Temperature Dependence of Ion and Water Diffusion in Crown Ether Loaded Nafion Matrix

4 AUTHORS:

Sanhita Chaudhury
Bhabha Atomic Research Centre
18 PUBLICATIONS   56 CITATIONS

SEE PROFILE

Arunasis Bhattacharyya
Bhabha Atomic Research Centre
55 PUBLICATIONS   789 CITATIONS

SEE PROFILE

Chhavi Agarwal
Bhabha Atomic Research Centre
37 PUBLICATIONS   148 CITATIONS

SEE PROFILE

Asimananda Goswami
Saha Institute of Nuclear Physics
265 PUBLICATIONS   1,811 CITATIONS

SEE PROFILE

Temperature Dependence of Ion and Water Diffusion in Crown Ether Loaded Nafion Matrix

Sanhita Chaudhury, A. Bhattacharya, Chhavi Agarwal, and A. Goswami*

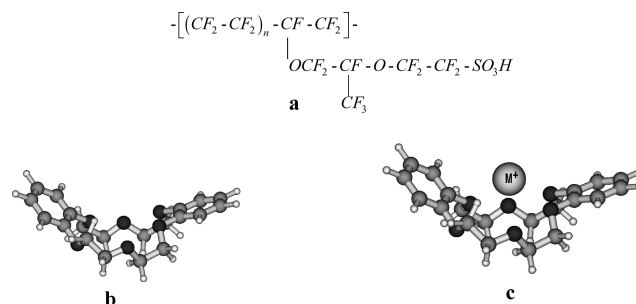Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

ABSTRACT: Temperature dependence study of the self-diffusion coefficient of Cs^+ ion in dibenzo-18-crown-6 (DB18C6) modified Nafion-117 (Cs-Naf-CR) was carried out in the temperature range of 50−65 °C. Temperature dependence of water diffusion in Cs-Naf-CR was also studied to understand the mechanism of cation and water transport in the membrane. Because of the very slow kinetics of isotopic exchange, self-diffusion measurement of Na^+ in Na-Naf-CR was carried out only at 60 °C. The result indicates that self-diffusion behavior is governed by the nature of the cation in which the crown ether was loaded in the membrane matrix. The activation energy of diffusion for Cs^+ ion and water in Cs-Naf-CR was found to be much higher than that in the pure Cs^+ form of Nafion (Cs-Naf). Water uptake of the membrane was also found to have reduced compared to Cs/Na-Naf. The results point to the binding of the ions by DB18C6 and the destruction of the water channels in the crown ether loaded membrane. The differential scanning calorimetry (DSC) data supports these observations.
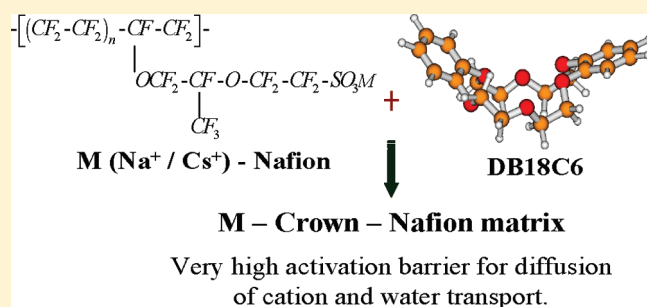
■ INTRODUCTION

Ion-exchange membranes are widely used in many separation processes based on the principle of Donnan and electrodialysis.[1] Their main use stems from the fact that they allow only the counterions to pass through while excluding the co-ions. Thus, they can be used as a separator between electrolytic solutions. The industrial applications of ion-exchange membranes include their use as separators in the chloralkali industry,[2] in battery cells, in pervaporation to dehydrate organic solvents,[3] etc. They are also used in the separation of CO_2 gases by carrier transport,[4] in sensors,[5] and in dehumidification of vapors.[6] In spite of their wide application in various fields, the ion-exchange membranes show very poor permselectivity between two different metal ions. Thus, the mutual separation of metal ions using ion-exchange membranes is not very efficient. One way to increase the metal ion selectivity is to incorporate some ligand within the membrane matrix having high selectivity for the metal ion of interest.

Crown ethers are an important class of molecules of both inherent and practical interest. The various ring size crown ethers or other complexing agents like calixerenes have a very good ability to selectively bind particular metal cations from solution depending upon the cavity size and solvents used. Various ion-selective electrodes have therefore been developed using those ligands.[7,8] Crown ethers mimic the ability of biological cation transport systems and of some antibiotics, which also bind metal cations selectively.[9] The major drawback associated with the separation of alkali metal ion using these ligands[10−13] is that they require an equivalent amount of counterion and the separation factor depends on the anion also.[14] Numerous attempts have been made in the literature[15−19] to study the competitive

transport of alkali metal ions by immobilizing the crown ether in the membrane matrix. The charge compensation of the metal ions was achieved by incorporating anionic functional groups either in the crown ether or in the polymer backbone of the membrane. Significant effect of the crown ethers on the transport selectivity was observed in the proton-driven cation transport experiments.[15] Increase in hydrophilicity of the membrane matrix resulted in higher transport rate, indicating the important role of water in the transport mechanism.[16]

Nafion-117 is a poly(perfluorosulfonic) acid ion-exchange membrane having a poly(tetrafluoroethylene) (PTFE) backbone with pendant side chains containing $-SO_3H$ groups (Figure 1a).

Figure 1. Structures of (a) Nafion, (b) DB18C6, and (c) metal complex of DB18C6.

In our earlier work with Nafion—crown ether system,[20] attempt was made to prepare an alkali metal ion selective membrane by loading dibenzo-18-crown-6 (DB18C6) in Nafion-117 cation-exchange membrane. Structure of DB18C6 and its corresponding metal ion complex are shown in Figure 1b and 1c respectively. It was observed that the transport behavior of the alkali metal ions in those membranes was strongly dependent on the cationic form of the membrane in which the crown ether was loaded. When the crown ether was loaded in the Li^+ form of the membrane (Li-Naf-CR), the entire ion-exchange sites were available for counterion exchange and the membrane showed enhanced selectivity for Cs^+ over Li^+. Complete ion-exchange equilibrium could be reached within a practical time scale because of favorable ion-exchange kinetics. On the other hand, when the crown ether was loaded in the Cs^+ form of the membrane (Cs-Naf-CR), all the ion-exchange sites were not available for counterion exchange due to drastic decrease of the mobility of the alkali metal ions in the membrane. This could be due to the strong binding of this crown for Cs^+, K^+, and Na^+ over Li^+ as observed in the literature.[21]

From the previous studies, however, it is not clear whether the cation-driven loading of DB18C6 in the Nafion-117 matrix provides template effect for improving the selectivity for other alkali metal ions, viz., Na^+ or K^+ vis-à-vis Cs^+ because of the too slow kinetics of isotopic exchange of these metal ions when DB18C6 was loaded in the cationic form of Nafion-117. DB18C6 is reported to bind Na^+ more strongly compared to Cs^+ as shown by the higher stability constant[22] in the former case. In the present work, experiments were therefore carried out to see the change in diffusional behavior for Cs^+ and Na^+ when DB18C6 is loaded in the respective cationic form of Nafion-117. Since the kinetics of isotopic exchange at room temperature with these membranes were too slow, self-diffusion experiments were carried out as a function of temperature to understand the mechanism of transport. Water plays an important role in the transport properties of Nafion-117 membrane. According to the cluster channel network model of Gierke,[23] the ions and water in the membrane form spherical clusters connected by narrow channels. During diffusion, the ions and water move through these water channels. Thus, for the cations of the same charge state, the strongly hydrated one diffuses faster through the membrane due to higher water content in the membrane. Also, the earlier works on temperature dependence of ion and water diffusion in Nafion matrix[24,25] show that activation energy for water diffusion in Nafion is comparable to that in pure water, indicating very little barrier for water transport in the membrane. In our earlier studies with the Nafion—crown ether system, the IR spectra[20] indicated less water content in the membrane matrix in the presence of crown ether. In the present work, the equilibrium water uptake in these membranes was measured. The effect of temperature on the self-diffusion coefficient of water in Cs-Naf-CR was also measured. The activation energy for self-diffusion of both Cs^+ and water was calculated and compared with that in Nafion-117 in absence of DB18C6. DSC measurements were also carried out to supplement the observations obtained from self-diffusion measurements. From the data, an attempt has been made to explain the membrane transport behavior in terms of hydration state of the membrane.

■ EXPERIMENTAL SECTION

Reagents and Chemicals. Nafion-117 ion-exchange membrane (purchased from Du Pont) with an equivalent weight of 1100 and thickness of 178 μm was used for the present set of experiments. The membrane samples were preconditioned to remove organic impurities following the method as described elsewhere.[26] The samples were refluxed in 5 M HNO_3 for 3 h. They were then treated with 0.5 M NaOH and 0.5 M HCl separately. Dibenzo-18-crown-6 (Analytical Reagent grade) used was procured from PCR Research Chemicals, Inc., Gainesville, FL. CsCl (99.999%, ultrapure grade) and NaCl (99.9%, Analytical Reagent grade) were procured from Sisco Research Lab., Mumbai, India, and SD Fine Chem. Ltd., India, respectively. Deionized water (18 MΩ/cm, Gradient A-10 model, Milli-Q, USA) was used in the present study. Radiotracers ^{137}Cs and ^{22}Na used in the present study were obtained from the Board of Radiation and Isotope Technology, Mumbai, India.

Incorporation of the Crown Ether. Incorporation of DB18C6 in the membrane samples having the desired ionic form was done following the method described in ref 20. The Nafion-117 samples in appropriate cationic form were placed in a saturated solution of DB18C6 in 200 mL of dimethylformamide for 24 h. The samples were subsequently removed from the solution, and excess solution was wiped out. The samples were washed thoroughly with deionized water and dried under vacuum.

Membrane Characterization. The weight of dry membrane was obtained by heating the membrane sample in Cs^+/Na^+ 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 these ionic forms. The extent of loading of DB18C6 was confirmed from the change in the dry weight of the sample before and after the loading of crown ether. The loading of DB18C6 was in the molar ratio of 1:1 with respect to Na^+, while it was 0.7:1.0 with respect to Cs^+. Infrared spectra of the membranes were also recorded using a Jasco Fourier transform IR spectrometer model JASCO FTIR4100 (Japan). The spectra obtained were similar to that shown in our earlier work.[20] The thickness of the membrane in appropriate ionic form was measured using a digital micrometer (Mitutoyo, Japan) which has an accuracy of 0.001 mm.

Differential Scanning Calorimetry (DSC). DSC measurements for the Cs^+/Na^+ form of Nafion with and without DB18C6 was done using a Mettler Toledo DSC 822 instrument at a heating rate of 10 °C/min within the temperature range of −10 to 300 °C. About 7—8.5 mg of membrane samples was used to record the scans. The scans were recorded under inert atmosphere with an empty aluminum pan as the reference. Indium was used as the calibration standard. The DSC traces were analyzed using the software supplied by Mettler Toledo.

Self-diffusion Measurement of Cations. For the self-diffusion study of radiotracer ions from the equilibrating solution into the membrane (absorption), the membrane sample (2 cm × 2 cm) in appropriate ionic form was placed in 30 mL of 0.01 N salt solution containing the radiotracer ions. The temperature of the solution was maintained using a constant temperature bath. During the course of the experiment, the temperature was monitored constantly using an external thermometer. The solution containing membrane sample was stirred vigorously (∼52 rad/s) to ensure that membrane diffusion was taking place. The sample was taken out at regular time intervals, washed thoroughly with deionized water to remove equilibrating solution clinging to the surface, and counted for γ-ray in a fixed geometry using a well-type NaI(Tl) detector connected to a 4k channel analyzer. The 661 and 511 keV peaks were monitored for ^{137}Cs and ^{22}Na, respectively. The membrane sample was placed again in the equilibrating solution after counting. This procedure was repeated until equilibrium uptake of radiotracer was reached. The actual residence

time of the membrane in equilibrating solution was used as the time of cation absorption. The Cs^+ ion self-diffusion measurement in Cs-Naf-CR was carried out at four different temperatures, viz., 50, 55, 60, and 65 °C. The experiments at each temperature were repeated to verify the reproducibility of the measurement. The dry weight of the membrane was taken before and after every experiment. It was observed that the weight of the membrane sample remained constant, indicating that crown ether did not come out of the membrane during the course of the experiment. A separate experiment was performed where Cs-Naf was spiked with ^{137}Cs radiotracer and subsequently used for loading DB18C6. Desorption of ^{137}Cs loaded in this membrane with CsCl as external solution was studied at 60 °C. It was observed that all the radiotracer could be removed and the desorption time scale was the same as observed in the previous experiment with Cs-Naf-CR at 60 °C. This result shows that all the Cs^+ ions in the DB18C6-modified Nafion-117 membrane are equivalent.

In the case of Na-Naf-CR, the self-diffusion study of Na^+ ion was carried out only at 60 °C since the kinetics was found to be too slow at lower temperatures. Even at 60 °C, it was not possible to reach complete equilibrium after a long time period. In order to obtain the fractional attainment of equilibrium as a function of time (t), the amount of radiotracer ions in the membrane at equilibrium ($t = \infty$) is required. This was found out indirectly, assuming that the amount of radiotracer ion in the membrane at infinite time is governed by the ratio of the amount of sodium ion in the membrane to that in the external solution. Total radioactivity added in the external salt solution was obtained by counting 100 μL of the solution in NaI(Tl) detector connected to a 4k channel analyzer. The number of available ion-exchange sites (mili equivalent) in the membrane was obtained from the dry weight of the membrane sample before incorporation of the crown ether. The equilibrium radioactivity in the membrane was obtained from the product of the ratio of Na^+ in the membrane to that in the external salt solution and the total activity present in the external salt solution. It was assumed that the uptake of radiotracer in the membrane did not alter the radioactivity concentration in the external salt solution.

Self-diffusion Measurement of Water in Cs-Naf-CR. In order to study the self-diffusion behavior of water in Cs-Naf-CR, the membrane sample (2 cm × 2 cm Cs-Naf-CR) was equilibrated in water spiked with ^3H (HTO) at a constant temperature with stirring for 2 h. After equilibration, the membrane was taken out and gently wiped with a filter paper to remove the water droplets attached to the surface. Then the sample was placed in 25 mL of deionized water which was kept at the same temperature at which equilibration of the membrane with HTO was carried out. The water was continuously stirred (~52 rad/s) during the course of the desorption experiment to minimize the film diffusion. The water diffusion rate in the membrane sample was measured by pipetting out 50 μL of the equilibrating solution after regular time intervals. The β activity of ^3H was measured by mixing the sample in a vial with 5 mL of scintillation cocktail-w (2,5-diphenyloxazole (PPO) = 0.7%, 1,4-di-2-(5-phenyloxazolylbenzene (POPOP) = 0.03%, naphthalene = 10%, and trinoctylphosphine oxide (TOPO) = 1% in 1,4-dioxane solvent), and counting the samples with a liquid scintillation analyzer. The water diffusion experiments were carried out at 27, 38, 45, 51, and 56 °C.

Membrane Water Content Measurement. The water content (cm³) of the membrane was obtained from the uptake of ^3H β activity at equilibrium in the membrane and the radioactivity
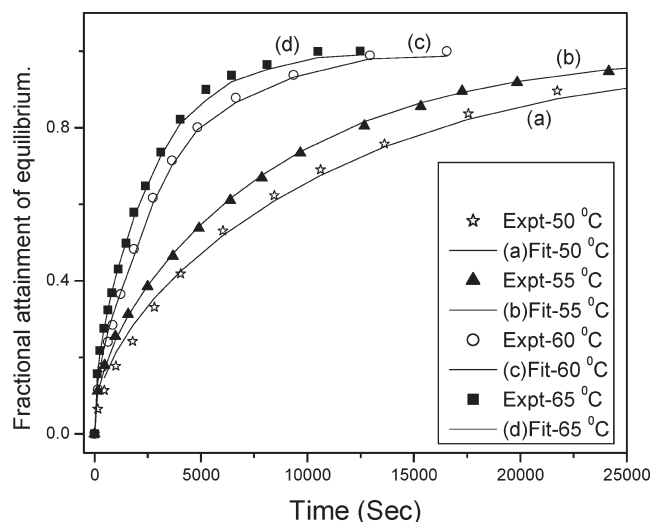
Figure 2. Self-diffusion profile of Cs^+ ion in Cs-Naf-CR at four different temperatures. The symbols are the experimental points, and the lines are the fitted lines to those experimental points.

Table 1. Variation of $D_{Cs^+}{}^m$ in Cs-Naf-CR as a Function of Different Temperatures

temp (°C)	50	55	60	65
$D_{Cs}^{+m} \times 10^6$ (cm²/s)	3.50×10^{-3}	5.13×10^{-3}	8.74×10^{-3}	1.32×10^{-2}

concentration of the ^3H-labeled water (HTO) used for equilibration. Assuming the density of water to be 1 g cm^{-3} in the membrane phase, and using the dry weight of the membrane after incorporation of the crown ether, the membrane water content ($n_{H_2O}/n_{SO_3^-}$) was obtained. In Cs-Naf-CR the water content was measured at 27, 38, 45, 51, and 56 °C while that for Na-Naf-CR was carried out only at 56 °C.

RESULTS AND DISCUSSION

Temperature Dependence of Self-diffusion of Cations in Cs-Naf-CR/Na-Naf-CR. Figure 2 shows the isotopic exchange kinetics studied for Cs-Naf-CR membrane at four different temperatures. As seen from the figure, there is a steady increase in isotopic exchange rate with increase in temperature, indicative of the existence of a barrier for diffusion. The value of the self-diffusion coefficient for Cs^+ ($D_{Cs^+}{}^m$) ion in this membrane at each temperature was obtained from a fit of the experimental data with the equation obtained from the analytical solution of Fick's second law[26]

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

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 (200 μm) in swollen condition. n^* and D were taken as free parameters and only first three terms in the eq 1 were used for fitting. The fitted
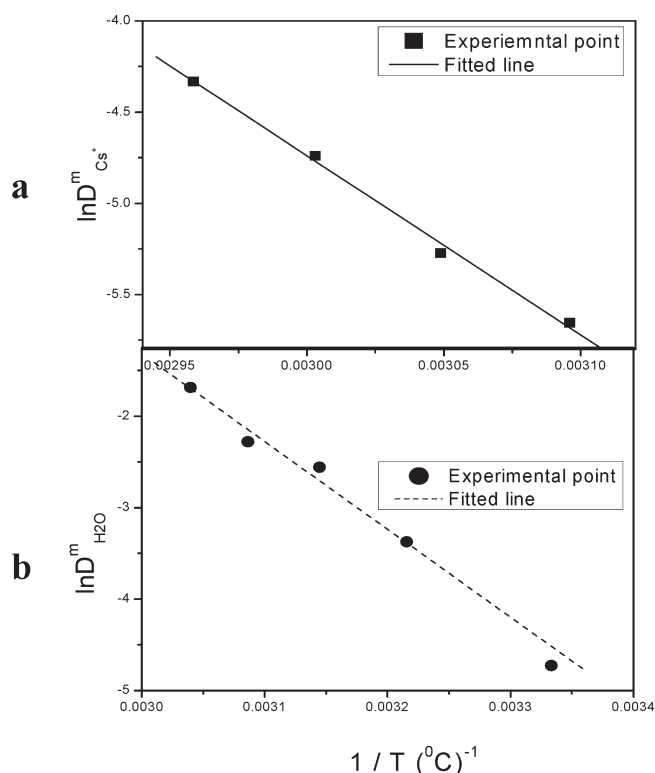
Figure 3. Variation of logarithm of self-diffusion coefficient of (a) Cs^+ (ln $D_{Cs^+}^m$) and of (b) water (ln $D_{H_2O}^m$) as a function of inverse of temperature.

Table 2. Activation Barrier for Cs^+ Ion and Water in Pure[24] and DB18C6-Modified Cs-Naf

| membrane	activation energy (kJ/mol)	
	Cs^+	H_2O
Cs-Naf	35.9	22.0
Cs-Naf-CR	80.1	79.8

line to these self-diffusion behaviors is also shown in Figure 2 along with the experimental points.

The $D_{Cs^+}^m$ values in Cs-Naf-CR obtained from the fit are given in Table 1. The Arhenius plot of the $D_{Cs^+}^m$ data is shown in Figure 3a. From the slope of this linear plot, the activation energy for diffusion of Cs^+ was obtained which is given in Table 2 along with the literature[24] reported activation energy for Cs-Naf (Nafion-120). The value of activation energy is seen to have increased by a factor of ∼2.2 in Cs-Naf-CR compared to Cs-Naf, accounting for the very slow diffusion rate of Cs^+ ion in Cs-Naf-CR at room temperature, as observed in our earlier work.[20] Such a large value of activation energy is typical of ionic diffusion in ionic crystal lattice rather than in swollen polymers.[24] This is indicative of significant change in the morphology and different mechanism of Cs^+ ion diffusion in the Cs-Naf-CR compared to Cs-Naf.

Attempt to carry out similar self-diffusion experiments with Na-Naf-CR was not possible at lower temperature as the isotopic exchange kinetics was too slow to reach complete equilibrium within a reasonable time scale. Figure 4 shows the comparison
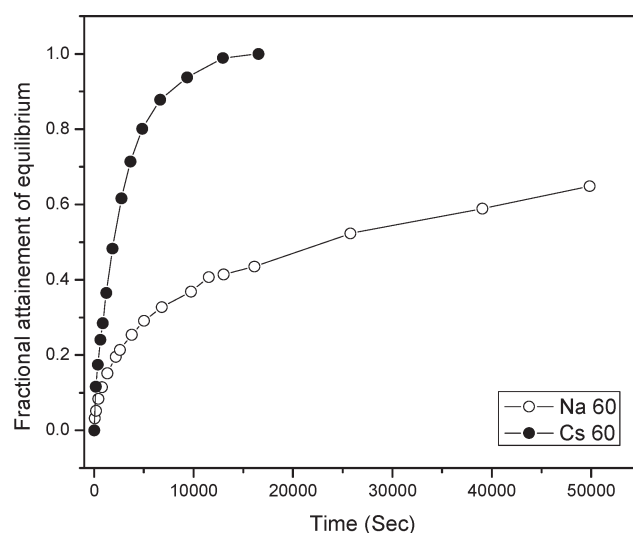
Figure 4. Comparison between Na^+ and Cs^+ self-diffusion profile at 60 °C.
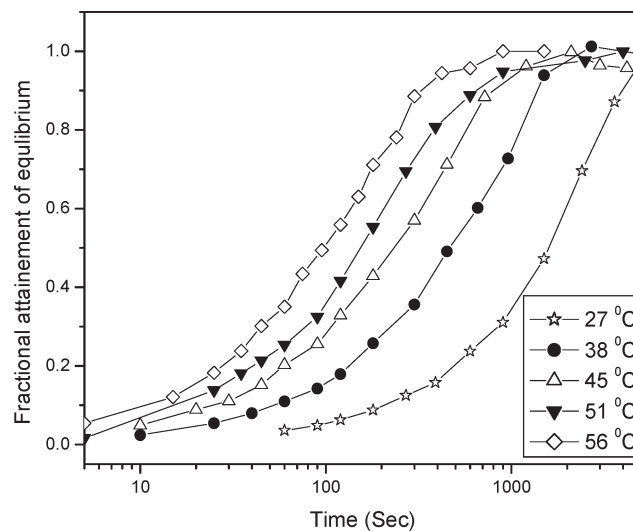
Figure 5. Self-diffusion profile of water in Cs-Naf-CR at five different temperatures.

between the isotopic exchange kinetics for Cs^+ and Na^+ with Cs-Naf-CR and Na-Naf-CR, respectively, at 60 °C. As can be seen from the figure, the Cs^+ isotopic exchange is complete within ∼20 000 s, while the Na^+ isotopic exchange is not complete even at 50 000 s. The lower mobility of Na^+ in Na-Naf-CR indicates higher activation energy for diffusion of Na^+ in Na-Naf-CR. This may reflect the stronger binding of Na^+ with the DB18C6 in the membrane matrix, retarding the mobility of the Na^+ ion.[22] There are literature reports[27−30] where selectivities of ion-exchange resins and ion-selective electrode have been enhanced by carrying out the measurement at elevated temperatures. It will be of interest to see whether the selectivity of this crown ether loaded membrane could be tuned by carrying out the transport study at higher temperature.

Temperature Dependence of Self-diffusion Behavior of Water. Figure 5 shows the self-diffusion behavior of water in Cs-Naf-CR studied with tritium-labeled water at five different

Table 3. Variation of $D_{H_2O}^m$ in Cs-Naf-CR as a Function of Different Temperatures

temp (°C)	27	38	45	51	56
$D_{H_2O}^m \times 10^6 (cm^2/s)$	8.88×10^{-3}	3.43×10^{-2}	7.74×10^{-2}	1.02×10^{-1}	1.85×10^{-1}

**Table 4. Water Content in Cs-Naf-CR at Different Temperatures**

temp (°C)	27	38	45	51	56
$n_{H_2O}/n_{SO_3^-}$	1.02	1.09	1.12	1.36	1.40

temperatures. Here again, the rate of $HTO_{(m)} \leftrightarrows H_2O_{(aq)}$ exchange increases with the rise in temperature. The values of $D_{H_2O}^m$, calculated from a fit of the experimental data with eq 1 are given in Table 3. The $D_{H_2O}^m$ values at a given temperature are ∼30 - 40 times higher than the $D_{Cs^+}^m$. It indicates that, as in the case of Cs-Naf, water diffusion in Cs-Naf-CR faces less hindrance than the diffusion of Cs$^+$ ion. However, all the values are substantially lower than the $D_{H_2O}^m$ in Cs-Naf, showing that the mobility of the water in Cs-Naf-CR is considerably hindered compared to that in Cs-Naf. The value of the activation energy, obtained from the Arhenius plot (Figure 3b), is also given in Table 2 along with the activation energy for Cs-Naf.[24] It is seen that the activation energy increases by a factor of ∼4 and is comparable to the activation energy for Cs$^+$ diffusion in Cs-Naf-CR. Such a high value of activation energy indicates that there is no continuous water channel in the Cs-Naf-CR.

Equilibrium uptake of water as a function of temperature in Cs-Naf-CR was also measured and the corresponding $n_{H_2O}/n_{SO_3^-}$ values are given in Table 4. As seen from the data, the water uptake has reduced significantly in Cs-Naf-CR over Cs-Naf, showing that dehydration of Cs$^+$ in Cs-Naf-CR has occurred. Reduction in water signal as observed from IR data[20] in Cs-Naf-CR as compared to Cs-Naf also confirms the increased hydrophobicity of the Nafion sample after incorporation of DB18C6 in the membrane matrix. This shows that complexation of DB18C6 with Cs$^+$ ion accompanied by the disruption of the water cluster channel network of Nafion-117 has taken place, thereby reducing the $D_{H_2O}^m$ significantly. The effect of water content in Nafion-117 on the self-diffusion coefficient of water was extensively studied by Zhao et al.[31] and it was concluded that the diffusivity changes significantly when $n_{H_2O}/n_{SO_3^-}$ becomes less than 4. At the $n_{H_2O}/n_{SO_3^-}$ values close to that in the present experiment (∼1), values of diffusion constants reported at different temperature are comparable to the values observed in the present experiments. This shows that, apart from the crown ether, water content in the membrane also plays an important role in the cation transport property of the membrane. These results explain why incorporation of hydrophilic species in the membrane increases the cation diffusion rate in the crown ether loaded membrane matrix.[16]

The cause of enhancement in the activation energy of Cs$^+$ ion in the DB18C6-loaded Nafion membrane compared to pure Nafion-117 could be due to enhancement in binding of the ion with the crown ether in the membrane matrix and also due to the reduction in water content in the membrane matrix due to loading of the crown ether, destroying water clusters in Cs-Naf.

In the case of Na-Naf-CR, equilibrium uptake of water was measured and the corresponding $n_{H_2O}/n_{SO_3^-}$ value was found to be 1.07. As can be seen from Table 4, the value is slightly lower than that of Cs-Naf-CR, indicating higher degree of dehydration of Na$^+$ in Na-Naf-CR as compared to Na-Naf which again reflects
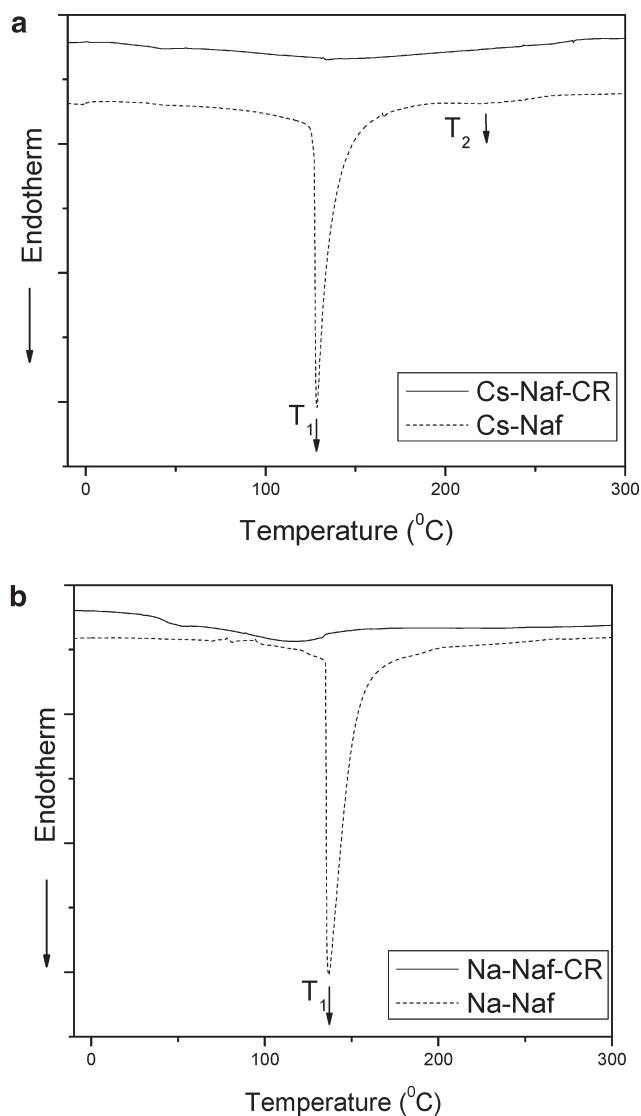
Figure 6. (a) DSC thermograms of Cs$^+$ form of Nafion membrane with and without DB18C6. (b) DSC thermograms of Na$^+$ form of Nafion membrane with and without DB18C6.

that DB18C6 binds more strongly with Na$^+$ ion in the membrane matrix. The higher $D_{Cs^+}^m$ as observed in our earlier work,[20] when DB18C6 was loaded in the Nafion-117 membrane in Li$^+$ form, could be due to at least partial retention of the water channels in Li-Naf-CR. This is due to the lower binding of DB18C6 with Li$^+$, thereby failing to completely dehydrate the Li$^+$ ion in the membrane matrix unlike Cs-Naf-CR and Na-Naf-CR.

Figure 6, a and b, depicts the DSC traces of pure and DB18C6-modified Cs$^+$/ Na$^+$ form of Nafion, respectively. In the case of Cs-Naf, one sharp endothermic peak at 128 °C and another broad endothermic peak at 242 °C have been observed while for Na-Naf only one sharp endothermic peak at 136 °C has been observed. This behavior of Cs$^+$/ Na$^+$ form of Nafion is well explained

in the literature.[32,33] Thus, the transition at ∼130 °C (T_1) has been associated with the transition into the ionic clusters and that at ∼245 °C (T_2) has been associated with the region of crystallite melting of the ionomers. The comparison of the DSC traces of Cs-Naf and Cs-Naf-CR shows that the sharp endothermic peak at 128 °C in Cs-Naf has almost disappeared in Cs-Naf-CR. As can be seen from Figure 6b, the same is true for Na-Naf-CR also. This change in DSC traces could be attributed to the absence of regions of water cluster channels after incorporation of DB18C6 in the Nafion-117 matrix. This corroborates our observations already obtained from equilibrium water uptake measurement and self-diffusion measurement of cations and water.

■ CONCLUSION

The mobility of ions (Cs$^+$/Na$^+$) and water has been found to reduce drastically in Cs-Naf-CR and Na-Naf-CR compared to the corresponding cationic form of pure Nafion-117. The temperature dependence of isotopic exchange of Cs$^+$ and Na$^+$ ion in Cs-Naf-CR and Na-Naf-CR, respectively, shows that there is a significant increase in the exchange rate with rise in temperature. From the temperature dependence of self-diffusion coefficient of Cs$^+$ and water in Cs-Naf-CR, the activation energy of diffusion for Cs$^+$ ion and water has been obtained. The values of activation energy for Cs$^+$ and water in Cs-Naf-CR are comparable and are much higher than that in the case of pure Nafion. This high value of activation barrier is comparable to that of ionic diffusion in ionic crystal lattice. Loading of DB18C6 in Nafion-117 enhances the hydrophobicity of the membrane matrix, thereby reducing the water uptake in the membranes. The DSC data shows disruption of water clusters in the membrane, and the attendant loss of plasticity which lowers the self-diffusion coefficient values. The results show the possibility of studying the selectivity of different alkali metal ions in these membranes at higher temperatures, which otherwise is not possible at room temperatures due to very slow kinetics.

■ 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) Eisenberg, A., Yeager, H. L., Eds. Perflourinated Ionomer Membranes; 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) Way, J. A.; Noble, R. D.; Reed, D. L.; Ginley, G. M.; Jarr, L. AIChE. J. 1987, 33, 480.
(5) Sakai, Y.; Sadaoka, Y.; Matsuguchi, M. J. Electrochem. Soc. 1989, 136, 171.
(6) Sata, T.; Tanimoto, M.; Kawamura, K.; Matsusaki, K. J. Colloid Interface Sci. 1999, 219, 310.
(7) Buhlmann, P.; Pretsch, E.; Bakker, E. Chem. Rev. 1998, 98, 1593.
(8) Xia, Z.; Badr, I. H. A.; Plummer, S. L.; Cullen, L.; Bachas, L. G. Anal. Sci. 1998, 14, 169.
(9) Dobler, M. Ionophores and their structures; Wiley: New York, 1981.
(10) Talanova, G. G.; Elkarim, N. S. A.; Hanes, R. E., Jr.; Hwang, H. S.; Rogers, R. D.; Bartsch, R. A. Anal. Chem. 1999, 71, 672.
(11) Gokel, G. W.; Leevy, W. M.; Weber, M. E. Chem. Rev. 2004, 104, 2723.
(12) Charewicz, W. A.; Bartsch, R. A. Anal. Chem. 1982, 54, 2300.
(13) Walkowiak, W.; Kang, S. I.; Stewart, L.; Ndip, G.; Bartsch, R. A. Anal. Chem. 1990, 62, 2022.
(14) Hankins, M. G.; Kim, Y. D.; Bartsch, R. A. J. Am. Chem. Soc. 1993, 115, 3370.
(15) Kimura, K.; Sakamoto, H.; Yoshinaga, M.; Shono, T. J. Chem Soc., Chem. Commun. 1983, 17, 978.
(16) Sakamoto, H.; Kimura, K.; Shono, T. Eur. Polym. J. 1986, 22, 97.
(17) Sata, T.; Tanimoto, M.; Kawamura, K.; Matsusaki, K. Colloid Polym. Sci. 2000, 278, 57.
(18) Sata, T.; Kawamura, K.; Higa, M.; Matsusaki, K. J. Membr. Sci. 2001, 183, 201.
(19) Nemat-Nasser, S.; Zamani, S.; Tor, Y. J. Appl. Phys. 2006, 99, 104902.
(20) Bhattacharya, A.; Goswami, A. J. Phys. Chem. B 2009, 113, 12958.
(21) Takeoka, S.; Sakai, H.; Tsuchida, E. Chem. Lett. 1990, 19, 1539.
(22) Katsura, S.; Ito, Y.; Takeda, Y. Inorg. Chim. Acta 2004, 357, 541.
(23) Hsu, W. Y.; Gierke, T. D. J. Membr. Sci. 1983, 13, 307.
(24) Yeager, H. L.; Steck, A. J. Electrochem. Soc.: Electrochem. Sci. Technol. 1981, 128, 1880.
(25) Saito, M.; Hayamimizu, K.; Okada, T. J. Phys. Chem. B 2005, 109, 3112.
(26) Goswami, A.; Acharya, A.; Pandey, A. K. J. Phys. Chem. B 2001, 105, 9196.
(27) Muraviev, D.; Gonzalo, A.; Valiente, M. Anal. Chem. 1995, 67, 3028.
(28) Zagorodni, A. A.; Muraviev, D. N.; Muhammed, M. Sep. Sci. Technol. 1997, 32, 413.
(29) Cerjan-Stefanovic, S.; Blanusa, M.; Kastelan-Macan, M.; Fresenius, Z. Anal. Chem. 1984, 319, 304.
(30) Zahran, E. M.; Gavalas, V.; Valiente, M.; Bachas, L. G. Anal. Chem. 2010, 82, 3622.
(31) Zhao, Q.; Majsztrik, P.; Benziger, J. J. Phys. Chem. B 2011, 115, 2717.
(32) Almeida, S. H.; Kawano, Y. J. Thermal Anal. Calorim. 1999, 58, 569.
(33) Stefanithis, I. D.; Mauritz, K. A. Macromolecules 1990, 23, 2397.

9400

dx.doi.org/10.1021/jp203821h |J. Phys. Chem. B 2011, 115, 9395–9400