High-Pressure Electrical Conductivity and NMR Studies in Variable Equivalent Weight NAFION Membranes

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ABSTRACT: Measurements of the electrical conductivity and proton and fluorine-19 NMR spin−lattice relaxation times (T_1) in acid form NAFION 105, 117, and 120 conditioned at various levels of relative humidity have been carried out. Complex impedance studies were made along the plane of the polymer film at frequencies from 10 to 10^8 Hz at room temperature and pressures up to 0.3 GPa. The NMR measurements were made at room temperature and pressures up to 0.25 GPa. Both types of measurement were also carried out on various concentrations of sulfuric acid in water. The electrical conductivity decreases with increasing pressure for low water content acid solutions and low water content NAFION samples. This behavior (positive activation volumes) is that expected for "normal" liquids and for ions in polymers where the motion of the ions is determined by the host matrix. However, for high water contents, the reverse is true. The electrical conductivity increases with increasing pressure which gives rise to a negative activation volume. The results show that at high water contents, the electrical conductivity mechanism in NAFION is essentially identical to that for a dilute acid where the transport is controlled by the aqueous component. The activation volumes extracted from the proton NMR T_1 data are in qualitative agreement with those obtained from the electrical conductivity measurements at intermediate and low water contents, suggesting that motion of the sulfonic acid-terminated pendant chains contributes to the conduction mechanism at low water contents.

Introduction

Because of their possible application in fuel cells, the electrical conductivity of ion exchange membranes such as NAFION is of interest. While many studies of the electrical conductivity in these types of material have been carried out,[1−14] relatively little work has been reported on the effect of high pressure on the conductivity. Molecular motions and ionic diffusion are associated with volume fluctuations that can be probed directly by employing pressure (rather than temperature) as the thermodynamic variable. Understanding of the proton transport mechanism in NAFION can be greatly facilitated by investigating these volume fluctuations. In a previous paper, the authors have presented some results for the effect of high pressure on the electrical conductivity and proton, deuteron, and oxygen-17 NMR spin−lattice relaxation times (T_1) of NAFION 117,[12] and in another paper, further measurements on NAFION 117 were reported along with measurements on other molecular weight materials.[13] As pointed out in the latter paper, it was of interest to carry out the electrical conductivity measurements on higher water content material. Those experiments have been completed, and the results are reported in the present paper. In addition, ^{1}H and ^{19}F T_1 data are presented, the former as a probe of water molecular motion and the latter reflecting relaxations of the main polymer and pendant chains.

Experimental Details

All studies were carried out on NAFION 105, 117, and 120 forms of NAFION manufactured by E. I. DuPont de Nemours. Under dry conditions, the NAFION 117, 105, and 120 samples are approximately 0.17, 0.145, and 0.26 mm thick, respectively, and their respective repeat unit equivalent weights are 1100, 1000, and 1200.

For the electrical conductivity studies of NAFION, the samples were approximately 4 cm long and 1 cm wide. Gold was vacuum-evaporated onto the ends of the sample. The gold completely covered the ends of the sample (both sides and edges), leaving a strip of NAFION approximately 3 cm long and 1 cm wide. This configuration has been shown to give good agreement with the bulk conductivity reported by other workers.[4]

For the atmospheric pressure measurements, the samples were placed in sealed jars containing saturated solutions of various salts to control the relative humidity. The ends of the samples were connected to alligator clips attached to the ends of electrical feedthroughs which were epoxied into the lid of the jar. All samples were pretreated as described previously.[4] In each case the samples were dried over phosphorus pentoxide and then successively conditioned at about 15, 25, 45, 75, and 100% relative humidities using saturated solutions as described above. The atmosphere in a glovebox was also adjusted to each relative humidity using the saturated solutions, and measurements of the dimensions and mass of the samples were carried out in the glovebox. The weight percent of water in the samples for the atmospheric pressure measurements was calculated by dividing the change in mass by the mass of the dry samples.

For the high-pressure electrical conductivity measurements, both the liquid and solid samples were isolated from the pressure fluid (Spinesstic 22) using techniques similar to those recently applied to gel electrolytes.[15] Briefly, the samples were sealed inside rubber tubing and then clamped onto the closure plug of a high-pressure vessel. In the case of the liquid samples, $^1/_8$ in. i.d. Viton tubing about 5 cm long was used, and stainless steel plugs were used in the ends of the tubing. In the case of the solid materials, four terminal measurements were carried out for one sample ($\lambda = 10$, NAFION 117).

The equivalent parallel capacitance and resistance of the samples were determined using a CGA-83 capacitance bridge ($10-10^5$ Hz) and/or a Hewlett-Packard 4194A impedance/gain-phase analyzer. All data were then transformed to the complex impedance, $Z^* = Z' - jZ''$.

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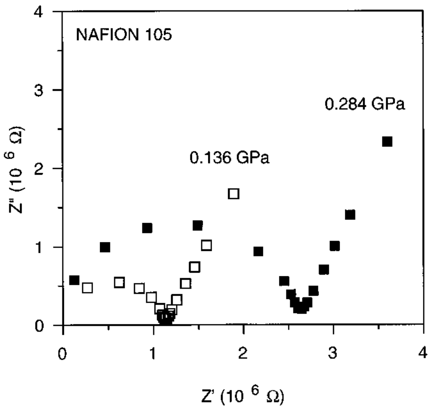

Figure 1. Complex impedance diagrams at two pressures for NAFION 105 containing 2.8 wt% ($\lambda = 1.6$) of water. The solid squares (0.2843 GPa) and open circles (0.1361 GPa) represent datum points obtained using a CGA-83 capacitance bridge. The frequencies increase from right to left, and the maximum frequency for that bridge is 10^5 Hz.

For ^{1}H NMR measurements, the samples were tightly sealed in Teflon tape immediately after determining their water uptake, and Fluorinert FC-72 (3M Co.) was employed as the pressure-transmitting fluid. Both the Teflon and Fluorinert were checked for absence of appreciable ^{1}H NMR signals. Proton T_1's were measured by inversion recovery at a Larmor frequency of 39 MHz, with a typical inverting pulse width of 10 μs. The variable pressure measurements on the acid solutions were accomplished by putting a small amount ($\approx$10 μL) of liquid into a two-piece Teflon piston-type cell. For ^{19}F T_1 measurements, also conducted at 39 MHz, the samples were sealed in a polyurethane rubber sheath, and Spinesstic 22 was utilized as the pressure-transmitting fluid. Some effects of pressure history were observed, in particular a slight decrease in activation volume (up to about 25%) after one or two pressure cycles. For consistency, all T_1's reported correspond to the decreasing pressure portion of the first cycle.

Results

Electrical Conductivity vs Water Content. Typical results for the electrical studies of NAFION are shown in Figure 1 in the form of complex impedance diagrams. In general, an impedance arc, attributable to the bulk properties of the material, is observed at the highest frequencies. In addition, a slanted line, due to electrode effects, is observed at the lowest frequencies. Because of the wide range of conductivity of the samples and different capabilities of the measuring instruments, different portions of the arc or line are observed for different samples at different water contents and pressures.

The data exhibit a slightly depressed semicircular arc, similar to that seen in other ion-conducting polymers.[16] This is consistent with the observation by various groups[4,11] that the electrical conductivity is attributable to a simple, frequency-independent conductivity mechanism. In the present work, all intercepts due to semicircular arcs were obtained graphically. The intercept of the impedance data with the Z' axis was taken to be the bulk resistance, R, of the sample. The conductance, $G = 1/R$, was then calculated from the intercept and transformed to the electrical conductivity, σ, via

$$\sigma = Gl/A \tag{1}$$

where A is the area of the sample and l is the length.

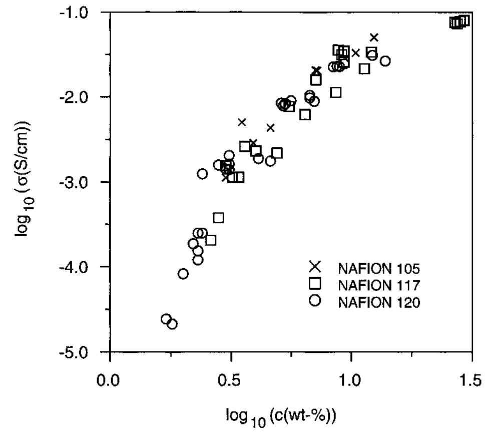

Figure 2. Electrical conductivity vs water content for various samples of NAFION 105, 117, and 120 at room temperature (about 298 K). All of the data for NAFION 105 are new. Some of the results for NAFION 117 and 120 are new, and the remainder are from ref 13.

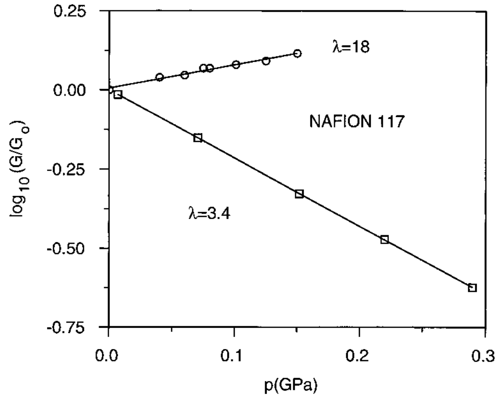

Figure 3. Relative electrical conductance vs pressure at room temperature (about 298 K) and various pressures for NAFION 117 containing water. The circles represent a high water content sample, $\lambda = 18$ waters per sulfonate, and the squares represent a low water content sample, $\lambda = 3.4$ waters per sulfonate. Also shown are the best-fit straight lines.

The results for the variation of the electrical conductivity with water content are shown in Figure 2. All of the data for NAFION 105 are new. Some of the results for NAFION 117 and 120 are new, and the remainder are from ref 13. (Two of the datum points from ref 13 are not included.) While NAFION 105 tends to exhibit a slightly higher conductivity, the different equivalent weight samples are almost indistinguishable when the conductivity data are plotted vs weight percent of water. However, for a given value of λ, which is the number of waters per sulfonate ion, the electrical conductivity is highest for NAFION 105 and lowest for NAFION 120.

Electrical Conductivity vs Pressure. Because of the steps required for loading the NAFION samples into the rubber tubing, it was possible that the water content of the sample could change during the process. Consequently, the electrical conductivity of the sample while it was inside the tubing was used to estimate the water content. The procedure was to calculate the electrical conductivity at approximately atmospheric pressure and then determine the water content from the empirical line shown in Figure 3 of ref 13. Consequently, the water contents reported in Table 1 represent indirect, albeit in situ, values of the water uptake divided by the mass of the dry samples.

Typical results for the variation of the electrical conductance with pressure are shown in Figure 3. As previously reported, the electrical conductance decreases with increasing pressure for low water content materi-

Table 1. Effect of Pressure on the Electrical Conductivity for Various Forms of NAFION with Different Water Content at Room Temperature

wt% H_2O	λ	$\partial \ln G/\partial p$ (GPa^{-1})	$\chi_T/3$ (GPa^{-1})	$\partial \ln \sigma/\partial p$ (GPa^{-1})	ΔV (cm^3/mol)
		NAFION 105			
2.8	1.6	−5.76	0.1	−5.66	+13.9
28.2	15.7	0.44	0.15	0.59	−1.45
		NAFION 117			
2.7	1.6	−4.76[a]	0.1	−4.66	11.4
3.5	2.1	−4.02[a]	0.1	−3.92	9.63
3.5	2.1	−4.06[a]	0.1	−3.96	9.72
4.0	2.4	−2.85[a]	0.1	−2.75	6.74
4.5	2.7	−2.80[b]	0.1	−2.70	6.63
5.6	3.4	−2.15[a]	0.1	−2.05	5.02
5.6	3.4	−2.15, −2.28[a]	0.1	−2.05, −2.18	5.02, 5.34
7.4	4.5	−1.18[b]	0.1	−1.08	2.63
16.4	10	0	0.15	0.15	−0.37
22.9	14	0.41	0.15	0.56	−1.38
24.5	15	0.29	0.15	0.44	−1.08
29.5	18	1.70	0.15	1.85	−4.55
		NAFION 120			
2.4	1.6	−6.54[a]	0.1	−6.44	15.8
2.8	1.9	−6.06[a]	0.1	−5.96	14.6
4.1	2.7	−3.09[a]	0.1	−2.99	7.33
4.2	2.8	−3.05[a]	0.1	−2.95	7.23
6.9	4.6	−1.02, −1.22[a]	0.1	−0.92, −1.12	2.24, 2.73
15.8	10.5	0.41	0.15	0.56	−1.38

[a] Reference 13. [b] Reference 12.

Table 2. Effect of Pressure on the Electrical Conductivity for Various Aqueous Solutions of Sulfuric Acid at Room Temperature

λ	$\partial \ln G/\partial p$ (GPa^{-1})	$\chi_T/3$ (GPa^{-1})	$\partial \ln \sigma/\partial p$ (GPa^{-1})	ΔV (cm^3/mol)
0	−0.75	0.15	−0.60	+1.48
2.2	0	0.15	+0.15	−0.37
9.6	0.54	0.15	+0.69	−1.70
14.8	0.80	0.15	+0.95	−2.34

als.[12,13] However, for high water content the behavior is opposite; i.e., the slope is positive. The values of the pressure variation of the conductance were calculated from best fits to the data, and the results are given in Table 1. The results for the various water/H_2SO_4 solutions are listed in Table 2.

Next, the pressure derivative of the electrical conductance was converted to pressure derivative of the electrical conductivity using

$$\left(\frac{\partial \ln \sigma}{\partial p}\right)_T = \left(\frac{\partial \ln G}{\partial p}\right)_T + \frac{\chi_T}{3} \tag{2}$$

where χ_T is the isothermal compressibility. Values of χ_T for the materials studied in the present work do not seem to be available. Consequently, the following approximations have been made. For the polymer at low water content, a value of $\chi_T = 0.3$/GPa was used, which is slightly larger than the value given for poly(tetrafluoroethylene).[17] For the high water content polymer and for the aqueous solutions of sulfuric acid a value of $\chi_T = 0.45$/GPa was used, which is the value for water.[18]

Finally, an activation volume was calculated from the pressure variation of the electrical conductivity via

$$\Delta V = -kT[\partial \ln \sigma/\partial p]_T \tag{3}$$

The results for NAFION are given in Table 1 and are plotted in Figure 4. The new and interesting feature, of course, is that at high water content the activation volume for NAFION is negative. It is noted that the fact that the activation volume is negative for high water content NAFION is not a consequence of estimating the compressibility. The reason is that, as can be seen from Table 1, for high water content NAFION, $\chi_T/3$ is a positive correction to a positive pressure derivative $(\partial \ln G/\partial p)_T$, and thus the only way that $\chi_T/3$ can change the sign of $(\partial \ln \sigma/\partial p)_T$, and hence ΔV, is if the compressibility is negative, which is unphysical. NMR results, which are also plotted in Figure 4, also reveal a decreasing activation volume with increasing water content, although the activation volume does not become negative even at the highest water concentrations. These observations are discussed later. The results for the water/H_2SO_4 solutions are listed in Table 2 and plotted in Figure 5.

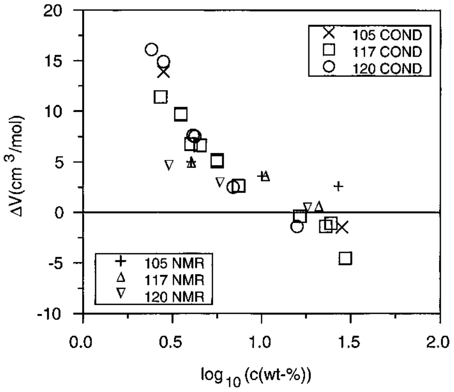

Figure 4. Activation volume vs water content in weight percent for various samples of NAFION 105, 117, and 120 at room temperature (about 298 K).

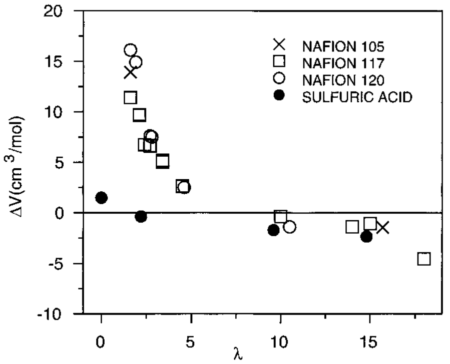

Figure 5. Activation volume vs water content in λ, which is the number of waters per sulfonate, for various samples of water in sulfuric acid and NAFION 105, 117, and 120 at room temperature (about 298 K).

NMR vs Pressure. In water-containing NAFION at room temperature, the so-called fast motion approximation, namely $\omega\tau_c \gg 1$, can be employed, where ω is the Larmor frequency and τ_c is the motional correlation time.[19] In this regime the spin-lattice relaxation rate $1/T_1$ is proportional to τ_c, and the activation volume for spin−lattice relaxation is given approximately by

$$\Delta V = -kT[\partial \ln T_1/\partial p]_T \tag{4}$$

Figure 6 displays T_1 vs pressure data for NAFION 105 (a), NAFION 117 (b), and NAFION 120 (c), for films with varying amounts of water. Least-squares straight-line fits to the data yield activation volumes that are listed in Table 3 and also plotted in Figure 4. While single, straight-line fits to some of the data (in particular

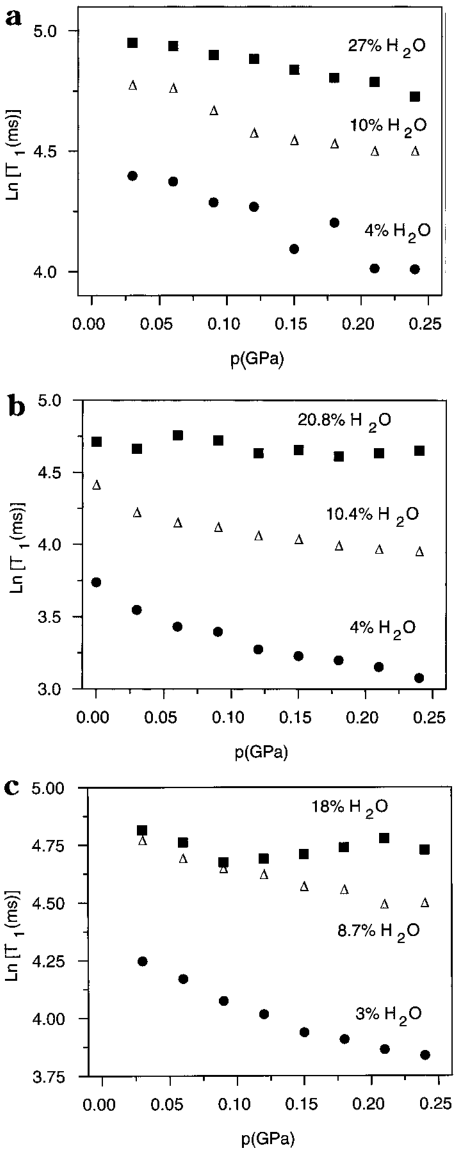

Figure 6. Proton NMR T_1 vs pressure for various equivalent weights of NAFION and water concentrations: (a) NAFION 105, (b) NAFION 117, and (c) NAFION 120.

Table 3. NMR Activation Volume

wt% H_2O	λ	ΔV (cm^3/mol)
	NAFION 105	
4	2.3	5.0 ± 0.2
10	5.7	3.6 ± 0.2
27	15.4	2.6 ± 0.3
	NAFION 117	
4	2.4	4.8 ± 0.4
10.4	6.2	3.5 ± 0.3
20.8	12.3	0.5 ± 1.0
	NAFION 120	
3	2.0	4.5 ± 0.4
8.7	5.8	2.8 ± 0.3
18	12.0	0.3 ± 1.0

10% water in Figure 6a, 4 and 10.4% in Figure 6b, and 18% in Figure 6c) are not entirely appropriate, the average slopes are still regarded as meaningful because of the trend of decreasing average slope with increasing water content. The ^{19}F T_1 vs pressure results are shown in Figure 7, again for NAFION 105 (a), NAFION 117 (b), and NAFION 120 (c). Because of substantial scatter within the very small variation of ^{19}F T_1 vs pressure, the corresponding activation volumes for most of the samples are not regarded as significantly different from zero. Least-squares fits for those samples that exhibit noticeable pressure dependence (NAFION 105 with 3% water and NAFION 117 with 4 and 22% water) yield activation volumes of about 1.5 ± 0.5 cm^3/mol.

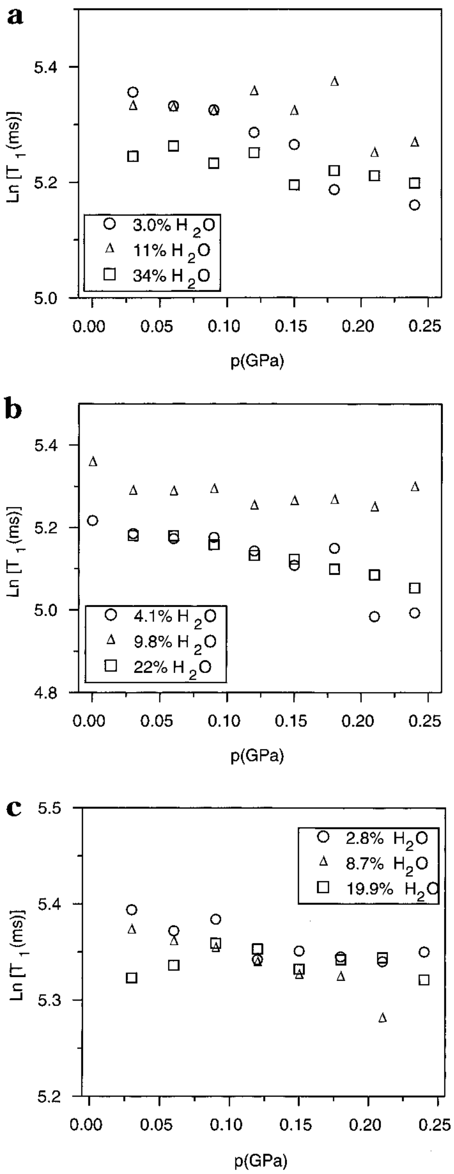

Figure 7. Fluorine-19 NMR T_1 vs pressure for various equivalent weights of NAFION and water concentrations: (a) NAFION 105, (b) NAFION 117, and (c) NAFION 120.

For comparison with the ^1H NMR results for NAFION, T_1 vs pressure data for two different water/H_2SO_4 solutions, corresponding to $\lambda = 5$ and $\lambda = 2$, are displayed in Figure 8. Again, because of the small fluctuations of the data about approximately zero slope, the activation volumes for water/H_2SO_4 solutions are regarded as essentially zero, at least in the pressure range employed in this investigation.

Discussion

NMR T_1 vs Pressure. For all three membranes, there are two clear trends regarding the ^1H NMR data: (i) T_1 increases with increasing water content; (ii) the activation volume increases with decreasing water content. The first observation simply reflects the decreased water molecular mobility at lower water content, which enhances the relaxation by decreasing τ_c

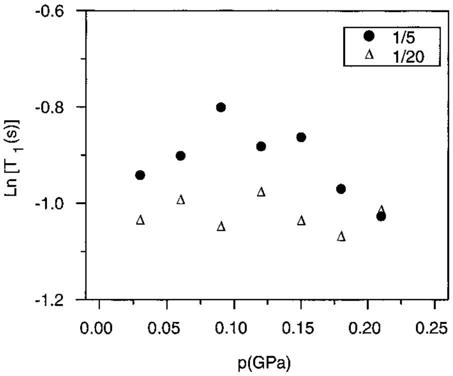

Figure 8. Proton NMR T_1 vs pressure for various amounts of sulfuric acid in water.

toward the value of ω^{-1}. The second trend is similar to that exhibited by the conductivity and will be discussed in more detail later. Briefly, at low water content water molecular relaxation requires some assistance from pendant chain motions, thus leading to increased activation volume. The activation volume at high water content, not surprisingly, approaches the value of liquid water (nearly zero in the current pressure range). The addition of H_2SO_4 to water does not appreciably change the activation volume, as indicated in Figure 8.

The ^{19}F relaxation data exhibit no clear trends, that is, T_1 is approximately independent of both water content and pressure. Given that over 80% of the fluorines reside in the relatively immobile (and, in the current pressure range, incompressible) PTFE backbone, this result is not entirely unexpected. For the samples that do show a slight pressure dependence, the small and positive activation volumes are indicative of restricted polymer chain motion under pressure.

Electrical Conductivity vs Water Content. As mentioned above, Figure 2 shows that the electrical conductivity of all three equivalent weights of polymer are essentially the same when they contain the same amount of water. That is not particularly surprising for low water content since there is little difference between the polymers, and it has been shown that at low water content electrical transport is governed by the polymer.[13] As will be shown in the next section, for high water content samples, the electrical conductivity is determined by the water itself, and thus varying the equivalent weight should have little effect.

Next, it should be apparent that for a given number of water molecules per sulfonate, constant λ, NAFION 105 has the highest conductivity while NAFION 120 has the lowest. This is expected since NAFION 105 will have the most protons (charge carriers) per unit volume and NAFION 120 will have the least.

Finally, Figure 2 shows that as the water content increases, the electrical conductivity increases relatively smoothly. The extent to which this behavior can be explained by present theories of NAFION (percolation, etc.) remains to be determined.

Electrical Conductivity vs Pressure. As has been previously shown,[1,12,13] NAFION exhibits two well-defined regions, one for $\lambda < 5$ (region i) and one for $\lambda > 5$ (region ii). These two regions are correlated with the ability of NAFION to absorb water from the vapor phase.[1] Specifically, Zawodzinski et al.[1] found that for $\lambda < 5$ water uptake occurs very slowly with increasing water vapor activity. This is the region corresponding to solvation of the proton and sulfonate ions. For $\lambda > 5$ of Zawodzinski et al.,[1] the polymer begins to swell rapidly as the water content increases. Consequently, in this regime the water begins to fill the space between the polymer chains.

Activation Volume, Region i. In a previous paper,[13] it was shown that in region i the activation volumes for NAFION 117 and 120 increase to large positive values as the water content decreases. The result for NAFION 105, listed in Table 1 and plotted in Figures 4 and 5, shows that it also exhibits a large activation volume at low water content. It was pointed out[13] that those activation volumes are typical of the values observed in the widely studied solvent-free polymer electrolytes.[16] This suggested that in region i electrical transport is controlled by segmental motions of the polymer. In the usual model of NAFION at low water content, there are "clusters" of water molecules and ions separated by polymer. The model, then, is that, for low water content NAFION, ions are moving through the amorphous polymeric regions between the "clusters", and it is the segmental motions of the polymer, presumably the pendant chains, which control this motion. The ^1H NMR activation volumes are highest in region i, although they do not rise to the extent that the conductivity values do as the water content is decreased. Again, this reflects the still dominant (even for $\lambda \approx 3$) contribution of water molecular motion, including rotation, to the T_1 process.

It is noted that this discussion of the activation volume assumes that there is no contribution from the formation of charge carriers; i.e., it is assumed that high pressure does not generate any charge carriers. In fact, the temperature variation of the electrical conductivity supports this conclusion since it has been shown that the electrical conductivity in dry NAFION exhibits non-Arrhenius VTF or WLF behavior,[20-22] and it is well-known that VTF behavior is typical of ion motion controlled by segmental motion of the polymer. This is, of course, the case in the widely studied solvent-free polymer electrolytes.[16] Also, Xu and co-workers have found VTF or WLF behavior in other ion-exchange membranes.[10,11,23] In addition, there are other polymer electrolytes similar to NAFION (stiff backbones and flexible side chains) which also exhibit VTF or WLF behavior.[24,25] In any of those cases, if the generation of charge carriers were dominant, the electrical conductivity would be expected to be Arrhenius. Consequently, it is concluded that, for low water content NAFION, the change of the electrical conductivity with pressure or temperature is attributable to changes in ion mobility only. Zawodzinski et al.[1] have also concluded that ionic mobility in low water content membranes is intimately tied to polymer motions.

The situation is not so clear for highly concentrated sulfuric acid. It is clear from either Table 2 or Figure 5 that a small, positive activation volume is found. It is tempting to again assign the positive activation volume to ion motion and assert that a small increase in volume is necessary for the ions to move through the sulfuric acid. However, as no data appear to exist concerning the variation of the dissociation constants or ionic concentration with pressure for concentrated sulfuric acid, no strong statement can be made at the present time. However, the large difference in the activation volumes for concentrated sulfuric acid and dry NAFION implies that there is little similarity between ion transport in the two materials.

Activation Volume, Region ii. It is clear from Figures 4 and 5 that for region ii the activation volume for

NAFION as deduced from the electrical conductivity is negative; i.e., the electrical conductivity increases as pressure increases. In a previous paper,[13] it was suggested that the electrical conductivity in this region is controlled more by the water than by the polymer. This is, of course, consistent with the characteristics of region ii since there is a substantial amount of water between the polymer chains. The model, then, is that the protons move through the water, which contains extra protons from the polymer, and thus the conductivity would be expected to approach that for water or a dilute acid.

In fact, the activation volume for water is negative. For example, on the basis of early data, Conway[26] concluded that the volume of activation is between -2.4 and -2.9 cm^3/mol. A more recent value as calculated from the data of Hamann[27] and presented by Holzapfel[28] is -10.6 cm^3/mol. Also, Quist et al.[29] found that for 0.002 424 m sulfuric acid at 70 °C $d \ln \sigma/dp = 1.5$/GPa, which leads to a value of about -4.3 cm^3/mol. Since none of those measurements on liquids were carried out under the conditions of the present work, the studies of sulfuric acid solutions reported here were undertaken. It is obvious from Table 1 and Figure 5 that the volume of activation for the aqueous sulfuric acid solutions studied in the present work is consistent with the results from similar previous work. Specifically, the activation volumes for the acid studied in the present work are somewhat less negative than the value from Quist et al., which is in turn less negative than the value for pure water; that is, it follows the variation in concentration. Most importantly, as is apparent from Figure 5, the activation volumes for the acid at high water concentrations are similar to that for NAFION containing large amounts of water. This provides evidence that at room temperature the electrical conductivity in NAFION with high water content is similar to that for the equivalent sulfuric acid aqueous solution.

Consequently, the usual interpretation of proton motion in aqueous solutions at room temperature also applies to NAFION. Specifically, proton motion is usually interpreted in terms of transfer from a hydronium ion , H_3O^+, to a water molecule.[26] It is straightforward to explain a negative activation volume in terms of this mechanism. The activation volume for ion motion is usually interpreted as the volume change when a diffusing species transfers from a “normal” position to an “activated” position (sometimes referred to as the “saddle point”). For this mechanism, the “normal” state consists of two parts, a hydronium ion and a water molecule. The “activated” state may be thought of as a single system, two water molecules sharing a proton. Because of the sharing, the “activated” state would be expected to have a smaller volume than the “normal” state, hence the negative volume of activation.

However, this model for the activation volume for region ii assumes that there is no contribution from the formation (or destruction) of charge carriers; i.e., it is assumed that high pressure does not change the number of charge carriers. In fact, that probably is not the case. For example, essentially all of the large negative activation volume for water is usually interpreted in terms of dissociation of the water molecules; i.e., the increase of electrical conductivity with pressure is usually attributed to an increase in the dissociation constant.[28] Further discussion of this point is given below, however, it is clear that a more sophisticated model for the activation volume for region ii is necessary.

Effect of Pressure on the Electrical Conductivity, Region i. An alternative approach is to analyze the results in terms of the effect of pressure on the electrical conductivity. Specifically, the electrical conductivity in a liquid can written as[30]

$$\sigma = (n_A {z_A}^2 \mu_A + n_B {z_B}^2 \mu_B) F^2 \tag{5}$$

where the μ_A and μ_B are the mobilities of ions A and B, n_A and n_B are the concentrations, z_A and z_B are the charge numbers, and F is the Faraday constant. For the sake of simplicity, it will be assumed that there is only one type of charge carrier. In the case of NAFION, that is a good approximation since only one type of charge carrier is usually considered, protons, and this leads to the following approximation for the pressure dependence of the electrical conductivity:

$$\left(\frac{\partial \ln \sigma}{\partial p}\right)_T = \left(\frac{\partial \ln N}{\partial p}\right)_T + \chi_T + \left(\frac{\partial \ln \mu}{\partial p}\right)_T \tag{6}$$

where N is the number of charge carriers.

Further, the mobility can be rewritten in terms of viscosity, η, via Stokes’ law

$$\mu = N_A/6\pi\eta r \tag{7}$$

Equation 7 is based on the assumption that the size of the moving object is much larger than the size of the particles which make up the medium that it is moving through. Of course, this is not strictly valid for ions moving through NAFION; however, it provides a framework for discussing the effect of pressure on the electrical conductivity since eq 7 leads to

$$\left(\frac{\partial \ln \sigma}{\partial p}\right)_T = \left(\frac{\partial \ln N}{\partial p}\right)_T + \chi_T - \left(\frac{\partial \ln \eta}{\partial p}\right)_T \tag{8}$$

Using either eq 6 or 8 it is straightforward to understand the large, negative pressure derivative of the electrical conductivity which is observed for low water content NAFION. As discussed above, the temperature variation of the electrical conductivity provides evidence that few carriers are generated as pressure increases. Consequently, it is reasonable to assume that the first term on the right-hand side of eq 6 or 8 is approximately zero. It could also be argued that pressure might increase the number of charge carriers since it is known that the dissociation constant of water increases as pressure increases,[28] and thus the first term in eq 6 or 8 might be positive. Next, the second term on the right-hand side of eq 6 or 8, the compressibility, is always positive. Consequently, the large decrease of electrical conductivity as pressure increases can be explained by either a large decrease in the mobility of the protons or a large increase in the viscosity of the medium. This is reasonable and is what is expected for normal materials. In fact, a large increase in viscosity with pressure in polymers[31] is usually attributed to viscosity associated with segmental motions, and thus proton motion in NAFION in region i can again be attributed to segmental motions.

Again, the situation is not so clear for highly concentrated sulfuric acid, for which a small negative pressure derivative of the electrical conductivity is found. According to eq 6 or 8 the positive compressibility leaves approximately -1.0 /GPa to be explained by changes in the concentration of charge carriers and changes in either the mobility or viscosity with pressure. It is reasonable that viscosity should increase and hence mobility should decrease as pressure increases. Further, it is also reasonable that the number of charge carriers should increase with increasing pressure as it does for dilute sulfuric acid.[29] In this model, then, the first term on the right-hand side of eqs 6 and 8 is positive, and hence the pressure derivative of the mobility or viscosity will be somewhat more negative than -1.0/GPa. However, at the present time no data appear to exist concerning either the variation of the dissociation constants or ionic concentration or the behavior of the viscosity with pressure for concentrated sulfuric acid. Consequently, no definitive statements can be made concerning the relative contributions of ionic concentration or mobility to the pressure derivative of the electrical conductivity for concentrated sulfuric acid.

Effect of Pressure on the Electrical Conductivity, Region ii. As is apparent from Tables 1 and 2, for NAFION in region ii and dilute sulfuric acid the logarithmic pressure derivative of the electrical conductivity (left-hand side of eqs 6 and 8) ranges from $+0.51$ to $+1.85$/GPa. Interestingly, a large fraction of this variation can be accounted for by the second term on the right-hand side of eqs 6 and 8, the isothermal compressibility which merely represents an increase in the concentration because the volume decreases as pressure increases. While the exact value is not known, in both cases it is probably very close to 0.45/GPa, which is the isothermal compressibility for water. That leaves from about $+0.06$ to $+1.45$/GPa to be accounted for by the effect of pressure on the number of ions and the mobility/viscosity.

As regards the first term in eqs 6 and 8, the effect of pressure on the number of ions, it is most likely that the number will increase because, as pointed out above, it is well-known that the dissociation constant of water increases as pressure increases.[28] However, the extent to which that is applicable to either the NAFION or sulfuric acid environment is not clear. In the case of NAFION, there are two sources of protons. Protons come either from the solvation of the sulfonate groups on the polymer or from the water itself. In the case of the sulfuric acid, again there are effectively two “sources” of protons since sulfuric acid contains two protons; i.e., ionization of the first proton from sulfuric acid is different from the second ionization. Consequently, the number of protons for those systems is not known let alone the variation of pressure, and thus all that can be said about the first term in eqs 6 and 8 is that it may be positive.

However, the residual pressure derivative of the electrical conductivity can be explained by the third term in eqs 6 and 8. If, for example, the number of ions increases strongly as pressure increases, it would require that the mobility decrease or the viscosity increase. In fact, under the thermodynamic conditions of the present work, 300 K and 0.001−0.25 GPa, the viscosity of water is known to increase with pressure,[32,33] and consequently the explanation would be straightforward. On the other hand, if the contribution due to the change in the number of ions with pressure were small, zero or even negative, it would require the mobility to increase or the viscosity to decrease as pressure increases. In fact, these are well-known phenomena for water since in the early work,[31,32] it was shown that below about 293 K and 0.1 GPa the viscosity of water does indeed decrease with increasing pressure. This is interpreted as pressure breaking the local structure of water, thereby making it easier for ion or molecular motion. Again, under the conditions of the present work the viscosity actually increases with pressure. However, there is little doubt that water continues to have structure to relatively high temperatures[34] and that that structure will be broken by pressure. It is not inconceivable that a decrease in local water structure could cause an increase in the mobility of ions with pressure yet not be strong enough to dominate the macroscopic viscosity; i.e., it is possible for both the mobility of ions and the macroscopic viscosity to increase with pressure. The remainder of the increase in the electrical conductivity with an increase of pressure could then be accounted for by a modified relationship between the viscosity and the mobility. Obviously, further work concerning this point is necessary.

The ^{1}H NMR relaxation is dominated by water molecular motion, particularly in region ii. The pressure-induced generation of charge carriers (the first term in eqs 6 and 8), which clearly increases the conductivity, would not be expected to have a significant effect on T_1. That is, if negative activation volumes (T_1 increasing with increasing pressure) were observed, this would most likely reflect mobility/viscosity effects. In fact, there is no evidence that the NMR activation volumes change sign as the water content of NAFION is increased; rather, they steadily approach zero, as is the case for the aqueous acid solutions. This tends to support the view that the first term in eqs 6 and 8, i.e., charge carrier generation, is primarily responsible for the negative conductivity activation volume in high water content NAFION and dilute aqueous H_2SO_4 solutions.

Conclusions

In summary, then, several results have been obtained via measurements of the electrical conductivity for different equivalent weight, water-containing NAFION samples and various concentrations of sulfuric acid at high pressure. The electrical conductivity decreases with increasing pressure for concentrated sulfuric acid and low water content NAFION samples. This behavior (positive activation volumes) is that expected for “normal” liquids and for ions in polymers where the motion of the ions is determined by segmental motions of the polymer. However, for high water contents in both NAFION and sulfuric acid, the reverse is true. The electrical conductivity increases with increasing pressure, which gives rise to a negative activation volume. The results show that at high water contents the electrical conductivity mechanism in NAFION is essentially identical to that for a dilute acid where the transport is controlled by the aqueous component. These conclusions are supported by proton NMR T_1 measurements, which yield decreasing activation volumes with increasing water content, approaching the value obtained for aqueous H_2SO_4 solutions.

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