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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.
Received April 15, 1982

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 α, β'', β', and γ in order of decreasing temperature.[2] The α relaxation has been assigned to the glass transition (T_g = 0 °C), β'' to motions of the fluorinated ether side chain, and β' to $(-CF_2-)_n$ backbone motions (akin to the γ relaxation in PTFE);[7] the γ 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 α 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 γ peak, which occurs at ~110 °C at 1 Hz, is presumed to manifest motions similar to those responsible for the γ relaxation in poly(tetrafluoroethylene) (PTFE).[6] While the γ relaxation is essentially unaffected by the presence of water, the α and β relaxations shift to lower temperatures with the addition of water in both the acid and its salts. The α and β 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	9.5×10^{18}	0.36
7% hydrated acid	1100	7.2×10^{18}	0.36
5% hydrated acid	1500	0	0.20
7% hydrated Fe^{3+} salt	1100	5.9×10^{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]

[†] Bell Laboratories, Murray Hill, NJ 07974.
[‡] Department of Chemistry, McGill University, Montreal, Quebec, Canada H3C 3G1.

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Table II
Temperatures (°C) at Which T_1 and $T_{1\rho}$ Minima and T_2 Transitions Occur[a]

sample	T_1(min) log ν_c (Hz) 7.75	$T_{1\rho}$(min) log ν_c (Hz) 4.6	T_2 transitions log ν_c (Hz)					relaxation processes
			3.6	3.7	3.8	3.9	4.0	
precursor		120						*b*
	~70	40/60	~50					α
		−15				~−10		β''
	40	(−40)					~−60	β'
	−25	(−80)						*b*
acid Nafion 1100 EW (7%)	120	~120		~120				α
		(70)						*b*
		(20)				~−20		K salt?
	~55	−20				~−20		γ
	(12)							*b*
	−25	~−80						*b*
							~−80	$T_g(H_2O) + \beta$
acid Nafion 1100 EW (25%)	145	~145	~135					α
		(55)			~55			*b*
	60	−20				~−40		γ
	−45	−80						*b*
							~−95	$T_g(H_2O) + \beta$

[a] Parentheses signify that the transitions are barely detectable and are therefore doubtful. [b] See text.

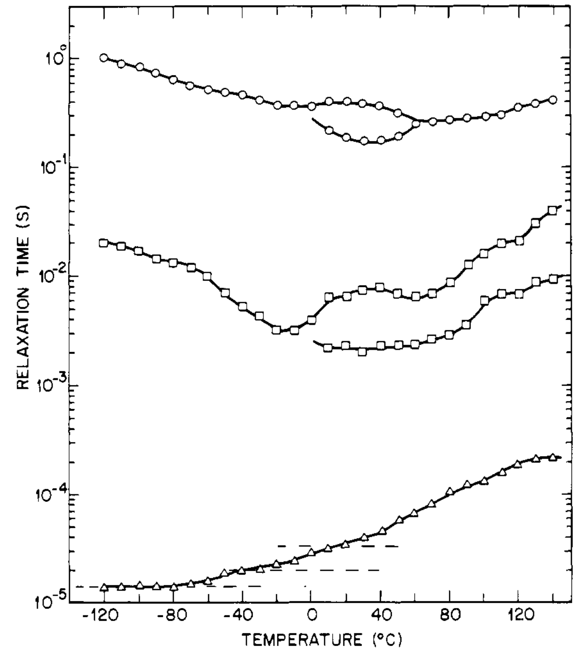

Figure 1. ^{19}F (40 MHz) T_1 (○), $T_{1\rho}$ (□), and T_2 (△) data for the Nafion precursor.

appears to be forming at ~140 °C. The data are consistent with the notion of one part of the polymer undergoing general motions typical of a glass transition while another part may be experiencing the more constrained motions responsible for the plateau. The two motions, however, cannot be very different in their degree of vigor; otherwise two T_2 components would be observed. On the other hand, there may be a broad distribution of motions active in the polymer at high temperatures. Without resolvable T_2 data at temperatures between +140 °C and the melting point, it is not possible, on the basis of NMR data, to confirm unambiguously the assignment of the α process as a true glass transition although it bears all the hallmarks of a T_g otherwise.

(iii) Nonexponential T_1 and $T_{1\rho}$ decay over part of the temperature range is indicative of a heterogeneous system. This is consistent with the phase-separated character postulated earlier.[2]

Correlation frequencies for the various motions have been extracted in the usual way[8] (Table II) and these are compared with dynamic mechanical and dielectric data on the transition map of Figure 2. Although the NMR points are in general agreement with earlier data, the way in which the β' locus has been drawn is arbitrary in the sense that this choice is dictated by the $T_{1\rho}$ point (N) at log ν_c = 4.6 and 1000/T = 4.3. This point has been estimated from the shoulder that is barely detectable on the low-temperature side of the $T_{1\rho}$ minimum at −20 °C. The T_1 and $T_{1\rho}$ data points at 1000/T = 4.0 and 5.2, respectively, indicate an additional relaxation process interposed between the β' and γ relaxations. Motions of SO_2F and/or CF_3 groups in the side chain are possible candidates. There is also a $T_{1\rho}$ minimum at 120 °C, pinpointing yet another source of relaxation on the high-temperature side of the α relaxation. This point coincides with the α process in FEP[7,10] and is almost certainly associated with $(-CF_2-)_n$ backbone motions. It is recalled that the α relaxation in FEP has been assigned to rotation-plus-translation (or helix conversion) of the $(-CF_2-)$ backbone chains.[10] Note, too, that a minimum was observed in the proton relaxation data for the acid Nafions in this temperature region.[1]

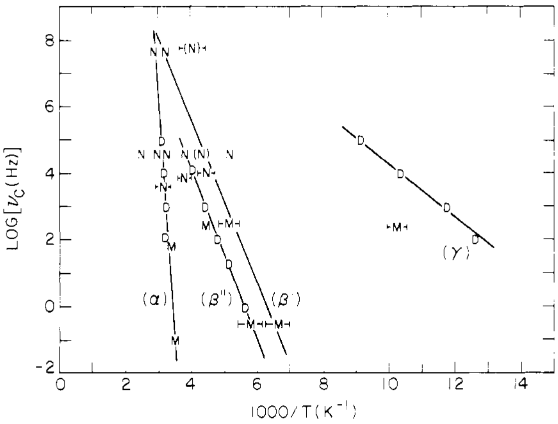

Figure 2. Transition map describing molecular motion in the Nafion precursor.

We shall return in subsequent discussion to molecular motional behavior of the precursor when comparisons are drawn with other Nafion materials studied.

Acid Nafions. Data for the acid Nafions of lower water content are presented in Figure 3. In contrast to the precursor, interpretation of ^{19}F data for the hydrated acid is complicated by three additional factors: (i) the effect

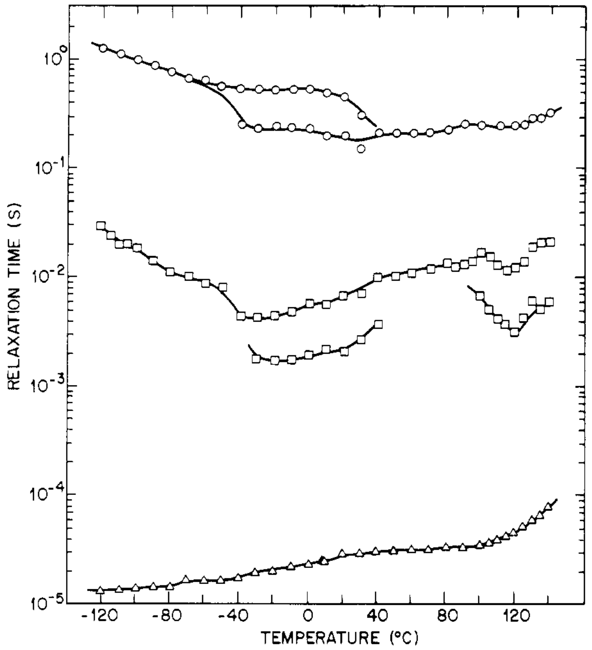

Figure 3. ^{19}F (40 MHz) T_1 (○), $T_{1\rho}$ (□), and T_2 (△) data for the acid Nafion with 7% water content.

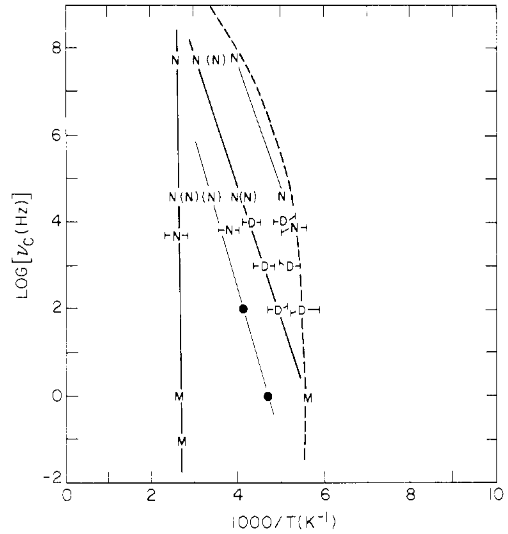

Figure 4. Transition map describing molecular motion in the acid Nafion (EW 1100) with 7% water content. The dashed line describes the glass transition process for the water (ref 6). The filled circles denote dielectric relaxation data for a K Nafion salt of comparable hydration.[3]

of water as a plasticizer, (ii) possible cross-relaxation effects between the ^{19}F and ^{1}H spin systems, and (iii) the effects of iron and potassium, which are present in appreciable amounts.

Analysis of molecular motion in the acid Nafion is conveniently approached through consideration of the transition map of Figure 4. The locus (dashed line) that describes the glass transition of the water, investigated earlier,[6] is included. Also included are the available data points for ~7% hydrated potassium salt.[3] In order of increasing temperature, the first set of data points characterizes the β relaxation and the water (or, more correctly, the salt) glass transition process. Note, however, that the T_1 (log ν_c = 7.75) and $T_{1\rho}$ (log ν_c = 4.6) points at 1000/T = 4.0 and 5.2, defining the second locus, are observed in both the acid Nafion with higher water content and in the precursor. If these points have the same molecular origin, as is probably the case, SO_2F motions, proposed in the last section as a possible candidate, is ruled out as the source of this relaxation. The third locus corresponds to the γ relaxation of the Yeo–Eisenberg paper[3] and probably also reflects specific side-chain motions. The fourth set of data points would appear to be associated with the presence of potassium salt while the high-temperature relaxation, designated α by Yeo and Eisenberg, is assigned to the glass transition (T_g = 110 °C) of the membrane. Again this locus almost exactly parallels the high-temperature relaxation in FEP associated with rotation-plus-translation of $(-CF_2-)_n$ backbone chains. Note, too, from the T_2 data of Figure 3 that motions of the backbone are much more curtailed compared with the precursor in the high-temperature region. This is reflected in the much higher glass transition temperature and is a particularly clear indicator of clustering in the acid Nafion.

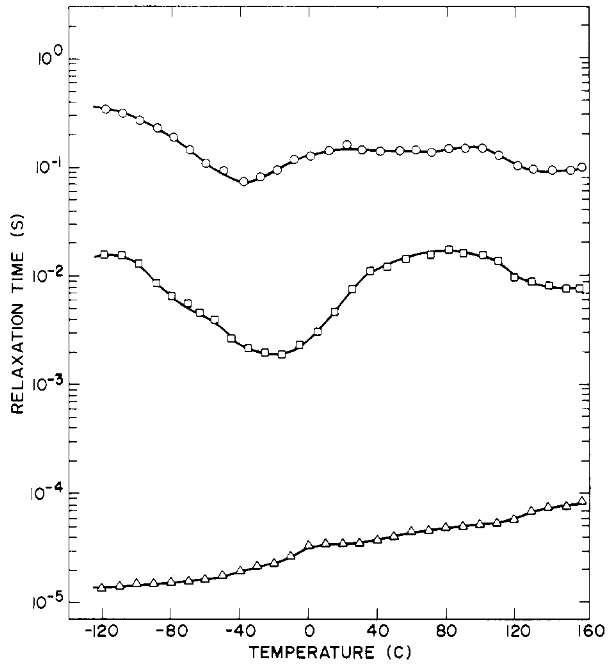

Figure 5. ^{19}F (40 MHz) T_1 (○), $T_{1\rho}$ (□), and T_2 (△) data for the acid Nafion with 25% water.

The observation of nonexponential T_1 and $T_{1\rho}$ decay is indicative of a heterogeneous system. While the usual interpretation of two regions relaxing at different rates and only weakly coupled by spin diffusion may be invoked,[8,11] another possibility must be considered in the present case. Part of the ^{19}F matrix may be more tightly coupled to efficiently relaxing iron impurities, giving rise to shorter relaxation times compared with those regions that are more remote from the iron sites. This aspect of data interpretation will be pursued further in the section dealing with the Fe^{3+} Nafion salt.

Data for the acid Nafion with 25% water content are presented in Figures 5 and 6. Generally, T_1 is shorter and T_2 is longer over the temperature range where molecular motions are activated. This is consistent with a freer motional environment, arising in part from plasticizing effects of the sizeable amount of water present. A shorter T_1 and $T_{1\rho}$ may also be due to coupling, via spin diffusion, to the efficiently relaxing iron atoms. In the context of the latter interpretation, the observation of single-component relaxation times would imply that most all ^{19}F nuclei are accessible to the iron relaxation sinks. As later discussion will show, this is not the case with the Fe^{3+}-exchanged salt. The locus (dashed line) corresponding to the glass transition for the water (and the β relaxation) has moved to lower temperatures, reflecting a lower T_g, as

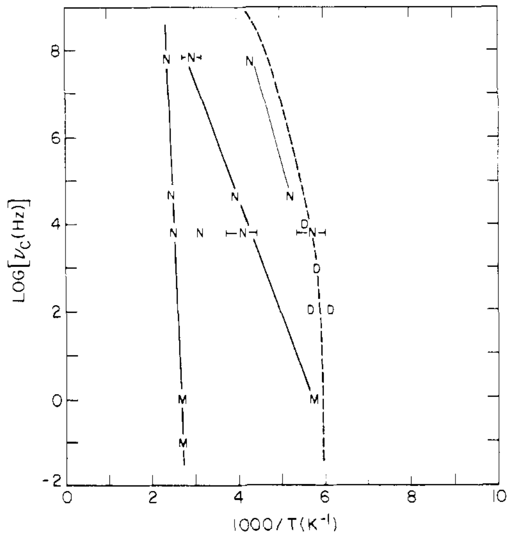

Figure 6. Transition map describing molecular motion in the acid Nafion (EW 1100) with 25% water. The dashed line describes the glass transition process for the water.[6]

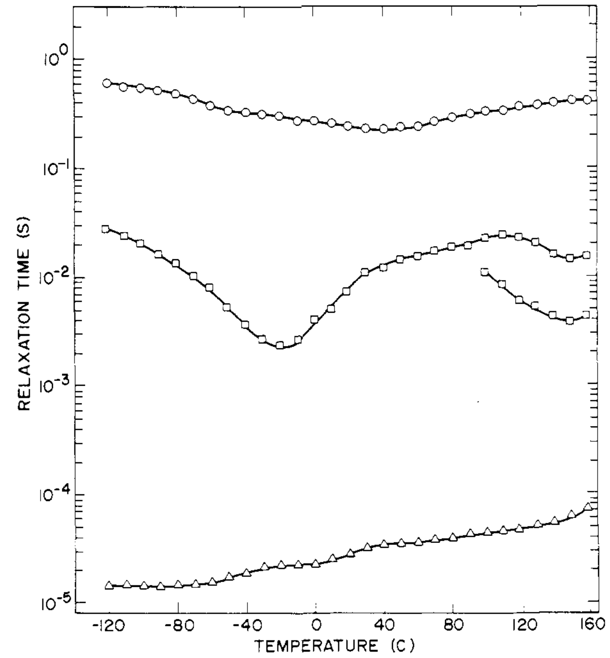

Figure 7. ^{19}F (40 MHz) T_1 (○), $T_{1\rho}$ (□), and T_2 (△) data for the acid Nafion (EW 1500) with 5% water content.

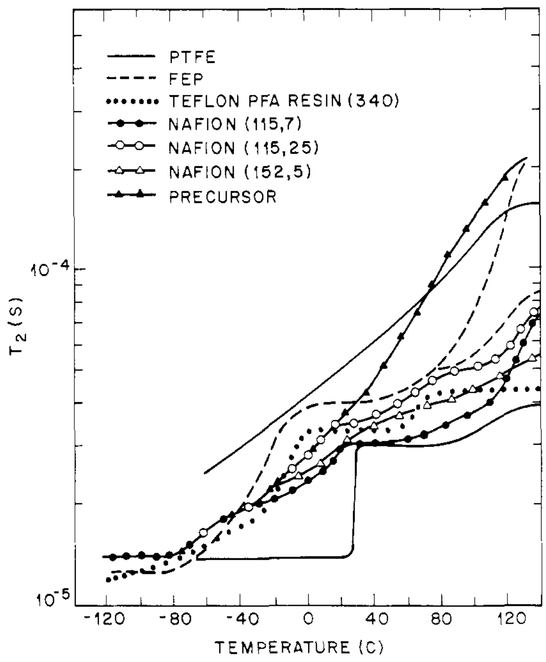

Figure 8. T_2 data for a number of fluorocarbons.

expected.[6] The α relaxation is affected slightly by the increased amount of water present and the γ relaxation not at all. The high-temperature T_1 and $T_{1\rho}$ minima associated with the α relaxation are broader and occur at somewhat higher temeperatures than in acid Nafion of lower water content. This observation supports the notion of weaker ionic interactions and matrix motions of a more general character induced by water plasticization. Structural differences in Nafions with high and low water contents are also evident in small-angle neutron scattering studies.[12] In the absence of relaxation data for a 25% hydrated potassium salt, it is not possible to determine the role of potassium in the sample. However, it is recalled that the β relaxation for the salt merges with the γ relaxation when the water content exceeds about 3.0 H_2O/SO_3H.[3] The origin of the T_2 data point corresponding to $\log \nu_c = 3.8$ at $1000/T = 3.1$ is obscure. It may be noted, however, that chemical exchange of water protons manifests itself in the proton T_2 data in this general temperature region.[1]

The acid Nafion of 1500 EW behaves in similar fashion to the 1100 EW sample, differing only in one or two points of detail (Figure 7). The T_2 response up to +120 °C, for example, indicates a mobility greater than that observed in an 1100 EW sample of comparable water content. This is consistent with the fact that there are fewer clustering centers to constrain matrix motion in the 1500 EW sample. The fact that T_2 for the 1500 EW acid falls below T_2 for the 1100 EW sample of comparable water content at temperatures greater than +120 °C is due to the observed shift to higher temperatures of the high-temperature transition in the 1500 EW acid. In this respect, the behavior of the 1500 EW material is similar to the 1100 EW sample of higher water content.

It is instructive to compare T_2 for a number of fluorocarbon materials (Figure 8).[9,10] This comparison demonstrates particularly clearly the effects of clustering and the concomitant restrictions imposed on molecular motion. The effect is most pronounced in the 1100 EW acid Nafion of lowest water content and becomes progressively less apparent in the 1500 EW sample and the 25% hydrated 1100 EW acid sample, respectively. It may be argued that plasticization effects due to water are largely responsible for the experimental observations. However, the precursor in which there is no water at all exhibits essentially unconstrained motion with increasing temperature, in support of the notion that there is no clustering in the precursor. Data for Teflon perfluoroalkoxy fluorocarbon resin Type 340 are also included for comparison. A more complete examination of motions in this polymer will appear elsewhere.

Fe^{3+}-Exchanged Salt. The discussion in the accompanying paper[1] alluded to a number of complexities that bedeviled interpretation of ^{1}H NMR data from the Fe^{3+} salt. Similar constraints apply in the present context but it is possible, nevertheless, to make a number of pertinent observations. The general lowering of T_1 and $T_{1\rho}$ compared with the acid Nafion data emphasizes the role of spin diffusion, which allows the iron to partially relax the ^{19}Fe nuclei (Figure 9). The two relaxation times are shorter at low temperature, where spin diffusion is more effective. Resolution of three T_1 components reflects the extremely heterogeneous nature of the Fe^{3+}-exchanged membrane,

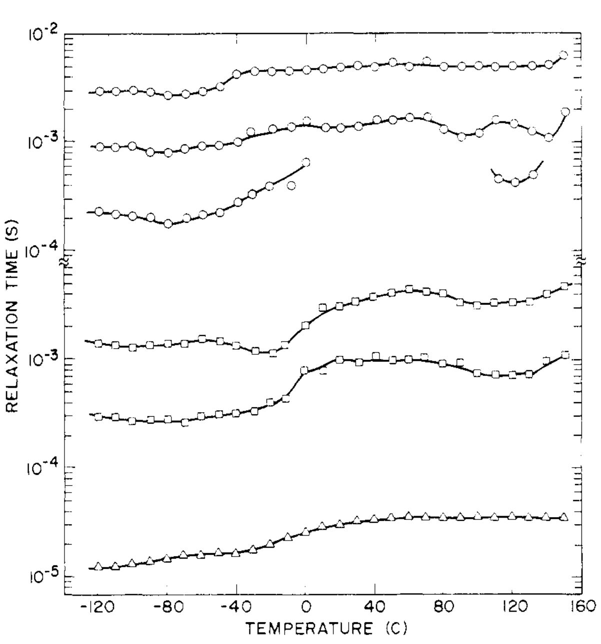

Figure 9. ^{19}F (40 MHz) T_1 (○), $T_{1\rho}$ (□), and T_2 (△) data for the Fe^{3+}-exchanged Nafion salt.

both in the morphological sense and in regard to the nature and behavior of the iron. It is recalled that there are (at least) two different kinds of iron atoms with different environments and associated water contents.[13] It may also be noted that nonexponential T_1 decay is predicted in solid systems in the case of diffusion-limited relaxation to paramagnetic sinks, for which magnetization recovers as $t^{1/2}$ for short times following saturation before assuming exponential decay behavior.[14,15] This mechanism may be operative in the Fe^{3+} salt.

Rodmacq and co-workers[13] have proposed a three-phase model of the Nafion membrane which is visualized in terms of (i) microcrystallites of the order of a few hundred angstroms in diameter, (ii) regions of an aqueous ionic cluster phase with a size of 20–35 Å containing about half of the iron in Fe^{2+} Nafion salts, (iii) an intermediate phase which contains less hydrated iron ions. The relative amount of iron in the clusters and the cluster size varies with water content. Mössbauer studies of Fe^{3+} Nafion salts have indicated that most of the iron is present as hydrated single ions or dimers in the aqueous phase.[16] More recently, Roche and co-workers[17] discussed a three-phase model involving crystalline, amorphous, and hydrophilic ionic phases.

Although one can develop a number of possible structural models to account for our experimental observations, it is more constructive, in the light of the NMR data, to examine the model of Rodmacq et al., which embodies the results of a comprehensive range of experiments. It is revealing to estimate roughly the maximum root-mean-square diffusive path length $\langle L^2\rangle^{1/2}$, which is related to the jump length l_0 ($\sim$1 Å), T_2, and the time t over which diffusion takes place:[8]

$$\langle L^2\rangle^{1/2} = \{6\langle l_0^2\rangle t/T_2\}^{1/2}$$

Setting $t = 3 \times 10^{-3}$ s, the magnitude of the longest T_1 component, one predicts a maximum diffusive path length of $\sim$35 Å. This implies that there cannot be any appreciable number of ^{19}F nuclei further removed from an iron relaxation sink than about 35 Å, which is inconsistent with a homogeneous microcrystalline phase of the diameter stipulated in the above model. In order to maintain the overall integrity of the model, a number of modifications can be visualized. Perhaps there are small aqueous inclusions containing iron within the crystallites or iron-bearing channels that penetrate into the microcrystallites. The notion of spherical crystallites of fixed diameter may also be inaccurate, and a different geometry such as a lamellar one, which allows for a lateral dimension of the order of 70 Å, is more appropriate. In any event the relaxation data for the Fe^{3+}-exchanged salt cannot be rationalized on the basis of a model that postulates the presence of uniform microcrystallites of the diameter proposed by Rodmacq and co-workers.

Summary

^{19}F T_1, T_2, and $T_{1\rho}$ NMR data have been analyzed to provide information on the molecular motional behavior of the backbone matrix in Nafion membranes. The results correlate well with those of other relaxation experiments. T_2 data are examined in the context of similar data from other fluorocarbons with the $-CF_2-$ repeat unit. Such a comparison highlights the motional constraint imposed by ion clustering in the 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.

Acknowledgment. It is a pleasure to acknowledge useful discussions with Dr. D. C. Douglass, Dr. D. W. McCall, and Professor J. M. D. Coey. We are grateful to S. M. Vincent for carrying out the X-ray fluorescence analysis of the Nafion membranes.

Registry No. Nafion EW 1100, 63496-24-2; Nafion EW 1500, 63496-25-3; Nafion iron salt, 81604-83-3; H_2O, 7732-18-5.

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