variance (0.25–0.5) of the autocorrelation function close to the critical point.

(c) The hydrodynamic correlation length $\xi_H$ is much larger than the critical correlation length measured from the angular disymmetry of the scattered light, which does not exceed 500 Å in the domain of $T - T_{sp}$ investigated here.[29,31] This explains that no deviation from the $k^2$ dependence was observed for the rate constant $\langle \Gamma \rangle$ in our experiments.

(d) The two straight lines of Figure 6, relative to samples of molecular weights 130 000 and $2 \times 10^6$, respectively, are shifted on the vertical scale by a factor of the order of 1.8, which is in reasonable agreement with the prediction 1.58 in eq 17.

## Conclusion

The main result of this paper concerns the concentration and molecular weight dependences of the diffusion constant, which can be represented on the form of a normalized hydrodynamic plot showing a minimum in the crossover region between the dilute and semidilute regimes.

The temperature dependence of the diffusion constant in the crossover region has also been analyzed in terms of the theories of critical fluctuations. The hydrodynamic correlation length measured in the vicinity of the critical point exceeds considerably the critical static correlation length because of virial effects on the friction coefficient. This difference between static and correlation length is likely to be also observed in the semidilute concentration range.

**Registry No.** Polystyrene, 9003-53-6; styrene–divinylbenzene copolymer, 9003-70-7.

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# A Study of the Behavior of Water in Nafion Membranes

**Noel G. Boyle,[†] Vincent J. McBrierty,[*,†] and Dean C. Douglass**

*Bell Laboratories, Murray Hill, New Jersey 07974.* *Received April 15, 1982*

ABSTRACT: This paper reports NMR data for perfluorosulfonate acid Nafion membranes containing various amounts of water. Results are also presented for $Fe^{3+}$- and $Na^+$-exchanged salts. The glasslike behavior at low temperatures is discussed. The data indicate that there is a distribution of heterogeneous water sites in the membranes and that fast exchange, on the NMR time scale, occurs between sites near room temperature and above. The presence of paramagnetic species in samples containing water, implied by the magnitude of the NMR relaxation times, is confirmed by X-ray fluorescence measurements, which reveal iron (and potassium) in significant amounts.

## Introduction

Many studies[1-13] have revealed the complex behavior of water associated with diverse solid media. Whether isolated in the vitreous or amorphous state[11] or incorporated in certain biological systems[5,8] or porous materials,[6,7,13] water manifests behavior essentially different from that observed in the bulk state. At low temperatures glasslike character is often observed.

Of interest in this paper is the behavior of water in the perfluorosulfonate membranes developed by the Du Pont company under the tradename Nafions. A preliminary report[14] has shown that water in Nafions also exhibits glasslike behavior at low temperatures and that data from NMR and neutron scattering experiments can be described

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[†] Department of Pure and Applied Physics, Trinity College, Dublin 2, Ireland.

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Table I
Concentrations of Water, Iron, and Potassium in the Nafion Samples Studied[a]

| sample no. | description | $[H_2O]/[SO_3H]$ | $[Fe]/[SO_3H]$ | $[Fe]/[H_2O]$ | [Fe] in sample, $cm^{-3}$ | [Fe] in water,[b] $cm^{-3}$ | [K]/[S][c] |
|---|---|---|---|---|---|---|---|
| 1 | 25% hydrated acid (115) | 15.3 | $8.7 \times 10^{-3}$ | $5.7 \times 10^{-4}$ | $9.5 \times 10^{18}$ | $1.9 \times 10^{19}$ | 0.43 |
| 2 | 7% hydrated acid (115) | 4.3 | $6.6 \times 10^{-3}$ | $1.5 \times 10^{-3}$ | $7.2 \times 10^{18}$ | $5.1 \times 10^{19}$ | 0.36 |
| 3 | 10% hydrated $Na^+$ salt (115) | 6.0 | $1.3 \times 10^{-3}$ | $2.1 \times 10^{-4}$ | $1.4 \times 10^{18}$ | $7.1 \times 10^{18}$ | 0.06 |
| 4 | 4% hydrated $Fe^{3+}$ salt (115) | 2.5 | 0.54 | 0.22 | $5.9 \times 10^{20}$ | $7.3 \times 10^{21}$ | |
| 5 | 8% hydrated acid (125) | 5.3 | | | | | 0.29 |

[a] Concentrations are reported relative to the dry material. [b] Assumes all the iron is present in the water. [c] Ratio of potassium to sulfur content.

by the WLF equation.[15] A glass transition temperature, $T_g$, of −105 °C is predicted for the water-saturated membrane. $T_g$ is higher for membranes containing less water or in the exchanged salt form. These observations are consistent with the known dependence of $T_g$ on molar salt fraction in salt–water mixtures[4] for which $T_g$ extrapolates to −134 °C, characteristic of vitreous water.

This report presents a more extensive study performed on a number of Nafion systems, utilizing primarily the nuclear magnetic resonance technique, and considers behavior at both high and low temperatures. The unusually short relaxation times reported in the earlier paper are discussed and results are presented for the $Fe^{3+}$ salt, which has an additional path for relaxation owing to the paramagnetic nature of the $Fe^{3+}$ cation.

It is known that the presence of water exerts a significant influence on the multiphase nature of Nafions[2,16-20] and is expected that a clearer understanding of the role of water will help resolve some of the vexing questions regarding the molecular structure and mode of operation of these commercially important materials.

## Experimental Section

Nafion is a perfluorosulfonate resin in which hydrophilic perfluorinated ether side chains terminated with $SO_3^-H^+$ are periodically attached to hydrophobic perfluoroethylene backbone molecules. The acid samples under investigation had equivalent weights of 1100 and 1200, respectively, that is, the weight of acid polymer per $SO_3H$ group. These Nafions are reported to be 5–10% crystalline with spherulitic structure and crystallite sizes of the order of 70 nm.[21] Samples exposed to ambient humidity contained ~7% by weight of water. A 25% hydrated sample was prepared by boiling the membrane in deionized water for 1 h, dried to remove excess surface water, and sealed in a tube suitable for NMR study.

In anticipation of our subsequent interpretation of data, which imply the presence of paramagnetic impurities in the Nafion (115) samples, an X-ray fluorescence analysis was carried out to check if, in fact, this were the case. Use of a milliprobe and a microdot standard of known concentration, revealed considerable amounts of iron and potassium. No iron was detected in Nafion (125). Quantitative estimates are listed in Table I. Also included are data pertinent to $Fe^{3+}$ Nafion and $Na^+$ Nafion salts prepared by soaking membranes in stirred 0.2 M $FeCl_3$ and 0.2 M NaCl solutions, respectively, for 12 h. Note that the iron content in the Na salt is reduced by a factor of 5 in the exchange process.

Spin–spin ($T_2$), spin–lattice ($T_1$), and rotating-frame ($T_{1\rho}$) data were recorded on a Bruker spectrometer. Methods of data acquisition and analysis have been described previously.[22] Briefly, $T_1$ was recorded at a resonant frequency of 40 MHz using a 180°–τ–90° pulse sequence.[23] The 90°–90° (phase shift) spin-locking sequence[24] provided $T_{1\rho}$ (at a $H_1$ radio-frequency field of 10 G). Short $T_2$ relaxation times were determined directly from the free induction decay following a 90° pulse while longer $T_2$'s required the 90°–τ–180° spin-echo sequence.[23]

## Results and Discussion

$T_1$, $T_2$, and $T_{1\rho}$ data for the 25% hydrated sample are presented as a function of temperature in Figure 1. The following features, listed in order of increasing temperature, are significant: (i) the nonexponential character of the three relaxation times on the low-temperature side of the glasslike transition near −80 °C; (ii) the magnitude of the ratio $T_1/T_2 = 2.6$ at the $T_1$ minimum (this exceeds the 1.6 predicted by the BPP theory, employing a single correlation time to describe the motion[13,25]); (iii) the comparable magnitudes of the three relaxation times at about −50 °C; (iv) the unusually short value of $T_1(\min) = 0.8$ ms at −65 °C; (v) the presence of the $T_2 = 5$ μs component between −60 and −10 °C; (vi) the shoulder that develops in $T_2$ near room temperature; (vii) the development of shallow $T_1$ and $T_{1\rho}$ minima near 80 °C; (viii) the nonexponential character of $T_1$ at temperatures in excess of 40 °C.

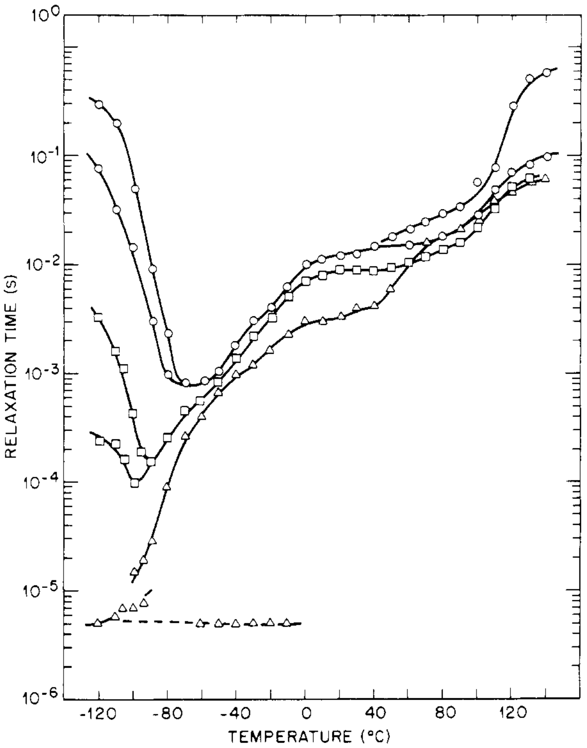

Figure 1. $T_1$ (○), $T_{1\rho}$ (□), and $T_2$ (△) data for the 25% hydrated acid Nafion (115).

The analytical framework developed to describe the behavior of water in other systems, concisely reviewed by Resing,[13] Pfeifer,[7] and Lechert,[6] accommodates points i, ii, and vi. Specific models have been developed by Woessner,[26] Zimmerman and Brittin,[27] Packer,[8] and Resing.[28,29] Resing adopts the notion that molecules are located at equilibrium sites separated from neighboring ones by potential barriers. Some sites have high enthalpies of adsorption and high barriers to translation and these would constitute the "bound" phase in the Zimmerman–Brittin sense.[27] Thus by invoking a broad distribution of correlation times and utilizing the Cohen and Turnbull[30] expression for the viscosity of liquids, Resing could quan-

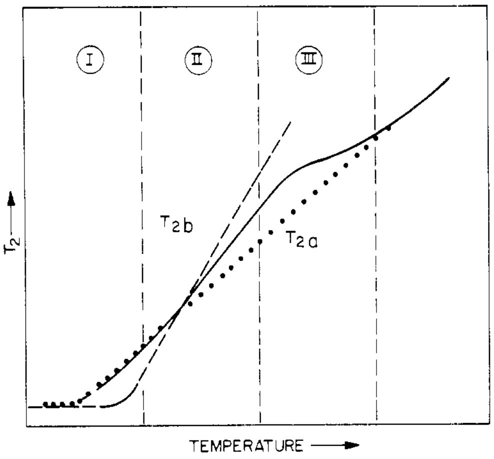

**Figure 2.** Schematic representation of $T_2$ behavior in acid Nafions. The solid curves represent the $T_2$ behavior predicted by the model. The behavior of component relaxation times $T_{2a}$ and $T_{2b}$ is explained in the text.

titatively account for the observed nonexponential $T_2$'s at temperatures below the $T_2$ transition near −75 °C, the ratio $T_1/T_2 > 1.6$ at the $T_1$ minimum, and the unusual behavior of $T_2$ just above the transtion. The formation of a $T_2$ shoulder, or indeed a $T_2$ maximum,[13] is a consequence of the onset of efficient chemical exchange between the bound states (short $T_2$) and the more mobile states (long $T_2$). This allows nuclei in the state characterized by the long $T_2$ to relax more rapidly, that is, with the shorter $T_2$. The distribution of barrier heights associated with the high-energy sites of the Resing model favors a plateau rather than a maximum.[13]

This model can be carried over to describe behavior in Nafion membranes. A wide range of experiments shows that water is not uniformly distributed in the Nafions, implying a distribution of sites.[2,20] Typically, infrared measurements reveal two environments for water molecules.[31] Distinctive changes in the response of the membrane also occur when the amount of water present exceeds the amount required to accommodate the first hydration layer.[2]

Figure 2 summarizes the proposed $T_2$ relaxation behavior in simplistic though graphic fashion. In region I two component relaxation times, $T_{2a}$ and $T_{2b}$, reflect two types of nonexchanging or slowly exchanging water molecules. If they were to remain noninteracting, they would exhibit the temperature dependence depicted by the dotted and dashed lines, respectively. Motion sets in to cause $T_2$ for the less tightly bound water molecules, $T_{2a}$, to increase. At a somewhat higher temperature the tightly bound water molecules begin to move with a characteristically higher activation energy. Indeed, the activation energies are sufficiently high as to cause $T_1$, $T_2$, and $T_{1\rho}$ to become comparable in magnitude immediately above the transition (point iii). In the transition region II, $T_{2a}$ and $T_{2b}$ are so close that they are unresolved. Note that one expects associated $T_{1\rho}$ and $T_1$ minima for the onset of these motions. Chemical exchange between the two types of water molecule, presumably arising from molecular diffusion, becomes efficient in region III and causes the average $T_2$ to be weighted toward the shorter (unresolved) component, thus forming the observed shoulder in the $T_2$-temperature curve. Since the correlation times associated with the two activated motional processes are approximately equal in the vicinity of the low-temperature $T_1$ minimum, this minimum is assumed to be a superposition of both events. Furthermore, the exchange process will show up in $T_1$ and $T_{1\rho}$ in the form of minima at some higher temperature. Broad minima at higher temperatures are indeed observed. A distribution of activation energies associated with the sites will presumably lead to a distribution of exchange rates, which accounts for the breadth of the minima.

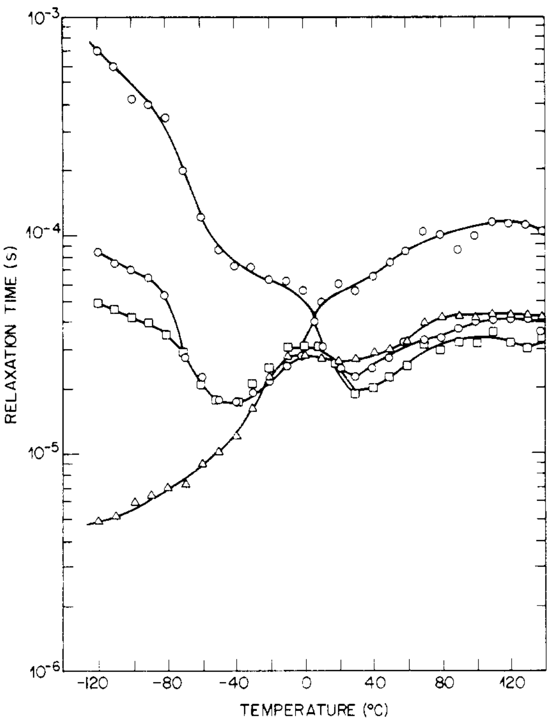

**Figure 3.** $T_1$ (○), $T_{1\rho}$ (□), and $T_2$ (△) data for the $Fe^{3+}$-exchanged Nafion salt.

Apart from the resolution of a very short $T_2$ in the temperature range −60 to −10 °C, almost certainly associated with frozen bulk water in the NMR sample tube (point v), the $T_2$ components that describe water molecules in their various environments are unresolved. Above 60 °C, $T_{1\rho}$, $T_2$, and the shorter $T_1$ component are comparable, as one would expect in the extreme narrowing regime.

The unusually high relaxation rates observed in samples 1–4 (such as the low-temperature $T_1(\mathrm{min}) = 0.8$ ms) imply an additional path for relaxation beyond nuclear-dipole interactions. The obvious candidate is the iron detected in the XRF spectra, which provides efficient sites for relaxation. It is reasonable to assume that the bulk of, if not all of, the impurity iron is in a water environment. This is certainly the case for iron-exchanged salts of Nafion. Mössbauer measurements on the $Fe^{3+}$ Nafion indicate that there are two, and sometimes three, distinct environments for the ferric ion.[32] One species is an isolated, hydrated $Fe^{3+}$ and another is a ferric dimer, probably oxygen bridged. The recoilless fraction of all the iron falls to zero below 0 °C, at a temperature close to $T_0$ given by the WLF plots,[14] which indicates that the ferric ions are all incorporated in the aqueous phase. Large ferric clusters may appear in reexchanged samples. The NMR data for the $Fe^{3+}$ Nafion salt presented in Figure 3 are largely consistent with these observations. If one assumes that all of the iron is accessible to the water, the observed relaxation times are consistent with an $Fe^{3+}$ concentration of $\sim 2 \times 10^{21}$ cm$^{-3}$.[33] This concentration is somewhat lower than the concentration of $7.3 \times 10^{21}$ cm$^{-3}$ determined from XRF analysis (Table I). While there is considerable uncertainty in the XRF estimates, it is tempting to suggest that not all the iron is equally accessible to water, perhaps indicating that the iron is not simply hydrated but present in clusters.

Table II
$T_1$ and $T_2$ Data[a]

| sample no. | $T_{1a}$, ms | $T_{2a}$, ms | $T_{1a}/T_{2a}$ | $T_{1b}$, ms | $T_{2b}$, ms | $T_1$(B), ms | $T_2$(B), ms |
|---|---|---|---|---|---|---|---|
| 1 | 0.8 | 0.3 | 2.7 | 12.0 | 3.3 | 5.0 | 3.0 |
| 2 | 1.0 | 0.3 | 3.3 | 1.0 | 1.0 | 2.0 | 1.0 |
|  |  |  |  | 2.3 | 1.0 |  |  |
| 3 | 1.7 | 0.2 | 8.5 | 7.0 | 5.5 | 10.0 | 8.0 |
|  | 3.8 | 0.5 | 7.6 |  |  |  |  |
| 4 | 1.7 | 1.2 | 1.4 | $5.7 \times 10^{-2}$ | $2.5 \times 10^{-2}$ | $10^{-2}$ | $7 \times 10^{-3}$ |
|  | 7.5 | 1.2 | 6.3 | $2.5 \times 10^{-2}$ | $2.5 \times 10^{-2}$ |  |  |
| 5 | 10.0 | 0.7 | 14.3 | 70.0 | 22.0 |  |  |
|  | 20.0 | 1.2 | 16.7 | 38.0 | 22.0 |  |  |

[a] $T_{1a}$ and $T_{2a}$ are experimental data at the temperature of the low-temperature $T_1$ minimum. $T_{1b}$, and $T_{2b}$ are room-temperature data (+25 °C). $T_1$(B) and $T_2$(B) are estimated from Bloembergen's data for $Fe^{3+}/H_2O$ solutions[33] and the $Fe^{3+}$ concentrations given in Table I.

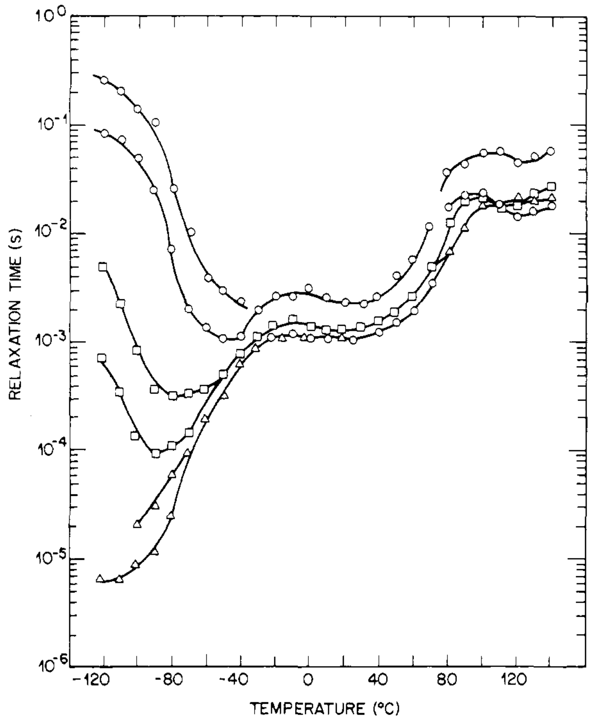

**Figure 4.** $T_1$ (○), $T_{1\rho}$ (□), and $T_2$ (△) data for the 7% hydrated acid Nafion (115).

Assuming that all the iron is in a water environment, $T_1$ and $T_2$ have been estimated from Bloembergen's results[33] for the four Nafion (115) samples (Table II). Predictions agree quite well with the experimental $T_1$ and $T_2$ data in the temperature region where the $T_2$ shoulder is formed, that is, the region where molecular diffusion if fully activated, notwithstanding the fact that differences in the dynamic behavior of water in the two experiments have been neglected.

The appearance of nonexponential $T_1$ decay at high temperatures in all probability stems from molecular diffusion processes with different activation energies. The respective $T_1$'s remain unresolved in the vicinity of the minima but as the temperature is increased the slopes of the $T_1$ vs. temperature curves, which provide a measure of the activation energies, become distinguishable.[34] It is plausible that $T_{1\rho}$ components remain unresolved. Similar arguments involving distributions of activated processes may also be responsible for the nonexponential $T_1$ behavior observed in the $Fe^{3+}$ Nafion salt (Figure 3). Undoubtedly, too, the characteristic relaxation behavior of the iron in different environments is significant.

The observation that $T_{1\rho} < T_2$ for temperatures between 60 and 110 °C in the sample containing 25% water is puzzling. However, many factors conspire to produce a situation that obfuscates interpretation. For example, the presence of a significant number of paramagnetic spins complicates interpretation of the usual 180°–$\tau$–90° spin-echo sequence from which $T_2$ is determined. Some of the proton spins are refocused, others are not. The assumption of a Lorentzian $T_2$ line shape may also contribute significant errors. Analogously, the characteristic longitudinal and transverse relaxation times of the iron in different environments are important parameters in determining proton relaxation in these systems. It is recalled that there is evidence of isolated, dimeric or clustered iron atoms in Fe-excahnged Nafion salts.[32] Note, too, that the host matrix begins to move appreciably in the high-temperature region.[35] It is evident therefore that interpretation of events at high temperatures remains speculative until these factors are carefully analyzed.

NMR data for sample 2 (Figure 4) broadly reflect behavior similar to that observed in the saturated sample. On points of detail, the low-temperature $T_2$ transition and associated $T_1$ and $T_{1\rho}$ minima occur at higher temperatures than for sample 1, reflecting a higher $T_g$ (−92 °C) as described in our first report.[14] The observation of nonexponential $T_1$ decay over virtually the entire temperature range would indicate, on the arguments presented above, that the activated processes are sufficiently different as to be manifested separately in the $T_1$ data. This is further supported by the persistence of nonexponential decay in $T_{1\rho}$ and $T_2$ to higher temperatures for the glasslike transition process. The observation of a $T_1$ component shorter than $T_{1\rho}$ and comparable to $T_2$ above −20 °C is a consequence of an inability to resolve separate components for $T_{1\rho}$ and $T_2$. The development of a high-temperature minimum in the three relaxation times at ~125 °C is also observed in fluorine resonance data, which reflect the behavior of the host matrix, and is probably associated with matrix motions. This aspect of the work will be reported in the accompanying paper.[35] On the reasonable assumption that water acts as a plasticizer for matrix motions, the corresponding minimum in sample 1 should occur at somewhat lower temperatures, perhaps the shallow minimum observed in the vicinity of 100 °C.

NMR results (Figure 5) for the Na salt (sample 3) fit into the general scenario outlined above. The NMR data indicate a higher glass transition temperature for the Na Nafion salt ($T_g$ = −73 °C) than either of the two hydrated acid Nafions.

Low-temperature $T_1$ minima for sample 5 (Figure 6) are an order of magnitude longer than corresponding $T_1$ for samples 1 and 2 and are comparable to $T_1$ for finely divided water adsorbed on charcoal.[13] These observations are consistent with the absence of detectable amounts of iron in the Nafion (125) membrane. Note, however, that

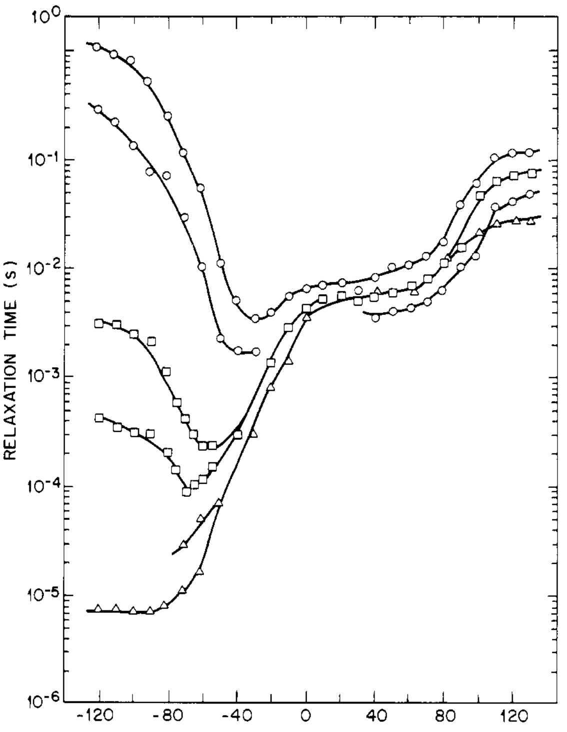

**Figure 5.** $T_1$ (○), $T_{1\rho}$ (□), and $T_2$ (△) data for the $Na^+$-exchanged Nafion salt.

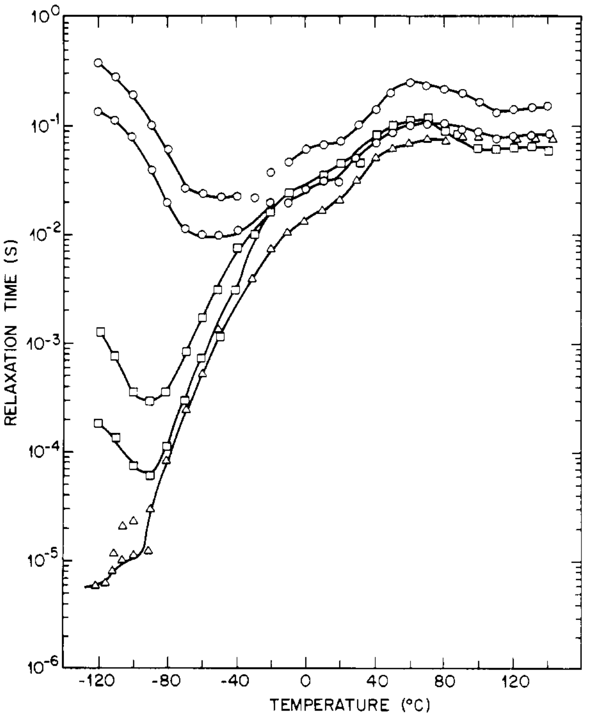

**Figure 6.** $T_1$ (○), $T_{1\rho}$ (□), and $T_2$ (△) data for an 8% hydrated acid Nafion (125).

corresponding $T_{1\rho}$ minima for samples 1, 2, and 4 are comparable, indicating that the $T_{1\rho}$ minima reflect relaxation dominated by molecular motion rather than by $Fe^{3+}$ interactions.

## Conclusions

NMR and X-ray fluorescence data shed light on the way in which water (or salt solution) behaves in Nafion membranes. The glasslike nature at low temperatures is in several respects similar to that observed in other systems containing finely divided water. Glass transition temperatures can be assigned in all cases except the $Fe^{3+}$ salt for which $T_1$, $T_{1\rho}$ minima, and $T_2$ transitions are not amenable to the usual interpretation. At higher temperatures, there is rapid chemical exchange between different water sites in the membrane. This is in accord with an earlier NMR study on a hydrated $Na^+$ Nafion salt.[20]

The magnitudes of NMR relaxation times provide the clue that there are significant amounts of paramegnetic species in the Nafion (115) membrane. The presence of iron and potassium, detected by X-ray fluorescence, may have bearing upon earlier interpretations of mechanical[16] and other properties of the membranes.

Mobile $T_2$'s of ~1 ms are too short to allow a determination of the coefficient of self-diffusion by the NMR technique. Such information would have been valuable in adjudicating between various proposals regarding the size of water clusters and the presence or absence of connecting water channels. The data presented are broadly consistent with current models describing the molecular architecture of Nafion membranes.[2,18,21] and will be discussed more fully in the light of $^{19}F$ resonance results in the accompanying paper.[35]

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**Registry No.** Nafion 115, 77950-55-1; Nafion 125, 65506-90-3; Nafion iron salt, 81604-83-3; Nafion sodium salt, 81604-84-4; K, 7440-09-7; $H_2O$, 7732-18-5.

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# NMR Investigation of Molecular Motion in Nafion Membranes

**Noel G. Boyle, Vincent J. McBrierty,*[†] and A. Eisenberg[‡]**

*Department of Pure and Applied Physics, Trinity College, Dublin 2, Ireland.*
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ABSTRACT: Molecular motions of the fluorocarbon backbone in Nafion membranes have been studied through its $^{19}$F NMR response. Results correlate well with those of other relaxation experiments. Collated $T_2$ data for a number of fluorocarbons with the $-CF_2-$ repeat unit highlight the motional constraints imposed by ion clustering in Nafions. Spin-diffusion considerations in the $Fe^{3+}$-exchanged salt provide some insight into the size and nature of $^{19}$F regions in the membrane.

## Introduction

The preceding paper[1] reports on the use of $^1$H NMR to explore the behavior of water in perfluorosulfonate Nafion membranes. Here we are concerned with the molecular motions of the membrane matrix as monitored by its $^{19}$F resonance response. NMR relaxation data complement earlier dynamic mechanical and dielectric measurements on the Nafion precursor,[2] the acid, and various of its salts[3–6] and provide a more complete description of molecular motion in the membrane.

The four relaxations observed in dielectric and mechanical data for the precursor are labeled $\alpha$, $\beta''$, $\beta'$, and $\gamma$ in order of decreasing temperature.[2] The $\alpha$ relaxation has been assigned to the glass transition ($T_g$ = 0 °C), $\beta''$ to motions of the fluorinated ether side chain, and $\beta'$ to $(-CF_2-)_n$ backbone motions (akin to the $\gamma$ relaxation in PTFE);[7] the $\gamma$ relaxation is believed to reflect motion of the side $SO_2F$ terminal groups.[2]

Three mechanical relaxation peaks have been observed in the acid and its salts.[3] The high-temperature $\alpha$ process is again assigned to the glass transition ($T_g$ values for the acid and its univalent salts are, respectively, 110 and ~220 °C). The $\gamma$ peak, which occurs at ~110 °C at 1 Hz, is presumed to manifest motions similar to those responsible for the $\gamma$ relaxation in poly(tetrafluoroethylene) (PTFE).[6] While the $\gamma$ relaxation is essentially unaffected by the presence of water, the $\alpha$ and $\beta$ relaxations shift to lower temperatures with the addition of water in both the acid and its salts. The $\alpha$ and $\beta$ peaks have been associated in the early study[3] with the glass transition of the matrix and of the ionic regions, respectively. This assignment has been reversed in more recent work.[4] Two dielectric peaks have been resolved, both of which shift to lower temperatures with increasing water content.

There is compelling evidence to support the view that ions in Nafions are clustered.[3–5] This will undoubtedly influence molecular motional behavior of the membranes, especially motions associated with the glass transition. Aspects such as these will be examined in the overall study of molecular motion in Nafions, which forms the main theme of this paper.

## Experimental Section

Although the Nafion materials under investigation have been described fully elsewhere,[1] some pertinent characteristics are listed in Table I. No attempt was made to wash out impurities prior to examination by NMR. X-ray fluorescence revealed the presence of iron and potassium in significant amounts.

Table I
Some Pertinent Data for the Nafion Samples Studied

| sample description | equiv wt | iron content, $cm^{-3}$ | [K]/[S] |
|---|---|---|---|
| precursor | 1200 | 0 | 0 |
| 25% hydrated acid | 1100 | $9.5 \times 10^{18}$ | 0.36 |
| 7% hydrated acid | 1100 | $7.2 \times 10^{18}$ | 0.36 |
| 5% hydrated acid | 1500 | 0 | 0.20 |
| 7% hydrated $Fe^{3+}$ salt | 1100 | $5.9 \times 10^{20}$ | ~0 |

Spin–spin ($T_2$), spin–lattice ($T_1$), and rotating-frame ($T_{1\rho}$) data were recorded for temperatures in the range −120 to +160 °C on a Bruker spectrometer operating at a resonant frequency of 40 MHz. The pulse sequences used to determine $T_1$, $T_2$, and $T_{1\rho}$ are described in the accompanying paper.[1] It is recalled that $T_2$, determined directly from the free induction decay following a $\pi/2$ pulse, is presumed to be the time for the signal amplitude to fall to $1/e$ of the initial observed magnitude. This procedure is only strictly correct for Lorentzian decays and represents an approximation when the decay has Gaussian character, as is usually the case at low temperatures. Furthermore, an inability to observe the first 5 μs (the recovery time of the spectrometer) of the decay results in an underestimate of $T_2$. However, the *change* in $T_2$ characteristic of the onset of a transition in a polymer may be readily detected even when the change in $T_2$ is small.

## Results and Discussion

**Precursor.** NMR data for the precursor, depicted as a function of temperature in Figure 1, give rise to a number of observations.

(i) The fact that $T_1$ remains relatively long (>0.1 s) and that minima are mostly ill-defined indicates either that few groups, isolated in the spin-diffusion sense, are participating in relaxation or that there are broad overlapping distributions of correlation times characterizing the various motions. The overall character of the $T_2$–temperature data[8] and earlier dynamic mechanical results[2] support the latter viewpoint.

(ii) Only one $T_2$ component, which increases almost monotonically with increasing temperature, is resolvable over the entire temperature range. The intermediate plateau regions, which delineate different relaxation processes, are ill-defined. The degree of motional vigor achieved at the highest temperatures studied is extensive though not liquid-like. A plateau in $T_2$, characteristic of other members of the $(-CF_2-)_n$ fluorocarbon family such as PTFE[9] or its hexafluoropropylene copolymer (FEP),[10]

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[†] Bell Laboratories, Murray Hill, NJ 07974.

[‡] Department of Chemistry, McGill University, Montreal, Quebec, Canada H3C 3G1.

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