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Transport Properties of Multivalent Cations in Nafion-117 Membrane with Mixed Ionic Composition

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ABSTRACT: The transport characteristics of multivalent cations like Ba^{2+} and Eu^{3+} have been studied in bi-ionic form of the Nafion-117 membrane. The membranes have been prepared by loading different proportions of H^+-Ba^{2+}/$Mg^{2+}-Ba^{2+}$/$Ba^{2+}-Eu^{3+}$/H^+-Eu^{3+}/Na^+-Eu^{3+}. The cationic compositions of the membranes have been determined from the measured ion exchange isotherms. Results show that the self-diffusion coefficient of Ba^{2+} (D_{Ba}) in $H-Ba$/$Mg-Ba$ systems as well as the self-diffusion coefficient of Eu^{3+} (D_{Eu}) in $H-Eu$/$Na-Eu$ systems are strongly dependent on the membrane ionic compositions and decreased continuously with increasing concentration of the highly hydrated ions (H^+/Na^+/Mg^{2+}) in the membrane. Increase in the proportion of H^+/Na^+/Mg^{2+} ions in the membrane increases the effective charge on the membrane matrix. This causes stronger electrostatic interaction of the less hydrated multivalent ions (Ba^{2+}/Eu^{3+}) with the membrane matrix charges, which ultimately results in their slower self-diffusion coefficients. The higher the valence, the stronger the electrostatic interaction is with the fixed ionic charges; hence, in general, D_{Eu} is affected more as compared to D_{Ba}. On the basis of the free-volume theory for polymers, the effective interaction potential (Φ) of the Ba^{2+} with the fixed ionic sites in the membrane has been calculated and found to be on the order of approximately millivolts. The higher the proportion of hydrated ion in the membrane, the higher the Φ is and the stronger the ion pair formation is with the fixed ionic sites in the membrane. However, in the Ba–Eu system, as the electrostatic interactions of the two ions with the membrane matrix are close, D_{Ba} and D_{Eu} are independent of the membrane ionic composition. The ionic composition dependence of D_{Ba} in the H–Ba system is reflected in the transport rate of Ba^{2+}, showing the importance of such measurements in understanding the transport characteristics of the membrane.
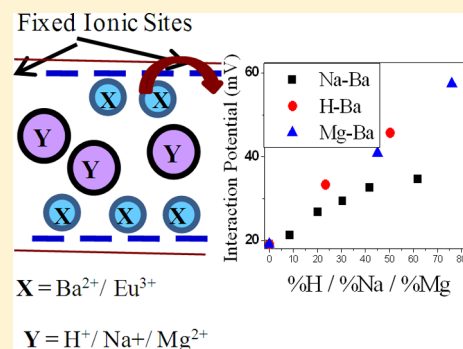
INTRODUCTION

Nafion is a widely used ion exchange membrane having a polytetrafluoroethylene matrix with pendant side chains containing $-SO_3H$ groups. This membrane is having large scale application in the polymer electrolyte fuel cell and chloro-alkali industry.[1−3] The high electrical conductivity, remarkable permselectivity, and excellent thermal and chemical stability of Nafion membranes compensate for their high cost. Extensive research has been carried out to understand the mechanism of diffusion of ions in the ion exchange membranes (IEMs) for designing membranes for specific applications. It has been observed that 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.[4] The self-diffusion coefficients (SDCs) of different ions in monocationic form of Nafion are well-reported in the literature.[5] The transport characteristics of a membrane containing two different cations provide more information than those containing a single cation.[4,6−8] However, it is not clearly known how the self-diffusion mobility of the counterion is modified in the presence of other counterions.

Okada et al.[7] have reported that the ionic mobilities of H^+ ion and alkali metal cations are independent of the ionic composition of the membrane. Similarly, Pourcelly et al.[8] also have observed that SDCs of Na^+ and Ca^{2+} are not dependent

on the ionic composition of the membrane. Literature reports[9,10] are available, where the effect of cation contamination on the transport properties of Nafion membrane has been studied using mathematical modeling. For full scale transport calculation using the Stefan Maxwell equation, the interdiffusion coefficient D_{ij} is required. In a binary cationic system, the SDCs of the individual cations (D_i or D_j) are one of the important input parameters, required for D_{ij} calculation.

In our earlier work,[11] the SDCs of cations (Na^+/Cs^+/Ba^{2+}) have been measured in mixed cationic compositions of the membrane. It has been found that, in Na–Ba system, SDC of Ba^{2+} (D_{Ba}) decreases continuously with increasing Na^+ content in the membrane, but the SDC of Na^+ is independent of membrane ionic composition. Similar observations have also been obtained for the Ag–Ba system, where D_{Ba} is found to decrease with increase in the Ag^+ content of the membrane. This ionic composition dependent self-diffusion behavior is ultimately reflected in the specific conductivity of the membrane. Thus, in the Na–Ba system, an increase in specific conductance with increase in Na^+ content of membrane has been found to be parabolic. Similar behavior of ionic conductance in the membrane MK-40 has been reported by

Table 1. Ionic Compositions of Equilibrating Solutions in Different Ionic Systems

syst	composition of equilibrating solution (Na^+/H^+:Eu^{3+})	syst	composition of equilibrating solution (Ba^{2+}:Eu^{3+})	syst	composition of equilibrating solution (H^+/Mg^{2+}:Ba^{2+})
Na–Eu	1:1	Ba–Eu	1:1	H–Ba	10:1
	4:1		4:1		50:1
	14:1				
	29:1				
H–Eu	20:1			Mg–Ba	4:1
	50:1				10:1
	100:1				

Karavanova and Yaroslavtsev.[12] On the other hand, for the Cs–Ba system,[11] the SDCs of both the ions have been found to be independent of the ionic composition of the membrane. The results have been interpreted on the basis of different transport pathways of the ions as well as their electrostatic interaction with the membrane matrix charges.

In the present work, in order to explore the effects of water uptake of the ions and its nature of interaction with the membrane matrix charges, on their SDCs, we have further studied the cationic composition dependence of the SDC of the multivalent ions (Ba^{2+} and Eu^{3+}) in bi-ionic form of Nafion-117 membrane. The membrane containing different proportions of X/Y ions and Eu^{3+}/Ba^{2+} ions are henceforth called the X–Eu or Y–Ba system, where X = H^+/Na^+/Ba^{2+} and Y = H^+/Mg^{2+}. In order to determine the membrane ionic composition, the ion exchange isotherms for all the systems in Nafion-117 membrane have been generated. The water uptakes of the membranes for different ionic compositions have also been measured. The results of the SDC measurement have been discussed on the basis of the tortuosity factor and the interaction of the cation with the fixed ionic sites. An attempt has been made to quantify the effective interaction potential of Ba^{2+} ion with the fixed ionic charges in the membrane in mixed cationic systems (Na–Ba/H–Ba/Mg–Ba). Further, the permeability coefficient (P_{Ba}) of Ba^{2+} for a particular membrane composition in H–Ba system as well as for pure Ba^{2+} form of the membrane has been obtained from the two compartment permeability experiment. An attempt has been made to correlate the SDC and the permeability coefficients of Ba^{2+}.

■ EXPERIMENTAL SECTION

Reagents and Chemicals. The metal salts NaCl, $BaCl_2$, $MgCl_2$, and $EuCl_3$, (99.999%, ultrapure grade) were procured from Sisco Research Lab., Mumbai, India. Deionized water (18 MΩ/cm, Gradient A-10 model, Milli-Q) and analytical grade HCl and HNO_3 (Merck, Germany) were used in the present study. Radiotracers ^{133}Ba and ^{152}Eu + ^{154}Eu, used in the present study, were obtained from Board of Radiation and Isotope Technology, Mumbai, India. Nafion-117 (purchased from Du Pont) ion exchange membrane with an equivalent weight of 1100 g and 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.[5] For the experiments involving Eu^{3+} ion, the salt solutions have been prepared in HCl (pH = 2.7).

Measurement of Self-Diffusion Coefficients and Ion Exchange Isotherm. For the Na–Eu system, four different equilibrating solutions containing different proportions (as shown in Table 1) of NaCl and $EuCl_3$ were prepared keeping the total ionic concentration fixed at 0.1 N. For each

equilibrating solution, the SDC of Eu^{3+} (D_{Eu}) was measured following the standard nonstationary radiotracer absorption method. In brief, the conditioned membrane sample (1 cm × 2 cm) in proton form was kept in well-stirred equilibrating solution at 27 °C for ~6 h. After equilibration, the membrane sample was taken out, and the required (^{152}Eu + ^{154}Eu) radiotracer was added to the solution. The further steps involved in the measurement of SDC were the same as described in ref 5.

The ion exchange isotherms of all the systems were obtained from the standard radiotracer method as described in ref 11. For other systems (H–Eu, Ba–Eu, H–Ba, and Mg–Ba), the same experimental procedure was followed to obtain D_{Eu} or D_{Ba}. The compositions of the different equilibrating solutions for all the systems are given in Table 1.

Two Compartment Permeation Experiment. In order to measure the permeability coefficients (P_{Ba}'s) of Ba^{2+}, cation permeation experiments were carried out in a two compartment cell separated by a Nafion-117 membrane having two different ionic compositions. In one case, the membrane was loaded with 100% Ba_{mem}, and in another case the membrane was loaded with 77% Ba_{mem} and 23% H_{mem}. The membrane active area was 5.3 cm^2, and volume of each compartment was 12 mL.

For the experiment involving 100% Ba_{mem}, each compartment of the cell was filled with 0.1 N $BaCl_2$ solution, and the feed solution was spiked with ^{133}Ba. The transport of Ba^{2+} from feed to receiver compartment was monitored by taking out 100 μL of aliquots from both the compartments at regular time intervals and counting the ^{133}Ba activity in NaI(Tl) detector. The solutions in both the compartments were stirred continuously to avoid any film controlled diffusion at the membrane interface.

For the experiment involving mixed ionic composition, the membrane in H^+ form was equilibrated for 6 h with a solution containing 0.1 N HCl and 0.1 N $BaCl_2$. The ratio of HCl and $BaCl_2$ in the equilibrating solution was taken in such a way that the membrane contains 77% Ba_{mem} and 23% H_{mem}. The pre-equilibrated membrane was used for the permeation experiment, and each compartment was filled with the same equilibrating solution. In order to ensure that there is no concentration gradient involved in the cation permeation, the same solution was used in both the compartments. The solution in the feed compartment was spiked with ^{133}Ba. The transport of Ba^{2+} from feed to receiver compartment was monitored by the same method as described in the previous section.

■ CALCULATION

Self-Diffusion Coefficients. The isotopic exchange profiles of Eu^{3+} in the Na–Eu system and in the Ba–Eu systems, as

obtained from present experiments, are shown in Figure 1 a,b, respectively. It is to be mentioned that the error bars associated

Figure 1. Isotopic exchange kinetics of Eu^{3+} for different ionic composition of the membrane in the (a) Na−Eu system and (b) Ba−Eu system.

with the experimental data points are of the size as the symbols and the quoted membrane composition is with respect to the total number of ion exchange sites in the membrane. The D_{Eu} values for different compositions of the membrane have been

obtained from a fit of the isotopic exchange data with the equation obtained from the analytical solution of Fick's second law given below.[5]

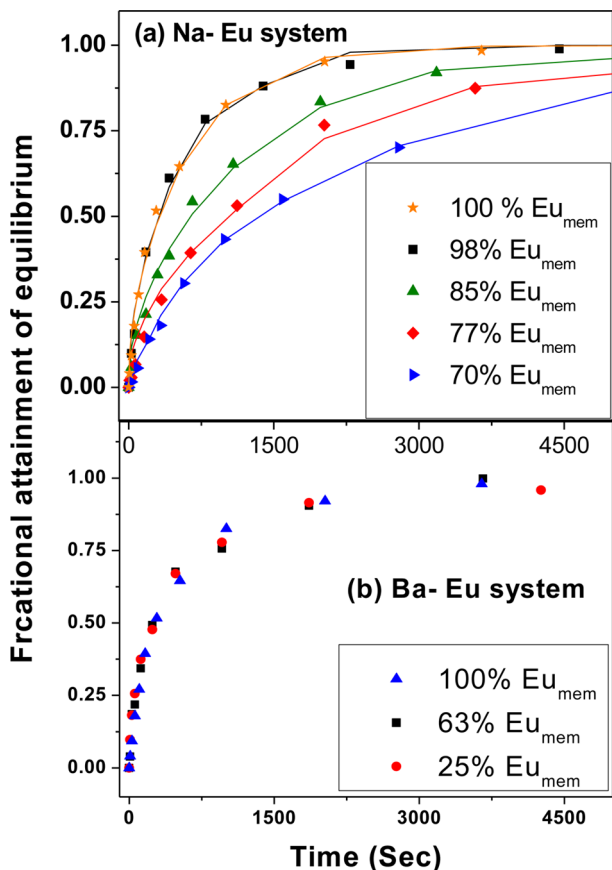$$n(t_k) = n^* \left[1 - \left(\frac{8}{\pi^2} \right) \left\{ \exp(-D\pi^2 t_k/L^2) + \frac{1}{9} \right. \right.$$
$$\left. \left. \exp(-9D\pi^2 t_k/L^2) + ... \right\} \right] \tag{1}$$

Here, 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 have been taken as free parameters, and only the first three terms in eq 1 have been used for fitting.
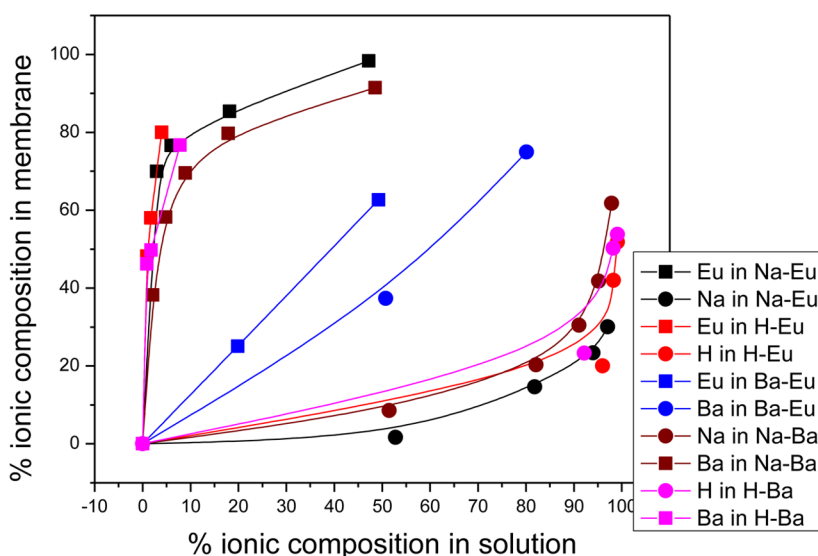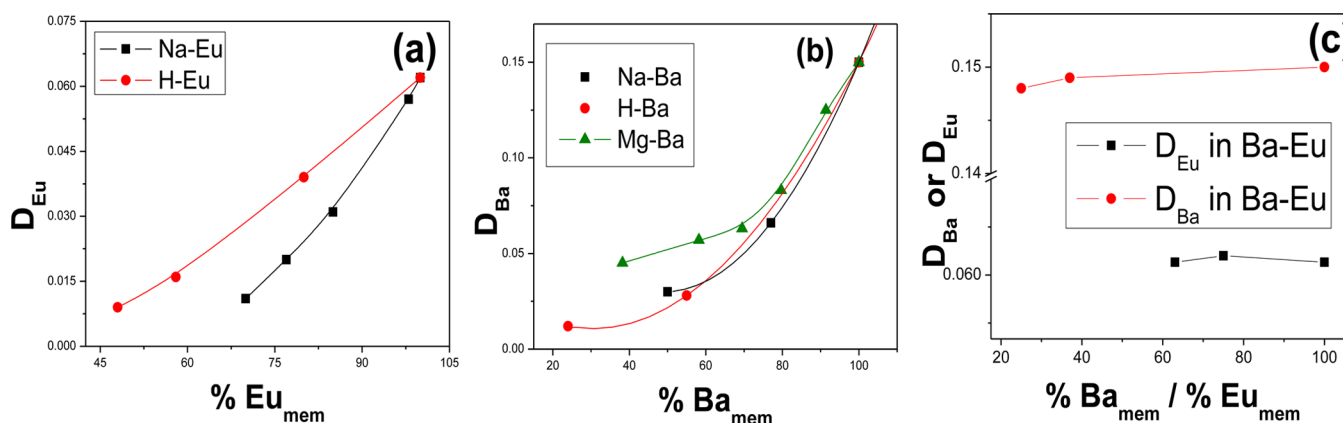
■ RESULTS AND DISCUSSION

The ion exchange isotherms for all the ionic systems are shown in Figure 2. In general, it indicates very high selectivity of Nafion-117 membrane for Ba^{2+} and Eu^{3+} ions over other H^+, Na^+, and Mg^{2+} ions. However, in the Ba−Eu system, the membrane shows comparable preference for both the counterions.

It is interesting to see from Figure 1 that, for the Na−Eu system, the rate of isotopic exchange of Eu^{3+} decreases significantly with increase in percentage of Na^+ in the membrane, whereas, for the Ba−Eu system, it is independent of the membrane cationic composition. In the H−Eu system, the variation of Eu^{3+} isotopic exchange profiles is similar to that in the Na−Eu system. Figure 3a shows the variation of D_{Eu} with change in membrane compositions in Na−Eu and H−Eu systems. It can be seen from the figure that D_{Eu} gradually decreases as % Na_{mem}/% H_{mem} increases. Compared to the SDC of Eu^{3+} (0.062×10^{-6} cm^2 s^{-1}) in the pure Eu^{3+} form of Nafion-117, the D_{Eu} is reduced by ∼82% and 86% for 30% Na_{mem} and 52% H_{mem}, respectively. The variation of D_{Ba} with change in membrane compositions in H−Ba and Mg−Ba systems has been shown in Figure 3b. It can be seen from the figure that D_{Ba} decreases with an increase in H^+/Mg^{2+} content in the membrane. The results obtained for Na−Eu, H−Eu, and

Figure 2. Ion exchange isotherms of different ionic systems in Nafion-117. The data of the Na−Ba system has been taken from ref 11.

Figure 3. Variation of SDC of Ba^{2+} (D_{Ba}) and Eu^{3+} (D_{Eu}) with change in membrane ionic composition in different systems. In part c, for Ba−Eu system, the SDC of one ion has been plotted against the composition of the other ion the membrane. The data for Na−Ba system has been taken from ref 11.
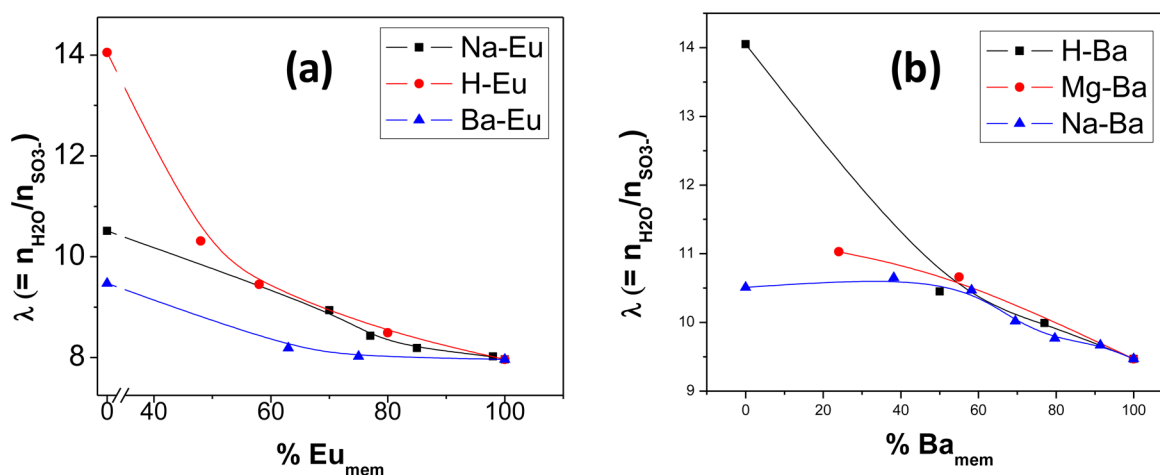
Figure 4. Water to exchange site mole ratio (λ) in Nafion-117 as a function of % Eu_{mem} or % Ba_{mem} in different systems. The data for Na−Ba system has been taken from ref 11.

H−Ba are in accordance with our earlier observations in Na−Ba and Ag−Ba systems, where the SDCs of multivalent ion decrease with increase in monovalent (Na^+/Ag^+) ion content in the membrane. It is to be noted that Mg^{2+}, in spite of being bivalent, affects the SDC of another bivalent ion Ba^{2+}. Surprisingly, for Ba−Eu system (Figure 3c), the SDCs of either ion are independent of membrane composition.

The SDC of a cation in an ion exchange membrane is influenced by (1) the tortuosity factor and (2) the electrostatic interaction of the cation with the fixed ionic sites in the membrane. The tortuosity is governed by the membrane water uptake, and the electrostatic interaction depends upon the valence state as well as hydration characteristics of the counterions. The electrostatic interaction may lead to formation of ion pairs with the fixed charges in the membrane. The probability of such ion pair formation increases with valence of the counterions and decreases with increasing hydration of the counterions. Thus, divalent and trivalent ions are expected to spend more time near the fixed matrix charges as compared to the monovalent ions. For them, a third parameter can also affect the SDC, which is the availability of more than one nearby vacant sites. In the mixed cationic system, probability of available nearby vacant sites decreases with decrease in concentration of multivalent ion. This factor has been observed to play a significant role in diffusion of

bivalent impurity ions in monovalent ionic crystals,[13,14] where the diffusion coefficient of bivalent ion is shown to decrease with decrease in impurity concentration. However, in our case, the mechanism of diffusion in ionic lattice may not be fully operative because of the presence of water in the membrane. Thus, ions may spend only a part of their time close to the ion exchange sites and diffuse through the central part of the water channel. This is validated by the fact that magnitudes of the SDCs of the cations in Nafion-117 membrane are much higher than the corresponding diffusion coefficients in an ionic crystal.

On the basis of these arguments, an attempt has been made to qualitatively explain the present observations. The water uptake ($\lambda = n_{H2O}/n_{SO3^-}$) of the membrane, as a function of membrane cationic compositions, is shown in Figure 4a,b. This indicates that water uptake in the membrane increases significantly as % of Na^+, H^+, and Mg^{2+} in the membrane increases relative to Ba^{2+} or Eu^{3+} ions. Pintauro and co-workers[6,15,16] have reported that the unfavorable hydration forces confine the highly hydrated cations to the central region of the water channel. Thus, the hydrated ions ($Na^+/H^+/Mg^{2+}$) are expected to remain dissociated in the water channel, and their SDCs are mostly therefore governed by the membrane tortuosity. As a result, the SDCs of these ions are nearly independent of membrane compositions.

Variation of D_{Ba} and D_{Eu} in the presence of $Na^+/H^+/Mg^{2+}$ in the membrane is distinctly different. They show a continuous decrease in SDC with increase in the proportion of the other ion in the membrane, similar to what is observed in an ionic crystal. These observations can be rationalized if we consider the observations reported by Pintauro and co-workers.[6,15,16] They revealed that a fraction of the less hydrated multivalent ions (Ba^{2+}/Eu^{3+}) exist as an ion pair with the fixed charges of the membrane matrix, and this fraction varies with the extent of monovalent cation present in the membrane. However, the highly hydrated ions ($H^+/Na^+/Mg^{2+}$) remain mostly dissociated in the water channel. Thus, as the proportion of highly hydrated ion in the membrane increases, the effective charge on the membrane matrix increases. This causes Ba^{2+}/Eu^{3+} ions to be attracted more toward the membrane matrix, and hence, their SDC decreases with increase in hydrated ion content in the membrane. Moreover, due to strong electrostatic interaction, the Ba^{2+}/Eu^{3+} ions spend a significant fraction of time close to the fixed ionic charges in the membrane. Accordingly, their diffusion may be affected by the availability of the required number of neighboring vacant sites and hence will depend upon the concentration of other ion in the membrane.

It is interesting to note that, in the Ba–Eu system, the SDCs of both cations are again independent of membrane composition. The ion exchange isotherm of the Ba–Eu system, as shown in Figure 2, indicates that the membrane has comparable preference for both ions. This indicates that the electrostatic interactions of the two ions with the membrane matrix are possibly close; i.e., they spent the same extent of time close to the ion exchange sites.

Figure 5 shows the variation of D_{Ba}/D^0_{Ba} and D_{Eu}/D^0_{Eu} in Na–Ba and Na–Eu systems, respectively. D^0_{Ba} and D^0_{Eu} are the
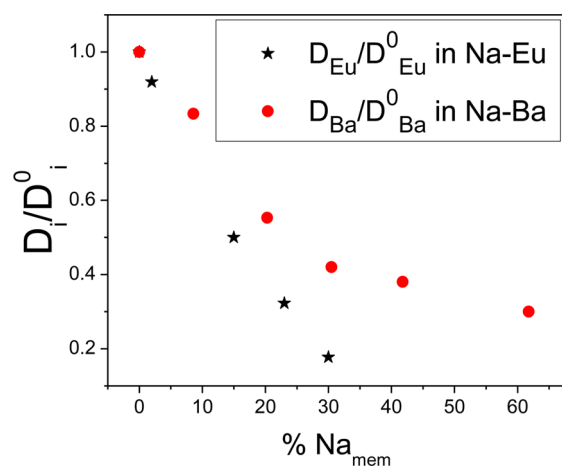
Figure 5. Variation of SDC of Eu^{3+} and Ba^{2+} (normalized with respect to that in the pristine membrane) with % Na_{mem} in Na–Eu and Na–Ba system. The data for Na–Ba system is taken from ref 11.

SDCs of the Ba^{2+} and Eu^{3+} ions in the pure Ba^{2+} and Eu^{3+} form of Nafion-117 membrane, respectively. For 30% Na_{mem}, D_{Eu} reduces by 82%, whereas D_{Ba}[11] reduces by 58%. As can be seen from Figure 4, the water uptake in the membrane for 30% Na_{mem} in Na–Ba as well as in the Na–Eu system is nearly the same. Thus, the tortuosity factors in both cases are almost comparable. However, Eu^{3+}, being a higher valent ion than Ba^{2+}, interacts more strongly with the fixed ionic sites in the membrane. Moreover, the factor related to the availability of

vacant sites will be more stringent in the case of Eu^{3+} than that in Ba^{2+}. Thus, for a particular % Na_{mem}, D_{Eu} is affected more as compared to D_{Ba}.

In order to obtain the interaction potential (Φ) of the ions with the fixed ionic sites in the membrane, an attempt has further been made to correlate the experimental SDCs of the ions with the free-volume fraction of polymer and the electrostatic interaction with the membrane matrix. For any diffusing cationic species in the membrane, the SDC (D_i) can be approximated as

$$D_i = (D_w)_i \exp(-\tau)\{\exp(-z_i e\Phi_i/kT)\} \quad (2)$$

where $(D_w)_i$ is the aqueous diffusion coefficient of the species, τ is a function of the polymer volume fraction (V_p), Z_i is the charge of the diffusing species, T is the absolute temperature, e is the electronic charge, and k is the Boltzmann constant. The τ dependent part of eq 2 gives the variation of D_i with the V_p of the membrane or tortuosity, while the Φ dependent part is the Boltzman factor, signifying the distribution of ions between the ionic sites and the water in the channels. The later one gives an idea about the charge unsaturation of the fixed ion exchange sites due to the presence of hydrated cations in the membrane. It is to be mentioned here that the effect of availability of neighboring vacant sites has been ignored. Most of the highly hydrated ions ($H^+/Na^+/Mg^{2+}$) remain dissociated in the water channels (away from the fixed ionic sites). Thus, their SDC is influenced only by the tortuosity factor. For them, eq 2 reduces to

$$D_i = (D_w)_i \exp(-\tau) \quad (3)$$

According to the free-volume theory of Yasuda et al.,[17] the tortuosity effect, which represents the lengthening of the path of moving ions, is fundamentally related to the polymer volume fraction in the polymer matrix, and the SDC (D) of cations can be written as

$$D = D_w \exp[-b(V_p/(1 - V_p))] \quad (4)$$

where D_w 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, obtained from a fit of the experimental data using eq 4. In the present context, free volume is essentially the volume fraction of water in the membrane, as determined by the water uptake capacity. In our earlier work, the variation of $\ln(D/D_w)$[5] with V_p of the membrane for different divalent and monovalent cations has been shown, and it has been observed that the SDCs of the divalent and monovalent cations varied linearly with free-volume fraction with different slopes. If it is assumed that, for a given V_p, the tortuosity factor is the same for monovalent and divalent ions, then the difference in the $\ln(D/D_w)$ of the monovalent and the divalent cations can be attributed to the higher interaction of the divalent cation with the fixed charges of the membrane.

In the present work, for a particular membrane composition, V_p is calculated from the volume of the water in the membrane and the volume of the wet membrane sample. From the plot of $\ln(D/D_w)$ of the monovalent ions,[5] the tortuosity factor has been obtained for that V_p. The interaction potential (Φ) for the less hydrated multivalent ions can thus be estimated from eq 2, using this tortuosity factor and the experimentally determined D_i. The individual D_w values have been obtained from the literature.[18] The calculated values of Φ of Ba^{2+} for different

ionic composition of the membrane in different systems (H−Ba/Mg−Ba/Na−Ba) are plotted in Figure 6. It can be seen that
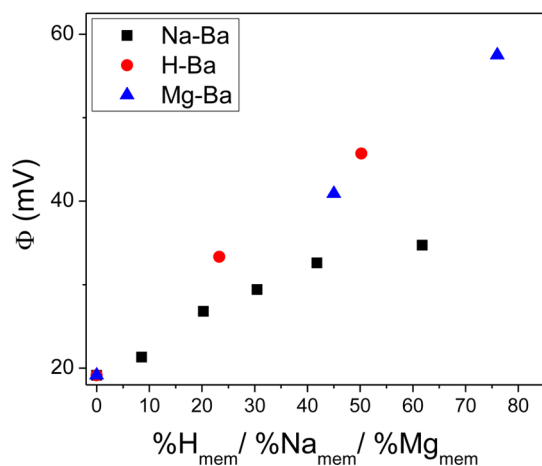
Figure 6. Variations of interaction potential (Φ) of Ba^{2+} with change in membrane ionic composition in different systems. The data for the Na−Ba system has been calculated using D_{Ba} from ref 11.

as the concentration of hydrated ion in the membrane increases, Φ increases. Thus, as H^+/Mg^{2+} is more hydrated than Na^+, Φ is comparatively higher in the H−Ba/Mg−Ba system than that in the Na−Ba system. As a result, for a particular percentage of H_{mem}/Na_{mem}, reduction in D_{Ba} is more prominent in the H−Ba system than that in the Na−Ba system.

In order to study the effect of the composition dependence of the D_{Ba} on the transport properties of the membrane, two compartment permeation experiments have been carried out at a given membrane composition in the H−Ba system as well as for the pure Ba^{2+} form of the membrane. Figure 7 shows the time dependence of the fraction (C_R/C_F) of the radiotracer (^{133}Ba) transported from feed to receiver for two different ionic
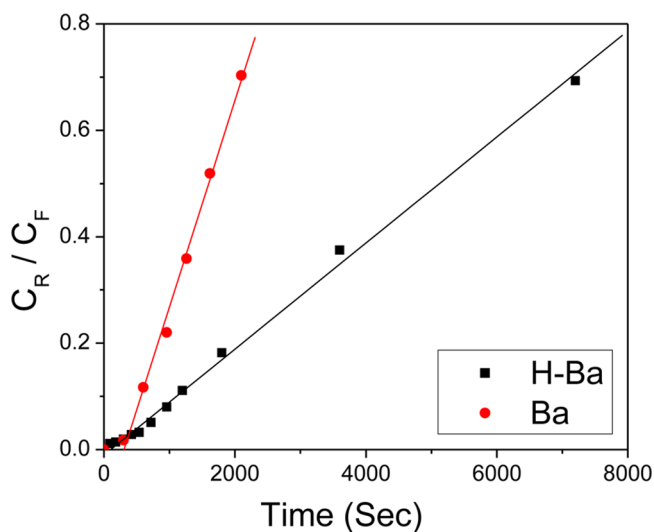
Figure 7. Time dependence of the ratio of Ba^{2+} concentration in the receiver compartment (C_R) to that in the feed compartment (C_F) in Nafion membrane. The circles correspond to 100% Ba_{mem}, and the squares correspond to the 23% H_{mem}−77% Ba_{mem}. The points are the experimental data, and the lines are the fitted profiles to those data points.

compositions of the membrane (i) 100% Ba_{mem} and (ii) 23% H_{mem}−77% Ba_{mem}).

From the slope of the plot, the permeability coefficient (P_{Ba}) of Ba^{2+} has been obtained using the following equation

$$P_{Ba} = (V/A)\left[\frac{d(C_R/C_F)_t}{dt}\right] \tag{5}$$

The experimentally obtained permeability coefficient values for the Ba^{2+} ion along with the corresponding SDCs for two different ionic compositions in the membrane are shown in Table 2. It is evident from the data that the permeability

Table 2. SDC and Permeability Coefficients of Ba^{2+} Ions in the H−Ba System

ionic composition (%) in membrane		$D_{Ba} \times 10^6$ (cm² s⁻¹)	$P_{Ba} \times 10^4$ (cm s⁻¹)
H^+	Ba^{2+}		
	100	0.150	7.94
23	77	0.066	2.26

coefficient of Ba^{2+} in Nafion-117 decreases in the presence of H^+ in the membrane. For 23% H_{mem}, there is ~3-fold decrease in the permeability coefficient of Ba^{2+} compared to that in the pure Ba^{2+} form of the membrane. It can also be seen from Table 2 that a decrease in P is mostly due to the decrease in D_{Ba}, and thus the ~2-fold decrease in D_{Ba} ultimately results in a ~3-fold decrease in P_{Ba}.

■ CONCLUSION

The equilibrium and transport properties of Nafion-117 membrane in mixed cationic composition have been studied using cations of different valence. The bivalent and the trivalent ions are found to have stronger absorption over the monovalent ions, though the preference between the bi- and the trivalent ions are not prominent. The water uptake (λ) of the membrane is strongly dependent on the cations present in the membrane. The SDCs of the Ba^{2+} and Eu^{3+} are significantly reduced in the presence of highly hydrated monovalent ions. Magnesium, though bivalent, behaves like monovalent ions in affecting the SDC of other multivalent ions studied. Results show that the more hydrated ions remain mostly dissociated in the water channel, while the less hydrated multivalent ions (Ba^{2+} and Eu^{3+}) mostly remain as contact ion pair with the fixed ionic charges in the membrane matrix, experiencing more friction during the transport. The presence of hydrated ions possibly increases the electrostatic attraction and also reduces the availability of neighboring vacant sites, both working in tandem to reduce the diffusion coefficient. On the contrary, between tri- and bivalent ions, the interdependency of SDC is nominal. The preference of Eu^{3+} over Ba^{2+} is also not significant, indicating that both the ions remain closely associated with the fixed charges due to their higher electrostatic interaction. They, therefore, do not exert mutual influence in modifying their transport behavior. Thus, the valence and the hydration characteristics of ions dictate the mutual dependence of SDC of the ions in Nafion-117 membrane.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Eisenberg, A.; Yeager, H. L. *Perfluorinated Ionomer Membranes*; ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982; p 41.

(2) Maeda, Y.; Tsuyumoto, M.; Karakane, H.; Tsugaya, H. Separation of Water-Ethanol Mixture by Pervaporation through Hydrolyzed Polyacrylonitrile Hollow Fiber Membranes. *Polym. J.* **1991**, *23*, 501−511.

(3) Sata, T. *Ion-Exchange Membranes-Preparation, Characterization, Modification and Application*; Royal Society of Chemistry: London, 2004.

(4) Yeager, H. L. Cation Exchange Selectivity of a Perfluorosulfonate Membrane; *Perfluorinated Ionomer Membranes*; ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982.

(5) Goswami, A.; Acharya, A.; Pandey, A. K. Study of Self-Diffusion of Monovalent and Divalent Cations in Nafion-117 Ion-Exchange Membrane. *J. Phys. Chem. B* **2001**, *105*, 9196−9201.

(6) Bontha, R.; Pintauro, P. N. Water Orientation and Ion Solvation Effects During Multicomponent Salt Partitioning in a Nafion Cation Exchange Membrane. *Chem. Eng. Sci.* **1994**, *49*, 3835−3851.

(7) Okada, T.; Satou, H.; Okuno, M.; Yuasa, M. Ion and Water Transport Characteristics of Perfluorosulfonated Ionomer Membranes with H^+ and Alkali Metal Cations. *J. Phys. Chem. B* **2002**, *106*, 1267−1273.

(8) Pourcelly, G.; Sistat, P.; Chapotot, A.; Gavach, C.; Nikonenko, V. Self Diffusion and Conductivity in Nafion Membranes in Contact with $NaCl+CaCl_2$ Solutions. *J. Membr. Sci.* **1996**, *110*, 69−78.

(9) Kienitz, B.; Baskaran, H.; Zawodzinski, T.; Pivovar, B. A Half Cell Model of Steady State PEM Fuel Cell Performance Degradation Under Contamination by Foreign Cationic Species. *ECS Trans.* **2007**, *11*, 777−788.

(10) Weber, A. Z.; Delacourt, C. Mathematical Modelling of Cation Contamination in a Proton-Exchange Membrane. *Fuel Cells* **2008**, *8*, 459−465.

(11) Chaudhury, S.; Agarwal, C.; Pandey, A. K.; Goswami, A. Self-Diffusion of Ions in Nafion-117 Membrane Having Mixed Ionic Composition. *J. Phys. Chem. B* **2012**, *116*, 1605−1611.

(12) Karavanova, Yu. A.; Yaroslavtsev, A. B. Diffusion Characteristics of Mixed-Cation Ion-Exchange Membranes. *Inorg. Mater.* **2010**, *46*, 789−792.

(13) Howard, R. E.; Lidiard, A. B. Matter Transport in Solids. *Rep. Prog. Phys.* **1964**, *27*, 161−240.

(14) Laskar, A. L. The Effect of Impurity Doping on the Diffusion of Sr^{2+} in AgCl. *J. Phys. C: Solid State Phys.* **1978**, *11*, 3397−3401.

(15) Pintauro, P. N.; Tandon, R.; Chao, L.; Xu, W.; Evilla, R. Equilibrium Partitioning of Monovalent/Divalent Cation-Salt Mixtures in Nafion Cation-Exchange Membranes. *J. Phys. Chem.* **1995**, *99*, 12915−12924.

(16) Tandon, R.; Pintauro, P. N. Divalent/Monovalent Cation Uptake Selectivity in a Nafion Cation-Exchange Membrane: Experimental and Modeling Studies. *J. Membr. Sci.* **1997**, *136*, 207−219.

(17) Yasuda, H.; Lamaze, C. E.; Ikenberry, L. D. Permeability of Solutes through Hydrated Polymer Membranes, Part I. Diffusion of Sodium Chloride. *Makromol. Chem.* **1968**, *118*, 19−35.

(18) Robinson, R. A.; Stokes, R. H.; *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1965; p 314.