Ion-transport characteristics in Nafion-117 membrane having mixed cationic composition

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Abstract

Membrane (Nafion-117) composition dependent self-diffusion studies of different cations (Na⁺ and Ba²⁺ ions) have been carried out, using radiotracer method. The choice of these two counterions in the membrane matrix was based on the fact, that these ions have significant difference in their self-diffusion coefficients in this membrane. Results indicate that the SDC of an ion in an ion exchange membrane, depends on the ionic composition of the membrane phase, and the mechanism of transport for bivalent ion is different from that of monovalent ion.

Introduction

Ion-exchange membranes can act as separators between two electrolyte solutions as they allow counter-ions to pass through while co-ions are excluded from the membrane. This property is utilized in the ion-exchange based separation processes as in Donnan dialysis and electrodialysis¹. Permeability of a diffusing species (permeant) in the membrane governs the transport flux across the membrane²,³. The permeability coefficient of a species depends on its diffusion coefficient (D) and partition coefficient in the membrane which is the ratio of concentration of permeant in the membrane to that of the permeant in solution outside the membrane. Ratio of permeability coefficient of the two diffusing species across the membrane, determines the separation factor. The knowledge of diffusion coefficients is therefore important for modelling membrane transport process.

Radiotracers are extensively used for ion diffusion studies. Self-diffusion behavior of monovalent and multivalent ions in the Nafion-117 membranes has been widely studied⁴,⁵. Self-Diffusion Coefficients (SDC) may be modified due to the presence of other ions in the membrane since ion exchange sites available for hopping reduce. However there is limited published experimental data, on SDC in membrane with mixed ionic composition. Okada et al⁶ determined ionic mobility in Nafion-117 in mixed ionic composition of H⁺ ion and alkali metal cations. They observed no significant change in ionic mobility, depending upon the ionic composition of the membrane. Pourcelly et al⁷ observed from radiotracer studies, that SDCs of Na⁺ and Ca²⁺ were independent of ionic composition of the membrane. In this paper, we report the measurement of SDC of Na⁺ and Ba²⁺ in Nafion-117 membrane, having varying ionic composition of Na⁺ and Ba²⁺. The results are discussed in terms of possible mechanism of transport of the monovalent and bivalent ions.
Experimental

Nafion-117 membrane pieces (2cm X 2cm) were refluxed in ~7M HNO₃ for 1 h, and conditioned with alternate equilibrations with NaOH and HCl. Three different equilibrating solutions containing 0.1N NaCl and 0.1N BaCl₂ in different proportions of 1:1, 4:1 and 8:1 were used, keeping the total ionic concentration fixed at 0.1N. For each of the equilibrating solution, two experiments were carried out, one for the Na⁺ ion and another for the Ba⁺² ion. For each experiment, the membrane sample was kept in well-stirred (~52 rad/s) equilibrating solution (30 ml) at 27°C for ~3 hrs, to eliminate film-controlled diffusion at the membrane solution interface. After equilibration, the membrane was taken out and required (²²Na or ¹³³Ba) radiotracers were added to the respective solution. Filter paper standards were prepared by taking pieces of filter paper of the same dimensions (2 cm×2 cm) as the membrane sample and adding 100 µL of the radiolabeled solution. Separate standards were prepared for Na and Ba. To study the diffusion kinetics of the respective ions, the membrane was kept into the radio labeled equilibrating solution with continuous stirring and taken out intermittently. The samples were then thoroughly washed with deionised water to remove equilibrating solution clinging to the surface and were counted for uptake of respective (Na or Ba) activity using a NaI(Tl) detector connected to a 4k channel analyzer. The membrane sample was again placed in the equilibrating solution after counting. Experiments with Na and Ba radiotracer were done separately because the 511 keV gamma ray of ²²Na can cause huge background in the low energy gamma rays of ¹³³Ba. The equilibrium uptake of the radiotracers in the membrane gave ionic composition in the membrane as well as that of equilibrating solution which was used to obtain ion exchange isotherm. The same procedure was followed for equilibrating solutions of different ionic compositions.

Results and Discussion

The ion exchange isotherm is shown in Fig. 1. The higher selectivity of the membrane for Ba⁺² ion over Na⁺ is apparent from the figure. The isotherm gave composition of the membrane and also the outside solutions, at which the isotopic exchange kinetics were studied. Fig. 2 shows the plot of kinetics of the isotopic exchange *Na⁺(l) ⇌ Na⁺(m) and *Ba⁺²( l) ⇌ Ba⁺²( m) respectively in three different equilibrating solution compositions, where * sign indicates the presence of radiotracer in the solution. It is seen from the figures, that the rate of isotopic exchange for Na⁺ ion does not change with change in ionic composition of the membrane.
composition of the membrane, while that of $\text{Ba}^{+2}$ ion decreases significantly with increase in $\text{Na}^{+}$ content in the membrane. The self diffusion coefficients of the $\text{Na}^{+}$ and $\text{Ba}^{+2}$ ions were obtained from the least square fit to the plot, using the analytical solution of the Fick’s second law as given by the equation:

$$n(t) = n^* \left[ 1 - \frac{8}{\pi^2} \left( \exp(-Dr_0^2/L^2) + \frac{1}{9} \exp(-9Dr_0^2/L^2) + \ldots \right) \right]$$

where $n^*$ is the total amount of the radiotracer ions in the membrane at equilibrium ($t = \infty$), $n(t)$ is the amount of radiotracer at any time $t$ in the membrane, $D$ is the diffusion coefficient and $L$ is the thickness of the membrane (200 mm). The $D$ values are given in Table 1 along with the ionic composition of the membrane obtained from the ion exchange isotherm studies.

Table 1: SDC values of $\text{Na}^{+}$ and $\text{Ba}^{+2}$ ions for different ionic composition of the membrane

<table>
<thead>
<tr>
<th>% Na$^{+}$ (membrane)</th>
<th>$D_{\text{Na}}^{+} \times 10^7$ (cm$^2$/sec)</th>
<th>$D_{\text{Ba}}^{+2} \times 10^7$ (cm$^2$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.55</td>
<td>9.4</td>
<td>1.2</td>
</tr>
<tr>
<td>20.26</td>
<td>9.6</td>
<td>0.84</td>
</tr>
<tr>
<td>30.44</td>
<td>9.2</td>
<td>0.64</td>
</tr>
</tbody>
</table>

For $\text{Na}^{+}$ ion, the $D$ values are reduced by about 8 % compared to the value of $1.03 \times 10^{-6}$ cm$^2$/sec for pure $\text{Na}$-form of membrane and it is independent of the composition of the membrane. For $\text{Ba}^{+2}$ ion, the $D$ values are reduced by a factor of about 2 compared to pure $\text{Ba}$-form of the membrane ($D = 1.4 \times 10^{-7}$ cm$^2$/sec) as the $\text{Na}$ content in the membrane increases from 8.5% to 30.4%. These results indicate that $\text{Na}^{+}$ ion possibly remains mostly dissociated in the water channels, and its transport is not hindered by the $\text{Ba}^{+2}$ ions which possibly remain in the proximity of the $-\text{SO}_3^-$ ions. Increase in the $\text{Na}$-content in the membrane, increases the average distance of hopping of the $\text{Ba}^{+2}$ ions and hence its diffusivity is strongly effected by the ionic composition of the membrane.

**Conclusion**

Result of the present work shows, that the SDC of an ion in an ion exchange membrane depends on the ionic composition of the membrane phase. The effect is stronger for bivalent ions as compared to monovalent ions. This shows the mechanism of transport for bivalent ion is different than that of monovalent ion.

**References**