

## ARTICLES

## High Pressure NMR Study of Water Self-Diffusion in NAFION-117 Membrane

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Measurements of the self-diffusion coefficient of water in NAFION-117 as a function of pressure have been carried out. The natural field gradient of a 7.3 T superconducting magnet was used for the diffusion measurement. The measurements were carried out at 288 K and variable pressure up to 0.25 GPa. The high-pressure diffusion data were obtained for four different water contents between 6.6 and 22 wt %. The calculated activation volume decreased from 13.2 to 2.7 cm<sup>3</sup>/mol as the water content increased from 6.6 to 22 wt %. These results agree with previously published activation volumes extracted from electric conductivity and NMR  $T_1$  measurements. It is suggested that segmental motions within the polymer play a significant role in the transport mechanism for low water content membranes, and that the transport mechanism for high water content membranes is similar to that in liquid bulk water.

## Introduction

There are a number of powerful NMR spectroscopic techniques that yield information for both structural and dynamic properties of materials. Additionally, diffusion and flow can be measured with good precision using NMR methods. When NMR is applied to the study of electrolytes, the gathered self-diffusion coefficients can be of great importance in characterizing ionic conduction and molecular motion. In this study, self-diffusion coefficients are measured and then used to evaluate mass transport in NAFION, a model material useful for hydrogen fuel cell applications. In general, the study of ion and molecular transport in polymers can be greatly assisted by employing pressure as the thermodynamic variable. Although many investigations of NMR self-diffusion and electrical conductivity have been carried out in proton conducting membranes,<sup>1–11</sup> and some electrical conductivity and NMR spin–lattice relaxation time ( $T_1$ ) studies as a function of applied pressure have been published,<sup>12–17</sup> to our knowledge, no work has been reported on the effect of high pressure on self-diffusion in a membrane. The NMR signal is dominated by water in the kinds of membranes used in fuel cells; nevertheless, it has been shown that water mobility is strongly correlated with electrical conductivity in these materials.<sup>2,7</sup> Molecular motions and ionic diffusion are associated with volume fluctuations that can be probed directly by employing pressure as the thermodynamic variable. It is of interest to compare these new results (pressure dependent diffusion measurements) with previous work reported for variable pressure electric conductivity and NMR  $T_1$  measurements for NAFION membranes at different water contents. Activation volumes for four different water concentrations in NAFION-117 are reported in the present work. Self-diffusion

measurements are customarily made by the pulsed gradient spin–echo method,<sup>20</sup> but in this work the static gradient associated with the fringe field of the NMR magnet was used. Two advantages of the static gradient are its typically much larger magnitude than obtainable with NMR probe gradient coils, and the relative ease of incorporating a pressure cell into the experiment.

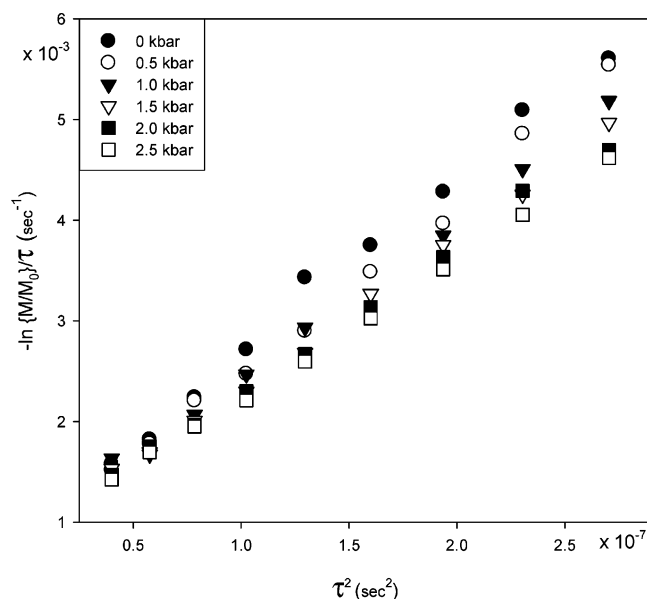
## Experimental Details

All studies were carried out on NAFION-117 supplied by E. I. du Pont de Nemours. Samples were made from 13 rectangular strips of film comprising a stack with dimensions 0.6 cm × 0.5 cm × 1.8 mm. Samples were first dried in a vacuum oven at 50 °C for several days and then saturated in distilled water for a few hours. After this preparation, the sample weight increased due to water uptake such that 100% × (weight of absorbed water)/(dry weight of NAFION) = 22%. Variation of the water uptake in samples was achieved by exposing the saturated sample (22 wt %) to the atmosphere for a limited time until the required water percentage was reached. For NMR measurements, the samples were hermetically sealed in thin polyethylene bags, which were shown to produce a negligible proton NMR background signal compared to the signal from the NAFION. This was necessary to isolate the sample from the pressure transmitting fluid (hydrogen-free FLUORINERT electronic fluid, FC-77 manufactured by 3M Co.).

The naturally existing field gradient of a conventional 7.3 T superconducting magnet was used for the measurements. The central field and gradient strength were varied continuously, within the limits of the magnet, by moving the NMR probe head within the bore of the magnet. The position of the NMR coil (which contains the sample) determines both the resonant frequency and the magnetic field gradient. A home-built

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**Figure 1.** Semilog plot of nuclear magnetization, as a function of the square of the pulse separation ( $\tau^2$ ) and pressure at 22 wt % water content in NAFION at temperature 288 K.

computer controlled motorized stage, capable of moving the probe in precise steps of 0.25 mm, was used to center the coil at a central field value of 1.7 T with a gradient strength ( $G = dB_z/dz$ ) of 0.253 T/cm. The latter quantity was determined experimentally using the standard self-diffusion coefficient of water.<sup>19</sup> Accurate variation of the pressure (0–2.5 kbar) was carried out using an ENERPAC 11-400 hydraulic system fitted to a sealed Cu–Be alloy high-pressure chamber (bomb) inside of which resides the NMR excitation coil and sample. Electronic leads between the coil and external matching and tuning capacitors was facilitated by a hermetic feedthrough.

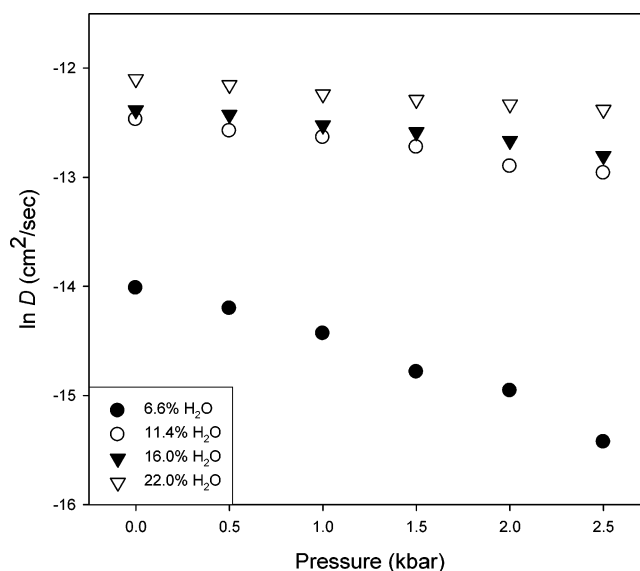
A home-built broadband NMR spectrometer operating at 72 MHz (the central field value corresponding to the position of the sample in the fringe-field) and utilizing a phase cycled spin–echo pulse sequence ( $\pi/2 - \tau - \pi - \tau - \text{acquire}$ ) was used to detect the proton echo signal from the sample. Pulse widths ( $\pi/2$ ) were typically of 2.5  $\mu\text{s}$  duration. Although it is acknowledged that this pulse width constitutes somewhat less than the full spectral coverage of all of the protons in the sample, estimated to be about 2 MHz (based on the  $\sim 2$  mm sample thickness and the  $\sim 0.025$  T/mm gradient), this value was chosen on the basis of the maximum signal amplitude obtainable for a given pulse separation.

## Results

Proton spin–echo intensities  $M(\tau)$  were measured as a function of the pulse separation,  $\tau$ , and self-diffusion coefficients  $D$  were extracted from the data using<sup>21</sup>

$$M(\tau) = M_0 \exp\{-(2/3)[3\tau/T_2 + (\gamma G)^2 D \tau^3]\} \quad (1)$$

In this expression  $M_0$  is the maximum magnetization (at  $\tau = 0$ ) and  $\gamma$  is the proton gyromagnetic ratio. To assist in the analysis, proton transverse relaxation times  $T_2$  were measured independently and the data were fit to a linearized version of eq 1 with slope =  $2(\gamma G)^2 D/3$  and intercept =  $2/T_2$ . In this way the diffusion coefficients were gathered with respect to applied pressure. Linearized results (i.e., data presented as a function of the square of the pulse separation,  $\tau^2$ ) and pressure at 22 wt % water content in NAFION are illustrated in Figure 1. The



**Figure 2.** Semilog plot of the self-diffusion coefficient ( $D$ ), as a function of pressure for different water contents in NAFION at temperature 288 K.

**TABLE 1: Activation Volumes for Different Water Contents in NAFION-117**

wt % H <sub>2</sub> O	activation vol (cm <sup>3</sup> /mol)
6.6	13.2 ± 1.0
11.4	4.8 ± 0.4
16.0	3.9 ± 0.3
22.0	2.7 ± 0.2

self-diffusion coefficients as a function of pressure for four different water contents in NAFION are plotted in Figure 2.

The data in Figure 2 can be further analyzed to yield the activation volume  $\Delta v$  associated with the diffusing water molecules according to

$$\Delta v = -kT \left( \frac{\partial \ln D}{\partial P} \right)_T \quad (2)$$

The activation volumes for four different water contents in NAFION-117 are given in Table 1.

## Discussion

The self-diffusion coefficient generally decreases with decreasing water content and also with increasing pressure as these yield greater restrictions for water molecular motions. In addition, the behavior of  $\Delta v$  versus water content (wt %) exhibits two well-defined regions: a low water content region, where  $\Delta v$  decreases rapidly with increasing water contents, and a high water content region, where  $\Delta v$  decreases further by a very small amount with increasing water content. This behavior has been previously observed by others in conductivity and  $T_1$  results.<sup>14,15</sup> It is important to point out that  $T_1$  is generally sensitive to fluctuations occurring on the time scale of the inverse of the NMR frequency and is thus responsive to short-range processes, whereas self-diffusion measurements probe typically longer ( $\sim 1$   $\mu\text{m}$ ) processes. Thus for example, molecular rotation, which is an effective relaxation means, could be expected to present a different activation volume than long-range translational motion. In the present case, a similar qualitative pressure dependence of the water molecular motion is revealed by both probes.

A relatively large  $\Delta v$  of 13 cm<sup>3</sup>/mol is observed for low water content. Similar values for  $\Delta v$  have been obtained from electrical

conductivity measurements of hydrated NAFION-117 films, and from  $^1\text{H}$  and  $^2\text{H}$  NMR spin–lattice relaxation measurements of comparably low water content films.<sup>12–16</sup> The observation that high activation volumes are often associated with solvent-free lithium polymer electrolytes suggests that ion transport in these cases is controlled by polymeric segmental motion.<sup>14–16</sup> Conductivity results for very low water content NAFION yield an activation volume of about  $50\text{ cm}^3/\text{mol}$ , consistent with values reported for lithium polymer electrolytes.<sup>22</sup> The highest activation volume presented here, though somewhat lower than the values usually associated with segmental motion are still consistent with the general view that NAFION with low water content can be viewed in terms of water molecule “clusters” and ions separated by polymer pendant chains. Conductivity takes place as protons move from cluster to cluster, as this motion is enhanced due to the segmental motion of the polymer.

At high water contents,  $\Delta v$  is relatively small and does not vary much with increasing water content. In a previous paper,<sup>14</sup> it was suggested that the electrical conductivity in this region is controlled more by bulk water than by the polymer. Zawodzinski et al. has also pointed out that the conductivity mechanism at high water content is expected to approach that of protons in bulk water due to the large number of pores within the polymer that are filled with water.<sup>1</sup> In fact, electrical conductivity of aqueous acid solutions tend to give small negative activation volumes, due to a compressibility factor (i.e., more ions per unit volume) that slightly outweighs the viscosity factor.<sup>15,23</sup> This is a complication that does not appear in the diffusion measurements, despite the correlation between water diffusivity and proton conductivity.

In our measurements the self-diffusion coefficient for the NAFION-117 sample with 22 wt % hydration decreased about 25% (from  $5.56 \times 10^{-6}\text{ cm}^2/\text{s}$  to  $4.20 \times 10^{-6}\text{ cm}^2/\text{s}$ ) as the pressure increased from 0 to 2.5 kbar. Upon comparison with the results for pure water, as given by Benedek and Purcell, the self-diffusion coefficient was observed to decrease by roughly 10% as the pressure increased by the same amount.<sup>18</sup> This shows that even though molecular motion at high water content is similar to that of bulk water, the polymer is still involved in the diffusion process. The advent of new polymer membranes that do not contain water for higher temperature fuel cell applications will require an understanding of alternative proton transport mechanisms, and it is expected that high-pressure NMR will become a very useful analytical tool in investigating these new materials.

## Summary

High-pressure NMR measurements of the water self-diffusion coefficient in NAFION were conducted in the nonuniform (fringe) region of a superconducting magnet. Activation volumes associated with water mobility have been obtained at several different water contents. The largest activation volume ( $13\text{ cm}^3/\text{mol}$ ) is found at the lowest water content (6.6%). As the water

content increases,  $\Delta v$  at first decreases rapidly and only gradually thereafter. This indicates that the transport mechanism in low water content films is significantly different than that at high water content, and possibly involves some contribution from segmental motions of the polymer. At higher water content, the change in  $\Delta v$  is comparatively small, suggesting that the transport mechanism in high water content membranes is dominated by bulk water. These new results, which are in good agreement with the previous studies of spin–lattice relaxation and electrical conductivity, illustrate how the pressure dependence of self-diffusion coefficients can be a useful tool in characterizing molecular motion in fuel cell membranes.

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