Polymer 40 (1999) 2481–2485

polymer

N.m.r. relaxation in Nafion—the low temperature regime

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Received 28 April 1997; revised 8 June 1998; accepted 15 June 1998

Abstract

The dynamical characteristics of water absorbed in Nafion are investigated using n.m.r. At temperatures below the dynamical transition temperature, T_t, relaxation rates indicate mobility associated with a fluid but the derived motional activation energies are similar to those of ice. This indicates a well ordered supercooled fluid consisting of hydrogen bonded water structures. The correlation time τ_c is found to have a Gaussian dependence on the surface area to volume ratio, unlike simple porous systems. We have shown that the surface area depends on $r^{2.5}$. We feel that this is due to the irregular nature of the surfaces of the clusters. © 1999 Published by Elsevier Science Ltd. All rights reserved.

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

1. Introduction

The dynamical behaviour of water absorbed in Nafion, as observed by n.m.r. relaxation, exhibits several unique features, as discussed in the previous paper [1]. Among these is an observed transition in the relaxation characteristics at a specific temperature, denoted, T_t. At temperatures above this transition, the absorbed water behaves very much like bulk water, and is modified only slightly by the presence of the polymer. The previous paper presents a detailed analysis of the relaxation of this regime.

At temperatures below this transition, the relaxation behaviour indicates significant change to the dynamical characteristics of the absorbed water. This paper discusses the nature of these dynamics. Nafion, sample preparation and experimental methods are described elsewhere [1].

It is well established that the nuclear magnetic relaxation rate of a gas or liquid is enhanced near an interface to a solid [2]. The correlation times of molecules at the surface, τ_{cs}, are generally longer than those in the bulk, τ_{cb}. The specific mechanism for the enhancement is generally not well understood, but it has been speculated that it is due either to the presence of paramagnetic sites on the solid surface or to the attractive van der Waals force between liquid and solid at the interface which hinders the molecular dynamics [3].

Magnetization evolution in confining pores is commonly modelled based on the work of Brownstein and Tarr [4], who investigated relaxation as a function of diffusion and geometry. Their results indicate that the observed relaxation is the average of the fluid and surface relaxation, weighted by the surface area to volume ratio. Using their approach, n.m.r. has been successfully employed as a probe of pore structure and size in saturated porous media, including oil sands [5], sedimentary rock [6–9] and porous glass [10,11]. There have also been several modifications reported recently which give extra consideration to bulk relaxation [12], consider a distribution of pore sizes [13], and expand the theory to encompass pulse field gradient techniques [14].

These models fail to describe the observed behaviour of water absorbed in Nafion. In this paper, a different approach is reported.

2. Analysis of the low temperature data

In this temperature regime, the characteristics of the data more closely resemble those predicted by the BPP [15] relaxation theory (see Fig. 1) than do the high temperature data. The minimum in the T_1 data and the convergence of the three data sets at higher temperatures are features of BPP relaxation. There are, however, two significant deviations from this relaxation model. The BPP theory predicts the existence of a minimum in $T_{1\rho}$. For a spin-locking field strength of 10 Gauss, the value of $T_{1\rho}$ at the minimum is expected to be lower than the minimum value of T_1 by a factor of 185. We did not observe the expected minima in the $T_{1\rho}$ data.

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0032-3861/99/$ - see front matter
PII: S0032-3861(98)00483-2

Also, the BPP relaxation model predicts that T_2 decreases monotonically with β ($\beta = 1000/T$). The data for the Nafion–water systems show distinct changes in the dependence of T_2 on β. Clearly, further contributing factors to the relaxation are indicated.

Goldmann–Shen [16] and Selective Inversion experiments were performed to detect the presence of cross-relaxation between the solid-like and liquid-like environments. No cross-relaxation was detected.

Above T_t, previous analysis [1] has suggested that the small fraction of protons associated with the ionic groups contribute to the observed T_2 and $T_{1\rho}$ relaxation behaviour. We expect a similar phenomenon to occur below T_t, but with a distinction. The SO_3H group becomes dissociated because of the large difference in the density of states between the SO_3H group and the water. That is, there are many more states available to the radical in solution then there are when it is attached to the backbone, and the equilibrium is biased very much towards the dissociated state. However, with decreasing temperatures, the density of states available in the water decreases very rapidly, and the equilibrium begins to favour the solid state. It is our suggestion that there is a temperature range over which the SO_3H groups go from being essentially fully dissociated to being fully associated. Below this temperature range, there is a large fraction of protons in a solid-like environment which contribute to the observed T_2 and $T_{1\rho}$ relaxation.

This temperature range will be defined by the properties of the absorbed water, which are functions of level of hydration. For simplicity it is assumed that the fraction of protons in solid-like sites increases linearly with temperature throughout this range. The observed relaxation rates are simply the weighted averages of the relaxation rates from the protons in solid-like and liquid-like environments. Relaxation of the protons in liquid-like sites is modelled using the BPP theory [15]. The motional correlation time, τ_c, is assumed to have an Arrhenius dependence on temperature.

The breadth of the minimum in T_1 indicates that a distribution of correlation times is required, so that

$$\frac{1}{T_1} = \int_0^\infty \frac{P(\tau_c)}{T_1(\tau_c)} d\tau_c \tag{1}$$

Similar expressions describe the rates $1/T_2$ and $1/T_{1\rho}$. For $P(\tau_c)$, it is common to assume a log-normal distribution [17] of the form

$$P(\tau_c) = \frac{\lambda}{\pi^{1/2}} e^{-s^2/\lambda^2} \tag{2}$$

where

$$S = \ln\left(\frac{\tau_c}{\bar{\tau}_c}\right) \tag{3}$$

and

$$\lambda^2 = \lambda_0^2 + \left(\frac{\lambda_Q}{RT}\right)^2 \tag{4}$$

with λ a parameter describing the width of the distribution,

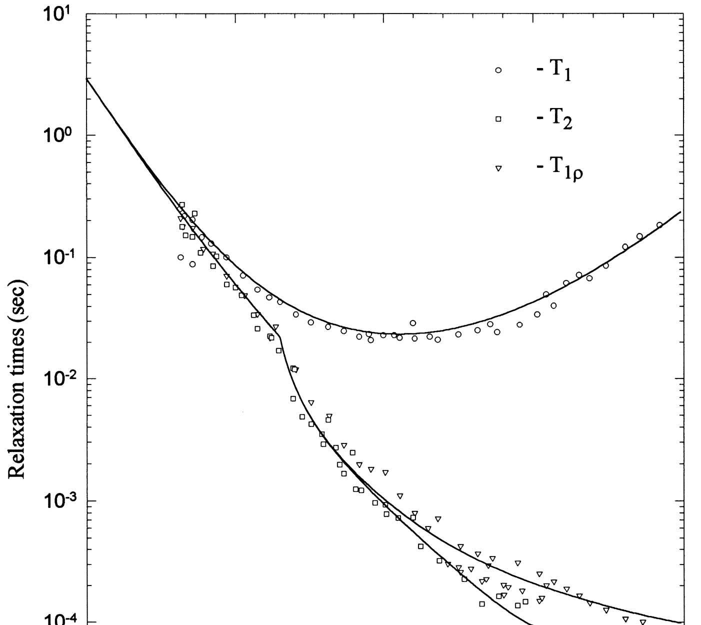

Fig. 1. Nafion hydrated to 15.9% H_2O. The solid lines represent the best fit to the model described in the text.

Table 1
Relaxation parameters associated with the liquid-like phase

Hydration level (%)	τ_o (s)	E_a (kcal)	λ_o, λ_Q
15.9	$(7.9 \pm 0.5) \times 10^{-24}$	14.5 ± 0.4	3.2 ± 0.3, 0
7.7	$(4.8 \pm 0.7) \times 10^{-23}$	14.2 ± 0.5	3.2 ± 0.3, 0
5.9	$(8.5 \pm 0.9) \times 10^{-23}$	14.5 ± 0.7	3.5 ± 0.5, 0
3.0	$(6.4 \pm 0.9) \times 10^{-21}$	14.0 ± 0.8	3.8 ± 0.6, 0
1.8	$(1.7 \pm 0.4) \times 10^{-19}$	13.6 ± 1.0	4.1 ± 0.8, 0
8.5 D_2O	$(4.4 \pm 1.5) \times 10^{-24}$	15.0 ± 1.0	3.1 ± 0.8, 0

and λ_0 and λ_Q the temperature independent and dependent contributions.

For the protons in solid-like sites, a single isotropic site is used. The motional correlation time is also assumed to have an Arrhenius temperature dependence. As is commonly done with this type of modelling, a lower limit was imposed on the value of T_2. This marks the onset of the rigid-lattice regime, in which T_2 changes very little; a value of 10 μs was used. The results of the modelling for Nafion hydrated to 15.9% H_2O are presented in Fig. 1. The solid lines represent the best fit of the model to the data. The change in the slope of the T_2 and $T_{1\rho}$ data coincides with the beginning of the reassociation of the acid groups. The parameters derived for the liquid-like relaxation are given in Table 1.

In this temperature regime the characteristics of the water absorbed in Nafion are somewhat anomalous. The activation energies deduced for the reorientational motion are large. Typically, O–H··O hydrogen bonds have energies of 3.5–4 kcal/mole. Within this phase, molecular reorientation requires the breaking of up to four hydrogen bonds. This high degree of bonding is indicative of a highly ordered phase. Similar behaviour is observed in normal ice [18], where four hydrogen bonds must be broken to accommodate reorientation.

Due to the temperature range involved and the peculiar ordered structure it is tempting to equate this water phase with ice. Ice, however, is characterized by a correlation time of approximately 10^{-6} s and is very rigid. This is reflected in a very short T_2 of several μs. Within this water phase, the observed T_2 is as high as 200 ms, and the calculated correlation time at − 20°C varies between samples from 10^{-10} to 10^{-11} s.

Water in this phase is a well-ordered supercooled fluid. Mobility is less than in either free water or the high temperature regime discussed in the previous paper, but much greater than in ice. It is our belief that water is forming complex cage-like structures, or clathrates, consisting of many molecules, and it is these we are seeing. Compound water within Nafion has previously been observed with infrared techniques [19–21]. Supercooling is maintained at much lower temperatures than expected for water in regular porous geometries [22]. It is believed that the irregularly shaped clusters within Nafion facilitate this supercooling. Modification is due to the presence of the surface. In these systems, the surface area to volume ratio is much higher than in simple geometries.

3. Variation with hydration

The results from Nafion hydrated to 7.7% H_2O are presented in Fig. 2. Similar features are noted at all levels of hydration. It is significant that within the liquid-like phase the motional activation energy and the breadth of the distribution in τ_c are invariant between samples. This indicates uniformity in the underlying relaxation processes. The dynamical mechanisms are independent of pore size; only the timescale is affected. The modifications in timescale, i.e. to the motional correlation times, are the result of changes in the ratio of surface area to volume within the clusters.

The moderating effects of the confining pores on the dynamical behaviour of the water can best be studied by examining the dependence of the motional correlation time τ_c on pore size. For illustrative purposes, τ_c has been calculated at − 20°C for all samples. This has been recorded in Table 2.

Existing models describing relaxation in porous geometries [4–14] fail in these Nafion–water systems. They predict that the observed relaxation is the weighted sum of relaxation from two regions, effectively a bimodal distribution of correlation times. The effect of altering the respective weighting in a bimodal distribution, as would

Table 2
The correlation time τ_c and pore size in Nafion at − 20°C

Hydration level (%)	Hydration level (n)	Pore diameter (Å)	τ_c (s) 253°K
15.9	11.6	27	6.5×10^{-12}
7.7	5.1	23	8.7×10^{-11}
5.9	3.8	22	2.8×10^{-10}
3.0	1.9	21	7.8×10^{-9}
1.8	1.1	20	6.6×10^{-7}
8.5 D_2O	5.1	23	3.9×10^{-11}

happen with varying hydration, is a marked change in the shape and width of the corresponding minimum in T_1. Such changes are absent from our data.

These models fail for several reasons, but we believe that the most important factor is the irregular nature of the surface of the pores in the Nafion–water systems. It has been indicated [19,23] that there is a high degree of intrusion of the fluorocarbon matrix into the pores. The resulting ‘fuzzy’ spheres have a ratio of surface area to volume considerably higher than for a perfect sphere. There is not an obvious distinction between a surface layer and a bulk phase. Instead, there is effectively one phase in which all water molecules spend some fraction of the time at or near a surface.

It is felt that the higher than average surface area within these pores is also the characteristic which inhibits the formation of ice at these low temperatures. This conclusion is based on the results of neutron scattering experiments on water absorbed in porous glass [24], where the confining geometries are less favourable to the formation of long orderly hexagonal channels which accompany the formation of hexagonal ice.

The dynamical behaviour, including the average reorientational correlation time, is a function of the fraction of time spent in proximity to the fluorocarbon phase. This is also observed in viscosity [25] and heat capacity [26] measurements of absorbed fluids, where these quantities are observed to increase in the vicinity of confining surfaces.

The pore size dependence of the correlation times observed in hydrated Nafion can be described by an empirical relationship. The bulk correlation time, τ_0, is modified by the presence of the surface to an extent dependent upon the fraction of time spent by water molecules in proximity to the surface. This is directly related to the amount of surface area available to each molecule, or the surface area to volume ratio. For a spherical pore, the volume is proportional to r^3 and the surface area is proportional to r^2. For a fuzzy sphere, this volume relation still holds if r is taken as an appropriate effective radius. The surface area, however, is directly affected by the degree of fuzziness, and the surface relation must be modified accordingly. It is assumed that the surface area is proportional to r^n. The surface area to volume ratio is then proportional to r^{n-3}. Further, it is assumed that there is a maximum value of surface area available to each water molecule. This is reflected in a minimum radius, r_0. The observed correlation times are fit to a Gaussian dependence

$$\tau = \tau_0 e^{Cx^2} \tag{5}$$

where

$$x = \left(\frac{r - r_o}{r_o}\right)^{n-3} \tag{6}$$

The denominator in Eq. (6) has been introduced to make x dimensionless. From the previous paper, $r_o = 9.7$ Å. The best fit to the data yields $\tau_o = 9.1 \times 10^{-13}$ s, $C = 0.74$, and

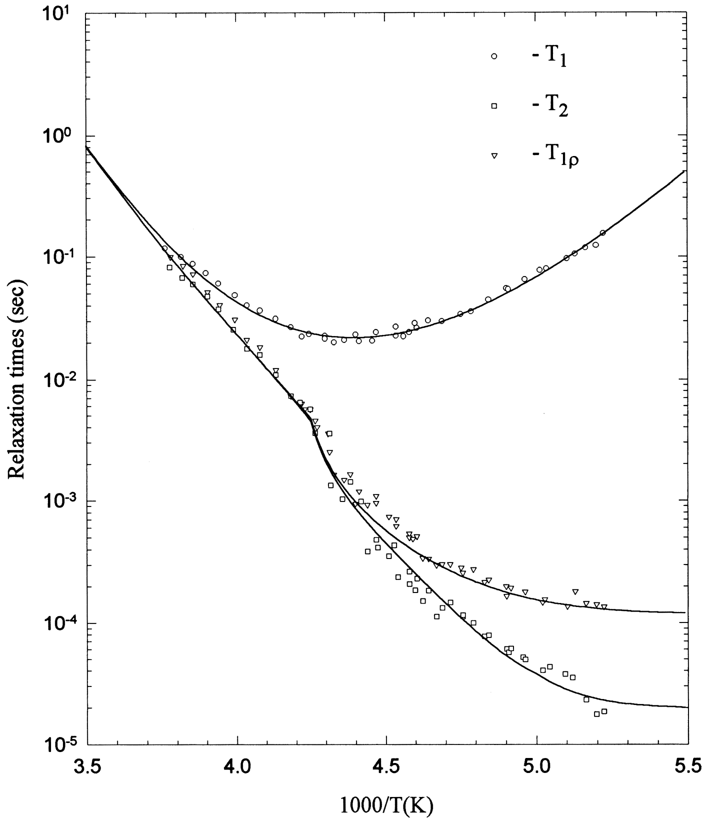

Fig. 2. Nafion hydrated to 7.7% H_2O. The solid lines represent the best fit to the model described in the text.

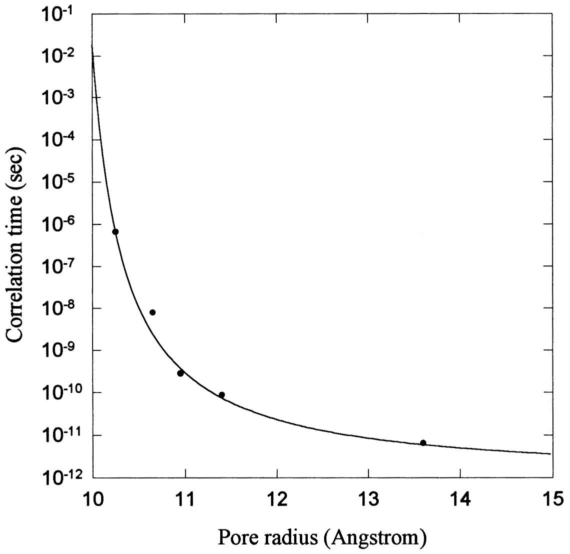

Fig. 3. The calculated correlation time in Nafion at − 20°C as a function of pore radius.

$n = 2.5$. This is presented in Fig. 3. Although it is difficult to extract reliable parameters from only five data points, the value obtained for τ_0 agrees well with the expected value for bulk water [27] of approximately 10^{-12} s.

The value obtained for the exponent n supports the view of the irregularly shaped cluster surfaces within Nafion. For a spherical pore, surface area is proportional to r^2 and volume is proportional to r^3. From the present results, the cluster surface area is proportional to $r^{2.5}$. As previously hypothesized, the surface area to volume ratio of the clusters within Nafion is unusually high.

The significant result of this exercise is that the motional correlation time of the water absorbed in Nafion clusters has a Gaussian dependence on the surface area to volume ratio. this has not been observed with conventional porous materials, and indicates that the irregularities inherent to the surface of the Nafion cluster dramatically alter the dynamical properties of the water.

In this low temperature regime, water absorbed in Nafion is characterized differently than in the high temperature extreme where its behaviour mimics that of bulk water. Here, water structures are formed, consisting of many molecules in well ordered clathrates with a high degree of hydrogen bonding, yet maintaining fluid-like dynamics. The irregular surfaces of the pores determine to a large extent the dynamical properties of the absorbed water, in particular the motional correlation time τ_c. They are also believed responsible for the apparent extreme supercooling.

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