

AD-A261 579



2

OFFICE OF NAVAL RESEARCH

GRANT # N00014-92-J-1629

R&T Code 4133037---01

Technical Report No. 2

Deuteron and Oxygen-17 NMR Studies of Molecular Motion
in Methanol-Saturated *Nafion* Membranes

by

R.S. Chen, J.R.P. Jayakody and S.G. Greenbaum

Prepared for Publication in

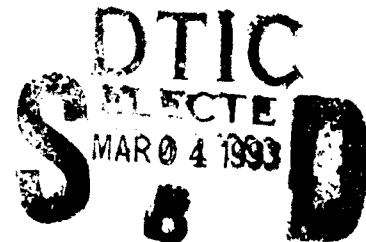
Materials Research Society Symposium on Solid State Ionics III

Hunter College of CUNY
Department of Physics
New York, NY 10021

January 25, 1993

Reproduction in whole or in part is permitted for any purpose of the United States Government.

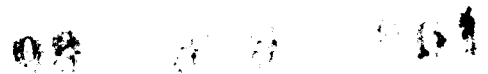
This document has been approved for public release and sale:
its distribution is unlimited.



93-04583



o.pk



REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. This report is the property of the U.S. Government. It is to be distributed and made available to the public without charge, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1 AGENCY USE ONLY (Leave blank)	2 REPORT DATE 25 January 1993	3 REPORT TYPE AND DATES COVERED Interim Technical Report 1, 1993	
4 TITLE AND SUBTITLE DEUTERON AND OXYGEN-17 NMR STUDIES OF MOLECULAR MOTION IN METHANOL-SATURATED NAFION MEMBRANES		5 FUNDING NUMBERS Grant number N00014-92-3-1629 R&T Code 4133037--01	
6 AUTHOR(S) R.S. Chen, J.R.P. Javakody and S.G. Greenbaum		8. PERFORMING ORGANIZATION REPORT NUMBER 2	
7 PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Physics Department, Hunter College of CUNY 695 Park Ave., New York, NY 10021		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
9 SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research, Chemistry Division 800 N. Quincy Street, Arlington, VA 22217-5660		11. SUPPLEMENTARY NOTES Presented at Materials Research Society Symposium on Solid State Ionics, Boston, MA, Dec. 1992; accepted for publication	
12a DISTRIBUTION AVAILABILITY STATEMENT Approved for public release and sale; distribution unlimited		12b. DISTRIBUTION CODE	
13 ABSTRACT (Maximum 200 words) <p style="text-align: center;">Deuteron and oxygen-17 NMR linewidth and spin-lattice relaxation measurements in <i>Nafion-117</i> films containing methanol at ~75% and ~100% saturation are reported. Molecular motion probed by room temperature measurements in stretched films and low T measurements in unstretched films is found to be quite rapid compared to previous results obtained for <i>Nafion-117</i> containing water.</p>			
14. SUBJECT TERMS Nafion; NMR; methanol; molecular motion		15. NUMBER OF PAGES 7	
17 SECURITY CLASSIFICATION OF REPORT unclassified		16. PRICE CODE	
18 SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT UL	

DEUTERON AND OXYGEN-17 NMR STUDIES OF MOLECULAR MOTION IN METHANOL-SATURATED NAFION MEMBRANES

R.S. CHEN, J.R.P. JAYAKODY and S.G. GREENBAUM
Physics Department, Hunter College of CUNY, New York, NY 10021

ABSTRACT

Deuteron and oxygen-17 NMR linewidth and spin-lattice relaxation measurements in *Nafion-117* films containing methanol at ~75% and ~100% saturation are reported. Molecular motion probed by room temperature measurements in stretched films and low T measurements in unstretched films is found to be quite rapid compared to previous results obtained for *Nafion-117* containing water.

Introduction

Perfluorinated ion-exchange membranes such as *Nafion* (DuPont) have been subject to a wide variety of intensive investigations because of their use as separators in present and future fuel cells.¹ Most of the efforts are geared toward applications involving hydrogen/oxygen fuel cells. The most important property of *Nafion* membranes in this capacity is their high proton transport number, which requires the presence of significant quantities of water (~20 wt%) in the membrane. Thus water molecular diffusion and charge transport across the membrane are, to some extent, correlated. One of the methods employed in measuring molecular and ionic diffusion is pulsed field gradient nuclear magnetic resonance (pfg NMR). One drawback (although sometimes this may be an advantage) of the technique is that it does not distinguish between charged and neutral diffusing species. The extent to which the mobilities of the two species (water molecules and protons) are correlated has been examined by pfg NMR by: (i) varying the H⁺ concentration by treating samples in different acidic environments;² (ii) varying the water concentration in the film.³

Alternatively, through the availability of water isotopically enriched in deuterium (with nuclear spin $I = 1$) or ¹⁷O ($I = 5/2$), NMR can be employed to study molecular dynamics by utilizing quadrupolar nuclei as probes. Although the very efficient and thus rapid relaxation associated with these nuclei often precludes pfg techniques, standard NMR spectroscopy is sufficiently rich in dynamical information. The authors have reported lineshape and spin-lattice relaxation (T_1) measurements in *Nafion-117* films containing D₂O and H₂¹⁷O (20% ¹⁷O-enrichment). One of the main results of this study was the observation of anisotropic molecular motion in the film plane, with dramatic enhancement of the anisotropy in modestly stretched films.⁴

The prospect of employing methanol directly as a fuel in low temperature fuel cells has obvious appeal, but there are formidable problems that must be addressed. Principal among these are the choice of a suitable catalyst to facilitate oxidation at the anode, and finding a membrane in which the methanol itself is inhibited from diffusing. In the latter case, methanol transporting across the membrane would be spontaneously oxidized at the cathode, leading to a chemical "short-circuit" in the fuel cell.⁵ In this work we employ NMR to investigate issues related to methanol molecular mobility in *Nafion-117* containing CH₃OD and CH₃¹⁷OH (15% ¹⁷O-enrichment).

Experimental Details

Nafion-117 sheets were obtained from DuPont and pretreated by boiling in dilute aqueous H₂SO₄ solution for 1 hour. Stretched films were prepared by gradually (over a period of several days) increasing the tension of a clamped and moistened film (dry films were found

to be too brittle to withstand the procedure) until ~40-50% elongation was achieved, and allowing the film to relax to a stable (over a timescale of about 1 week) configuration of about 15% elongation. The films were cut into rectangular pieces which were then assembled into a stack and loaded into open-ended 7mm outer diameter pyrex NMR tubes. The samples were dried for at least 4 hours in a roughing vacuum or over P₂O₅ at room temperature, and then exposed to methanol (either CH₃OD or 15% enriched CH₃¹⁷OH) vapor in sealed bottles. Immediately after determining the methanol weight uptake of the samples with a microbalance, the sample tubes were tightly sealed. Samples equilibrated for 24 hours contained 22-25 wt% methanol and were regarded as saturated. Films of methanol content of ~17 wt% were prepared by restricting the vapor exposure time to about 15 hours. Unstretched samples containing methanol were prepared by the same procedure. Deuteron and oxygen-17 NMR data were obtained at a field of 7 T with a Novex spectrometer interfaced to a LeCroy 9400 digital oscilloscope and a microcomputer. Both single-pulse and quadrupole-echo sequences were utilized for linewidth measurements, and spin-lattice relaxation times (T₁) were measured by inversion recovery. Pulse widths corresponding to $\pi/2$ flip angles were approximately 8 μ s. The recovery profiles were exponential over the entire temperature range of this investigation (160 - 300K). Temperature control (± 2 K) was achieved by N₂ flow regulation.

Results and Discussion

Room temperature deuteron NMR spectra of *Nafion-117* films containing 24 wt% CH₃OD are shown in Fig. 1, for both unstretched (a) and 11% stretched (b) samples. The angles listed between the spectra correspond to the relative orientation of the external magnetic field and the stretch direction. For the spectra in 1(a) (nominally unstretched), the stretch direction is assumed to be along the circumference of the rolled sheets obtained from the manufacturer. Comparison of the spectra in (a) and (b) clearly demonstrates that some molecular anisotropy is generated by stretching. The splitting in (b) appears to follow the $3 \cos^2\theta - 1$ dependence of quadrupole-perturbed Zeeman Hamiltonian. Close examination of the spectra in (a) also shows some anisotropy (though much smaller than (b)) according to the minimum linewidth being observed at the angle at which the quadrupole splitting vanishes (54°, sometimes referred to as the "magic angle"). However, it is necessary to point out that stretched films containing a comparable molecular concentration of D₂O (15 wt%) exhibited splittings an order of magnitude larger than shown in (b).⁴ In order to appreciate the degree of anisotropy exhibited here it is useful to mention that the full splitting that would result from the quadrupole interaction of a rigid O-D bond is on the order of 200 kHz.⁶ Thus nearly all of the anisotropy is averaged out by molecular motion, more so for CH₃OD than for D₂O.

Room temperature oxygen-17 NMR spectra of unstretched (a) and stretched (b) *Nafion-117* films containing 22 wt% CH₃¹⁷OH (at 15% enrichment) are displayed in Fig. 2. No angular dependence is apparent, even in the stretched samples. This is in stark contrast to the situation observed in stretched samples containing 16 wt% H₂¹⁷O, in which well-defined quadrupole "satellite" transitions, corresponding to transitions between m_l sublevels other than the central ($\pm 1/2$) one, with an overall spectral width of about 10 kHz, were observed.⁴ Although some of the anisotropy could be masked by lifetime broadening of the rapidly relaxing ¹⁷O nuclei (this will be discussed in somewhat more detail later), it is clear that methanol molecular motion retains almost none of the anisotropy generated in the stretched perfluoropolymer host, again in contrast to the situation concerning water molecular motion.

Distribution/	
Availability Code	
Dist	Special
A-1	

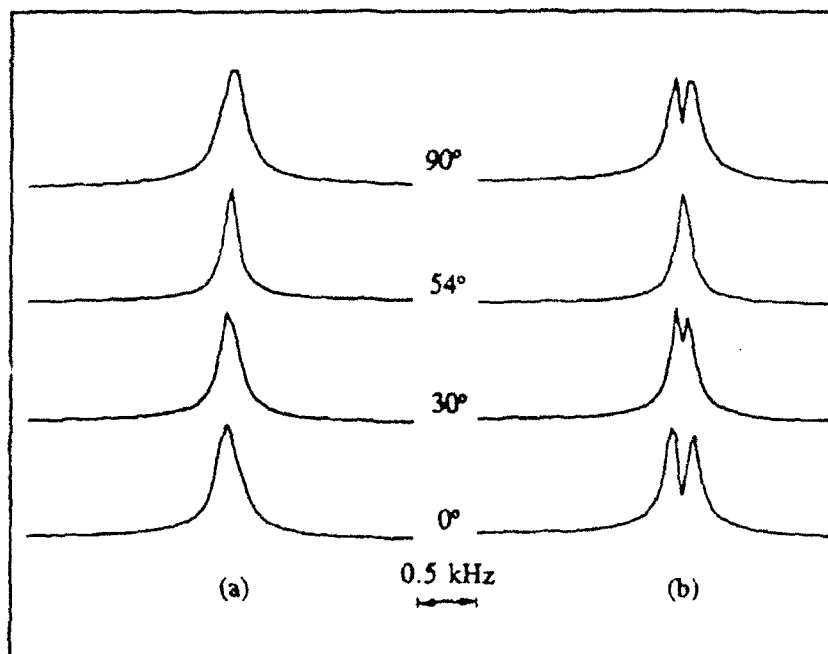


Figure 1. Deuteron NMR spectra of *Nafion-117* containing 24 wt% CH_3OD . (a) unstretched; (b) 11% stretched. The angles listed refer to the relative orientation of the stretch direction and the external magnetic field.

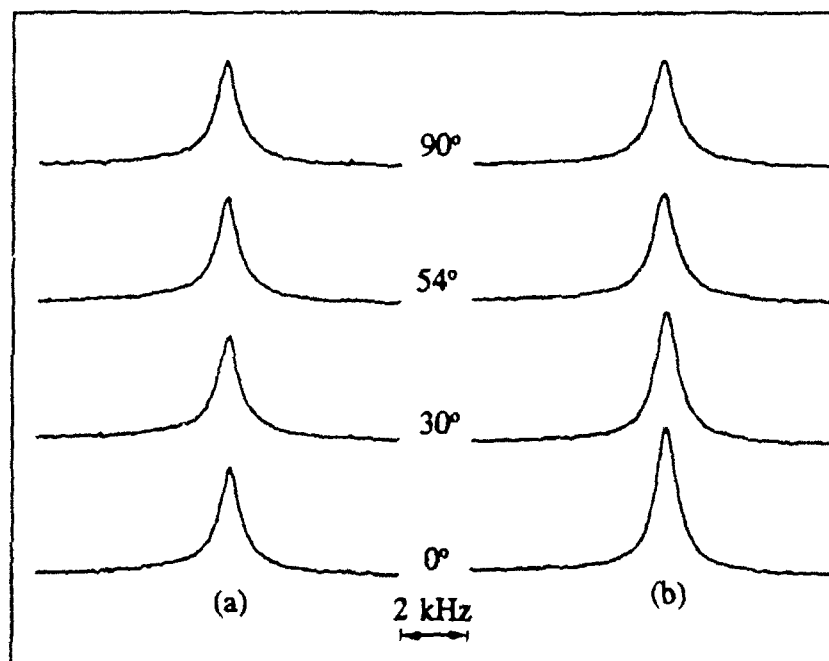


Figure 2. Oxygen-17 NMR spectra of unstretched (a) and stretched (b) *Nafion-117* films containing 22 wt% of 15%-enriched H_2^{17}O , under conditions described in Fig. 1 caption.

In order to obtain additional information regarding the dynamics of methanol in *Nafion*, variable temperature linewidth and T_1 measurements were performed. For linewidth measurements, unstretched samples oriented close to the magic angle were utilized in order to suppress the small anisotropies shown in Fig. 1. Arrhenius plots of deuteron linewidth of two samples, one saturated with CH_3OD (24 wt%) and the other containing 17 wt%, are displayed in Fig. 3. The linewidth of the 17 wt% sample is characterized by a low activation

energy (~ 0.05 eV) region above 240 K, steepening to ~ 0.20 eV between 180 and 240 K. The sample exhibits a highly unusual line-narrowing phenomenon as T is decreased below 170K. The origin of this line-narrowing is presently unknown, but could possibly be attributed to a subtle phase transition. The 24 wt% sample follows the same kind of behavior as the unsaturated one, but all of the features are shifted to lower T by some 5 - 10 K. It is interesting that at the lowest temperature at which measurements were made (140 K), the linewidth was still observed to be an order of magnitude smaller than that corresponding to a rigid quadrupole interaction for an O-D bond. In *Nafion* containing D_2O , the full rigid deuteron linewidth was observed at around 190 K.⁴ Thus molecular motion is frozen out at much higher T in the *Nafion*-water system than in *Nafion*-methanol. Arrhenius plots of T_1 of these samples are shown in Fig. 4. Again, the two curves exhibit similar behavior with the features, most notably the T_1 minimum, of the 24 wt% sample shifted to lower T (by 5 - 10 K) relative to the 17 wt% sample.

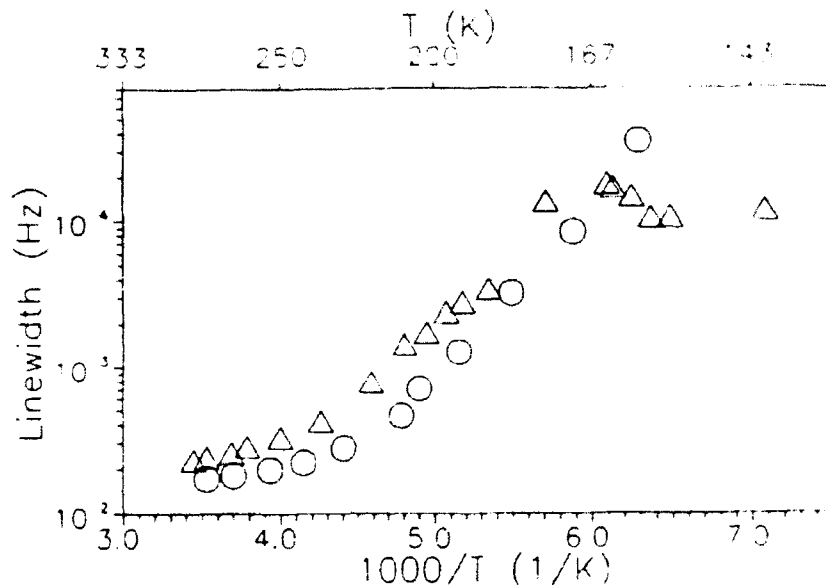


Figure 3. Arrhenius plots of deuteron NMR linewidth in *Nafion-117* containing 17 wt% (triangles) and 24 wt% (circles) CH_3OD .

Although the molecular motion time-scale probed by linewidth and T_1 are considerably different (10^{2-5} Hz in the former and 10^{7-8} Hz in the latter), the dominant motional process responsible for both linewidth and T_1 behavior is assumed to be molecular rotation, as in the case of liquid CH_3OD .⁷ Molecular rotation provides an even more efficient relaxation pathway for $CH_3^{17}O$ because of the considerably larger (than deuterons in the same molecule) quadrupole interaction experienced by the ^{17}O nucleus. Figure 5 displays Arrhenius plots of ^{17}O T_1 in *Nafion-117* samples containing 22 wt% and 18 wt% CH_3OH enriched 15% in ^{17}O . At temperatures below ~ 220 K, T_1 cannot be measured reliably because it becomes comparable to the width of the inverting pulse ($\sim 20 \mu s$). Oxygen-17 linewidths of the same samples are plotted in Fig. 6. It is interesting to note that the ^{17}O linewidths are determined, in large part, by lifetime (i.e. T_1) effects. For example the T_1 contribution to the linewidth, which can be estimated as $(\pi T_1)^{-1}$, is approximately half of the total linewidth at 295 K. This is at least partly responsible for the absence of ^{17}O spectral anisotropies in Fig. 2. Not surprisingly, the activation energies which characterize the T_1 and linewidth temperature dependencies are quite similar (~ 0.20 eV).

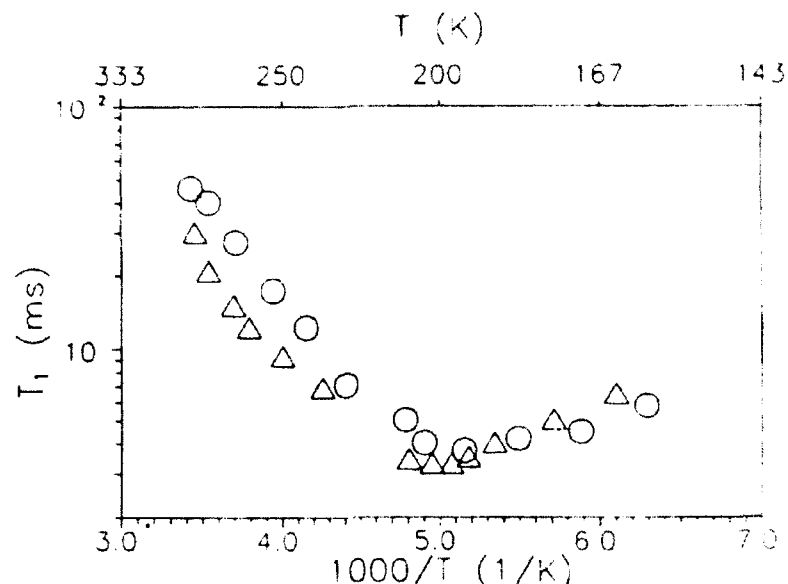


Figure 4. Arrhenius plots of deuteron spin-lattice relaxation time T_1 in *Nafion-117* containing 17 wt% (triangles) and 24% (circles) CH_3OD .

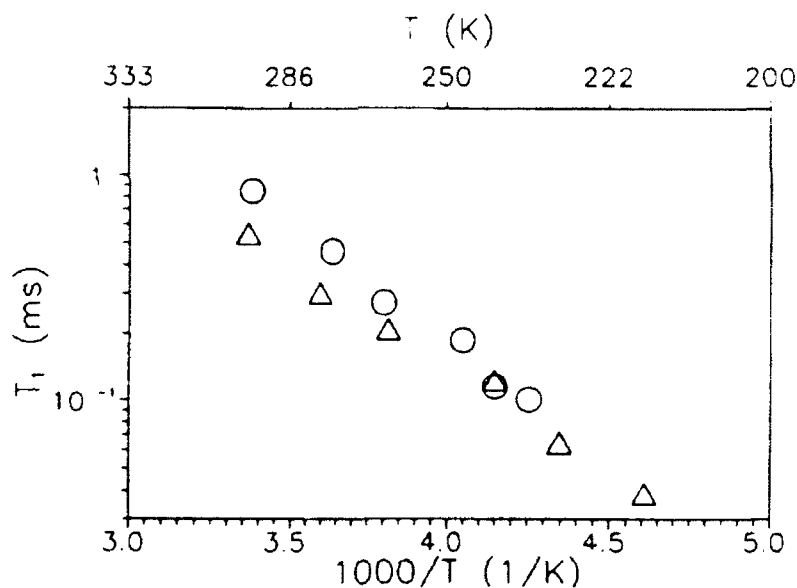


Figure 5. Arrhenius plots of ^{17}O spin-lattice relaxation time in *Nafion-117* containing 18 wt% (triangles) and 22 wt% (circles) of 15% ^{17}O -enriched CH_3OH .

The general shapes of the linewidth curves in Fig. 6 follow the temperature dependence predicted for a second-order quadrupole broadened central transition (lifetime effects are included), shown schematically in Fig. 7.⁸ The high- T region, equivalent to short motional correlation time τ , corresponds to the extreme narrowing limit $\omega_L \tau \ll 1$, where ω_L is the Larmor (NMR measurement) frequency. As T is lowered (or τ increased) the linewidth reaches a maximum associated with the T_1 minimum occurring at ca. $\omega_L \tau = 1$. This, of course, represents the lifetime contribution to the linewidth discussed above. Lowering T further reduces the linewidth until a minimum is reached, corresponding to a τ -value of the

order of $1/\omega_Q$, where ω_Q is the strength of the quadrupole interaction (on the order of several MHz at lower T). Further reduction in T (increase in τ) broadens the line until the rigid limit of the second-order linewidth, ω_Q^2/ω_L is reached. As in the case of the deuteron NMR results, the oxygen-17 linewidths of the two samples follow similar trends, with the main features of the higher methanol-content sample shifted to lower T. Thus the molecular dynamics at a given temperature are somewhat faster in the saturated sample.

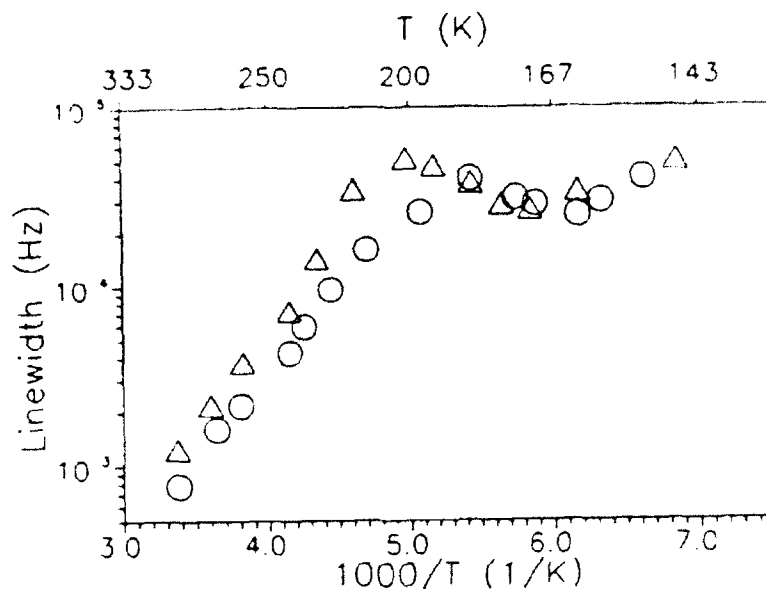


Figure 6. Arrhenius plots of ^{17}O linewidth in *Nafion-117* containing 18 wt% (triangles) and 22 wt% (circles) of 15% ^{17}O -enriched CH_3OH .

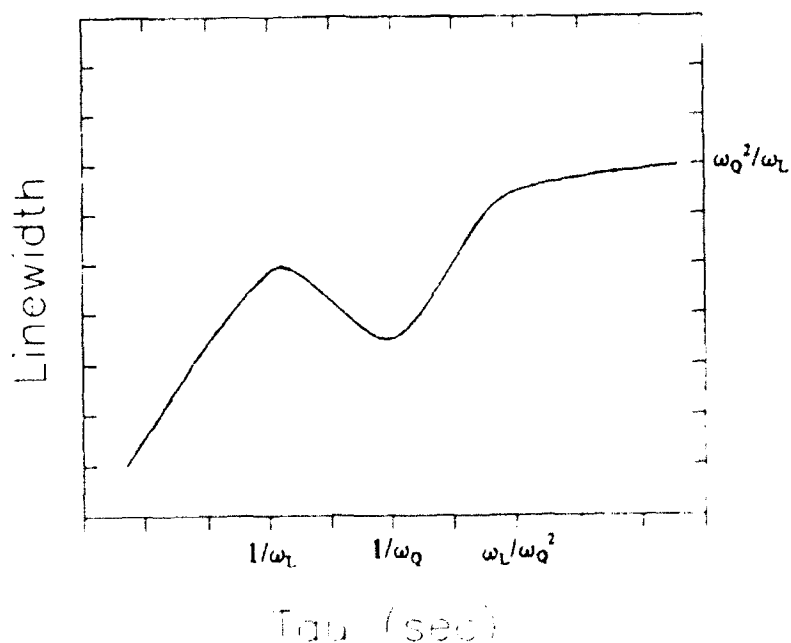


Figure 7. Predicted behavior of the linewidth of the central transition for a half-integer spin quadrupolar nucleus, as a function of molecular correlation time. Adapted from reference 8.

Although there is no simple and direct relationship between relaxation processes dominated by molecular rotation and methanol diffusion across the membrane (pfg proton NMR would be useful in this regard), the results reported here clearly suggest that methanol is highly mobile in *Nafion-117*, considerably more so than water. A brief summary of the experimental evidence supporting this conclusion is given: (i) near absence of anisotropic molecular motion in stretched films; (ii) deuteron linewidth at 140 K is still an order of magnitude smaller than that corresponding to a rigid O-D bond; (iii) molecular dynamics are somewhat faster at higher methanol content. Previous considerations of *Nafion-117* as membrane separator in a methanol fuel cell led to diffusion measurements and mathematical modelling. The main conclusion of this study was that methanol transport across the membrane is probably too high, thus other membrane separators were deemed more promising.⁵ The results reported in the present investigation are not inconsistent with this assessment.

Acknowledgements

The authors acknowledge Dr. W.E. O'Grady of the US Naval Research Laboratory for useful discussions regarding methanol fuel cells. This work was supported, in part, by a grant from the US Office of Naval Research.

References

1. S.J. Sondheimer, N.J. Bunce and C.A. Fyfe, *J. Macromol. Sci. - Rev. in Macromol. Chem. and Phys.* **C26**, 353 (1986).
2. R.C.T. Slade, J. Barker and J.H. Strange, *Solid State Ionics* **35**, 11 (1989).
3. T.A. Zawodzinski, Jr., M. Neeman, L.O. Sillerud and S. Gottesfeld, *J. Phys. Chem.* **95**, 6040 (1991).
4. R.S. Chen, J.R.P. Jayakody, S.G. Greenbaum, Y.S. Pak, G. Xu, M.G. McLin and J.J. Fontanella, *J. Electrochem. Soc.*, in press.
5. M. W. Verbrugge, *ibid.* **136**, 417 (1989).
6. L.W. Jelinski, in High-Resolution NMR Spectroscopy of Synthetic Polymers in Bulk, L. Komoroski, ed., VCH Publishers, New York (1986), Ch. 10.
7. D.E. O'Reilly and E.M. Peterson, *J. Chem. Phys.* **55**, 2155 (1971).
8. (a) A. Baram, Z. Luz and S. Alexander, *ibid.* **58**, 4558 (1973); (b) A. Vega, presented at the Bat-Sheva Workshop on New Developments and Applications in ESR and NMR Spectroscopy, Israel, 1990 (unpublished).