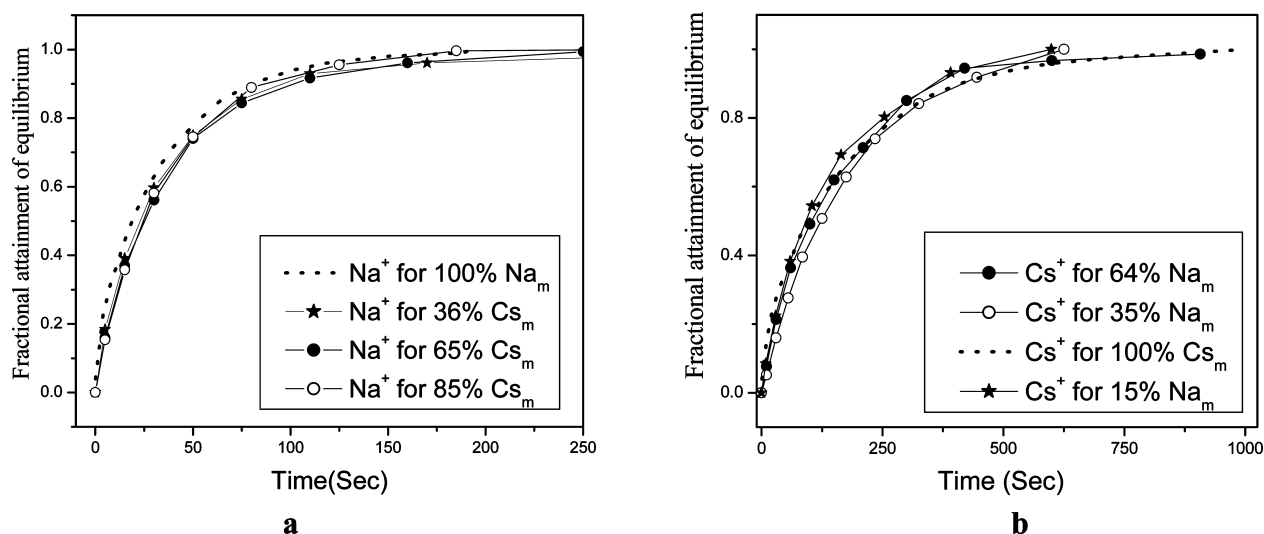

a

b

Figure 2. Diffusion kinetics of (a) Na$^+$ and (b) Cs$^+$ for different ionic compositions of the membrane in the Na−Cs system.
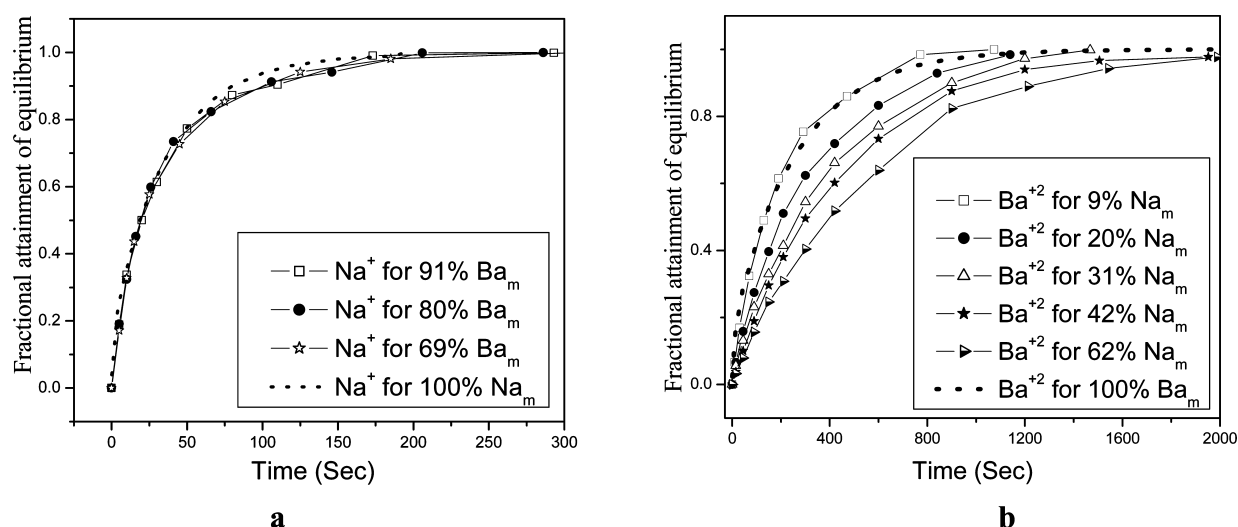
Figure 3. Diffusion kinetics of (a) Na$^+$ and (b) Ba^{2+} for different ionic compositions of the membrane in the Na−Ba system.

in the net water content of the membrane. These observations agree with those of Yeager and Steck.[11] The observations obtained for the Cs−Ba system can also be explained due to the different locations of the ions in the membrane.

For the Na−Ba system, both ions move through the water-rich region of the membrane, but the Na$^+$ ion possibly remains mostly dissociated in the water channels, and its transport is not hindered by the Ba^{2+} ion which, being a divalent one, possibly remains in the proximity of the −SO$_3^-$ ion.[14] On the other hand, diffusion of Ba^{2+} ions may be regarded as a lattice diffusion, and increase in the Na$^+$ content of the membrane increases the average spacing between two successive Ba^{2+} ions. This enhanced hopping distance with increased Na$^+$ content may strongly affect the diffusivity of the Ba^{2+} ions. The same reason can explain the change in D_{Ba} in the Ag−Ba system.

A representative set of Nyquist plots obtained from the ac impedance measurements for Nafion-117 loaded with different proportions of Na$^+$ and Ba^{2+} ions are shown in Figure 4.
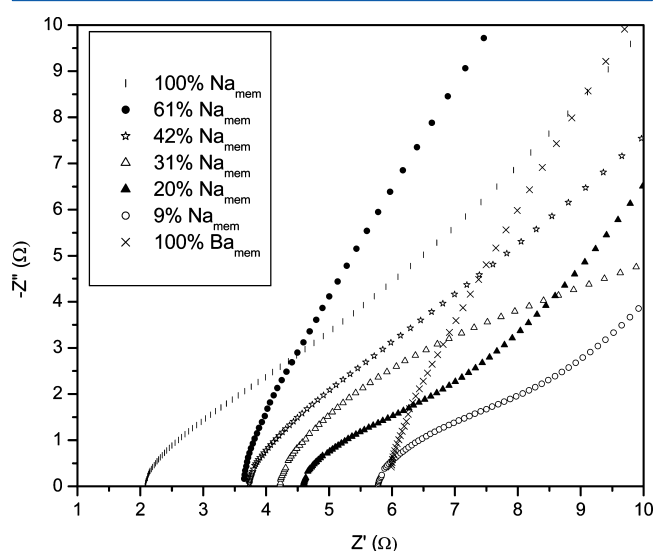

Figure 4. Nyquist plots obtained from impedance measurements for Nafion-117 loaded with different proportions of Na$^+$ and Ba^{2+} ions. Z' and Z'' are the real and imaginary components respectively of the impedance as a function of frequency.

The κ_{imp} values as a function of ionic composition of the membrane for the Na−Ba and Na−Cs systems are shown in Tables 1 and 2, respectively. The corresponding κ_{cal} values obtained using eqs 3 and 4 are also included in Tables 1 and 2. A list of SDCs of Na$^+$ obtained from radiotracer measurements and specific conductivities of the Na$^+$ form of Nafion-117 membrane in different sources are shown in Table 5. It is seen

Table 5. Comparison of SDCs of Na$^+$ Obtained from Radiotracer Measurements and Specific Conductivities of Na$^+$ Form of Nafion-117 Membrane

	SDC ($\times 10^6$ cm^2 s^{-1})		
no.	radiotracer measurement	impedance measurement	κ_{imp} ($\times 10^2$ S cm^{-1})
I^{a,f}	0.94−0.98	−	−
II^b	1.8	1.7	0.8
III^{c,f}	−	1.1	0.5
IV^d	−	6.5	3.0
present work	1.0^e	2.6	1.3

^{a}Reference 11. ^{b}Reference 17. ^{c}Reference 21. ^{d}Reference 27. ^{e}Reference 15. ^{f}Nafion-120.

from Table 5 that there is a good consistency in the SDCs obtained from radiotracer measurement, but the specific conductivities obtained from impedance measurements show wide divergence in different literature sources. There are not enough data from the literature where the measured diffusion coefficient has been correlated to the measured specific conductivity of the membrane. Millet[21] has shown that D_{Na} calculated from the specific conductivity is comparable to that given in ref 11. Pourcelly et al.[17] have also determined D_{Na} from specific conductivity data, and the value differed by a factor of 1.8 from the quoted literature.[15] In the present work, the data given in Tables 1 and 2 indicate that there is an ∼2.5 times difference between the κ_{imp} and κ_{cal} values for the pure Na$^+$ form of the membrane in both Na−Ba and Na−Cs systems.

The values of κ_{imp}, normalized at the calculated specific conductivity of the pure Na$^+$ form of Nafion-117, are plotted as a function of Na$^+$ content in the membrane in Figures 5 and 6 for the Na−Ba and Na−Cs systems, respectively. The corresponding κ_{cal} values using eqs 3 and 4 are also shown in
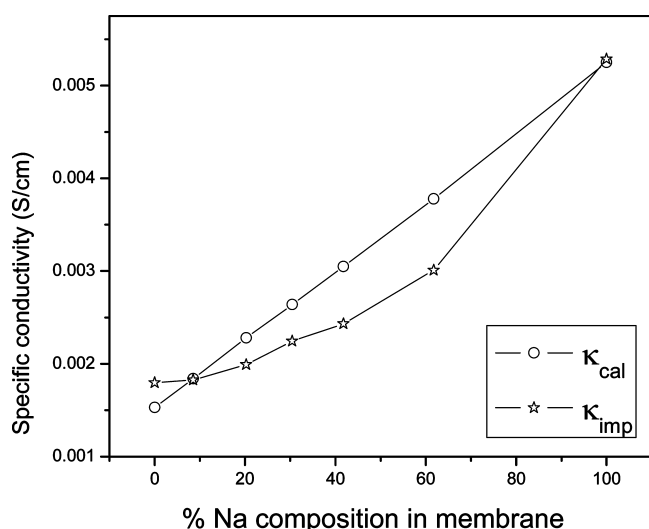
Figure 5. Specific conductivities of Nafion-117 membrane containing different proportions of Na^+ and Ba^{2+} ions.
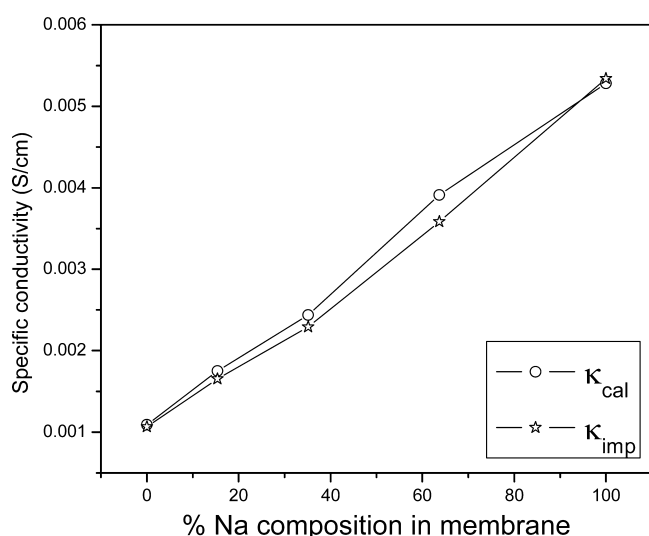

Figure 6. Specific conductivities of Nafion-117 membrane containing different proportions of Na^+ and Cs^+ ions.

Figures 5 and 6. As expected from eqs 3 and 4, there is a linear increase in κ_{cal} with an increase in the Na^+ content of the membrane for both types of ionic systems. For the Na−Cs system, the increment in κ_{imp} follows the same linear trend as that of the corresponding κ_{cal}. This linear trend essentially indicates that there is no mutual interaction of the ions when they move in the membrane. However, for the Na−Ba system, κ_{imp} increases in a parabolic fashion.[18,27,28] The deviation from linearity in the Na−Ba system is indicative of interaction between the diffusing ions in the membrane.[27] However, in the present case, the self-diffusion data show that diffusion of Na^+ ions is not affected by the Ba^{2+} ions, while the diffusion of the latter is strongly influenced by the former one. This essentially shows that the observed deviation from linearity as a function of ionic composition need not necessarily result from the change in SDC of both components in the membrane due to their mutual interaction. Other factors such as different extent of interaction of the cations with the fixed charges of the membrane can also play a role. A clear understanding of the cause of diffusional differences of different types of ions may permit diffusional discriminations to be designed into polymer membranes for specific separations.

■ CONCLUSION

Results of the present work show that the SDC of an ion in Nafion-117 membrane may be influenced by the ionic composition of the membrane phase, depending upon the path of transport of the two cations within the membrane. If the two ions are moving through different pathways in a bi-ionic system, then none of the SDCs of the cations are affected, whereas if they are moving through an overlapping path, then, depending upon the electrostatic binding of the cation with the fixed charge group of the membrane, the SDCs will be affected. This ionic composition dependent self-diffusion behavior of either cation is ultimately reflected in the specific conductivity of the system.

■ AUTHOR INFORMATION

Corresponding Author
*Fax: +91-22-25505150/25505151. Tel.: +91-22-25593688. E-mail: agoswami@barc.gov.in.

■ REFERENCES

(1) Sata, T. *Ion-Exchange Membranes——Preparation, Characterization, Modification and Application*; Royal Society of Chemistry: London, 2004.
(2) *Perflourinated Ionomer Membranes*; Eisenberg, A., Yeager, H. L., Eds.; ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982; p 41.
(3) Maeda, Y.; Tsuyumoto, M.; Karakane, H.; Tsugaya, H. *Polym. J.* **1991**, *23*, 501.
(4) Yasuda, H.; Lamaze, C. E.; Peterlin, A. *J. Polym. Sci., Part A-2* **1971**, *9*, 1117.
(5) Crank, J.; Park, G. S. *Diffusion in Polymer*; Academic Press: London, 1968; Chapter 1.
(6) Heitner-Wirguin, C. *J. Membr. Sci.* **1996**, *120*, 1.
(7) Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535.
(8) Suresh, G.; Scindia, Y. M.; Pandey, A. K.; Goswami, A. *J. Phys. Chem. B* **2004**, *108*, 4104.
(9) Sodaye, S.; Pandey, A. K.; Goswami, A. *J. Phys. Chem. B* **2009**, *113*, 12482.
(10) Hsu, W. Y.; Gierke, T. D. *J. Membr. Sci.* **1983**, *13*, 307.
(11) Yeager, H. L.; Steck, A. *J. Electrochem. Soc.* **1981**, *128*, 1880.
(12) Robertson, M. A. F.; Yeager, H. L. *Macromolecules* **1996**, *29*, 5166.
(13) Pintauro, P. N.; Tandon, R.; Chao, L.; Xu, W.; Evilla, R. *J. Phys. Chem.* **1995**, *99*, 12915.
(14) Tandon, R.; Pintauro, P. N. *J. Membr. Sci.* **1997**, *136*, 207.
(15) Goswami, A.; Acharya, A.; Pandey, A. K. *J. Phys. Chem. B* **2001**, *105*, 9196.
(16) Okada, T.; Satou, H.; Okuno, M.; Yuasa, M. *J. Phys. Chem. B* **2002**, *106*, 1267.
(17) Pourcelly, G.; Sistat, P.; Chapotot, A.; Gavach, C.; Nikonenko, V. *J. Membr. Sci.* **1996**, *110*, 69.
(18) Karavanova, Yu. A.; Yaroslavtsev, A. B. *Inorg. Mater.* **2010**, *46*, 789.
(19) Sodaye, S.; Agarwal, C.; Goswami, A. *J. Membr. Sci.* **2008**, *314*, 221.
(20) Chaudhury, S.; Agarwal, C.; Pandey, A. K.; Aher, V. T.; Panicker, L.; Ramagiri, S. V.; Bellare, J. R.; Goswami, A. *J. Membr. Sci.* **2011**, *382*, 262.
(21) Millet, P. *J. Membr. Sci.* **1990**, *50*, 325.
(22) Pourcelly, G.; Oikonomou, A.; Gavach, C.; Hurwitz, H. D. *J. Electroanal. Chem.* **1990**, *287*, 43.
(23) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1965; p 314.

(24) Gavach, C.; Pamboutzoglou, G.; Nedyalkov, M.; Pourcelly, G. *J. Membr. Sci.* **1989**, *45*, 37.

(25) Subrahmanian, V.; Lakshminarayanaiah, N. *J. Phys. Chem.* **1968**, *72*, 4314.

(26) Nwal Amang, D.; Alexandrova, S.; Sghaetzel, P. *Electrochim. Acta* **2003**, *48*, 2563.

(27) Okada, T.; Moller-Holst, S.; Gorseth, O.; Kjelstrup, S. *J. Electroanal. Chem.* **1998**, *442*, 137.

(28) Hirofumi, M.; Miyoshi, H.; Yamagami, M.; Chubachi, M.; Kataoka, T. *J. Chem. Eng. Data* **1994**, *39*, 595.