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ELECTRICAL CONDUCTIVITY AND NMR STUDIES OF METHANOL/WATER MIXTURES IN NAFION MEMBRANES

by

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Complex impedance studies have been carried out in acid form NAFION 117 treated with various amounts of methanol and methanol-water mixtures. At room temperature and atmospheric pressure the conductivity for NAFION treated with "pure" methanol is about a factor of ten less than for NAFION which contains the same wt.-% of water. In samples treated with the water-methanol mixtures, the conductivity is lower than for samples having the same total wt.-% of water. However, for low mixed fluid wt-% the conductivity is significantly higher than for samples with the same amount of water, only, as was in the mix. This enhancement of conductivity over that for the corresponding water uptake is attributed to a plasticizing effect of the methanol facilitating the segmental motion of the polymer. At higher water concentrations, the conductivity is generally lower in the mixed solution-treated samples than in samples treated with the corresponding amount of water. This is to be expected since in this regime, proton conduction occurs in fluid-rich regions, which in the solution case includes a large fraction of methanol. For a 40 wt.-% 1.4:1 molar ratio film, the studies were carried out at pressures up to 0.3 GPa It is found that the electrical conductivity decreases with increasing pressure. Both the electrical conductivity and the activation volume are similar to the result for NAFION containing the same amount of water only. Deuteron NMR spin-lattice relaxation measurements of isotopically enriched methanol/water mixtures in NAFION 117 at elevated pressure demonstrate greater molecular-level interactions between methanol and NAFION than between water and NAFION. This is consistent with the plasticizing effect observed in the conductivity results.

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ELECTRICAL CONDUCTIVITY AND NMR STUDIES OF METHANOL/WATER MIXTURES IN *NAFION* MEMBRANES

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Abstract- Complex impedance studies have been carried out in acid form *NAFION* 117 treated with various amounts of methanol *and* methanol-water mixtures. At room temperature and atmospheric pressure the conductivity for *NAFION* treated with "pure" methanol is about a factor of ten less than for *NAFION* which contains the same wt.-% of water. In samples treated with the water-methanol mixtures, the conductivity is lower than for samples having the same total wt.-% of water. However, for low mixed fluid wt-% the conductivity is significantly higher than for samples with the same amount of water, only, as was in the mix. This enhancement of conductivity over that for the corresponding water uptake is attributed to a plasticizing effect of the methanol facilitating the segmental motion of the polymer. At higher water concentrations, the conductivity is generally lower in the mixed solution-treated samples than in samples treated with the corresponding amount of water. This is to be expected since in this regime, proton conduction occurs in fluid-rich regions, which in the solution case includes a large fraction of methanol. For a 40 wt.-% 1.4:1 molar ratio film, the studies were carried out at pressures up to 0.3 GPa. It is found that the electrical conductivity decreases with increasing pressure. Both the electrical conductivity and the activation volume are similar to the result for *NAFION* containing the same amount of water only. Deuteron NMR spin-lattice relaxation measurements of isotopically enriched methanol/water mixtures in *NAFION* 117 at elevated pressure demonstrate greater molecular-level interactions between methanol and *NAFION* than between water and *NAFION*. This is consistent with the plasticizing effect observed in the conductivity results.

Keywords: *NAFION*, electrical conductivity, deuteron NMR, methanol, activation volume, high pressure

INTRODUCTION

Because of their possible application in fuel cells, ion exchange membranes such as *NAFION* are of interest. Consequently, many studies of the electrical conductivity in these types of material containing water have been carried out [1-15]. However, it appears that no data have been reported for electrical conductivity in the presence of methanol even though other types of results, such as NMR [16], swelling [17] and transport [18] studies have recently begun to appear. This kind of information is of increasing importance in view of applications in direct methanol fuel cells. However, in such applications, *NAFION* is hampered by large methanol cross-over problems.[18] In the present work, various solutions of methanol and water have been added to *NAFION* 117 and studies of the electrical conductivity of *NAFION* at room temperature and atmospheric pressure and at elevated pressure have been carried out. High pressure deuteron NMR measurements were also carried out in *NAFION* containing ^{2}H-enriched mixtures of methanol and water.

EXPERIMENTAL

All studies were carried out on *NAFION* 117 manufactured by E. I. DuPont de Nemours. The equivalent weight is 1100 and under dry conditions, the samples are approximately 0.17 mm thick. The samples were on the order of 4 cm long and 1 cm wide. Gold was vacuum evaporated onto the ends of the sample. The gold completely covered the ends of the sample (both sides and edges) leaving a strip of *NAFION* approximately 3.5 cm long and 1 cm wide. This configuration has been shown to give good agreement with the bulk conductivity reported by other workers [4].

For the atmospheric pressure measurements, the samples were dried over phosphorous pentoxide then placed inside a glove box containing open containers of the appropriate mixture of methanol and water, thus maintaining a saturated atmosphere. The ratios were adjusted according to the different vapor pressures of methanol and water. The sample was placed in contact with a measured quantity of the mixture and allowed to absorb the liquid. No attempt was made to carry out the experiments under ultra dry conditions and thus there is probably a small but significant amount of water in the methanol. None of the conclusions of the present work are affected by that fact. The sample was weighed and the dimensions taken immediately prior to the impedance measurement being made while the samples remained inside the glove box. Therefore the sample was maintained in the appropriate relative methanol-water atmosphere throughout the procedure. The wt-% uptake of the solution by the samples was calculated by dividing the change in mass by the mass of the dry samples.

The equivalent parallel capacitance and resistance of the samples were determined using a CGA-83 Capacitance bridge (10-10^5 Hz) and/or a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer. All data were then transformed to the complex impedance, $Z^* = Z'-jZ''$.

The data were plotted as complex impedance diagrams, the forms for which are similar to those shown previously for *NAFION* 117 under other conditions [12] and to those seen in ion conducting polymers [20]. In general, an impedance arc, attributable to the bulk properties of the material, is observed at the highest frequencies. This is consistent with the observation by various groups [4,11] that the electrical conductivity is attributable to a simple, frequency independent conductivity mechanism. In addition, a slanted line, due to electrode effects, is observed at the lowest frequencies. Because of the wide range of conductivity of the samples and different capabilities of the measuring instruments, different portions of the arc or line are observed for different samples at different solution contents and pressures.

In the present work, all intercepts due to semicircular arcs were obtained graphically. The intercept of the impedance data with the Z' axis was taken to be the bulk resistance, R, of the sample. The conductance, G=1/R, was then calculated from the intercept and transformed to the electrical conductivity, σ, via

$$\sigma = G\,l/A. \qquad (1)$$

where A is the area of the sample and l is the length.

For the high pressure electrical conductivity measurements, the samples were isolated from the pressure fluid using techniques similar to those recently applied to gel electrolytes [19] and *NAFION* containing water [15]. Briefly, the samples were sealed inside rubber tubing with platinum electrodes projecting through the ends. 40 wt-% of a solution of a 1.4:1 molar (3:1 by volume, 2.4:1 by weight) methanol-water solution was injected into the sample holder. The samples were then clamped onto the closure plug of a high pressure vessel and the conductance was measured at various pressures.

For deuteron NMR studies, strips of dried *NAFION* 117 were immersed in various mixtues of CH_3OD and D_2O for at least 24 hours, removed from the liquid and quickly blotted dry (to eliminate most of the free surface liquid), and then sealed in short lengths (~8mm) of silicone tubing. The high pressure measurements were carried out on a *Novex* NMR spectrometer at a ^2H resonance frequency of 31 MHz, with a home-built high pressure NMR probe; *Fluorinert* FC-77 (3M) was utilized as the pressure transmitting fluid. Spin-lattice relaxation time (T_1) data were obtained by inversion recovery, as pressure was increased then decreased. Only modest pressure history effects were noted and, for consistency, all reported values correspond to the decreasing pressure part of the experiment. High pressure measurements of the corresponding free liquids, sealed in silicone, were also taken.

RESULTS AND DISCUSSION

Electrical Conductivity vs. Water Content

The electrical conductivity results for samples treated with methanol and a 1:1 molar ratio methanol-water mixture are shown in Figure 1. For comparison, the results for the conductivity of *NAFION* treated with water only [15] are also shown. The conductivity is about an order of magnitude lower than is observed for *NAFION* treated with the same amount of water. However, when the conductivity is plotted against *water* content, as is also shown in Figure 1, at low solution content, it is significantly higher than for water alone. Part of the effect is, of course, due to the conductivity associated with the "pure" methanol in the sample. However, a residual conductivity remains. This is attributed to a plasticizing effect of the methanol. Specifically, it has been suggested that for low water contents, electrical conductivity in *NAFION* takes place via segmental motions (presumably the side chains) of the polymer [1,13,15]. The interpretation, then is that the addition of methanol increases the segmental motions of the polymer thereby increasing the electrical conductivity.

It is also clear from Figure 1 that the behavior is different at high solution contents. The plot of solution conductivity vs. *water* content shows that there is a tendency for the conductivity to be the same if not lower than for water alone. Again, this is consistent with previous results. It has been suggested that at high water contents the conductivity is controlled by the liquid phase rather than the polymer [1,13,15]. Since the electrical conductivity of methanol is lower than for water, it would be expected that the conductivity of the solution, and hence for solution in *NAFION*, should be smaller than for water alone.

Electrical Conductivity vs. Pressure

The results for the variation of the electrical conductance with pressure are shown in Figure 2. The value of the pressure variation of the conductance was calculated from a best-fit to the data and the result is that dlnG/dp = -0.55/GPa. Next, the pressure derivative of the electrical conductance was converted to pressure derivative of the electrical conductivity using:

$$\left(\frac{\partial \ln \sigma}{\partial p}\right)_T = \left(\frac{\partial \ln G}{\partial p}\right)_T + \frac{\chi_T}{3} \qquad (2)$$

where χ_T is the isothermal compressibility. Since the isothermal compressibility of the polymer under the conditions of the experiment is not known, the value for water, χ_T=0.45/GPa [22], was used and thus a value of dlnσ/dp = -0.4/GPa is obtained. Finally, an activation volume was calculated from the pressure variation of the electrical conductivity via:

$$\Delta V = -kT\,[d\ln\sigma/dp]_T. \qquad (3)$$

The result is that $\Delta V = +0.99\ \text{cm}^3/\text{mol}$. In contrast to the results for water in *NAFION*, the activation volume is positive even though the sample contains 40 wt.-% of fluid. For water in *NAFION*, the activation volume is negative for water contents above about 15 wt.-%. However, the 40 wt.-% mixture contains about 11.7 wt.-% of water and the activation volume for the mixture is approximately equal to that for a sample containing 11.7 wt.-% of water only. In order to show this, the activation volume for the mixture has been added to data from References 13 and 15 and the resultant plot is shown in Figure 3. However, the similarity in the activation volumes is probably fortuitous because it was found that the electrical conductivity, itself, for 40 wt.-% of a 1.4:1 molar methanol-water solution in *NAFION* is approximately the same as for 11.7 wt.-% water in *NAFION*. It will be of interest to carry out experiments on other concentrations of 1.4:1 solution in *NAFION* as well as for other solution compositions.

^{2}H NMR Spin-Lattice Relaxation vs. Pressure

Deuteron T_1 values as a function of pressure are plotted in Fig. 4, for *NAFION*-117 equilibrated in different CH_3OD/D_2O mixtures. A clear trend of decreasing T_1 with increasing volume (or mole) fraction of methanol, at any given pressure, is observed. Rotational reorientation of water and methanol molecules produces large fluctuations in the deuteron quadrupole coupling interaction, and is the primary relaxation mechanism. At ambient temperature this motion is very rapid, although less so than in the corresponding free liquids, and leads to T_1 values that are above the T_1 minimum (which would accur at much lower temperature). Hence decreasing T_1 corresponds to a *decreasing* molecular reorientation rate. The decrease in molecular rotation rate can possibly have implications for the proton transport mechanism, in which rotation of water molecules plays a róle.[12] It is interesting that the T_1 values of liquid D_2O and liquid CH_3OD, and their pressure dependencies, plotted in Fig. 5, are quite close to each other. Therefore the above trend provides evidence that methanol experiences stronger interaction with the *NAFION* internal structure, leading to greater reorientation restrictions, than water. This molecular-level interaction is undoubtedly related to the plasticizing action of the methanol. Activation volumes for spin-latttice relaxation can be defined by analogy with eq.(3) as:

$$\Delta V = -kT\, d[\ln(T_1)]/dP \qquad (4)$$

The results drawn from the data in Fig. 4 are plotted in Fig. 6. Despite the considerable error bars, it is clear that the *NAFION* containing 100% methanol exhibits the highest activation volume (consistent with the largest slope in Fig.4). The data for pure liquid methanol and water (Fig. 5), in fact, yield slightly negative activation volumes over the range of pressure studied; the result for liquid D_2O is in agreement with previously reported work [2~~3~~2], while the liquid methanol and water/methanol mixture results are new. As mentioned previously, larger activation volumes are associated with reorientation of larger molecular subunits, i.e. pendant chains. The electrical conductivity results above suggest that the methanol can act as a plasticizer, thus increasing the mobility of the pendant chains. This is consistent with the present NMR outcome, whereby the enhanced pendant chain motion in the *NAFION* with 100% methanol exhibits the largest pressure dependence.

CONCLUSIONS

In summary, then, several results have been obtained via measurements of the electrical conductivity of methanol and methanol/water solutions in *NAFION*. The conductivity in samples treated with methanol alone has been shown to be significantly lower than in *NAFION* treated with water. The conductivity of *NAFION* when treated with water/methanol mixes is also lower than for water alone, when the solution uptake is large. However, at low solution uptake, the conductivity is significantly higher than would be expected on the basis of the total amounts of water and methanol. This is attributed to plasticization by the methanol. NMR results provide further evidence of this plasticization effect, via decreased molecular reorientational rate and larger activation volumes for methanol-rich samples. In the higher water content regime, where proton transport occurs in the fluid rich regions, the presence of methanol leads to a reduction in the electrical conductivity.

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FIGURE CAPTIONS

Figure 1. Electrical conductivity vs. liquid content for various samples of NAFION 117 at room temperature (about 298 K).

Figure 2. Electrical conductance vs. pressure at room temperature (about 298 K) and various pressures for NAFION 117 containing 40 wt-% of a 1.4:1 methanol:water solution. The squares represent the data and the line is the best-fit straight line.

Figure 3. Activation volume vs. water content in wt-% for various samples of NAFION 105, 117 and 120 at room temperature (about 298 K). The solid symbol represents a NAFION 117 sample soaked in a 1.4:1 methanol:water solution. The wt-% for that sample is also the water content.

Fig Captions cont'd

4. Deuteron T_1 pressure dependencies of *NAFION-117* containing different ratios (by volume) of D_2O/CH_3OD.

5. Deuteron T_1 pressure dependencies of mixtures of D_2O and CH_3OD for different volume ratios.

6. Deuteron spin-lattice activation volumes calculated from the data in Fig. 4.

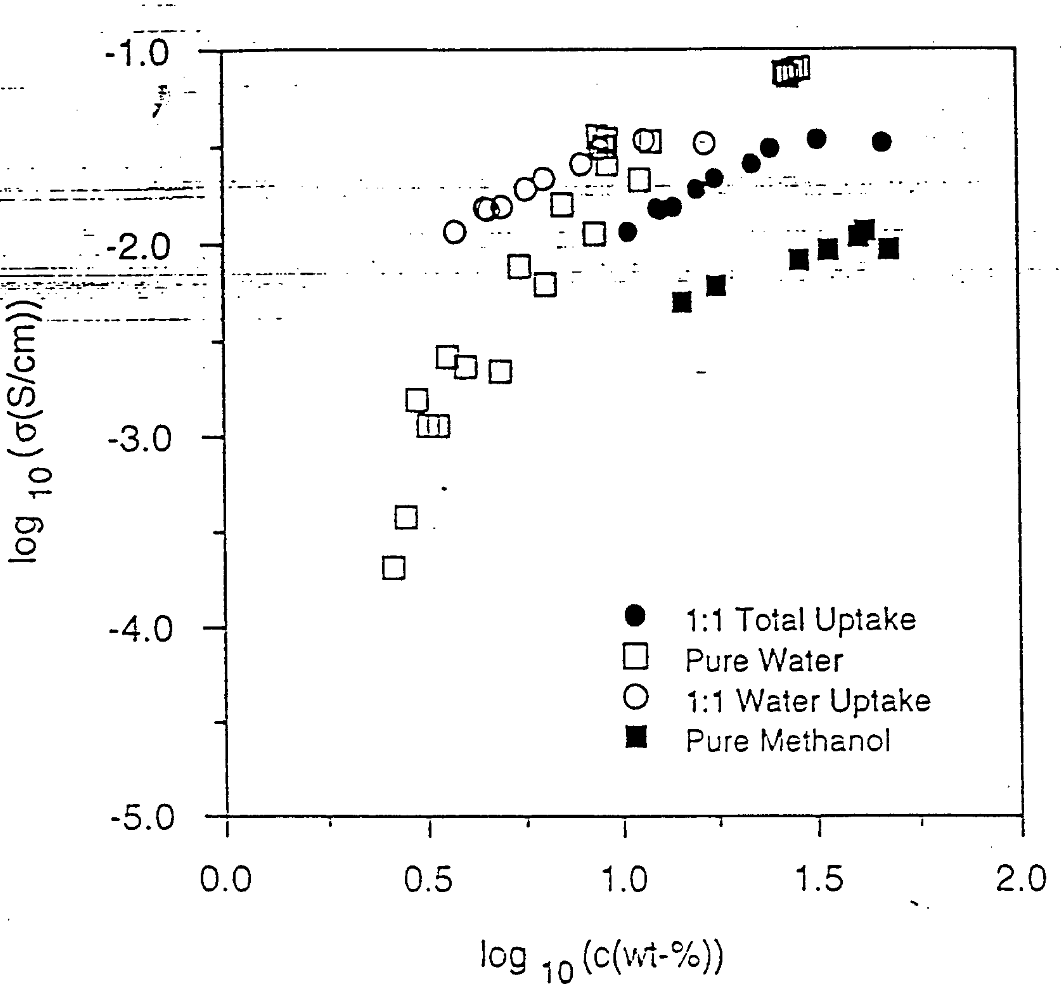

-1.0
-2.0
-3.0
-4.0
-5.0
0.0
0.5
1.0
1.5
2.0
log 10 (σ(S/cm))
log 10 (c(wt-%))
● 1:1 Total Uptake
□ Pure Water
○ 1:1 Water Uptake
■ Pure Methanol

Fig 1

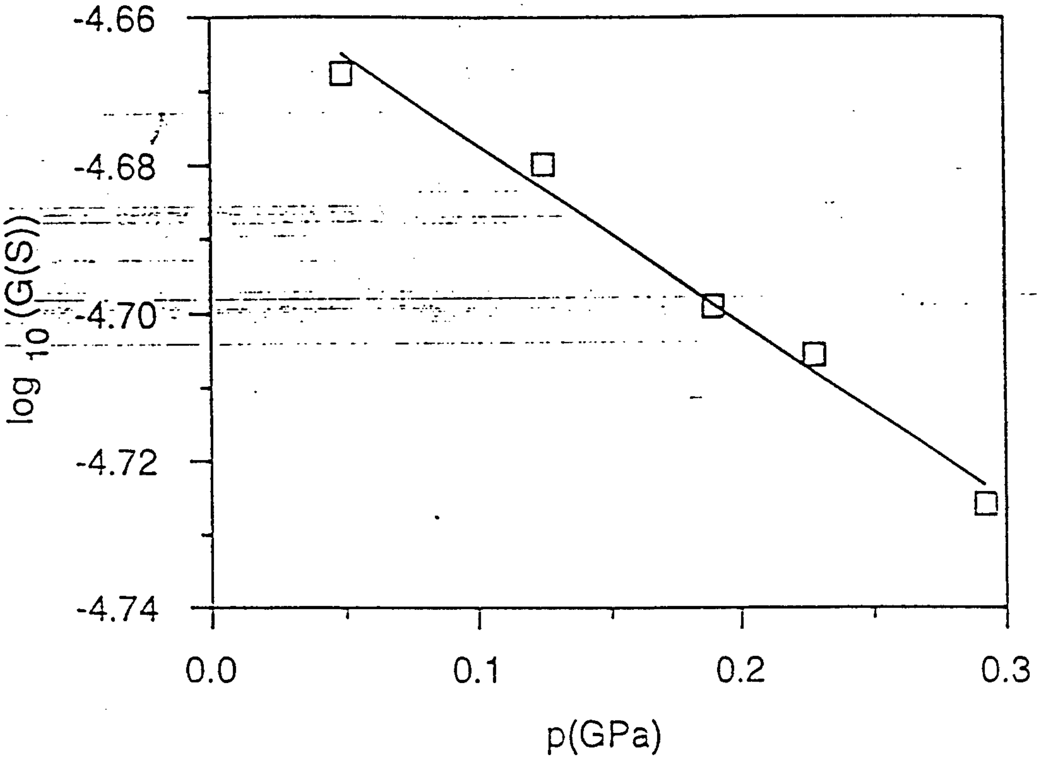
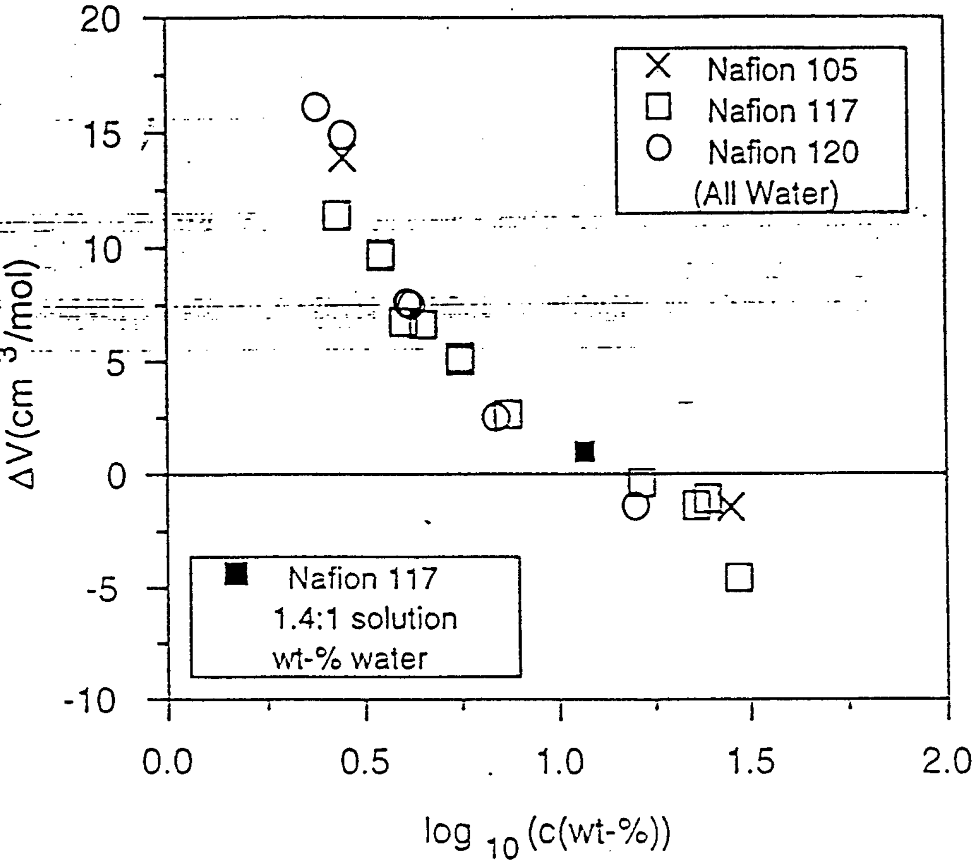


Fig 2



20
15
10
5
0
-5
-10
ΔV(cm 3/mol)
0.0
0.5
1.0
1.5
2.0
log 10 (c(wt-%))
× Nafion 105
□ Nafion 117
○ Nafion 120
(All Water)
■ Nafion 117
1.4:1 solution
wt-% water

Fig 3

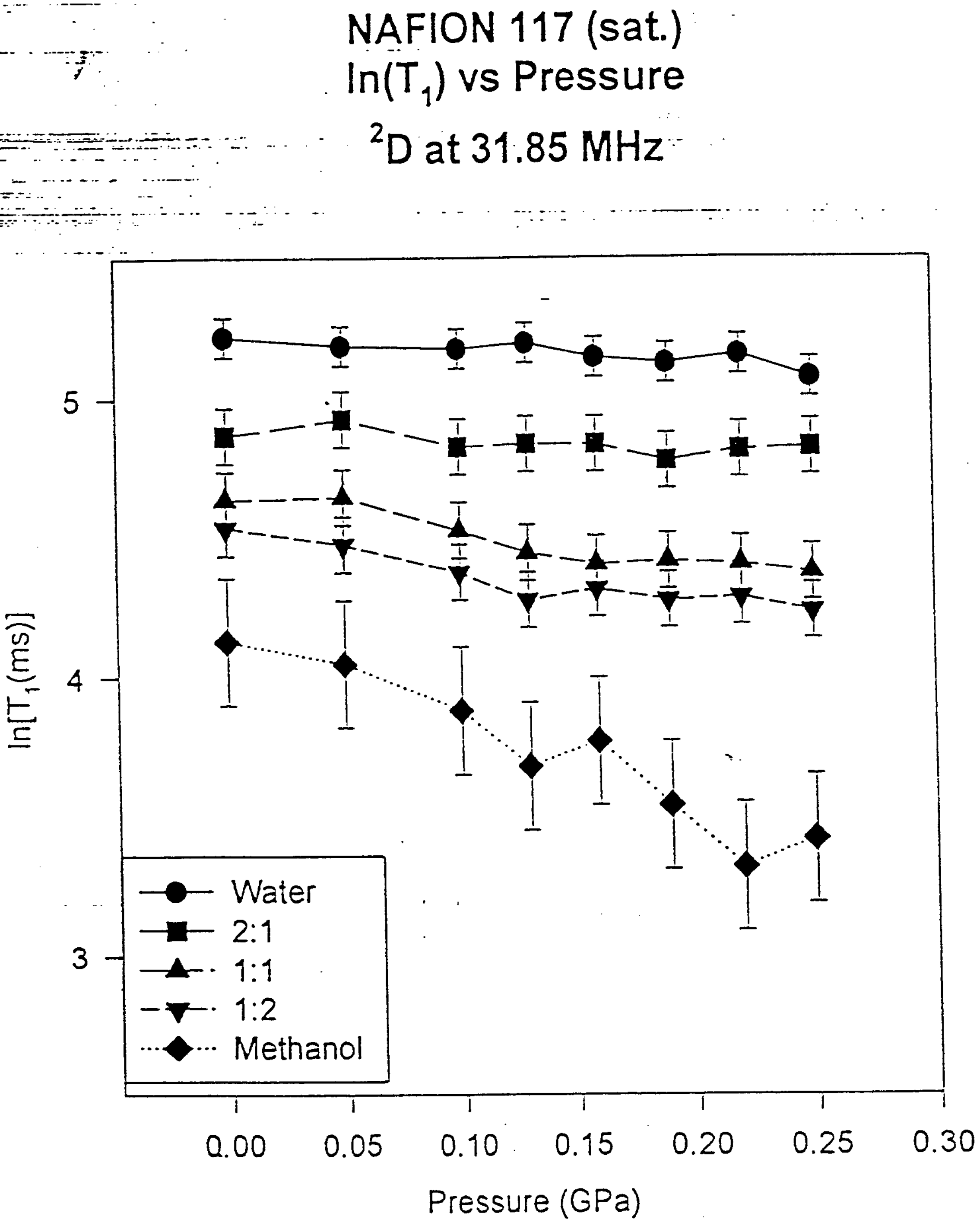

NAFION 117 (sat.)
ln(T_1) vs Pressure
^{2}D at 31.85 MHz
ln[T_1(ms)]
5
4
3
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Pressure (GPa)
Water
2:1
1:1
1:2
Methanol

Fig 4.

NAFION 117 + D_2O:CH_3OD
^{2}D NMR Activation Vol. vs Water Content

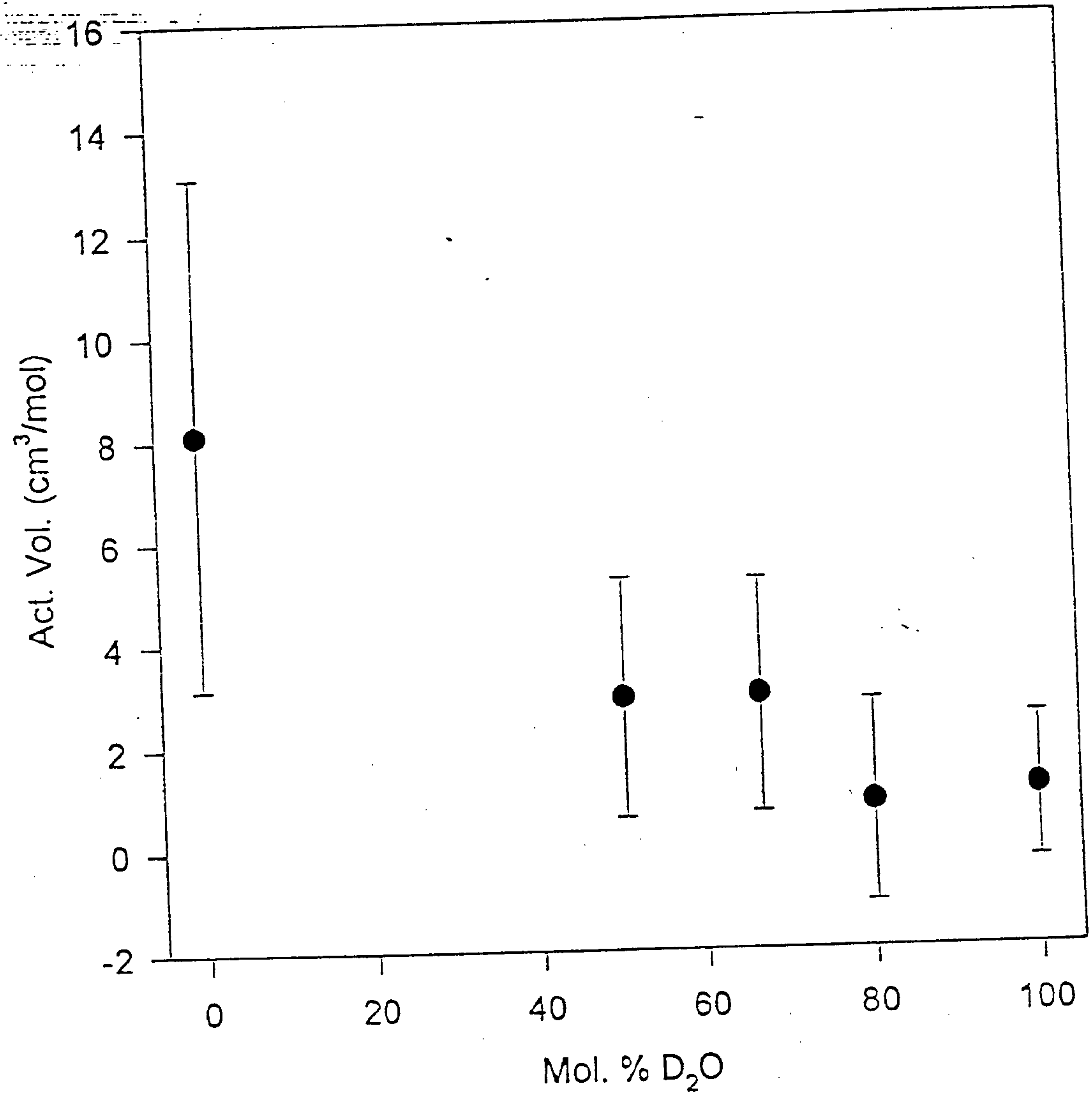


Fig 5

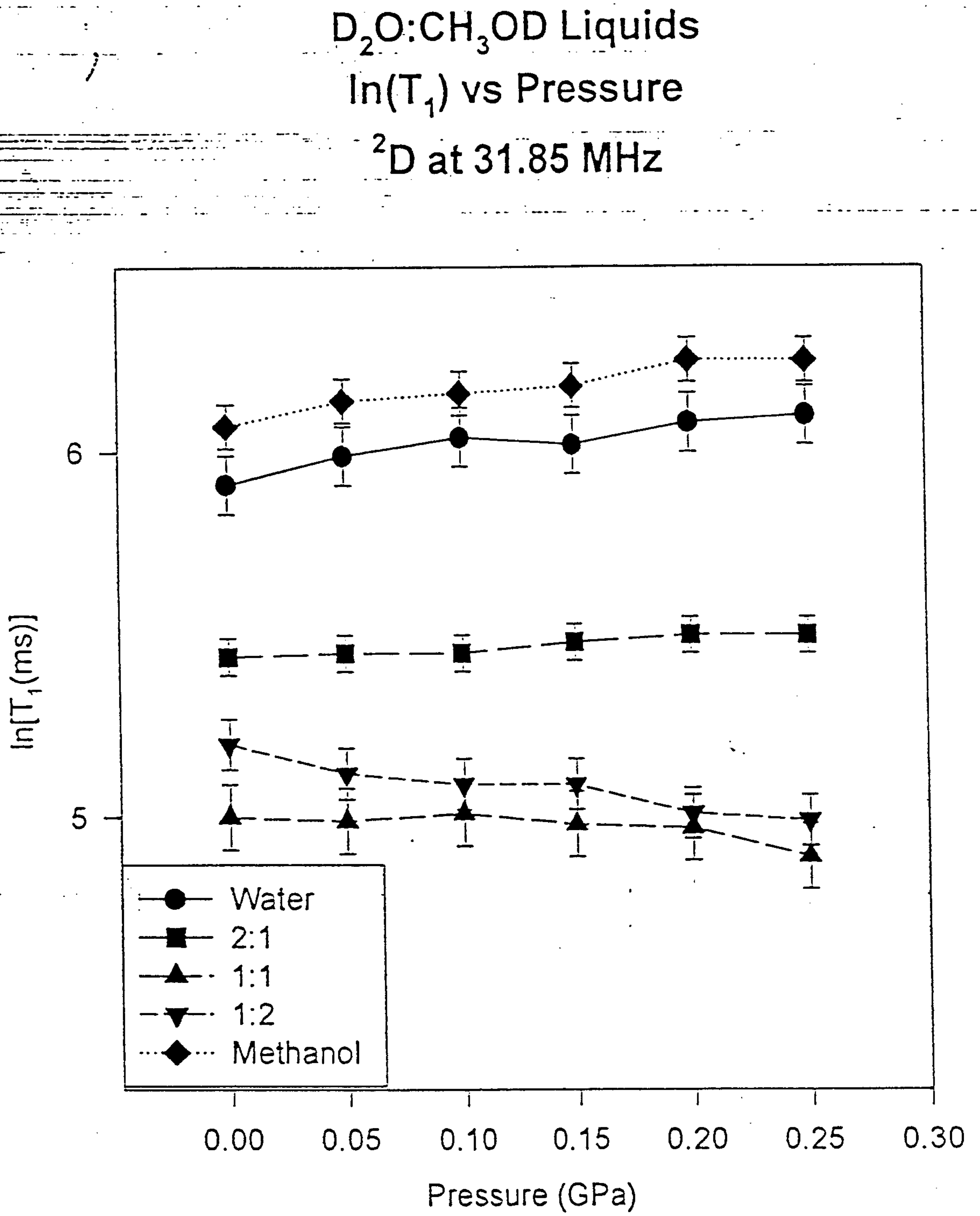

D2O:CH3OD Liquids
ln(T1) vs Pressure
2D at 31.85 MHz
ln[T1(ms)]
6
5
Water
2:1
1:1
1:2
Methanol
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Pressure (GPa)

Fig 6