Effect of Cation Driven Loading of Dibenzo-18-Crown-6 in Nafion-117 Membrane on the Diffusion and Transport Behavior of Alkali Metal Ions

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The possibility of enhancing the selectivity to separate the alkali metal ions was studied by loading dibenzo-18-crown-6 (DB18C6) in Li^+, Na^+, K^+, and Cs^+ form of cation exchange membrane, Nafion-117 (M−Naf−Cr where M = Li, Na, K, and Cs). DB18C6 was incorporated in Nafion-117 in corresponding ionic forms. Presence of DB18C6 in Nafion-117 was confirmed by FTIR. Self-diffusion and ion exchange kinetics of the alkali metal ions were studied in these membranes. It was observed that the diffusion in the membrane slowed down drastically from Li^+ to all other monovalent alkali metal ions. Two compartment cell experiments were done with DB18C6 loaded Cs^+-form of Nafion-117 (Cs−Naf−Cr) membrane to study the transport of Na^+ and Cs^+ ions. No transport of ions was observed. When the same experiment were performed by replacing Li^+ of Li−Naf−Cr with Cs^+ (Cs−Li−Naf−Cr), transport of Cs^+ and H^+ were observed at much faster time scale compared to Cs−Naf−Cr. The selectivity of Cs^+ over Li^+ was enhanced by a factor of about 6 when Li−Naf−Cr was used in place Li^+ form of Nafion-117 for the transport experiments.

Introduction

Ion exchange membranes have been widely used in various industrial fields and have become one of the essential materials in separation processes. They are used as separators of electrolyte solutions in chlor-alkali industry, as well as in electrodialysis to concentrate or desalinate electrolyte solutions, in diffusion dialysis to recover acids or alkalis from waste solutions, and in pervaporation to dehydrate organic solvents.[1] Further applications of the membranes are in the dehumidification of vapors,[2] in the separation of acidic gas such as carbon dioxide by carrier transport,[3] and as sensing materials.[4] Though the performance of ion exchange membranes has been vastly improved in recent years, conventional ion exchange membranes are still ineffective for removing or concentrating specific ions with the same charge from a mixture due to poor perm-selectivity for specific ions. Mutual separation of the alkali metal ions is therefore difficult using the ion exchange membranes, unless their selectivity is enhanced for a particular metal ion by incorporating a suitable ligand either by physical or chemical means. A number of crown ethers, calixarenes, and cryptands are highly selective for particular alkali metal ions. Various ion selective electrodes have therefore been developed and used employing that macrocyclic ligands.[5,6] Separation processes of the alkali metal ions using these macrocyclic ligands have been attempted employing solvent extraction and membrane-based techniques.[7−10] The major drawback of those ligands for the separation process is the requirement of equivalent amount of counterion, viz. nitrate, chloride, or perchlorate and the separation factor depends on the anion also.[11] The necessecity of the excess of counterion can be avoided either by attaching ionizable group such as carboxylate, sulfonate group to the crown ether and the calixarene moiety[12−14] or by incorporating those macrocyclic ligands in a matrix which already contains ionizable groups, viz. ion exchange resins or membranes.[2,15−17]

Nafion-117, a perfluorosulphonate ionomer, is extensively used in polymer electrolyte fuel cell, chlor-alkali industries, and Donnan dialysis based applications[18,19] and can be a good host for these ligands. According to cluster channel network model, the transport of ions through the Nafion membrane occurs through water swollen ionic clusters, connected by narrow channels.[20] However, it has been suggested that the clusters may not be spherical in shape and there may be a local intrusion of fluorocarbon phase in hydrated ionic clusters.[21] A three phase submicrostructure model of Nafion membrane, consisting of fluorocarbon crystallites, ionic hydrophilic clusters and an amorphous hydrophobic region (with lower ionic and water content) has been proposed by Yeager et al.[22] and Pineri et al.[23] Morphology and properties of Nafion membrane has been extensively reviewed recently by Mauritz and Moore.[24] Different species has been introduced in Nafion to modify its transport properties for its use in fuel cell,[25−28] in chemical sensors[29] and ion selective electrodes.[30] Dibenzo-18-crown-6 (DB18C6) has been found to be selective for Cs^+, K^+, and Na^+ over Li^+ ion.[31] Takeoka et al.[32] studied the relative mobility of different alkali metal cations in Nafion-117 loaded with 15-crown-5 and 18-crown-6 by impedance measurement. It was observed that the mobility of Li^+ was much higher compared to Na^+ and K^+. There is no literature available on the cation driven loading of the crown ether in ion exchange membranes and its effect on the transport properties of the membrane. In the present paper, an attempt has been made to incorporate the crown ether (DB18C6) in the membrane loaded with different monovalent cations to study the possibility of making template for a particular cation. The study of transport behavior of different alkali metal ions was carried out to ascertain the effect of templating depending upon the cationic form used for incorporating the crown ether. The results of characterization of the membranes using different techniques

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are reported. Transport properties of the membranes were studied with different alkali metal ions. Finally, results of diffusion dialysis experiment to see the prospect of separation of Li$^+$/Cs$^+$ using the crown ether loaded membrane is reported.

Experimental Section

Reagents and Chemicals. Dibenzo-18-crown-6 (Analytical Reagent grade) used was procured from PCR Research Chemicals, Inc./Gainesville, FL. CsCl (99.999%, ultrapure grade) and KCl (99.9%, Analytical Reagent grade) were procured from Sisco Research Lab., Mumbai, India. NaCl (99.9%, Analytical Reagent grade) and LiCl (99.9%, Analytical Reagent grade) were procured from SD Fine Chem. Ltd., India and Chemco Fine Chemicals, Mumbai, India respectively. HCl (37%, Proanalysi) was procured from Merck KGaA, Darmstadt, Germany. Deionized water (18 MΩ/cm, Gradient A-10 model, Milli-Q, U.S.A.) were used in the present study. Nafion-117 ion exchange membrane with an equivalent weight of 1100 and thickness of 178 μm was used. The membranes were treated to remove organic impurities as described in the literature.[33] It was then conditioned with 0.5 M HCl and 0.5 M NaOH followed by equilibration with 0.5 mol/L of relevant salt solution for 18−24 h at room temperature (27 °C) for converting the membrane into the appropriate ionic form. Radiotracers ^{137}Cs and ^{22}Na used in the present study were obtained from Board of Radiation and Isotope Technology, Mumbai, India.

Loading of Crown Ether in the Nafion-117 Membrane. Crown ether was incorporated in the membrane by soaking Nafion-117 loaded with different alkali metal ions, viz. Li$^+$, Na$^+$, K$^+$, and Cs$^+$ in a large volume (∼300 mL) of 0.4 mM DB18C6 solution in dimethyl formamide for 24 h. The membrane was subsequently removed from the solution, and excess solution was then wiped out. The membrane was then washed thoroughly with demineralized water and dried under vacuum.

Characterization of the Crown Ether−Loaded Membrane. *FTIR Studies.* Infrared spectra were recorded using a Jasco Fourier transform IR spectrometer model JASCO FT-IR4100 (Japan). Spectra of Cs−Nafion and Li−Naf−Cr were taken with smaller aperture (0.5 and 0.9 mm, respectively) to avoid the flooding of detector due to broad absorption band of water.

Thermogravimatric (TG) studies. The nonisothermal thermogravimetric (TG) measurements were carried out with Mettler thermogravimetric analyzer (TG 50) coupled with a Mettler TC 10A processor. The temperature calibrations were carried out according to the instrument manual. The experimental data collected were transferred to a computer and analyses were carried out by Mettler STAR^e program.[34] Approximately 10 mg of the polymer samples were taken in an open alumina crucible and the degradation profiles were recorded from 25 to 600 °C at a heating rate of 10 °C min^{-1}. The decomposition was carried out in an inert dynamic atmosphere of high purity nitrogen set at a flow rate of 50 mL min^{-1}.

Diffusion Studies. For the diffusion studies of radiotracer ions from the equilibrating solution into the membrane (absorption), the membrane sample in appropriate form was placed in 25 mL of salt solution containing the radiotracer ions at room temperature (27 °C). The concentration of salt in equilibrating solution was kept at 0.025 M to maximize the absorption of radiotracer ions into the membrane. The solution containing membrane sample was stirred vigorously
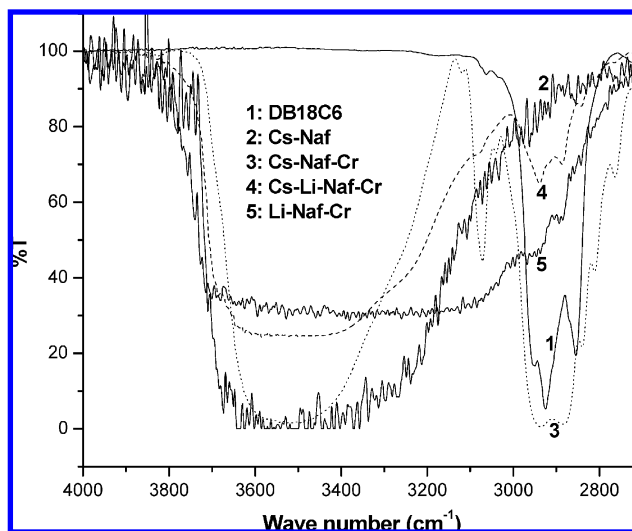
Figure 1. FTIR spectra of DB18C6 and Nafion-117 in different cationic form in absence and presence of DB18C6.

to ensure the boundary conditions, that is, membrane diffusion is taking place. The membrane sample was taken out at regular time intervals, washed thoroughly with deionized water and counted for γ-ray in the 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 replaced again in the equilibrating solution after counting. The actual residence time of the membrane in the equilibrating solution was used as the time of cation absorption. Desorption experiments were carried out in a similar way. The details of the experiment have been described elsewhere.[33]

Transport Studies for the Cations. Transport studies were carried out in a two compartment dialysis cell separated by Nafion-117 membrane in appropriate form. Volume of each compartment was 25 mL. The solution in each compartment was continuously stirred during the course of the experiment to minimize the film diffusion. The solution in one of the compartments was initially spiked with appropriate radiotracer. The radioactivity in each compartment was subsequently measured by pippetting out 100 μL of solution at regular time intervals and counting for γ-ray activity until the equilibrium is reached. The transport of H$^+$ ion was monitored by titrating 100 μL solution from each compartment by 0.1 M NaOH.

Results and Discussion

Figure 1 shows the FTIR spectra of Cs$^+$ form of Nafion-117-, DB18C6-, and DB18C6-loaded Nafion-117 membranes in different cationic form. It is seen from the figure that the Cs−Naf has a broad absorption band at 3000−3800 cm^{-1} indicating the presence of water in the membrane matrix. Pure DB18C6 possesses a characteristic absorption peak at 2930 cm^{-1} due to the C−H stretching, which is absent in the Cs−Naf. Both Cs−Naf−Cr and Cs−Li−Naf−Cr show the DB18C6 peak for C−H stretching at 2930 cm^{-1}. Li−Naf−Cr contains significant amount of water as seen from very broad absorption band in the 3000−3800 cm^{-1} region which mask the DB18C6 peak. Water content is seen to have reduced in the Cs−Naf−Cr and Cs−Li−Naf−Cr, thereby making the DB18C6 peak visible. Apparently the DB18C6 peak is weaker in Cs−Li−Naf−Cr
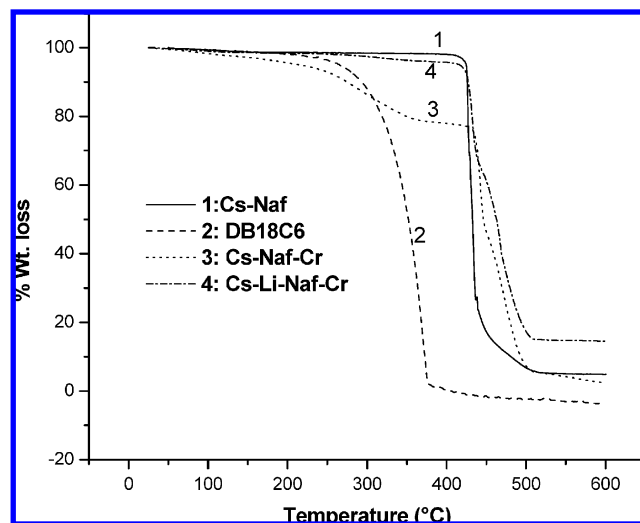
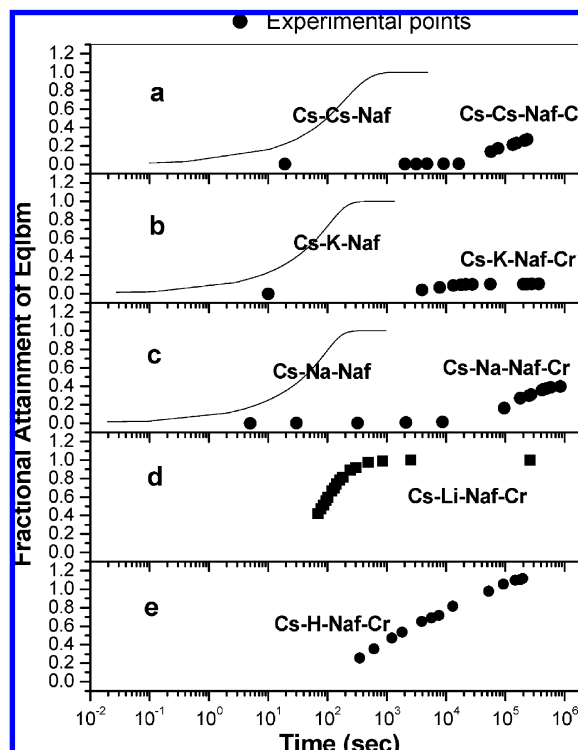**Figure 2.** Thermogravimatric plots of Nafion-117 in different forms.

Figure 3. Cs^+ sorption in M−Naf−Cr membrane in different cationic form. Solid lines indicate the Cs^+ sorption profile in the different cationic form of pure Nafion-117 obtained from Nernst−Planck equation (with known diffusion coefficient of the ions) for ion exchange kinetics.

compared to Cs−Naf−Cr indicating the lower concentration of DB18C6 in Cs−Li−Naf−Cr.

TG data of Nafion-117 membranes in various forms are shown in Figure 2. Cs−Nafion decomposes above 400 °C, while DB18C6 starts decomposing at ∼200 °C and the decomposition completes around ∼375 °C. It is seen that Cs−Naf−Cr loses significant weight (∼20%) before 400 °C showing the decomposition of DB18C6 in the membrane. Weight loss is less than 5% before 400 °C for both Li−Naf−Cr and Cs−Li−Naf−Cr. This shows the concentration of DB18C6 in Cs−Naf−Cr is higher compared to Li−Naf−Cr. This enhanced loading can be attributed to the higher affinity of this crown ether for Cs^+ over Li^+.

Diffusion Studies. Figure 3 shows the isotopic and ion exchange kinetics studied with M−Naf−Cr membranes. It is seen from Figure 3a that the $Cs^+_{(m)} \rightleftharpoons Cs^+_{(s)}$ isotopic exchange rate is very slow and is not complete even after several days. The extent of slowing down is evident from a comparison of the graph for $Cs^+_{(m)} \rightleftharpoons Cs^+_{(s)}$ isotopic exchange for pure Nafion-117 (solid line in Figure 3a) calculated using literature value[33] of self-diffusion coefficient of Cs^+ and using the equation

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

where $n(t_k)$ and n^* are the amounts of radiotracer (M*) in the equilibrating solution at fixed time t_k and t_∞, respectively, D^m is the self-diffusion coefficient of the metal ion in the membrane, and L is the thickness of the membrane. For Cs−Naf, the exchange is complete in ∼500 s. The reduction in mobility of Cs^+ in Cs−Naf−Cr indicates either there is a change in morphology of the membrane making most of the ion exchange sites inaccessible for exchange or there is significant increase in interaction of Cs^+ ion (increase in affinity) with crown ether loaded membrane, thereby reducing its mobility in the membrane.

When attempt is made to replace K^+ and Na^+ ions with Cs^+ in K−Naf−Cr and Na−Naf−Cr membrane, the attain-

ment of equilibrium is equally slow (Figure 3b,c) like isotopic exchange of $Cs^+_{(s)} \rightleftharpoons Cs^+_{(m)}$ in Cs−Naf−Cr. In these cases also, the equilibrium is not attained after several days. With K^+, about 20% ion exchange sites is replaced while with Na^+, ∼40% ion exchange sites is replaced. The ion exchange kinetics for exchange of Cs^+ with Na−Naf and K−Naf, calculated from the Nernst−Plank equation[35] using literature values[33] of self-diffusion coefficients, are also shown as solid lines in the Figure 3b,c. The calculated rate of exchange is much faster than what is observed in Na−Naf−Cr and K−Naf−Cr. Incomplete equilibration possibly indicates that all the ion exchange sites are not available for exchange. Since radiotracers enter from both the surfaces of the plain sheet of membrane in the diffusion experiment, it is not possible to conclude whether a fraction of ion exchange sites are replaced uniformly throughout the membrane, or the entering ions remained confined near the surface of the membrane due to reduced mobility because of higher interaction with the modified membrane matrix.

The result of ion exchange kinetics is completely different with Li−Naf−Cr membrane. Here entire Li^+ ion is replaceable with Cs^+, and the kinetics is rather fast (Figure 4a), though slower (solid line in the figure) than the calculated value for Li−Naf from the Nernst-Plank equation[35] using literature values[33,36] of self-diffusion coefficients. The kinetics of reverse exchange with the membrane loaded with Cs^+ ($Li^+ \rightleftharpoons Cs^+$ in Cs−Li−Naf−Cr) was also carried out and the result is shown in Figure 4b. The rate is slower than the forward exchange indicating the lower mobility of the Cs^+ ion in the membrane. However, Cs^+ ions were completely replaceable with Li^+ ions. The exchange with H−Naf−Cr is shown in the Figure 3e. It is interesting to see the rate of exchange is
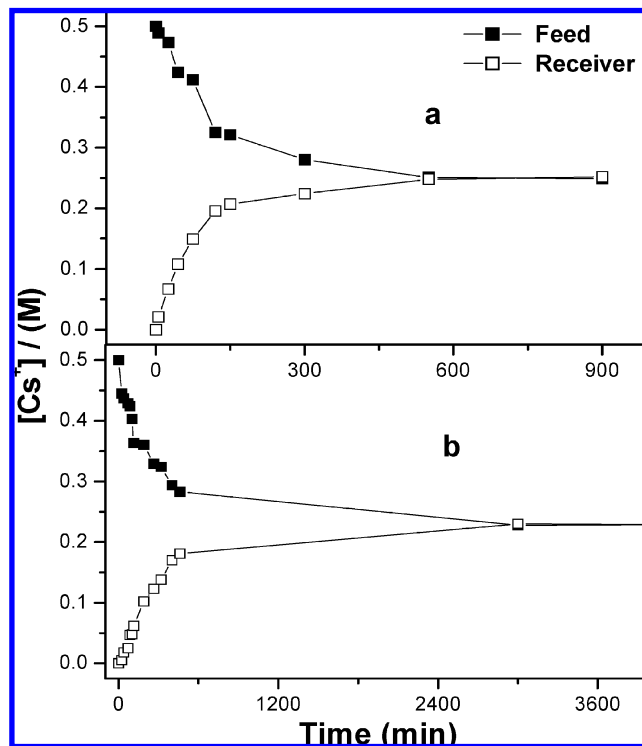
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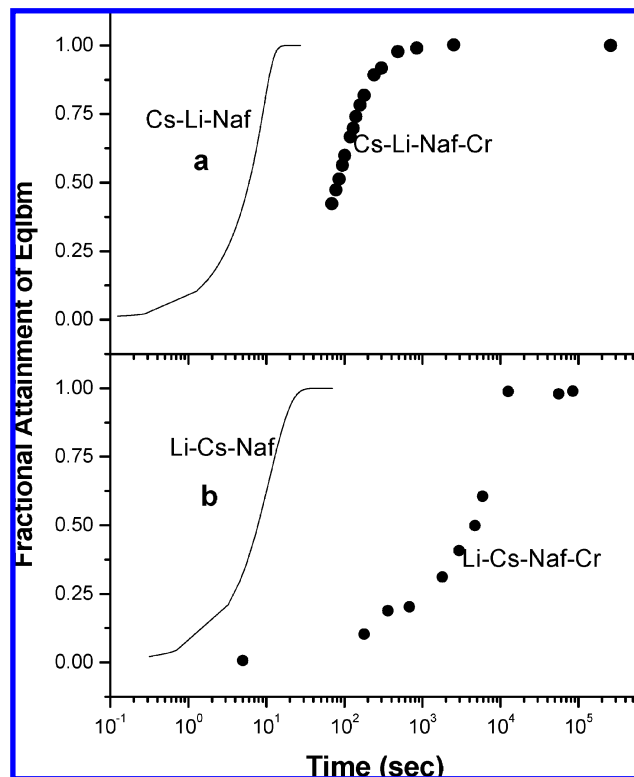
Figure 4. Comparison of the ion exchange kinetics between (a) Cs^+ sorption in the Li–Naf–Cr and (b) Li^+ sorption in the Cs–Li–Naf–Cr; solid lines indicate the sorption profile in the different cationic form of pure Nafion-117 obtained from Nernst–Planck equation (with known diffusion coeff. of the ions) for ion exchange kinetics.

Figure 5. Cs^+ transport through (a) H–Naf–Cr and (b) Cs–Li–Naf–Cr in two compartment cell experiment; feed, 0.5 M CsCl; receiver, 0.5 M HCl (solid line is eye guide through the points).

slower than that with Li–Naf–Cr (Figure 3d). The results of the isotopic and ion exchange kinetics show that the diffusion of ions depend on the ionic form of the membrane which was used to load the crown ether. The lower degree of loading of DB18C6 and presence of higher amount of water in the Li^+ form of Nafion-117 membrane as indicated by TG and FTIR studies may be responsible for the observed difference.

Transport Studies. Diffusion study shows that 20–40% of the ion exchange sites of Na–Naf–Cr, K–Naf–Cr, and Cs–Naf–Cr are replaceable by Cs^+ ion. In order to see whether this would permit the transport of Cs^+ ions through this membrane, two compartment cell experiments have been carried out.

When the Cs–Naf–Cr membrane has been used, and ion exchange has been studied using 0.5 M CsCl + 0.5 M NaCl in the feed compartment and 1 M HCl in the receiver compartment, no transport has been observed over a period of several days. This shows that the membrane is not permeable to Na^+/Cs^+ ions. Thus it can be concluded that exchange that is observed in diffusion experiment is not uniform over the entire membrane volume. The exchange takes place in a localized region near the surface due to stronger interaction of the Cs^+ ions with the membrane, reducing its mobility in the membrane.

When two compartment cell experiment has been carried out with H–Naf–Cr membrane, using 0.5 M CsCl in the feed compartment and 0.5 M HCl in the receiver compartment, the Donnan equilibrium is established indicating that the membrane is permeable to both Cs^+ and H^+ ions as shown in Figure 5a. Similarly, when the Cs–Li–Naf–Cr membrane has been used

in two compartment cell experiment between 0.5 M CsCl and 0.5 M HCl, Donnan equilibrium is established as shown in Figure 5b. This shows that the membrane is permeable to both Cs^+/H^+ ions and the result corroborates the observation of diffusion experiment.

Li–Naf–Cr membrane has been used between 0.25 M CsCl + 0.25 M LiCl and 0.5 M HCl to study the competitive transport of Cs^+/Li^+ ion through the membrane. The percent transport of Cs^+ and Li^+ ion as a function of time through these membranes is given in Table 1. As seen, Cs^+ ion transports at a faster rate than Li^+ through the membrane. In fact Cs^+ transport to the receiver side is complete before Li^+ starts diffusing out appreciably. In the long run, Donnan equilibrium is established. The permeability coefficient (P) of Cs^+ and Li^+ is related to the slopes of the corresponding curves in Figure 6 as[37,38]

$$P = (VL/A)\left[\frac{d([M]_R/[M]_F)_t}{dt}\right] \qquad (2)$$

Where A is the membrane surface area, V is the volume of each cell compartment. $[M]_R$ and $[M]_F$ are the concentration of metal ion (M^+) in the receiver and feed compartment respectively at time "t". The mutual selectivity (P_{Cs}/P_{Li}) for a given form of Nafion-117 was obtained from the ratio of the slopes (S) of Figure 6 as listed in Table 2. It is seen from the table that there is an enhancement in selectivity by a factor of about 6 with Li–Naf–Cr as compared to Li–Naf. The permeability coefficient of an ion is determined by the product of the diffusion coefficient and its partition coefficient between the membrane and solution phase. Since the experimental self-diffusion coefficient of Cs^+ ion is smaller than that of Li^+ ion, it is expected to move slower through the membrane compared to Li^+ ion.

TABLE 1: Competitive Transport of Cs$^+$ and Li$^+$ through the Li$^+$ Form of Nafion-117 in Presence and Absence of DB18C6

| | Li−Nafion−Cr | | | | Li−Nafion | | |
| | % transport | | | | % transport | | |
time (min)	Li$^+$	Cs$^+$	Cs/Li	time (min)	Li$^+$	Cs$^+$	Cs/Li
15	12.8	6.4	0.5	5	10	4.4	0.44
90	12.8	27.2	2.125	15	12	16	1.333
170	12.4	39.6	3.194	25	12.4	20.8	1.677
290	12	50	4.167	40	21.2	27.6	1.302
350	14.8	53.2	3.595	85	32.4	38	1.173
1860	53.6	46.8	0.873	1440	56	38.8	0.693

Thus the observed behavior of faster transport of Cs$^+$can only be explained if the partition coefficient of Cs$^+$ is much higher than Li$^+$ ion, so that most of the ion exchange sites of the membrane is occupied by Cs$^+$ ions. This would give higher flux and transport rate of Cs$^+$ over Li$^+$ enhancing its selectivity. It is to be noted in this context that DB18C6 shows higher selectivity for Cs$^+$ over Li$^+$ in solvent extraction experiment.[31] The lower mobility of Cs$^+$ compared to Li$^+$ through the Cs−Li−Naf−Cr as observed from diffusion experiment is also indicative of higher interaction of Cs$^+$ with DB18C6 giving higher partition coefficient.
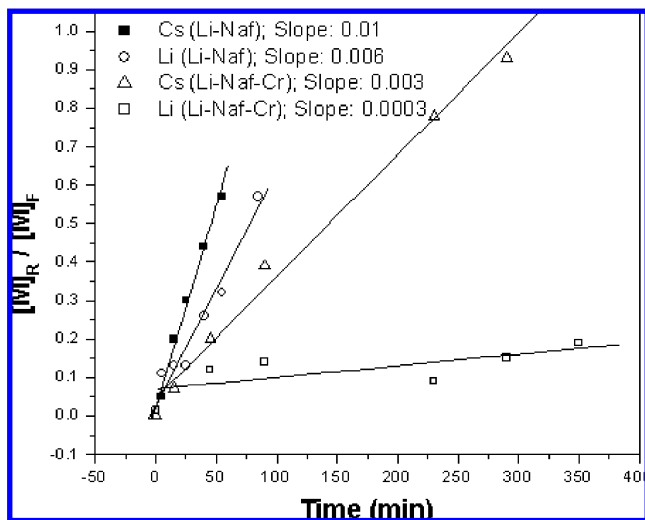
Conclusion

DB18C6 was incorporated in Nafion-117 cation exchange membrane loaded with different alkali metal cations to study the templating effect on their transport process through the membrane. When Na$^+$, K$^+$, and Cs$^+$ loaded membrane was incorporated with DB18C6, the mobility of the ions was found to be extremely small compared to pure Nafion-117. This can be due to the result of strong templating effect in presence of those alkali metal ions due to their stronger interaction with DB18C6. However, Li$^+$ and H$^+$ form of

Figure 6. Effect of loading of DB18C6 in the Li$^+$ form of Nafion-117 on the selectivity of Cs$^+$ over Li$^+$; feed, 0.25 M CsCl + 0.25 M LiCl; receiver, 0.5 M HCl.

TABLE 2: Enhancement in Selectivity for Cs$^+$ over Li$^+$ in Presence of DB18C6 in the Nafion-117 Matrix

| Li−Naf−Cr | | | Li−Nafion | | | selectivity ratio |
| slope (S) | | selectivity | slope (s) | | selectivity | |
Cs$^+$	Li$^+$	(P$_{Cs}$/P$_{Li}$)	Cs$^+$	Li$^+$	(P$_{Cs}$/P$_{Li}$)	(Li−Naf−Cr/ Li−Naf)
0.003	0.0003	10	0.01	0.006	1.67	6

membrane loaded with DB18C6 allowed transport of Li$^+$, H$^+$, and Cs$^+$ ions. Significant enhancement of selectivity for Cs$^+$ over Li$^+$ was observed in the DB18C6 form of Li$^+$ loaded membrane. This shows that this membrane can be used for separation of Cs$^+$ over Li$^+$. The result shows that the cation driven loading of crown ether has some templating effect which leads to enhancement of the selectivity for a particular cation.

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