The State of Water in Swollen Ionomers Containing Sulfonic Acid Salts

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Synopsis

The proton magnetic resonance relaxation times and heat capacity of water in perfluoroethylene sulfonic acid (Nafion), chlorosulfonated polyethylene (SPE), and sulfonated polysulfone (SPS) were measured as a function of temperature. Only the relaxation data for water present in Nafion conformed to the BPP model. The data indicate that the presence of fine pores, $\sim$12 Å in diameter, causes water–surface interactions to play a significant role. For materials with the same pore size, a difference in spin-lattice relaxation time T_1 may be correlated to the Flory–Huggins parameter χ calculated for the interaction of water with the neutral portion of the polymer backbone. Only a part of the water present in Nafion and SPE undergoes freezing, while no transition was observed for water in SPS for temperatures down to −60°C. For Nafion and SPE, the heat of fusion ΔH_f calculated from combined FID data and the DSC study was $\simeq$20 cal/g.

INTRODUCTION

Research on the structure and properties of solid-state ion-containing polymers has been carried out in several laboratories. The structural aspects have been studied by using direct techniques such as small-angle x-ray scattering,[1] and electron microscopy,[2] as well as indirect techniques such as water absorption studies.[3] The object of these studies has been to obtain some insight into ionic organization within the solid material.

In many ion-containing polymers, aggregation of the charge groups occurs, a phenomenon which can be expected on the basis of low dielectric constant of the matrix. The size and number of these aggregates depends on both ionic concentration and rigidity of the polymer chain. Water also plays an important role in this process. If carboxyl groups (weak acid) are present in the ionomer material, then low levels of humidity will enhance the intensity of the x-ray peak generated by the aggregates' presence, but saturation with water destroys it.[2] Marx et al.[4] reported that although plasticization with water increases the extent of acid group aggregation, water saturation completely destroys these aggregates.

The water absorption in perfluorosulfonic acid membranes (du Pont trade name Nafion) was studied by Hopfinger et al.,[5] who found that upon aggregate formation a loss of water molecules occurs. This is considered to be the result of strong dipole–dipole interactions which force water molecules from between the interacting dipole units.

In the present work we have tried to follow the influence of the morphology on the state of water in several ion-containing polymers. The presence of charged

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groups forces the water into the matrix, while at the same time the water interacts with neutral portions of the polymer chains. Thus, it is of interest to consider how morphologic structure versus the chemical nature of the matrix influences the state of water.

For this purpose we chose Nafion, chlorosulfonated polyethylene (SPE), and sulfonated polysulfone (SPS). The backbone of the constituent chain of Nafion consists of perfluoroethylene units, while the side chain is of the form

$$-(OCF_2-CF)_x-OCF_2-CF_2-SO_3H$$
$$\underset{\displaystyle CF_3}{|}$$
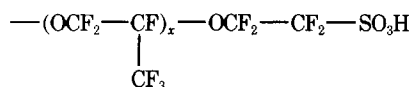
where x is small. The SPS can be considered as a copolymer of the sulfonated and nonsulfonated units of the form
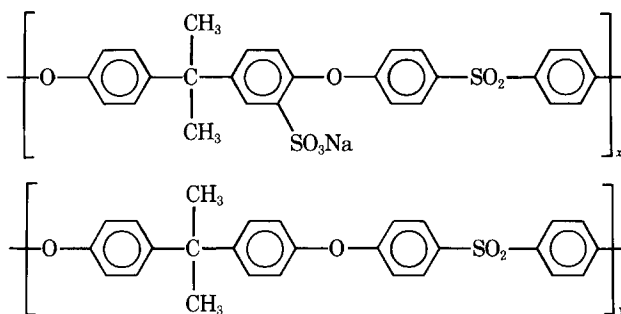
One primary common feature of the materials studied is the presence of sulfonic groups in approximately the same concentration (Table I). In addition, it is believed that in Nafion these groups are aggregated,[6] a conclusion which can also be drawn in the case of SPS[7] and SPE.[8] Thirdly, the volume fraction of water in each matrix is almost identical. Finally, of interest to the total study we have conducted with respect to the transport properties of such polymers, all these materials are quite permselective.

The physical methods chosen to examine the state (or states) of water were

TABLE I
Spin–Lattice Relaxation time T_1 (20°C) for Water Protons in Different Systems

Material	IEC, (meq/g)	Water uptake, %	Moles water/mole exchange site	Pore diameter, Å	T_1, sec
Water	—	—	—	—	2.6[a]
Nafion	0.83[b]	24[b]	16	12[b]	0.098
SPE	0.8[c]	15[d]	10.0	12	0.056
SPS	1.21[e]	29[e]	13	12[e]	0.026
Dowex-50	3[f]		15[f]		0.750[f]

[a] From Ref. 13.
[b] From Ref. 14.
[c] From Ref. 8.
[d] Determined in our laboratory.
[e] From Ref. 7
[f] From Ref. 15.

a pulsed NMR technique and differential scanning calorimetry (DSC). Whenever changes in the motion of molecules are involved, nuclear spin relaxation spectroscopy can be an important technique to probe molecular dynamics. The detailed description of the theory can be found elsewhere.[9] It is worthwhile, however, to briefly review the meaning of the physical parameters measured. The longitudinal (spin–lattice) relaxation time T_1 represents a measure of the time required for energy to pass from the spin system to other degrees of freedom. The transverse (spin–spin) relaxation time T_2 refers to thermal equilibrium within the spin system itself. According to the theory of nuclear magnetic relaxation of Solomon,[10] T_1 and T_2 are functions of a correlation time τ_c. The correlation time is the time a molecule takes to turn through a radian or to move through a distance comparable with its own dimension.

Using DSC, one can measure the amount of heat absorption as a function of temperature and consequently detect both the presence and magnitude of phase transitions (such as freezing) which the water may undergo.

EXPERIMENTAL

Ion Exchange Membrane Samples

SPS was obtained by sulfonation of polysulfone resin P-1700 (Union Carbide). The sulfonation was carried out in 1,2-dichloroethane with chlorosulfonic acid according to the method described elsewhere.[11] Nafion 125 was obtained from the Research and Development Division, du Pont. The SPE membrane was prepared by Dr. R. M. Messalem of the Research and Development Authority of Ben-Gurion University, Beer Sheba.

All the ion exchange membranes used in experiments were converted to the Na^+ form by exchange with a $0.5M$ solution of NaCl. Prior to exchange, Nafion membranes were pretreated by boiling with water according to the suggested du Pont procedure.[12] The samples in their Na^+ form were stored in water nearly 24 hr, carefully dried on the surface, and put in the NMR tube or DSC pan.

The ion exchange capacities (IEC) and water uptake of the samples are listed in Table I.

NMR Experiments

The magnetic relaxation data were obtained as a function of temperature at a resonance frequency of 60 MHz on a Bruker pulsed NMR spectrometer E-K-R 3225. The strength (H_0) of the steady magnetic field is provided by an electromagnet, model V4012 AHR.

Sample temperature was controlled by flowing nitrogen gas, thermally regulated by a Bruker B-ST 100/700 heating unit, around the sample.

The spin–lattice relaxation time T_1 was measured with a $180°–\tau–90°$ pulse sequence. T_1 was calculated from the plotted slope of expression (1)

$$\ln \left[\frac{M(0) - M(\tau)}{2M(0)} \right] = \frac{-\tau}{T_1} \tag{1}$$

where τ is the time between 180 and 90° pulses, $M(\tau)$ is the height of free induction decay (FID) following the 90° pulse, and $M(0)$ is the height of the FID in the absence of the 180° pulse.

The spin–spin relaxation time T_2 was measured by a Carr–Purcell $90°$–τ–$180°$ pulse sequence,[15] in which T_2 was obtained from the echo envelope according to

$$\tilde{M}(\tau) = M(0) \exp(-\tau/T_2) \tag{2}$$

where $\tilde{M}(\tau)$ is the decay height at time τ.

The *FID* following the $90°$ pulse was time averaged in order to enhance the signal/noise ratio by using a signal analyzer (HP-5480A). The height of the *FID* is equal to the signal height on the vertical axis at time zero.

From a summation of errors, we estimate the uncertainty in T_1 at ±10–15% and in T_2 at $\pm15\%$.

In a typical trial, the sample was cooled until $-60°C$ and kept at this temperature for 30 min. The temperature was then raised in stepwise fashion and kept constant for 15–20 min before making measurements.

As a control, we verified that dry samples (heated overnight at $50°C$ in vacuo and in the presence of P_2O_5) exhibit no signal. Atomic absorbtion analysis on the sodium form of SPS indicated the level of iron impurities to be below the limit of detection, 2 ppm.

DSC Measurements

Differential scanning calorimetry was performed on a du Pont model 990 thermal analyzer. For a typical run, the sample weight was approximately 8 mg, and a dry membrane was used as a blank. The sample was cooled to $-75°C$ and kept at this temperature for 30 min before the DSC run was recorded. The heat of transition (ΔH) was calculated according to the expression

$$\Delta H(\text{mcal}) = \frac{\text{SB} \times C\ 60(\text{sec})}{A} \tag{3}$$

where S is the peak area (cm^2), A is the heating rate (deg/min), C is the sensitivity (mcal/sec cm), and B has the dimensions of deg/cm. An estimate of errors suggests that the ΔH measurements were accurate to within $\pm5\%$.

RESULTS AND DISCUSSION

Nuclear Magnetic Resonance

Water absorbed by a membrane containing fixed charges may be compared with water adsorbed by a heterogeneous surface. A part of the water is associated with ionic species, i.e., fixed charge groups and counterions; part interacts with an organic matrix; while still another part conserves some hydrogen bonding structure, perhaps similar to that of bulk water.

A theoretical model was proposed by Bloembergen, Purcell, and Pound (BPP),[17] which predicts the temperature dependence of relaxation processes for water adsorbed on a surface. Thus, we shall consider our experimental data in the light of this model.

Application of the BPP Theoretical Model

The BPP model shows that the nuclear magnetic resonance relaxation times are in certain cases related to the motion of the molecules which contain the nuclei. In this context, the model has been used to explain results obtained from an NMR study of various molecules, especially water, adsorbed on a surface.[18] The model's fundamental assumption is that nuclear dipole–dipole relaxation represents the dominant relaxation mechanism. As a test of this assumption for the present work, D_2O was used to replace part of the water present in a sample. Because of the much smaller dipole moment of the deuterium, the relaxation time for protons in this case should increase. Indeed, we observed that when 50% of the water present in the membrane is D_2O, T_1 increases by 35% for Nafion but only by 15% for SPS and SPE.

This result suggests that of the three systems examined, the conclusions of the BPP model are most applicable to Nafion. The dependence of T_1 and T_2 versus reciprocal temperature for Nafion is shown in Figure 1. The plot of T_2 for water protons in Nafion shows a continuous decline versus reciprocal temperature, while a minimum in the dependence of T_1 is clearly distinguishable at $\sim 250°K$. The existence of this minimum is predicted by the intramolecular dipolar relaxation mechanism. Furthermore, the T_1/T_2 ratio at this minimum should be equal to 1.6 if only one environmental state exists with a single correlation time.[17] According to this model, at the temperature corresponding to the minimum T_1, the relationship given in eq. (4) is fulfilled:
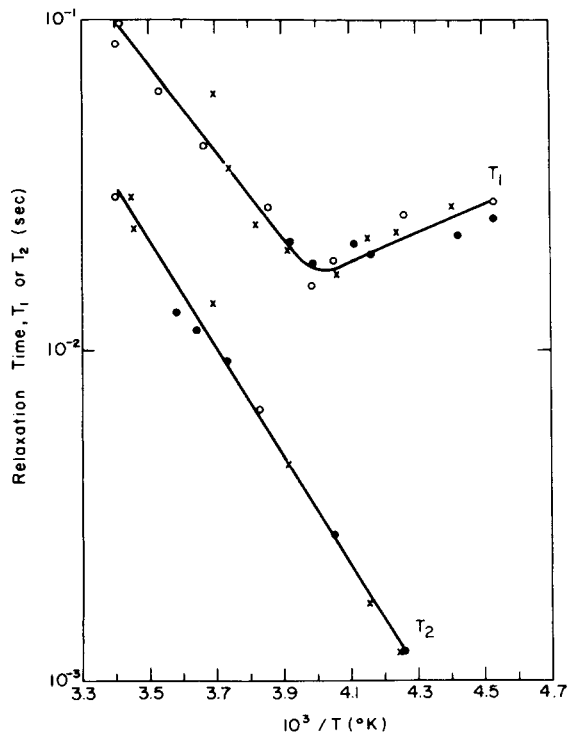
$$\omega \tau_c = 0.6158 \tag{4}$$

Fig. 1. NMR relaxation times for water absorbed by Nafion: (x, ○, ●) different samples.

independent of whether or not a distribution of correlation times is assumed. From eq. (4), with $\omega = 2\pi \times 60 \times 10^6$ rad/sec for this experiment, τ_c calculated for Nafion is equal to 1.7×10^{-9} sec. This value is two orders of magnitude longer than for supercooled water, but four orders of magnitude shorter than for ice (for the same temperature).[18] Thus, the water which remains mobile at this temperature in Nafion is closer to the state of supercooled water than to ice.

The T_1/T_2 ratio at the minimum, T_1, is much greater than 1.6, a fact which indicates that a number of environmental states exist for water in Nafion. However, the existence of different environmental states requires some inequality between parameters describing a molecular motion (correlation time, etc.) in which each state would be expected to have its own characteristic T_1 and T_2. Thus, to explain the experimentally observed single relaxation times T_1 and T_2, one must assume that a fast exchange occurs between water molecules associated with different environmental states. If the rate of such exchange is faster than the relaxation rate for any given state, some average value of T_1 and T_2 is obtained.

Let us now examine the dependence of T_1 and T_2 versus reciprocal temperature for SPE and SPS (Figs. 2 and 3). As one might expect from the results of the experiment with D_2O, T_1 does not follow the parabolic dependence predicted by the BPP model. Some other relaxation mechanism must therefore influence the relaxation for the majority of the water protons in SPE and SPS.

In searching for effects which facilitate nuclear spin relaxation, we require mechanisms which can induce nuclear spin transitions between two energy levels.
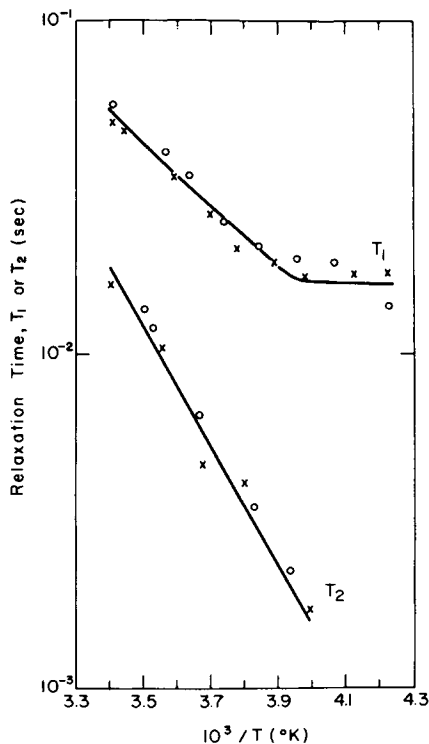

Fig. 2. NMR relaxation times for water absorbed by SPE: (x, O) different samples.
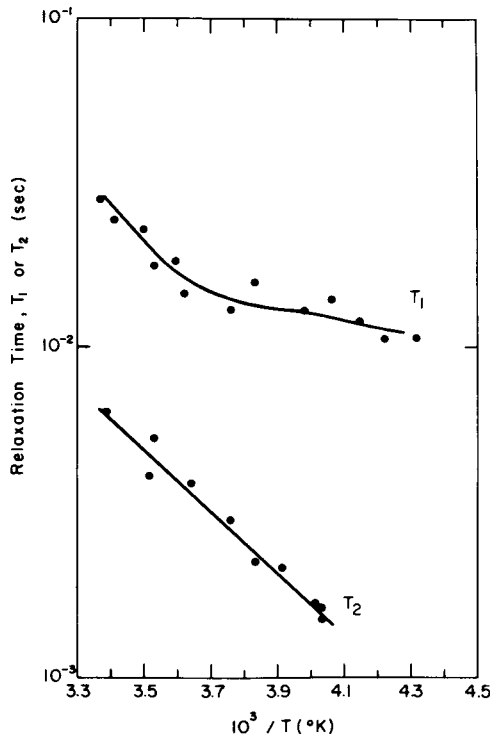
Fig. 3. NMR relaxation times for water absorbed by SPS.

Any fluctuation of magnetic intensity at a nucleus can cause spin transitions if it has components of a suitable frequency. One possibility considered was the influence of paramagnetic impurities (Fe, Mg, Cu, etc.). However, this does not seem likely for the following reasons. Firstly, no presence of iron could be detected in the SPS sample, for example (see experimental section). Secondly, a sample of SPS was equilibrated with $0.1N$ solution of ethylenediaminetetraacetic acid disodium salt (EDTA) for 24 hr. After this treatment, the membrane was placed in water and the spin–lattice relaxation time was measured. The value obtained did not differ significantly from that obtained before treatment for EDTA (28 ± 4 vs. 26 ± 4 msec). Thus, some more fundamental explanation is still required.

Role of Clusters, Pore Size, and Matrix

If one examines the values of the spin–lattice relaxation times shown in Table I, one observes that the values for protons in the ionomeric membranes are considerably lower than those obtained for water in a conventional ion exchange resin containing a similar ratio of moles of water per exchange site (e.g., Dowex-50, cation exchange resin with sulfonic acid groups on a polystyrene backbone[15]). The question arises, then, whether or not this difference is due to a special state of water surrounding the ion exchange groups which may be present as clusters or multiplets in ionomeric materials.

As pointed out earlier,[5] upon multiplet formation, water molecules are forced out to allow increased dipole–dipole interactions between the ion pairs which

form multiplets; i.e., the role of multiplets, as far as it may concern the state of water, is to decrease the hydration shell size of the ions and, consequently, increase water–ion interactions. Hypothesizing the increase of these interactions as the major reason determining water behavior, it would be reasonable to expect (1) equal values of relaxation times for matrices with equal distributions of ion exchange groups as monomers, multiplets, and clusters; (2) the same underlying mechanism for the dominant relaxation process of water protons; and (3) equivalent types of temperature dependence (for T_1 and T_2). However, none of the above conditions appear to be met for the three materials studied. On this basis, we conclude that the presence of ion exchange group aggregates cannot be the dominant factor determining water behavior in ionomeric materials.

Among the other potential factors influencing the state of water, one must consider the pore size. SPS, Nafion, and SPE all have pore diameters of molecular dimensions (Table I).[7,14] Therefore, surface effects can have a much larger degree of influence on the average state of the water molecules because surface water layers no longer merge into bulk water. The quantitative characterization of these interactions is very difficult. However, in order to judge the extent to which they are different for different matrixes having the same fixed ion exchange groups, we can calculate the Flory–Huggins parameter χ for the interaction between water molecules and the neutral polymer matrix corresponding to each ionomer, e.g., poly(tetrafluoroethylene) for Nafion, poly(vinyl chloride) for SPE, and polysulfone for SPS.

The volume fraction of solvent, ϕ, contained in a swollen nonionic polymer in equilibrium with a poor swelling agent is[19]

$$\phi = \exp\left(-1 - \chi + \frac{V_1}{V_2}\right) \tag{5}$$

where V_1 and V_2 are molar volumes of solvent and polymer, respectively; or

$$\chi = \frac{V_1}{V_2} - 1 - \ln \phi \tag{6}$$

To calculate χ from eq. (6), ϕ was calculated from data for water uptake[20] and polymer density, while $V_1/V_2 \ll 1$ and does not influence the results for our case.

Of course, the absolute value of the χ parameter so calculated is suspect in terms of its molecular meaning, because the fundamental assumptions in the Flory–Huggins theory do not take into account hydrogen bonding effects in solvents such as water. Nonetheless, as a means of establishing the relative order of the favorability of the thermodynamic interaction for the series water/Teflon, water/PVC, and water/polysulfone, it is probably justified (and in any case the only method available).

The calculated values of χ are shown in Table II. Referring back to Table I, it is clearly seen that the less thermodynamically favorable the water–matrix interactions (i.e., the higher the value of χ), the greater the value of T_1. To our knowledge, the existence of a connection between a pure thermodynamic parameter and an NMR relaxation rate has never before been suggested. Obviously, to make such a connection more convincing, one has to measure relaxation times for water absorbed by the actual neutral matrix (i.e., poly(vinyl chloride), polysulfone, Teflon, etc.). However, since their absorbed water content

Polymer	volume fraction of water ϕ	χ
Poly(tetrafluoroethylene)	$< 10^{-4}$	$> +8.2$
Poly(vinyl chloride)	2.6×10^{-4}	$+7.3$
Polysulfone	22×10^{-4}	$+5.1$

is very low, such an experiment does not seem to be technically possible at this time. Keeping in mind that the value of T_1 is connected to the extent of freedom of rotational or translational motion, in retrospect the relation between χ and T_1 might have been anticipated. Recent work[21] has shown the same type of connection between the thermodynamic activity of water absorbed by different polymers and the rates of water diffusion.

Free Induction Decay Study

To search for the existance of a phase transition, one may use the height of an *FID*, i.e. $M(0)$, which is proportional to the number of mobile protons, since the less mobile fraction decays before the receiver recovers from a saturation after the 90° pulse.

$M(0)$ can be referred to some reference temperature, e.g., $(M(0)$ (298 K), which then defines a relative fraction of mobile protons, f_m. The plot of $f_m = M(0)/M(0)(298$ K) versus reciprocal temperature (Fig. 4) shows that about 50 and 20% of the total number of water protons in Nafion and SPE respectively became significantly less mobile around 0°, while for SPS, f_m remains constant over the range +20 to −50°C. These observations lead to the question as to whether or not we can consider the data in Figure 4 to be indicative of freezing by a part of the water in Nafion and SPE.

The smooth decrease of T_1 and T_2 versus reciprocal temperature for Nafion, SPS, and SPE (Figs. 1–3) does not contain any features typical of freezing in the sense that one does not observe a typical first-order phase transition. One anticipates a sharp discontinuity in the dependence of T_1 and T_2 at a phase tran-
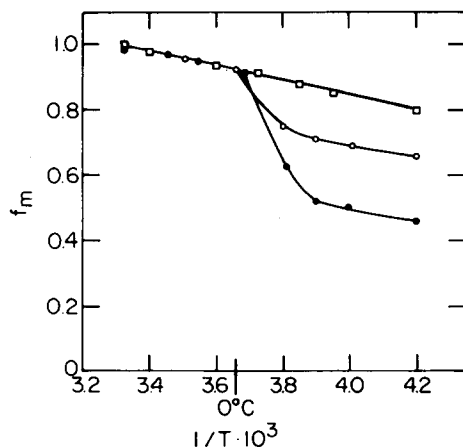

Fig. 4. Temperature corrected f_m vs. reciprocal temperature: ($\square$) SPS; ($\bullet$) SPE; ($\bigcirc$) Nafion.

sition temperature, as, for example, when bulk water freezes, there is a drop of five orders of magnitude in T_2. However, the behavior noted in Figures 1–3 is also found for water within porous glasses with a pore diameter of 200 Å,[22] in which T_2 decreases only two orders of magnitude while T_1 decreases continuously. For a porous glass with a pore diameter of 24 Å, a smooth decline in T_2 and T_1 versus reciprocal temperature was observed,[22] similar to that in Figures 2 and 3. This finding was explained as the result of structural ordering in the small pores, while the presence of bulk and ordered water was assumed in glasses with larger pores.[22]

As mentioned previously, a strong interaction exists between the ions and the polymer matrix and water absorbed by this matrix. These interactions destroy the characteristic hydrogen bonding structure of water molecules which are present in bulk water. Figure 4 clearly shows that part of the water becomes immobile in Nafion and SPE at ~0°C, but the absence of a sharp discontinuity in the dependence of T_1 and T_2 upon temperature does not allow us to straightforwardly interpret this finding as a simple freezing first-order phase transition. To decide the nature of the observed phenomena, we used differential scanning calorimentry—the conventional tool to detect phase transitions.

Differential Scanning Calorimetry

As Figure 5 shows, a broad maximum in the heat uptake-versus-temperature curve appeared within the temperature range of −20 to −1°C and of −15 to −1°C for swollen Nafion and SPE, respectively, while no peak appeared for SPS. Heats of transition (cal/g), calculated from eq. (3), are summarized in Table III and are found to be independent of experimental parameters, such as the heating rate. The shape of the peak and the independence of calculated amount of the heat absorbed on the heating rate permit us to conclude that the observed broad endothermic transition for Nafion and SPE most likely represents a diffuse first-order transition for water freezing from a number of different states. This is of course in agreement with our earlier conclusion from the NMR data that the water exists in several different states and a fast exchange occurs between these states.

In principle, one could also use the data to calculate the amount of the freezing water, provided that the value of the heat of fusion is known. However, the value of 79.9 cal/g for the heat of fusion for water in a membrane is clearly not justified, since the general phenomenon of a lowered heat of fusion can be anticipated from the work on water adsorbed on a silica surface.[23] Using NMR data from the free induction decay study we can instead calculate the heat of the phase transition. It can be seen from Table IV that the values obtained are substantially lower than those of bulk water and show a dependence on the pore size.

It is interesting to note that heats of fusion obtained for water present in Nafion and SPE are identical within experimental error. This suggests that in both membranes nearly the same number of hydrogen bonds between water molecules undergoes rearrangement upon phase transition. On the other hand, with respect to the mobility of the water molecules (measured in terms of T_1), motion is more restricted for water molecules in SPE than for those in Nafion. This observation suggests that an additional restriction of rotational and translational motion of water molecules comes from the stronger water–matrix interactions
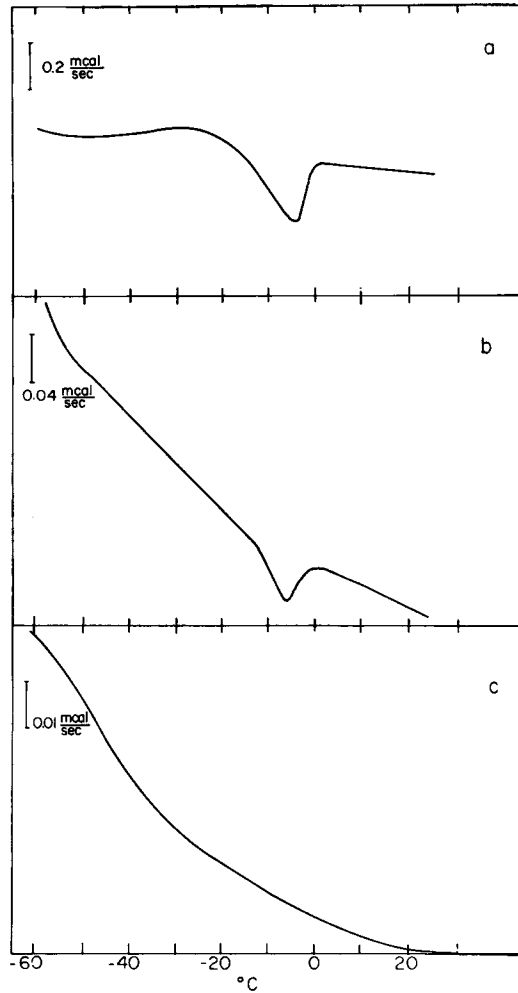
Fig. 5. DSC scan of wet membranes as function of temperature: (a) Nafion membrane; (b) SPE membrane; (c) SPS membrane.

for SPE in comparison with Nafion, and it is in agreement with the conclusions drawn in the previous section.

SUMMARY AND CONCLUSIONS

(1) The BPP model of dipole–dipole relaxation is only applicable to systems such as Nafion in which the water–organic matrix interactions are thermodynamically very weak. For systems with stronger interactions, e.g., SPE and SPS,

TABLE III
Heat Absorption for Water in Nafion

Weight membrane + water, mg	Weight water, mg	Rate of heating, °C/min	ΔH observed, $\times 10^3$ cal	ΔH, cal/g
12.9	2.6	5	28.2	10.8
11.4	2.3	20	25.6	11.1

TABLE IV
Heat of Fusion for Water in Systems of Different Pore Size

Material	Pore diameter, Å	ΔH_f, cal/g
SPS	12	—
Nafion	12	23
SPE		25
CA-20-T-IL-80[a]	< 500	34
CA-20-T-IL-95[a]	500–1000	61

[a] Cellulose acetate membranes of different pore size.[24,25]

the relaxation behavior no longer follows the BPP model, and a new model is required.

(2) T_1 was qualitatively found to depend on the Flory–Huggins χ parameter for the interaction between the water and the organic portion of the matrix.

(3) NMR and heat of fusion data indicate that the presence of small pores and interaction between the water and the organic matrix are the most significant factors that influence the state of water absorbed by the membrane   The presence of charged group aggregates does not appear to play an important role.

(4) The NMR study indicates that a number of environmental states for water exist in Nafion and that a fast exchange occurs between these states.

(5) The heats of fusion obtained for water in Nafion and SPE suggest that water present in membranes within fine pores behaves as a liquid which is significantly different in its physical properties from those of bulk water.

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