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# Electrodriven Ion Transport through Crown Ether–Nafion Composite Membrane: Enhanced Selectivity of $\text{Cs}^+$ over $\text{Na}^+$ by Ion Gating at the Surface

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## S Supporting Information

**ABSTRACT:** Two types of  $\text{Cs}^+$  ion-selective crown ether–Nafion composite membranes have been prepared. In one case, the dibenzo-21-crown-7 (DB21C7) has been incorporated uniformly in the  $\text{Cs}^+$  form of Nafion-117 membrane in varying molar ratio with respect to  $\text{Cs}^+$ , and in the other case,  $\text{Cs}^+$  driven loading of DB21C7 has been confined (ion gating) to a very small thickness ( $25\ \mu\text{m}$ ) from one of the surfaces of the Nafion-117 membrane. The surface confinement of  $\text{Cs}^+$  in the ion-gated membrane has been studied by energy dispersive X-ray spectroscopy and secondary ion mass spectrometry. The cation ( $\text{Cs}^+/\text{Na}^+$ ) transport properties of the membranes have been studied under application of electric field. In the uniformly crown-ether-loaded membranes (Cs-Naf-CR), the decrease in crown ether molar ratio has been found to increase the mobility of  $\text{Cs}^+$  through the membrane at the cost of mutual cationic selectivity ( $\text{Cs}^+$  over  $\text{Na}^+$ ). On the other hand, enhanced selectivity of  $\text{Cs}^+$  over  $\text{Na}^+$  with significant cationic transport at room temperature has been obtained with the ion-gated membrane (Cs-H-Naf-CR). When applied to the simulated nuclear waste solution, selective transport of  $\text{Cs}^+$  has also been obtained using this gated membrane even in the presence of very high  $\text{Na}^+$  ( $\text{Cs}^+:\text{Na}^+ = 1:1428$ ) concentration in aqueous solution.

## INTRODUCTION

Because of their permselective property, ion-exchange membranes (IEM) find wide applications in fuel cells, chlor-alkali industry,<sup>1</sup> electro-dialysis,<sup>2</sup> diffusion dialysis, etc. However, IEMs are rarely used in metal ion separations because of their poor selectivity. Attempts have been made to enhance the selectivity of IEMs by incorporating various ligands. Alkali metal ion-selective crown ethers, calixarenes, and cryptands are well-known in the literature, and use of these ligands in membranes for development of various ion-selective electrodes has been studied.<sup>3,4</sup> The requirement of an equivalent amount of counterion, viz. nitrate, chloride, or perchlorate, is the major drawback of these ligand-based separation processes.<sup>5–8</sup> Cation-exchange membranes can provide the negative charge required by the metal ion–crown ether complex, obviating the need of additional counter-anions. In this context, there are several studies on the competitive transport of alkali metal ions by immobilizing the crown ether in the IEM matrix.<sup>9–13</sup> Nafion-117 is a widely used and well-studied IEM which consists of a polytetrafluoroethylene backbone with pendant side chains containing  $-\text{SO}_3\text{H}$  groups. Different attempts have been made to modify the transport properties of Nafion for its use in fuel cells,<sup>14–17</sup> chemical sensors,<sup>18</sup> and ion-selective electrodes<sup>19</sup> by incorporating suitable crown ethers in the membrane.

In our earlier attempt,<sup>20,21</sup> dibenzo-18-crown-6 (DB18C6) was incorporated in Nafion-117 cation-exchange membrane to prepare an alkali metal ion-selective membrane. It has been observed that the transport behavior of the alkali metal ions in those membranes is strongly dependent on the cationic form of the membrane in which the crown ether is loaded. The result indicates that the cation-driven loading of crown ether can have a templating effect. This leads to enhancement of the selectivity

for a particular cation. It has also been observed that the permeability of the cations ( $\text{Cs}^+$  and  $\text{Na}^+$ ) in the  $\text{Cs}^+/\text{Na}^+$  templated crown-ether-loaded Nafion-117 membranes are too low to be of any practical use. On introduction of crown ethers in the Nafion-117 matrix, the membrane becomes highly hydrophobic and loses plasticity which lowers the self-diffusion coefficients and hence the permeability.<sup>22</sup> This is a general problem with the IEM, that the enhanced selectivity of an ion is usually accompanied by reduction in mobility of the ion. Therefore, enhancement in the permeability with high selectivity is a challenge for use of IEM in separating ions of similar charge.

Also, in Donnan dialysis, permeation of ion from feed to receiver phase through IEM requires counter transport of another ion from receiver to feed phase to maintain electrical neutrality. This counterion transport will be prevented by an ideal specific ion-selective membrane. Thus, conventional Donnan dialytic separation with a highly ion-selective membrane is not possible. This problem can be circumvented if an electric field is applied across the membrane so that the anion in the feed compartment is oxidized at the anode and the cation moves to the receiver phase without requiring any counter transport, as in electrodialysis. The use of an electric field thus eliminates the need for adding salt or stripping agent in the receiver side. Application of an electric field also enhances the cation flux, which leads to quantitative cation transport under practical time scale. This kind of membrane-based analyte preconcentration method under the influence of

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an electric field (electromembrane extraction) is currently receiving attention.<sup>23–27</sup>

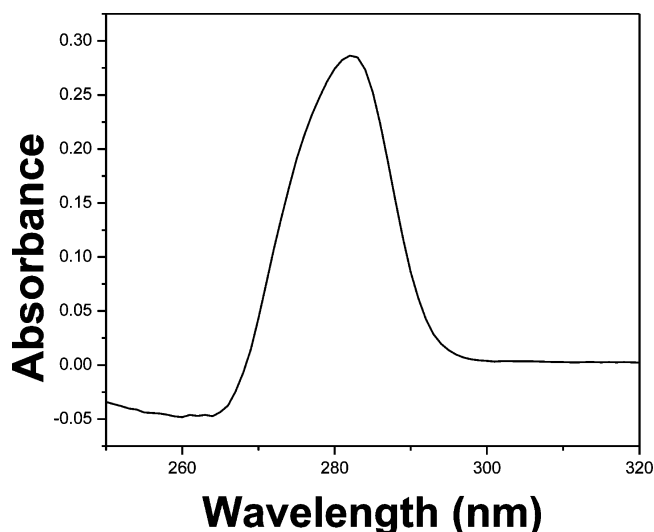
The aim of the present work is to obtain a highly  $\text{Cs}^+$  ion-selective IEM with significant permeability that can be used for separation of  $\text{Cs}^+$  from a liquid radioactive waste having high  $\text{Na}^+$  concentration. With this in view, in the present work, a  $\text{Cs}^+$  selective dibenzo-21-crown-7 (DB21C7=CR) has been incorporated uniformly in  $\text{Cs}^+$  form of Nafion-117 membrane in varying molar ratio ( $N = n_{\text{CR}}/n_{\text{Cs}^+}$ ) with respect to  $\text{Cs}^+$  in the membrane. The  $\text{Cs}^+_{\text{sol}} \rightleftharpoons \text{Cs}^+_{\text{mem}}$  (sol, solution; mem, membrane) isotope exchange kinetics and  $\text{Na}^+_{\text{sol}} \rightleftharpoons \text{Cs}^+_{\text{mem}}$  ion-exchange kinetics in these homogeneously crown-ether-loaded membranes (Cs-Naf-CR) have been studied to assess the transport rate of the ions in these membranes. A crown ether–Nafion composite membrane has also been prepared by incorporating DB21C7 in a thin surface layer (few micrometers) of Nafion-117 membrane (ion gating). The surface confinement of  $\text{Cs}^+$  in this ion-gated membrane (Cs-H-Naf-CR) has been studied using energy dispersive X-ray spectroscopy (EDS) and time of flight secondary ion mass spectrometry (ToFSIMS). A comparative account of these 2 types of membranes (Cs-Naf-CR and Cs-H-Naf-CR) for electrodriven selective transport of  $\text{Cs}^+$  from  $\text{Na}^+$  is also presented. The suitability of this membrane for selective removal of  $^{137}\text{Cs}$  from a simulated nuclear waste solution has also been studied. The results have been discussed in terms of cationic diffusivity and selectivity.

## EXPERIMENTAL SECTION

**Reagents and Chemicals.** Dibenzo-21-crown-7 (analytical reagent grade) has been procured from Sigma-Aldrich. Nafion-117 ion-exchange membrane (purchased from Du Pont) with an equivalent weight of 1100 and thickness of  $178\ \mu\text{m}$  (in fully dried condition) has been used for the present set of experiments. Preconditioning of the membrane samples is done following the method described elsewhere.<sup>28</sup>  $\text{CsNO}_3$ ,  $\text{CsCl}$  (99.999%, ultrapure grade),  $\text{NaCl}$ , and  $\text{NaNO}_3$  (99.9%, analytical reagent grade) have been procured from Sisco Research Lab., Mumbai, India and SD Fine Chem. Ltd., India, respectively. Deionized water ( $18\ \text{M}\Omega/\text{cm}$ , Gradient A-10 model, Milli-Q, U.S.) is used in the present study. Radiotracers ( $^{137}\text{Cs}$  and  $^{22}\text{Na}$ ) used in the present study have been obtained from Board of Radiation and Isotope Technology, Mumbai, India.

**Incorporation and Quantification of the Crown Ether in Cs-Naf-CR.** The loading of crown ether in Cs-Naf has been done by soaking the membrane in 15 mL of DB21C7/dimethylformamide (DMF) solution for 24 h. The samples have been washed thoroughly with deionized water and heated at  $70\ ^\circ\text{C}$  under vacuum. The extent of loading of crown ether in the membrane has been controlled by varying the dissolved amount of DB21C7 in DMF, so that the mole ratio of  $\text{Cs}^+$  in the membrane and dissolved DB21C7 in solution varies from 1:1 to 4:1. The quantification of the crown ether in the membrane matrix has been done by a gravimetric method as well as by UV–visible spectrophotometry, where the spectra of the left-over DB21C7 in DMF solution (after crown ether loading in the membrane) have been used for the quantification. A representative UV–visible spectrum ( $\lambda_{\text{max}} = 281\ \text{nm}$ ) for  $2.0 \times 10^{-4}\ \text{M}$  solution of DB21C7 in DMF is shown in Figure 1.

In the gravimetric method, the dry weights of the membranes before and after loading of the DB21C7 have been used to



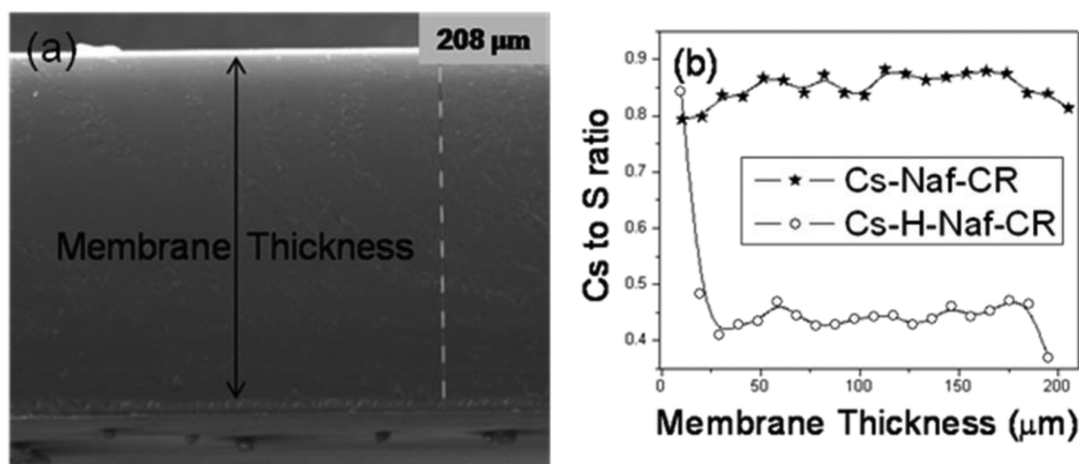
**Figure 1.** UV–visible spectrum acquired for  $2.0 \times 10^{-4}\ \text{M}$  DB21C7 solution in DMF.

calculate  $N$ . The weight of the dry membrane has been obtained by heating the membrane sample for 6–8 h at  $70\ ^\circ\text{C}$  under vacuum. The values of  $N$  obtained from the UV–visible spectrophotometric and the gravimetric methods agree well.

**Preparation and Characterization of Cs-H-Naf-CR.** The  $\text{Cs}^+$ -gated membrane (Cs-H-Naf-CR) has been prepared by first exposing H-Naf (pure Nafion-117) membrane to  $0.1\ \text{M}$   $\text{CsCl}$  solution from one surface for 15 s. The exposure time is decided from the  $\text{Cs}^+ \rightleftharpoons \text{H}^+$  ion-exchange kinetics as given elsewhere.<sup>29</sup> This partially  $\text{Cs}^+$ -loaded membrane is immediately placed in a DB21C7-DMF solution so that the motion of  $\text{Cs}^+$  ions is arrested by DB21C7 in DMF medium. The amount of crown ether in the DMF solution is in a stoichiometric ratio of 1:1 to the total ion-exchange sites in the membrane. The annealing of the crown-ether-loaded membrane has been done by heating the membrane sample at  $70\ ^\circ\text{C}$  under vacuum.<sup>21</sup> As calculated from gravimetric and UV–visible spectrophotometric measurement, the value of  $n_{\text{CR}}/n_{\text{IES}}$  ( $n_{\text{IES}}$  is the number of ion-exchange sites in the membrane) in the Cs-H-Naf-CR membrane has been found to be 0.32.

The distribution of  $\text{Cs}^+$  ions along the thickness of this membrane has been studied by EDS and ToFSIMS methods. The EDS analysis has been carried out using a Cam Scan spectrometric unit (model 3100) with 20 kV voltage and  $150\ \mu\text{A}$  beam current. The scanning has been done along the thickness of the membrane in 20 steps (each step covered a  $10\ \mu\text{m}$  length). At each step, data has been acquired for 1 min. For comparison purposes, this analysis is also carried out for Cs-Naf-CR (uniform  $\text{Cs}^+$  ion distribution throughout the membrane thickness).

Figure 2a shows the cross sectional view of the Cs-Naf-CR membrane ( $N = 0.8$ ) under scanning electron microscope. The number of steps that has been taken to cover the full thickness of the membrane for EDS analysis is also marked in the image. The Cs to S (each S atom corresponds to one ion-exchange site in the membrane) atom percent ratio (as obtained from EDS analysis) in Cs-Naf-CR ( $N = 0.8$ ) and Cs-H-Naf-CR are shown in Figure 2b. The constant Cs to S atom percent ratio in Cs-Naf-CR indicates homogeneous distribution of  $\text{Cs}^+$  throughout the membrane thickness. The sharp fall in Cs/S ratio in Cs-H-Naf-CR in the first few micrometers ( $25\ \mu\text{m}$ ) indicates that  $\text{Cs}^+$



**Figure 2.** (a) Microscopic image of the cross section of Cs-Naf-CR along which EDS analysis has been carried out. (b) Atom percent ratio of Cs to S (as obtained from EDS analysis) in Cs-Naf-CR ( $N = 0.8$ ) and Cs-H-Naf-CR.

is loaded only in the initial  $\sim 25 \mu\text{m}$  thickness. The EDS analysis shows that  $\text{Cs}^+$  is confined only within  $25 \mu\text{m}$  from the surface.

The detail of the characterization of this membrane by ToFSIMS has been given in Supporting Information.

**Measurement of Isotope Exchange and Ion-Exchange Kinetics.** The  $\text{Cs}_{\text{sol}}^+ \rightleftharpoons \text{Cs}_{\text{mem}}^+$  isotopic exchange and  $\text{Na}_{\text{sol}}^+ \rightleftharpoons \text{Cs}_{\text{mem}}^+$  ion-exchange measurements in the partially crown-ether-loaded Cs-Naf-CR membranes have been carried out at room temperature following the standard radiotracer method as described elsewhere.<sup>21</sup> The details of the method have been given in Supporting Information.

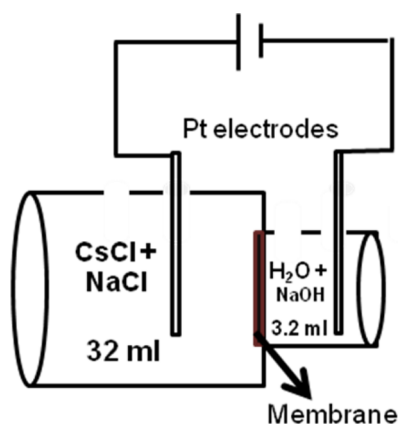
**Transport Study.** In order to study the selective transport of  $\text{Cs}^+$  over  $\text{Na}^+$  (using Cs-Naf/Cs-Naf-CR/Cs-H-Naf-CR membranes), two-compartment permeation experiments have been carried out at room temperature. During the experiment, an electric field (4 V) has been applied across the membrane using two Pt electrodes. The membrane active surface area is  $1.8 \text{ cm}^2$ . A schematic diagram of the experimental arrangement is shown in Figure 3. To achieve volume reduction along with selective transport, the volume ratio of feed to receiver compartment has been kept to be 10.<sup>26</sup> A mixture (32 mL) of NaCl and CsCl has been used in the feed and deionized water (3.2 mL) spiked with NaOH (0.04 mmol) has been used in the receiver compartment. Two different mole ratios of  $\text{Cs}^+$

and  $\text{Na}^+$  (1:1 or 1:4) have been used in the feed compartment. The  $\text{Cs}^+$ -gated surface of the membrane is exposed to the feed solution which is tagged with  $^{22}\text{Na}$  and  $^{137}\text{Cs}$  tracer. The solutions in both compartments have been stirred ( $\sim 300 \text{ rpm}$ ) continuously to avoid any film-controlled diffusion at the membrane interface. Amount of  $\text{Na}^+$  and  $\text{Cs}^+$  transferred from the feed to the receiver side has been monitored by taking out  $200 \mu\text{L}$  aliquots from both compartments at regular time intervals and counting the  $^{22}\text{Na}$  and  $^{137}\text{Cs}$  activity in an HPGe detector. For comparison of the results, one of the transport experiments ( $\text{Cs}^+:\text{Na}^+ = 1:1$  in feed solution) has been repeated with Cs-Naf, keeping other conditions unaltered.

A transport experiment has also been carried out for the simulated effluent solution of resorcinol formaldehyde polycondensate resin (RFPR, intermediate level nuclear waste treated with RFPR) with the feed composition being  $0.1 \text{ M NaNO}_3$  and  $3.5 \times 10^{-4} \text{ M CsNO}_3$  in  $0.4 \text{ M HNO}_3$ .<sup>30</sup> During the course of the experiment it is observed that the crown ether is leaching out from the membrane possibly because of the strong interaction between  $\text{HNO}_3$  and DB21C7. The feed solution has thus been neutralized with NaOH ( $\text{pH} \sim 7$ ) before the experiment is carried out. The final feed composition for this simulated waste is  $0.5 \text{ M NaNO}_3$  and  $3.5 \times 10^{-4} \text{ M CsNO}_3$ .

## RESULTS AND DISCUSSION

**Cs-Naf-CR.** Four Cs-Naf-CR membranes have been prepared containing different mole ratios ( $N = 0.80, 0.66, 0.36, 0.21$ ) of DB21C7 with respect to  $\text{Cs}^+$ . The  $\text{Cs}_{\text{sol}}^+ \rightleftharpoons \text{Cs}_{\text{mem}}^+$  isotopic exchange in Cs-Naf-CR membrane ( $N = 0.8$ ) is too slow to be observed at room temperature. However, for other Cs-Naf-CR membranes with lower ( $<0.8$ )  $N$ , the  $\text{Cs}_{\text{sol}}^+ \rightleftharpoons \text{Cs}_{\text{mem}}^+$  isotopic exchange takes place at room temperature. The  $\text{Cs}_{\text{sol}}^+ \rightleftharpoons \text{Cs}_{\text{mem}}^+$  isotopic exchange profiles and the  $\text{Na}_{\text{sol}}^+ \rightleftharpoons \text{Cs}_{\text{mem}}^+$  ion-exchange profiles in these partially DB21C7-loaded Cs-Naf-CR membranes are shown in panels a and b of Figure 4, respectively. The arrows in the figures show the extent of sites available for isotopic/ion exchange. The results show that the mobility of  $\text{Cs}^+$  in the Cs-Naf-CR membrane decreases with an increase in  $N$  and that the fraction of isotopic exchange sites available for  $\text{Cs}_{\text{sol}}^+ \rightleftharpoons \text{Cs}_{\text{mem}}^+$  exchange decreases. It is also seen from the figures that the  $\text{Na}_{\text{sol}}^+ \rightleftharpoons \text{Cs}_{\text{mem}}^+$  exchange profiles are faster than the corresponding  $\text{Cs}_{\text{sol}}^+ \rightleftharpoons \text{Cs}_{\text{mem}}^+$



**Figure 3.** Experimental arrangement for transport studies under applied electric field.

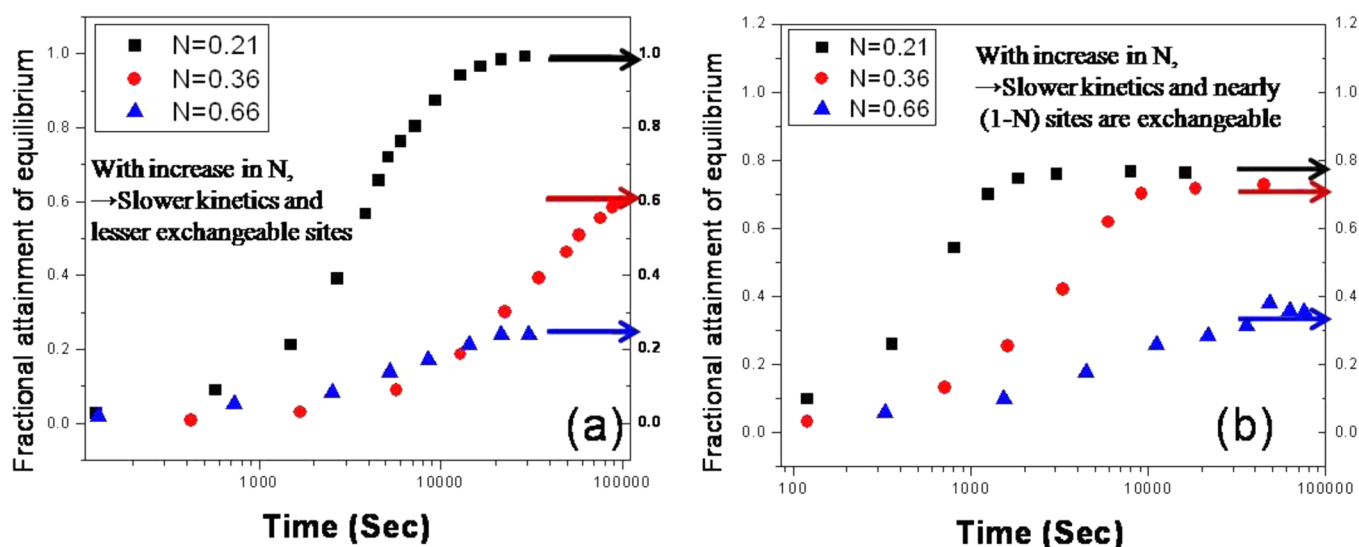


Figure 4. Room-temperature (a)  $\text{Cs}^+_{\text{sol}} \rightleftharpoons \text{Cs}^+_{\text{mem}}$  isotopic exchange profiles and (b)  $\text{Na}^+_{\text{sol}} \rightleftharpoons \text{Cs}^+_{\text{mem}}$  ion-exchange profiles in Cs-Naf-CR membranes with different  $N$ . The arrows indicate the fraction of exchangeable sites in the membrane at room temperature.

Table 1. Time-Dependent Relative Cation Transport (%  $\text{Cs}^+/\% \text{Na}^+$ ) for Different Membranes<sup>a</sup>

Cs-Naf		Cs-Naf-CR ( $N = 0.36$ )		Cs-H-Naf-CR	
time (min)	relative cation transport (% $\text{Cs}^+/\% \text{Na}^+$ )	time (min)	relative cation transport (% $\text{Cs}^+/\% \text{Na}^+$ )	time (min)	relative cation transport (% $\text{Cs}^+/\% \text{Na}^+$ )
90	0.91	60	0.87	210	4.08
210	1.12	150	0.99	420	4.49
330	0.87	210	1.05	1380	4.39
450	1.03	360	1.06	1635	4.03
1410	1.05	435	1.03	1860	3.91

<sup>a</sup>The experiments have been carried out at 4 V with the feed solution having 5 mmol  $\text{Cs}^+$  and 5 mmol  $\text{Na}^+$ .

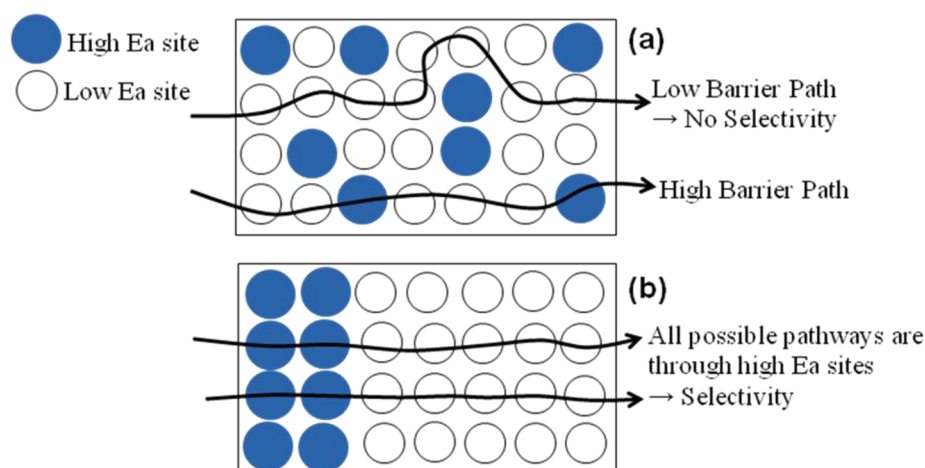


Figure 5. Cation transport paths in (a) uniformly crown-ether-loaded Cs-Naf-CR membrane and (b) ion-gated Cs-H-Naf-CR membrane.

exchange. However,  $\text{Na}^+_{\text{sol}} \rightleftharpoons \text{Cs}^+_{\text{mem}}$  exchange proceeds to the extent that can be expected from the fraction of sites free of crown ether ( $1 - N$ ). This shows that there are two different types of  $\text{Cs}^+$  ionic sites in these Cs-Naf-CR membranes: one is associated with crown ether, and the other is free of crown ether. As seen from the profiles in Figure 4a, with increasing  $N$ , the crown ether associated sites are increasingly difficult for  $\text{Cs}^+_{\text{sol}} \rightleftharpoons \text{Cs}^+_{\text{mem}}$  exchange because of changes in membrane morphology.<sup>21</sup>

The time-dependent relative cation transport (%  $\text{Cs}^+/\% \text{Na}^+$ ) for different membranes (Cs-Naf, Cs-Naf-CR ( $N = 0.36$ ),

and Cs-H-Naf-CR) are shown in Table 1. The data shown in the table are for the experiments that have been carried out at 4 V with the feed solution having 5 mmol  $\text{Cs}^+$  and 5 mmol  $\text{Na}^+$ . As can be seen from this table, transport selectivity of  $\text{Cs}^+$  over  $\text{Na}^+$  has not been observed in the two-compartment transport experiments for the Cs-Naf and Cs-Naf-CR ( $N = 0.36$ ) membranes. The absence of selective transport in Cs-Naf-CR membranes can be understood on the basis of the presence of two types of ion-exchange sites in these membranes as explained earlier. The sites free of crown ether provide transport pathways like pure Nafion-117 with lower activation



**Table 2.** Details of the Two-Compartment Transport Experiments Carried out at 4 V along with Corresponding Enrichment Factor of  $\text{Cs}^+$  over  $\text{Na}^+$  and Permeability Coefficient of  $\text{Cs}^+$ 

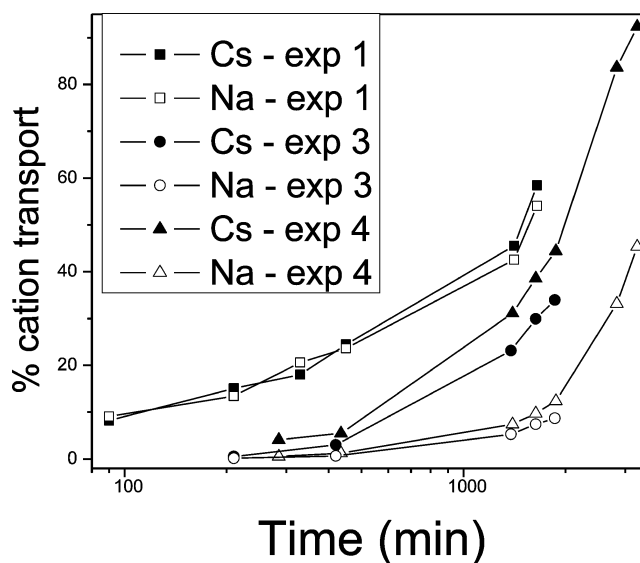
experiment no.	feed composition (mmol)		membrane	enrichment factor ( $\epsilon$ )	permeability coefficient of $\text{Cs}^+$ (cm/s)
	$\text{Cs}^+$	$\text{Na}^+$			
1	5	5	Cs-Naf	$1.0 \pm 0.1$	$4.2 \times 10^{-5}$
2	5	5	Cs-Naf-CR ( $N = 0.36$ )	$1.0 \pm 0.1$	$4.7 \times 10^{-5}$
3	5	5	Cs-H-Naf-CR	$4.5 \pm 0.1$	$2.0 \times 10^{-5}$
4	2	8	Cs-H-Naf-CR	$4.3 \pm 0.1$	$2.7 \times 10^{-5}$
5	0.0084	12	Cs-H-Naf-CR	$2.3 \pm 0.1$	—

barrier ( $E_a$ ) and lower selectivity. On the other hand, the diffusion involving crown ether associated ion-exchange sites have very high activation barrier (templating effect) for diffusion and high selectivity. These two transport pathways in Cs-Naf-CR membranes are represented schematically in Figure 5a. Because both ion-exchange sites are randomly distributed throughout the membrane, transport of most of the ions occurs involving the lower activation barrier sites, resulting in transport behavior (no selectivity) similar to that of pure Nafion-117.

**Ion-Gated Membrane (Cs-H-Naf-CR).** Transport experiments have been carried out with the membrane having one of the surface layers ( $\sim 25 \mu\text{m}$ ) loaded with DB21C7 templated  $\text{Cs}^+$ . The schematic representation of the cation transport pathway in this ion-gated membrane is shown in Figure 5b. Because all the ions have to pass through the crown-ether-loaded ion-exchange sites, a high degree of selectivity toward  $\text{Cs}^+$  is expected. However, the thin layer may enhance the permeability, allowing faster transport compared to that of the fully crown-ether-loaded membranes.

As shown in Table 1, the relative cation transport (%  $\text{Cs}^+/\text{Na}^+$ ) in Cs-H-Naf-CR is much higher than that of Cs-Naf and Cs-Naf-CR ( $N = 0.36$ ). This indicates selective transport of  $\text{Cs}^+$  over  $\text{Na}^+$  through Cs-H-Naf-CR, which otherwise is not observed with the other two membranes. Nearly constant relative cation transport throughout the experimental time scale, as shown in the table, indicates that the enhanced selectivity of Cs-H-Naf-CR is not ascribed to initial transient ion exchange. The results of the experiments carried out using different feed compositions as well as different membranes are given in Table 2. The different experiments carried out are identified with the corresponding experiment numbers in this table. Enrichment factor  $\epsilon$ , as shown in the table, is defined as the ratio of percentage cation transport (%  $\text{Cs}^+/\text{Na}^+$ ) at a particular time. A higher enrichment factor ( $\epsilon > 1$ ) indicates higher selectivity in transport of  $\text{Cs}^+$  over  $\text{Na}^+$  to the receiver side. The errors shown on the enrichment factors are the corresponding absolute errors on the measured data and have been calculated from the radioactivity counting statistics. The permeability coefficients  $P$  for  $\text{Cs}^+$  ion in the different experiments are also shown in this table. As can be seen from this table,  $P$  for Cs-H-Naf-CR is 2 times lower than that with Cs-Naf. This indicates that the permeation rate is comparable to that of Nafion, which is industrially used in a large scale.

The cation transport rates for different feed compositions are shown in Figure 6. With the  $\text{Cs}^+$  form of Nafion-117 membrane (Cs-Naf), after 7 h, 24%  $\text{Cs}^+$  and 23%  $\text{Na}^+$  has been transported to the receiver side without any enrichment ( $\epsilon = 1.0$ ). For the experiments with Cs-H-Naf-CR (experiments 3 and 4), at the same time scale (7 h), the percentage  $\text{Cs}^+/\text{Na}^+$  transported are 3/0.6 and 5.5/1.6, respectively, which shows the effect of crown

**Figure 6.** Cation ( $\text{Cs}^+/\text{Na}^+$ ) transport profiles under different experimental conditions.

ether on the cationic mobility. The percentages, as shown in Figure 6, are with respect to the initial amount of cations in the feed side that are available for transport. In the receiver compartment, along with the volume reduction factor of 10, the observed enrichment factor of  $\text{Cs}^+$  over  $\text{Na}^+$  for third and fourth experiment are  $4.5 \pm 0.1$  and  $4.3 \pm 0.1$ , respectively. The results indicate that ion gating of the membrane with crown ether has imparted enhanced selectivity over that of pure Nafion-117 and enhanced transport rate over that of partial but uniformly crown-ether-loaded membrane. Nearly 100% cation transport shows the effect of electrically driven transport.

The results of the transport experiment (experiment 5) carried out for simulated effluent solution of resorcinol formaldehyde polycondensate resin (RFPR)<sup>30</sup> are also shown in Table 2. It can be seen from the data that here also an enrichment factor of  $2.3 \pm 0.1$  has been observed for  $\text{Cs}^+$  over  $\text{Na}^+$ . This indicates that the selective transport of  $\text{Cs}^+$  in this ion-gated membrane is possible despite such a high ( $\text{Cs}^+:\text{Na}^+ = 1:1428$ )  $\text{Na}^+$  concentration in aqueous solution.

## CONCLUSION

Homogeneous loading of crown ether in the bulk of the membrane at different molar ratios of crown ether (with respect to  $\text{Cs}^+$ ) enhance the cationic mobility with reduced selectivity. The problem of enhanced selectivity at the cost of mobility has been successfully overcome by confinement of the templating (with crown ether) only at the surface ion-exchange sites. In this ion-gated membrane, the combined effect of selectivity due to the templating effect of the surface screening layer and the

significant mobility of the cation in the bulk under applied electric potential results in selective and quantitative transport of  $\text{Cs}^+$  over  $\text{Na}^+$  at a practical time scale. Further enhancement in transport selectivity is expected with more selective crown ether or calix crown ligand and subsequent tuning of the screening layer thickness. Electrodialytic separation of ions with the same charge state can be carried out with this kind of modified ion-exchange membrane.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Characterization of Cs-H-Naf-CR by ToFSIMS method and the description of the isotopic and ion-exchange kinetics measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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