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Polymer 40 (1999) 2471–2480

polymer

An n.m.r. investigation of the dynamical characteristics of water absorbed in Nafion

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Received 28 April 1998; revised 8 June 1998; accepted 15 June 1998

Abstract

Proton and deuterium spin–lattice relaxation times (T_1), spin–spin relaxation times (T_2), and rotating frame spin–lattice relaxation times ($T_{1\rho}$) and Fluorine T_1 and T_2 were measured as a function of hydration and temperature in hydrated Nafion. The proton and deuterium data display an apparent dynamical transition which we have attributed to a change in the degree of order within the aqueous phase. The temperature at which this transition occurs, T_t, is a function of the level of hydration, increasing for decreasing hydration. Above T_t, the relaxation processes are similar to those observed in bulk water. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: n.m.r.; Nafion; Relaxation

1. Introduction

Although it is well known that the properties of a liquid can be modified by its confinement in very small spaces, attempts to unravel the role of geometry in modifying the behaviour of a confined fluid have proven to be difficult and frequently controversial [1].

Studies of critical phenomena have shown that a liquid phase transition may be strongly modified or even suppressed if its confining geometry is smaller than the thermal correlation length of the confined fluid [2]. In particular, one of the consequences of cooling a liquid in ultrasmall geometries is the appearance of extreme supercooling, or depression of the freezing point far below the expected three-dimensional solidification temperature. There has been much speculation concerning the origin of this phenomenon, attributing it to possible finite size effects, size limited fluctuations, interactions with the substrate, effects of random fields, nucleation from the pore walls and surface induced disorder [1]. Despite these efforts, a comprehensive understanding of the phenomenon has yet to evolve.

The observed supercooling of fluids in porous geometries is of fundamental importance, but it is by no means the only thermodynamic property to be affected by confinement within a pore. Modifications of fluid density, compressibility, expansivity, heat capacity, velocity of sound propagation, vapour pressure, chemical potential and dielectric constant have been documented [3]. Transport properties of confined liquids show similar modifications. Diffusivity, viscosity, electrical conductivity, dielectric relaxation, sound absorption, nuclear spin relaxation times and chemical shifts, electron spin relaxation and chemical relaxation all exhibit anomalous behaviour when confined to restricted geometries.

Water exhibits especially unique behaviour when confined in porous geometries — a consequence of the tendency of water molecules to form larger hydrogen bonded structures. The depression of the freezing point increases with decreasing pore diameter [1]. Compressibility, viscosity and specific heat rise exponentially with decreasing temperature, giving an apparent singularity at approximately −45°C. The density of water goes through a maximum at 4°C and falls off as a sixth order polynomial with decreasing temperature [4]. The dynamical characteristics of water in confining geometries do not lend themselves to a straightforward elucidation.

To further elucidate the behaviour of water in these environments, a nuclear magnetic resonance (n.m.r.) investigation of water absorbed in the ionic polymer Nafion was undertaken. N.m.r. is well suited to the study of molecular dynamics in liquids. The timescale of molecular motions in the liquid state lie within the range easily observed by n.m.r. [5].

^{1}H and ^{2}H spin–lattice relaxation times (T_1), spin–spin relaxation times (T_2), and rotating frame spin–lattice relaxation times ($T_{1\rho}$) were measured as a function of hydration

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PII: S0032-3861(98)00484-4

and temperature. Also, Fluorine T_1 and T_2 were measured as functions of hydration and temperature.

Nafion is an ionic polymer composed primarily of a fluorocarbon backbone, yet is characterized by unique electrochemical behaviour. It readily absorbs water and is electrically and ionically conductive. Electrochemical activity in Nafion is centred around ionic side chains, which form an inverted micellular structure in the presence of water. The number and sizes of these clusters is determined by the level of polymer hydration. Cluster diameters ranging from 20 to 50 Å have been observed [6–10], containing up to 100 pairs of ionic sites, with up to 20 water molecules around each site.

A distinct change in the relaxation behaviour in these Nafion–water systems is observed at a temperature which is dependent on the level of absorbed water. Here this ‘transition’ temperature is denoted T_t. Different relaxation processes are indicated above and below this temperature, and the data are therefore treated separately in each temperature regime. In this paper, relaxation in the temperature regime above the transition is analyzed. Low temperature relaxation is discussed in the accompanying article.

2. Experimental

Nafion 117 was purchased from the Sigma Chemical Company (St. Louis, Mo.) in the form of a sheet approximately 8 in × 10 in × 0.007 in. The manufacturing process is known to leave many impurities [11–14], most importantly paramagnetic contaminants which are particularly damaging to an n.m.r. experiment. An extensive purification procedure was developed to ensure the removal of these impurities.

All glass sample tubes and any assorted glassware used in preparation of the samples were first soaked in a 50% sulphuric – 50% nitric acid solution for 24 h and then rinsed in distilled–deionized water. Next they were immersed in a 0.01 M EDTA solution for a further 24 h, followed by a thorough rinse.

The first stage in the purification of Nafion is designed to convert all active sites to their acid form, that is $SO_3^- H^+$. When received from the supplier, many of these sites contain other cations, particularly Na^+ and K^+. Strips of Nafion 1 cm wide are cut from the raw sheet. These are soaked in 2 M HCl at a temperature of 80°C for 2 h to exchange all cations with H^+. The Nafion is then repeatedly boiled in fresh distilled–deionized water to remove any residual HCl.

The next step in the purification process is designed to remove paramagnetic impurities introduced during the manufacture of Nafion. This is achieved via chelation with EDTA. The Nafion strips are soaked in a 0.01 M EDTA solution for 24 h followed by repeated boiling in distilled–deionized water to remove residual EDTA. The effectiveness of this procedure in removing paramagnetic impurities was verified using Electron Paramagnetic Resonance. Within the limits of the sensitivity of the spectrometer, approximately 10^{14} spins, no paramagnetic nuclei were detected.

As a side effect of the synthesis of Nafion, there exists in the raw polymer light weight oligomers and precursor fragments [13,14]. These are responsible for its cloudy or translucent appearance. To remove these the Nafion strips are immersed in a 50% ethanol–50% water solution in a sonic bath for 2 h, followed by repeated boiling in fresh distilled–deionized water.

For each sample a strip of Nafion with dimensions 1 cm × 25 cm with a mass of approximately 600 mg was used. Accurate determination of the dry weight of Nafion is difficult since the standard drying techniques of exposing the sample to vacuum pressures of 10^{-3} Torr or heating to 105°C, fail to remove all of the water from Nafion [15, 16]. Up to one water molecule per SO_3H group may remain within the polymer. This unique characteristic of Nafion is not well understood but it is felt by us that as drying progresses, the inter-cluster channels constrict and some clusters become isolated within the matrix, unable to yield their water.

Heating the Nafion samples at 140°C while at a vacuum pressure of 10^{-3} Torr for 24 h gives the most satisfactory dehydration. The sample weight obtained from this process is taken to be the dry sample weight. Above 130°C little extra water is removed with increasing temperature, while above 180°C the polymer begins to darken irreversibly and eventually becomes black.

For the lower hydration levels, re-hydration was carried out in a sealed, partially evacuated desiccator. The water content of each sample was determined by suspending it above a saturated salt solution which allowed only a specific relative humidity. Different levels of hydration were achieved using different salts.

For hydration levels above 8%, or approximately five water molecules per sulphonate group, vapour phase hydration proves insufficient. The Nafion samples must be boiled in distilled–deionized water which markedly increases absorption and gives levels up to approximately 20% or 15 water molecules per sulphonate group. Intermediate hydration levels are achieved via subsequent partial dehydration.

Following hydration, the Nafion strips were rolled up and placed into preweighed 10 mm glass tubes which were then flame sealed for preservation.

A final weighing of the sealed sample gives the hydration level, expressed as the weight of the water as a percentage of the total weight. Samples with levels ranging from 1.8% to 16% were prepared.

Proton and fluorine n.m.r. measurements were performed at 30 MHz. Deuterium measurements were performed at 30.6 MHz. The inversion recovery sequence, 180°-τ-90°, was used for T_1 measurement. Spin–spin relaxation times were obtained from the $T_{2\ \mathrm{FID}}$ sequence or, when longer relaxation times warranted, from the $T_{2\ \mathrm{CPMG}}$ sequence.

Table 1
The 'transition' temperature, T_t, in hydrated Nafion

Hydration level	Transition $\beta = 1000/T$	Transition temperature
15.9% H_2O	3.80 ± 0.03	−10 ± 2°C
7.7% H_2O	3.75 ± 0.07	−7 ± 5°C
5.9% H_2O	3.50 ± 0.10	13 ± 8°C
7.7% D_2O	3.79 ± 0.06	−9 ± 4°C

3. Analysis of the high temperature data

In all the samples and at virtually all temperatures the n.m.r. decay and recovery exhibited single exponential behaviour. This is an indication that relaxation occurs at a single site, at multiple sites with identical n.m.r. parameters, or at multiple sites experiencing fast exchange with each other. In such a complex water–polymer system as this, it is our belief that the true case is the latter.

The relaxation behaviour deviates notably from that predicted for BPP [17] relaxation behaviour (Fig. 1). This manifests itself in several ways, the most significant of which is a change in slope which occurs at about − 10°C ($1000/T = 3.8$). At this temperature, denoted here as T_t, the slopes of the T_1, T_2 and $T_{1\rho}$ vs $\beta = 1000/T$ plots change sharply. This change is accompanied by an approximately 7% drop in signal intensity from the high temperature side to the low temperature side, and yet there is no discontinuity in the actual relaxation times.

Equally significant, for temperatures higher than T_t the relaxation times T_2 and $T_{1\rho}$ diverge from T_1. In BPP relaxation, in this high temperature 'motionally narrowed' regime, the three relaxation times converge to a single value.

A similar behaviour is observed in all the data sets. T_t is dependent on the level of hydration, shifting to higher temperatures with decreasing moisture content. So significant is this shift that the 'transition' is barely discernable at the lowest hydration level; it occurs near the high temperature limit of the data.

T_t was determined from the zero crossing of the second derivative of the measured T_1 values with respect to β. The results, as well as estimates of the experimental uncertainty, are given in Table 1.

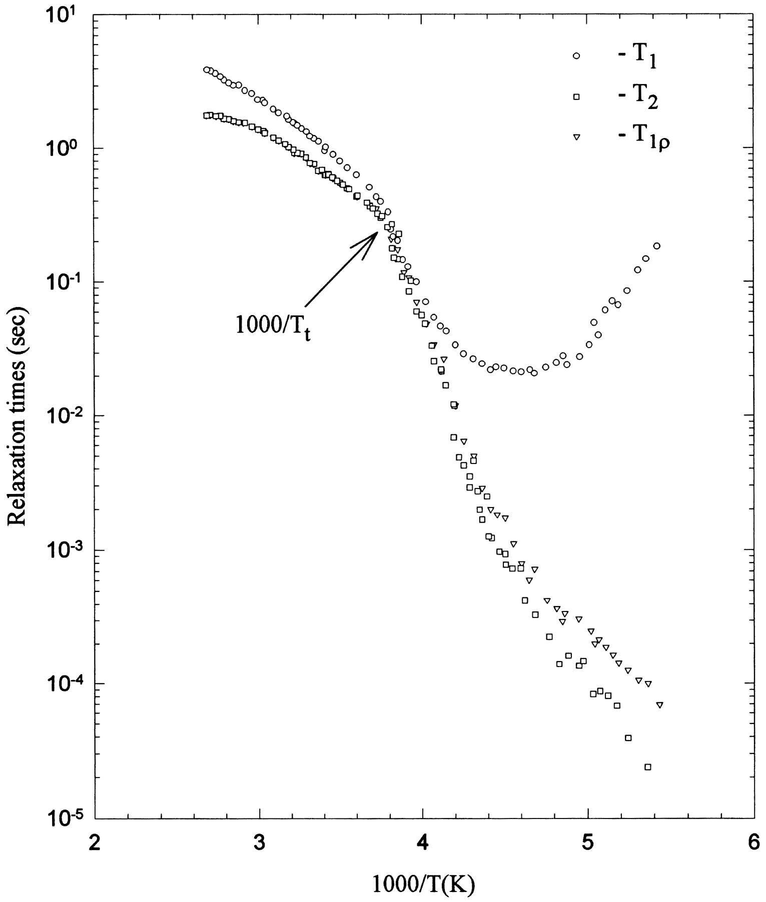

Fig. 1. Relaxation times T_1, T_2, and $T_{1\rho}$ vs 1000/T (K) for Nafion hydrated to 15.9% H_2O.

The transition in these systems may occur either in the aqueous or the fluorocarbon phase. In the event of the latter, it is expected that this would be directly reflected as a transition in the fluorine relaxation behaviour. In the case of an aqueous phase transition, the effect on the fluorine relaxation would be more subtle.

Fluorine T_1 and T_2 data are plotted in Fig. 2 as functions of reciprocal temperature and hydration, in both H_2O and D_2O hydrated Nafion samples. The T_1 data display a broad minimum which is a characteristic response for large polymers. T_2 is very short and changes little with temperature, which is also characteristic of solid polymers.

It is important to note that the fluorine T_1 and T_2 values are independent of the level of hydration. Also, there is no distinction between H_2O and D_2O hydration. The fluorine relaxation processes in the polymer are completely unaffected by the presence or absence of a hydrating medium. In contrast, ^1H and ^2H relaxation in the aqueous phase is strongly moderated by the presence of the polymer.

An inspection of the fluorine data shows no discontinuities which could be associated with a change in the fluorocarbon matrix. While this does not rule out the possibility of a phase transition, it suggests that the observed ‘transition’ is of a dynamical nature rather than structural.

The value of T_t is approximately 10°K higher in D_2O hydrated Nafion than in the corresponding sample hydrated with H_2O. This is undoubtably due to the larger moment of inertia of the D_2O molecules. A similar phenomenon is observed in the melting and boiling temperatures of the two species, which are increased by 3.8° and 1.4°, respectively, in D_2O.

4. The apparent phase transition

It is commonly assumed that the reorientational correlation time has an Arrhenius dependence on temperature, so that the slope of the relaxation data in plots such as these represent the reorientational activation energy. Above T_t the slopes of the T_1, T_2 and $T_{1\rho}$ data are relatively low, giving a small activation energy. This is characteristic of water molecules with a high degree of mobility, i.e. a low hydrogen bond density.

Below T_t the slope of the data is many times higher, indicative of a situation in which molecular motion is very restricted, i.e. a higher hydrogen bond density.

It is seen that water absorbed in Nafion is in a very mobile state at temperatures above T_t, but is in a well ordered state with a high hydrogen bond density at temperatures below T_t. It is tempting at first to attribute this behaviour to the freezing of the absorbed water. However, this is easily discounted on two points. First, the measured T_2 values (up to 200 ms)

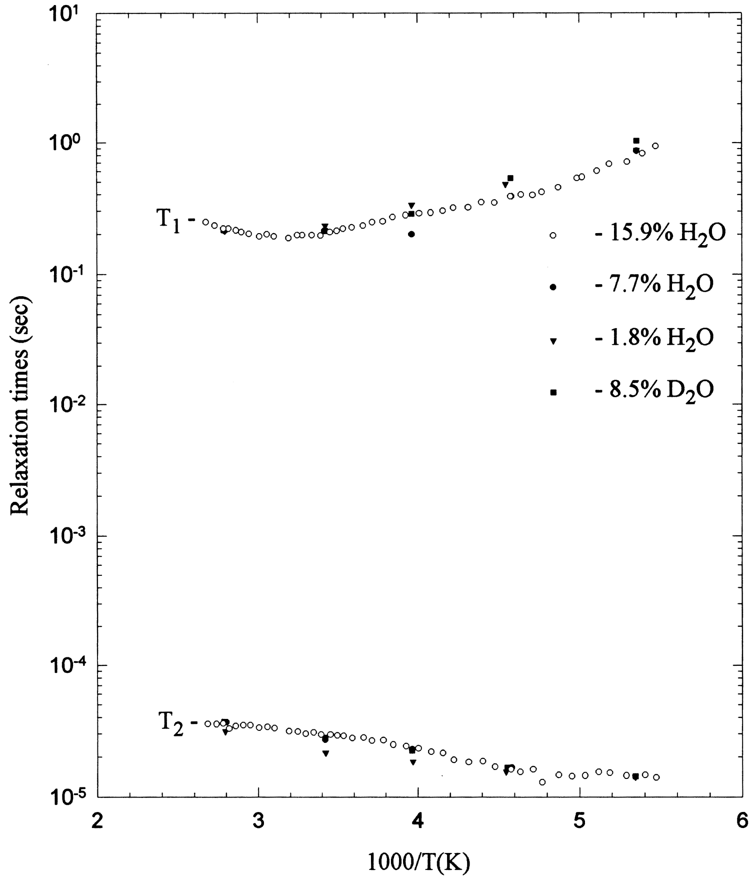

Fig. 2. Fluorine relaxation times T_1 and T_2 vs 1000/T (K) for Nafion of varying hydration.

are far too long to be associated with ice (T_2 approximately 10 μs). Second, the transition occurs at higher temperatures with decreasing hydration and is observed as high as 13°C, clearly not a freezing phenomenon.

The transition in the relaxation behaviour is clearly not due to structural reordering in the Nafion itself. Evidence of a phase transition is noticeably absent in the fluorine relaxation data in Fig. 2. The dynamical 'transition' is also not a characteristic of bulk water, since such behaviour is not observed in n.m.r. experiments on bulk water [18–20]. The unusual phenomenon such as shown in Fig. 1 represent the effects of the confining geometry on the motional freedom of the absorbed water.

A similar effect has been observed in microcalorimetric studies of Nafion [21]. An endothermic peak occurs at about − 15°C in Nafion hydrated to 15%. Similar peaks are observed at hydration levels above 8%, but none can be distinguished below this level.

The explanation given to the observed endothermic peak involves the freezing of excess water within the Nafion pores. While our analysis does not substantiate this interpretation, there is an indication of an increase in the degree of ordering and in the hydrogen bond density within the water.

5. Analysis of the data

For particles with spin 1/2, the relaxation rates are given by [17]:

$$\frac{1}{T_1}=\frac{3\gamma^4\hbar^2}{10r^6}\left[\frac{\tau_c}{1+\omega_0^2\tau_c^2}+\frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right] \quad (1)$$

$$\frac{1}{T_2}=\frac{3\gamma^4\hbar^2}{20r^6}\left[3\tau_c+\frac{5\tau_c}{1+\omega_0^2\tau_c^2}+\frac{2\tau_c}{1+4\omega_0^2\tau_c^2}\right] \quad (2)$$

$$\frac{1}{T_{1\rho}}=\frac{3\gamma^4\hbar^2}{20r^6}\left[\frac{3\tau_c}{1+4\omega_1^2\tau_c^2}+\frac{5\tau_c}{1+\omega_0^2\tau_c^2}+\frac{2\tau_c}{1+4\omega_0^2\tau_c^2}\right] \quad (3)$$

Here, γ is the nuclear gyromagnetic ratio, r is the internuclear separation, ω_o is the nuclear Larmor frequency and τ_c is the correlation time of the motion involved.

In the high temperature extreme, i.e. when $\omega_o\tau_c \ll 1$, this theory predicts that the relaxation times T_1, T_2 and $T_{1\rho}$ are inversely proportional to the correlation time τ_c. The common assumption that the correlation time has an Arrhenius dependence on temperature clearly fails here. Under this assumption, T_1 increases exponentially with reciprocal temperature, something not observed in this data.

It has been noted that there are several unusual features in the temperature dependence of the n.m.r. relaxation times for hydrated Nafion. There are indications of additional contributions to the relaxation mechanisms which vary with temperature and make differing contributions to the relaxation rates. Because of these extra mechanisms, the T_1 data are analyzed separately from the T_2 and $T_{1\rho}$ data.

The behaviour observed in the T_1 data is similar to that exhibited by bulk water [18]. For demonstrative purposes, the T_1 values for bulk water are included in the analysis (see Figs 3 and 4). With the exception of a scaling of the temperature axis, there is a remarkable similarity among the temperature dependencies of the respective relaxation times.

Attempts to model the relaxation times of water or Nafion–water systems based on hard sphere approximations, e.g. the Debye–Stokes formalism, are unsuccessful simply because water molecules are not very well approximated as non- interacting hard spheres. There have been several instances where this has been recognized and corrections attempted.

Speedy [22] and Lüdemann [23] have examined corrections to molecular self diffusion for non-polar, polar and hydrogen bonded molecules. In their findings, the non-polar molecules tetrafluoromethane and methane could be approximated as interacting hard spheres. Liquids containing polar molecules tended to deviate from hard sphere liquids, particularly at lower temperatures. This was attributed to attractive interactions and modelled by the attractive part of a Lennard–Jones potential.

It is their conclusion that these descriptions must fail for hydrogen bonded liquids like the monoalcohols or water. In this class of liquids the isobaric temperature dependence can only be represented empirically. For low pressure supercooled water isobars are well represented by the dynamic scaling law originally introduced by Speedy and Angell [24] to describe the temperature dependence of the isothermal compressibility of supercooled water. More recently, this formalism has been successfully used to model the average hydrogen bond lifetime in supercooled water as obtained from molecular dynamics simulations [25].

Lang and Lüdemann have used this power law expression extensively to model the reorientational correlation time in supercooled water [20,26–28]. It was used to explain the behaviour of ^{1}H, ^{2}H and ^{17}O spin lattice relaxation measurements in water as a function of pressure and temperature. Here,

$$\tau_c=\tau_o\left(\frac{T_s}{T-T_s}\right)^{\gamma} \quad (4)$$

and T_s, the singularity temperature, is interpreted as the low temperature mechanical stability limit of the liquid. It is important to note that the singularity at T_s is a different phenomenon than the transition at T_t, which is a dynamical transition in the Nafion–water systems.

The nature of this singularity has been the subject of some discussion [3,24,29–31]. Extensive modelling has predicted a supercooled liquid catastrophe in the viscosity, isothermal compressibility, self diffusion, dielectric relaxation, heat capacity and thermal expansion of supercooled water. The singularity temperature is usually predicted to be − 45°C ± 4°C. It is significant that this is approximately 5°C lower than the homogeneous nucleation temperature, the lowest

Table 2
The parameters representing the best fit of Eq. (4) to water and hydrated Nafion

Hydration level	τ_o (sec)	T_s (K)	γ
Water	$(6.1 \pm .1) \times 10^{-13}$	224 ± 2	1.82 ± .04
15.9% H_2O	$(1.7 \pm .2) \times 10^{-12}$	233 ± 2	1.64 ± .06
7.7% H_2O	$(2.9 \pm .4) \times 10^{-12}$	240 ± 4	1.73 ± .10
5.9% H_2O	$(3.6 \pm .6) \times 10^{-12}$	240 ± 5	2.05 ± .15
D_2O	$(3.7 \pm .1) \times 10^{-13}$	230 ± 2	1.82 ± .04
8.5%	$(4.0 \pm .5) \times 10^{-13}$	244 ± 4	2.19 ± .12

temperature to which water can theoretically be supercooled. The singularity can therefore never be experimentally observed. In our case, the absorbed water remains unfrozen to much lower temperatures, but undergoes a dynamical transition into another behavioural regime at temperatures above the singularity temperature.

Eq. (4) was used to model the reorientational correlation time of water in the Nafion–water systems, and the results are presented in Table 2, and graphically in Figs 3 and 4.

The singularity temperature, T_s, tends to increase slightly with decreasing hydration, with respect to bulk water. This can be interpreted as the effect of the restricting pores on the mobility of the water molecules. As pore size is reduced, so is the motional freedom. The singularity temperature represents the temperature at which molecular reorientation will be frozen out. Since the confining boundaries aid in reducing the degree of mobility, T_s will therefore be higher.

The value of T_s for D_2O hydrated Nafion is slightly higher than the corresponding H_2O hydrated sample. This is a result of the higher moment of inertia associated with D_2O. T_s is significantly higher than in pure D_2O due to the effects of the confining geometry of the pores.

For comparative purposes, the most meaningful result of the fitting exercises is the actual correlation time, τ_c. The nature of the dependence of τ_c on the pore size will be determined by the moderating effects of the confining geometries on the properties of the absorbed water. Elucidation of these effects will be facilitated by an understanding of this dependence.

Pore radii in hydrated Nafion are functions of the moisture content. Data are not available for the form of Nafion

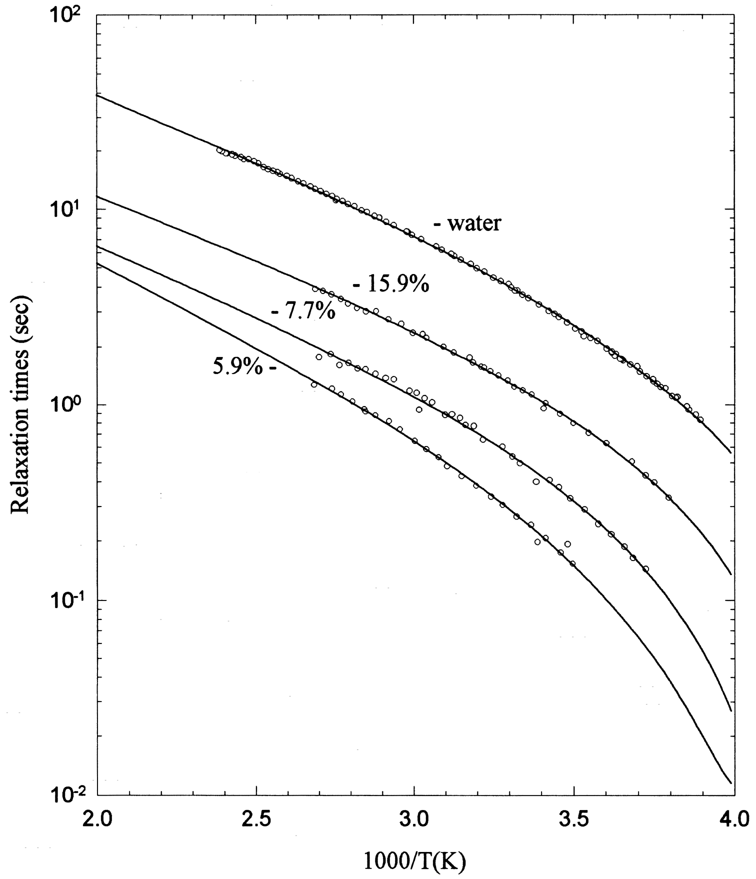

Fig. 3. T_1 values for water and Nafion hydrated to 15.9%, 7.7% and 5.9% H_2O. The solid lines represent the best fit to the model described in the text.

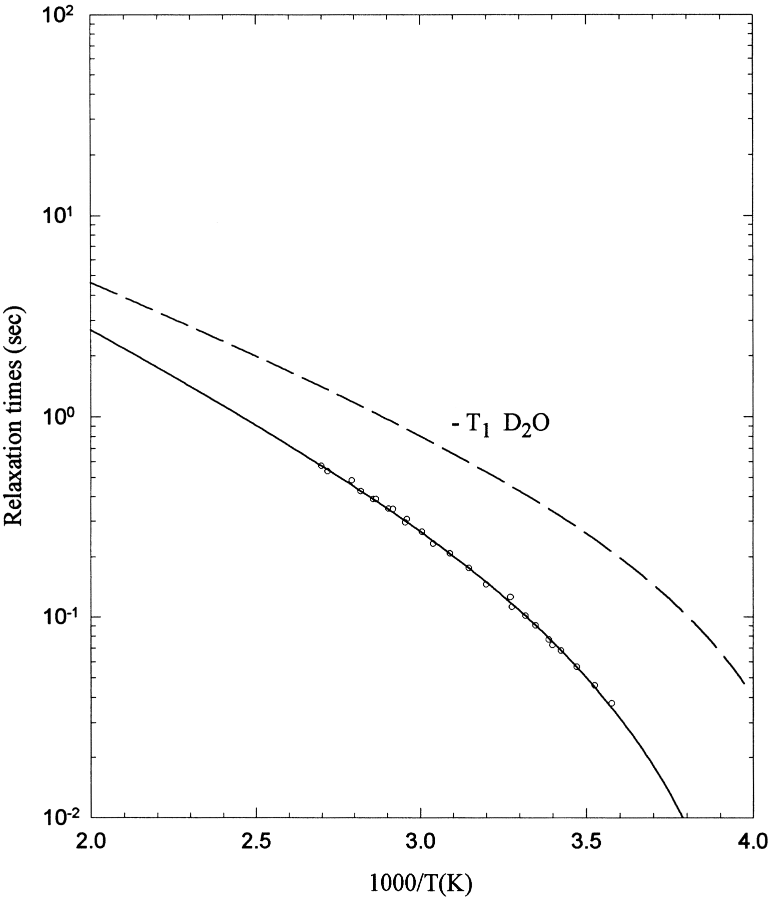

Fig. 4. T_1 values for Nafion hydrated to 5.8% D_2O. The solid line represents the best fit to the model described in the text. The dashed line is the predicted behaviour for pure D_2O [26].

used here, with a molecular weight of 1100 g/mol, but are for Nafion with a molecular weight of 1200 g/mol [8]. Although the cluster sizes will be smaller for the heavier form, it is expected that the differences will be small, and trends similar. Therefore, the values published for the pore diameters of the heavier form of Nafion will be used here.

The available data can be fit to a straight line of the form

$$d(\text{Å}) = 0.68n + 19.3 \tag{5}$$

where n is the number of water molecules per SO_3H group. From this the diameter of the clusters in the three Nafion samples presented are calculated.

The correlation time τ_c has been calculated as a function of hydration and pore diameter at 20°C and 90°C. These are presented in Table 3. The correlation time in bulk water [32] is characteristically about 10^{-12} s; in bound or surface water about 10^{-11} to 10^{-9} s, and in bonded water 10^{-7} s.

It is interesting to note that the correlation time of water absorbed in these pores is within an order of magnitude of the correlation time of bulk water. At the highest level of hydration, it is only twice that of free water. In terms of motional freedom, the absorbed water is affected relatively little by the presence of the Nafion. Clearly the water in the pores is behaving very much like bulk water. This is in contrast to surface hydration, where absorbed water behaves more like bound water than bulk water.

From a calculation of the ratio of the correlation time at a particular level of hydration to that of water, it is seen that it

Table 3
The correlation time τ_c and pore size in Nafion at 20°C and 90°C

Hydration level-%	Hydration level-*n*	Pore diameter (Å)	τ_c (sec) 293 K	τ_c (sec) 363 K
Water	Water	n/a	5.1×10^{-12}	1.4×10^{-12}
15.9% H_2O	11.6	27	1.6×10^{-11}	4.5×10^{-12}
7.7% H_2O	5.1	23	4.0×10^{-11}	9.0×10^{-12}
5.9% H_2O	3.8	22	8.0×10^{-11}	1.4×10^{-11}
D_2O	D_2O	n/a	3.9×10^{-12}	1.0×10^{-12}
8.5% D_2O	5.1	23	1.3×10^{-11}	1.9×10^{-12}

is essentially independent of temperature. The correlation time of the absorbed water at any particular temperature is simply the correlation time of bulk water at that temperature multiplied by a scaling constant. This again indicates that the absorbed water is behaving very much as free water with a minimum of modification from the Nafion, except for the confining effects of the pores, which lengthen the value of τ.

6. Analysis of the T_2 and $T_{1\rho}$ data

The BPP relaxation theory predicts that in the high temperature extreme, T_1, T_2 and $T_{1\rho}$ all converge to a single value. Since this is not the case here, the presence of additional contributions to the relaxation processes is indicated. It is significant that there is no difference between the T_2 and $T_{1\rho}$ values and that they diverge together from T_1. This indicates that the spin–spin and low field spin–lattice relaxation are affected in the same way by the additional relaxation mechanisms, while high field spin–lattice relaxation is unaffected. This implies that there are additional low frequency contributions to the spectral density functions.

The relaxation data from the Nafion water system are successfully modelled by assuming fast exchange with protons in a solid-like environment via:

$$\frac{1}{(T_{1,2,1\rho})_{\mathrm{obs}}} = \frac{f}{(T_{1,2,1\rho})_a} + \frac{1-f}{(T_{1,2,1\rho})_b} \tag{6}$$

where $(T_{1,2,1\rho})_{a,b}$ are the intrinsic relaxation times of sites a and b, and f is the fractional amount of site a.

In the Nafion–water system, the only location for protons in a solid-like configuration is the SO_3H groups. However, these are acid groups which dissociate in an aqueous environment and the fraction of these sites which at any one time contain a proton must be very small. Relaxation at these sites must be very efficient to significantly influence the global relaxation behaviour.

For the purposes of modelling, it will be assumed that the intrinsic water T_1 is the observed value, and that exchange affects only T_2 and $T_{1\rho}$. Since it is expected that the system will be in the motionally narrowed regime, it is also assumed that the intrinsic T_2 and $T_{1\rho}$ values of the water are equal to the T_1 values.

The intrinsic relaxation times of the protons in the solid-like environment are unknown, and cannot be readily determined. This is inconsequential in the case of the T_1 data where the T_1 values in the solid and liquid environments are expected to be reasonably close. The small fraction of solid-like sites will have a negligible effect on the observed T_1. As for T_2 and $T_{1\rho}$ of the protons in the solid- like sites, since the observed relaxation times are identical and it is assumed that the intrinsic water T_2 and $T_{1\rho}$ are equal, the intrinsic solid T_2 and $T_{1\rho}$ must also be equal. It will also be assumed that for the protons in the solid-like environments τ_c has an Arrhenius temperature dependence.

While it is straightforward to determine the weighted contribution to the relaxation from the solid-like site, f and τ_o cannot be determined separately. It is possible, however, to obtain an estimate of the magnitude of the fractional size if a typical value for the solid T_2 at room temperature is assumed, say 5 μs. The fraction of the acid sites which are not dissociated is found to be $< 10^{-4}$. In other words, the acid sites are ionized more than 99.99% of the time.

The activation energy associated with reorientation of the solid-like site is readily extracted. These are given in Table 4 and the corresponding results of the model are presented in Fig. 5. The value in D_2O hydrated Nafion is larger than the corresponding sample hydrated with H_2O due to the larger moment of inertia. The moment of inertia of an SO_3D group rotating about the principal axis is approximately 40% greater than an SO_3H rotating in a similar fashion.

Over this limited set of samples, the activation energy associated with the protons in the solid-like sites is approximately proportional to the inverse of the level of hydration. This is due to the reduced mobility associated with the presence of the confining pores. At lower levels of hydration, i.e. with decreasing cluster sizes, it has been shown that the reorientational correlation time of the mobile water decreases with decreasing pore size. This increases the probability of hydrogen bond formation with neighbouring groups, including the SO_3H groups. Reorientation of the protons in the solid-like sites requires the breaking of these bonds, which form more readily in smaller sized clusters. The activation energy associated with this motion increases with decreasing hydration levels.

Table 4
The activation energy associated with the reorientation of the protons in the solid-like sites as a function of hydration

Hydration level	Activation energy (kcal/mol)
15.9% H_2O	1.9 ± .2
7.7% H_2O	4.4 ± .4
5.9% H_2O	5.5 ± .6
8.5% D_2O	5.5 ± .6

7. Conclusions

The molecular dynamics of water absorbed in the ionic polymer Nafion were investigated using pulse nuclear magnetic relaxation techniques. Nafion, a form of perfluorosulphonic acid, is characterized by unique electrochemical properties.

At the outset a thorough purification procedure was developed. Nafion is a complex system, and as received from the supplier is known to be contaminated with a variety of impurities. Among these, some are paramagnetic and particularly damaging to an n.m.r. experiment; a fact not taken into account in much of the earlier n.m.r. work with Nafion.

Water absorbed in Nafion creates an environment of clusters embedded in the fluorocarbon matrix. Above the

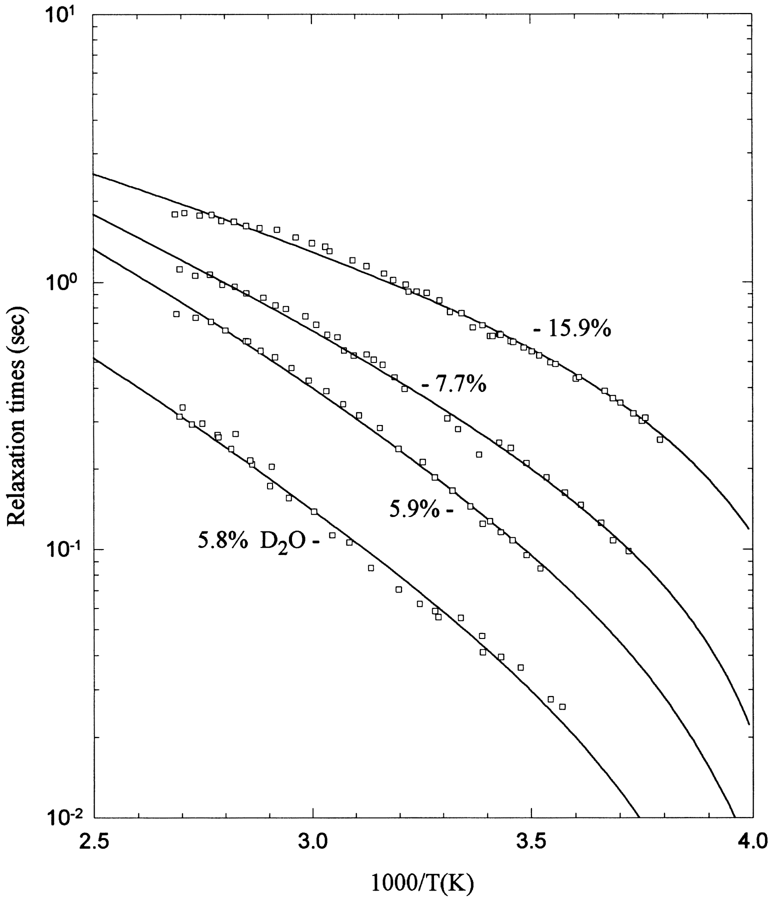

Fig. 5. T_2 values for water and Nafion hydrated to 15.9%, 7.7%, 5.9% H_2O and 5.8% D_2O. The solid lines represent the best fit to the model described in the text.

temperature T_t, water in these clusters behaves very much like pure water. The dependence on temperature of the spin–lattice relaxation time mirrors that in samples of bulk water. The reorientational correlation times are modified due to the confining geometry of the pores. This modification takes the form of a scaling factor which is a function of the pore diameter. Similar characteristics are displayed for both H_2O and D_2O hydrated Nafion, modified only by the difference in the respective moments of inertia.

The behaviour of the T_2 and $T_{1\rho}$ relaxation times can be explained as due to an interaction between the polymer and the water in the form of exchange. The reorientational activation energy of protons in the solid groups is derived from this interaction. It is a function of the level of hydration, and has a similar dependence on hydration as does the transition temperature T_t. This is a measure of the restriction of molecular motion due to the presence of the pores.

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