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Self-diffusion of water, ethanol and decafluropentane in perfluorosulfonate ionomer by pulse field gradient NMR

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Abstract

Self-diffusion constants for water, ethanol and decafluoropentane were measured in the perfluorosulfonate ionomer Nafion^{R} using pulse field gradient proton NMR. Measurements were made as a function of concentration, temperature and diffusion time. For water, diffusion constants ranged from 10^{-4} to 10^{-7} cm^2/s. A reasonable interpretation could be developed using free volume theory if the concentration was scaled by considering only the ionomeric pendant group as the accessible domain. The temperature dependence could be summarized in terms of the WLF equation. For ethanol, the self-diffusion constants are comparable in magnitude to those of water but the concentration dependence is stronger and the temperature dependence weaker. Free volume theory provides a poor framework for summarizing the concentration and temperature dependence of the diffusion of ethanol in Nafion. In an accompanying report, fluorine-19 spin diffusion and fluorine-19 line shape data indicate larger morphological changes in Nafion upon addition of ethanol and greater plasticization of the pendant group domain. The larger morphological changes are thought to contribute to the concentration dependence of diffusion making free volume theory inapplicable. The decafluoropentane diffusion constants appear to depend on the time scale over which the diffusion is observed. This is not true for the other two penetrants, which are considered to be primarily located in domains comprised of the sulfonate groups and side chains. The decafluropentane is likely to be located in amorphous domains composed of the CF_2 groups. The dependence of the self-diffusion constant of the decafluoropentane on diffusion time indicates that the domain or phase supporting transport is poorly interconnected. At long diffusion times, the product of the self-diffusion constant and the diffusion time becomes constant which is associated with restricted diffusion.

Keywords: Nafion; NMR; Diffusion

1. Introduction

The transport of ions through the perfluorosulfonate ionomer Nafion (Dupont trademark) has been widely studied because of the electrochemical applications of this material in such areas as ion selective electrodes and fuel cells [1,2,3]. The permeability of Nafion to low molecular weight gases has also been measured since membranes of this material also show selectivity again with possible applications [4]. The transport of water [5], and low molecular weight alcohols [6] across Nafion membranes has been observed to be very rapid which allows for the prospect of the separation of water from organic molecules which do not contain ionizable or hydrogen bonding protons. However, it is difficult to extract a diffusion constant from permeability measurements in a complex material like Nafion since a number of corrections are required [7].

Self-diffusion constants can be directly determined by pulse field gradient NMR measurements. Careful measurements of this type have been made for water in Nafion as a function of chemical activity [8]. However, a larger range of measurements for different types of molecules as a function of temperature and concentration would be useful. If Nafion is strongly plasticized, it might be possible to consider diffusion in terms of typical polymeric interpretational approaches such as free volume theory for concentration dependence and WLF for temperature dependence [9,10]. This approach is applicable for diffusion of a penetrant in a matrix undergoing segmental motion [11]. Free volume concepts would not be expected to apply to the viscoelastic response of bulk Nafion but they may allow for a reasonable interpretation of the environment experienced by a small solvent molecule diffusing through a plasticized region in Nafion. The application of these interpretational approaches is complicated by the complex morphology of Nafion and by morphological changes induced by the addition of a strongly interacting solvent. To clarify this aspect, a

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morphological study based on fluorine-19 spin diffusion was made and reported in an accompanying report [12].

The self-diffusion constant of ethanol is also considered here since it is comparable to that of water and the morphology of Nafion in the presence of ethanol is determined in the accompanying morphological study as well. Solvents are expected to produce morphological changes in the ionomer and each solvent could induce different changes [13]. Thus it will be helpful to compare self-diffusion, morphology and permeability. To achieve the latter comparison, permeability measurements were performed on the same commercial samples of Nafion and are reported elsewhere [7]. In the interpretation of permeability, it is helpful to have an independent measurement of the self-diffusion constant as well as morphological information.

In contrast to the behavior of water and ethanol, penetrants which are presumed to interact more strongly with the hydrophilic regions of Nafion, it would be informative to study a penetrant which is hydrophobic in character and interacts more favorably with the perfluoroethylenic regions. The partially fluorinated pentane, $CF_3CHFCHFCF_2CF_3$, is absorbed to a small extent in Nafion and its translational diffusion can also be probed though the concentration range is limited.

The morphology of ionomers and Nafion in particular is an area of considerable activity over the years and there has been an ongoing interplay of diffusion measurements and morphological measurements [14]. The experimental approach that has had the most impact on the morphological models of Nafion and other ionomers is small angle X-ray scattering (SAXS). The salt forms of Nafion display an 'ionic peak' which has been widely considered as a spherical cluster of cations and the associated anion from the pendant group of Nafion. Water and other hydrogen bonding solvents are considered to be sorbed into these clusters. However to account for the rapid diffusion of water, the existence of channels between the clusters has been proposed. The channels have also been considered as the source of selectivity in the transport of ions through Nafion. The material outside the clusters is considered to be largely composed of perfluoroethylene groups, which are present in both crystalline and amorphous forms. The cluster concept has been embellished over the years and various forms of this model could be used to interpret the volume fraction of clusters, which support transport. Some local arrangement of the clusters relative to each other is required for this and one model [15] uses spheres on a diamond lattice and allows for long range disorder.

From the point of view of fluorine-19 spin diffusion measurements and xenon-129 chemical shifts reported in the accompanying report, there are two main sorption environments in Nafion as in the cluster model. However, the NMR data do not require the existence of spherical clusters to be interpreted and indeed Eisenberg [16] in reviewing the morphological studies concludes that the clusters could be a continuous phase since there is no evidence for the existence of channels. Thus for the purposes of interpreting the self-diffusion data of water and ethanol, a continuous phase consisting of ionic groups and/or pendant groups will be considered as the environment primarily supporting the transport of water and ethanol. This environment will be considered as having a random spatial character. There is the possibility that the pathway for diffusion in such a system will be tortuous or otherwise impeded by domains less permeable to these molecules. Pulse gradient diffusion measurements can detect tortuosity [17,18] or restricted diffusion [19] in multiphase systems since the apparent diffusion constant could depend on the overall time scale of the experiment. This is especially likely if the phase supporting transport is a minor component of the system. This experimental signature will be checked as measurements are made. In this regard, the behavior of the partially fluorinated pentane, which presumably penetrates the amorphous perfluoroethylenic regions of the polymer, will contrast with the phase consisting of the pendant groups and probe the other region not involved in the rapid transport of hydrogen bonding solvents.

Why might free volume and WLF type behavior be encountered? In the pendant group/ionic group phase in the presence of solvents, some part of the polymeric system could undergo local segmental motion. On the length scale of the penetrant, the friction experienced might then be similar to that of a swollen polymeric rubber undergoing segmental motion. However the pendant group phase is quite rigid in the absence of solvents like water and ethanol. Thus segmental motion would cease at low concentrations unlike a rubber and one should therefore expect that a free volume extrapolation to zero concentration would not be meaningful. However the nature of solvent motion at moderate to high levels within the pendant group domain might still be considered in a free volume framework. Since the system as a whole does not consist of a single phase, the bulk viscoelastic response will not be that of a swollen polymeric rubber but at the local level it may be a satisfactory approach. Again the presence of tortuosity or restricted diffusion [17–19] leads to an experimental signature in the PFG data and in relating self-diffusion to a property such as permeability this factor must be included as well.

2. Experimental

Diffusion experiments were performed on Bruker MSL 300 and Varian Inova 400 spectrometers with a high resolution gradient accessories and gradient probes. The Bruker system was used for the water measurements and the Varian system for the ethanol and decafluoropentane measurements. The well known Stejskal–Tanner pulse sequence $\pi/2–G(\delta)–\pi–G(\delta)–$(echo) was used to measure the diffusion constant of both water and ethanol and the stimulated echo sequence $\pi/2–G(\delta)–\pi/2–\tau–\pi/2–G(\delta)–$(echo) was

used when diffusion was slow and long times between gradient pulses were required [19]. In the case of ethanol the aliphatic resonances only were used in all the determinations: the inclusion of the OH resonance yielded faster diffusion coefficients due to exchange processes. The strength of the magnetic field gradients was varied from 14 to 140 Gauss/cm. The length of δ was in the range 1 to 5 ms and the time between gradient pulses, Δ, was in the range 3–600 ms. The length scale of diffusion is microns given this time scale and diffusion constants in the range of 10^{-5} to 10^{-8} cm^2/s.

Nafion in the hydrogen form was purchased from Aldrich and has an equivalent weight of 1250 g per ionic unit. The Nafion was dried in a vacuum oven for several days at a temperature of 80°C to remove most of the residual water. Known weights of either water, ethanol or decafluoropentane were then added to a sample of Nafion in an NMR tube which was then sealed. The sample was allowed to equilibrate at a temperature of 50°C for several days. After equilibration the diffusion constant measured did not change over a period of months.

3. Results

Fig. 1 displays the self-diffusion constants for water as a function of concentration at a series of temperatures. Fig. 2 is a similar plot for the self-diffusion of ethanol in Nafion. Fig. 3 is a plot of the apparent diffusion constant as a function of Δ, the time scale of the diffusion measurement, for ethanol and the decafluoropentane.

4. Interpretation

The concentration dependence of the diffusion coefficients at a given temperature can be expressed using Fujita free volume theory [9–11] as

$$\ln \frac{D}{D_0} = \frac{((f_s/B_d) - (f_p/B_d))\phi_s}{(f_p/B_d)^2 + (f_p/B_d)((f_s/B_d) - (f_p/B_d))\phi_s}, \qquad (1)$$

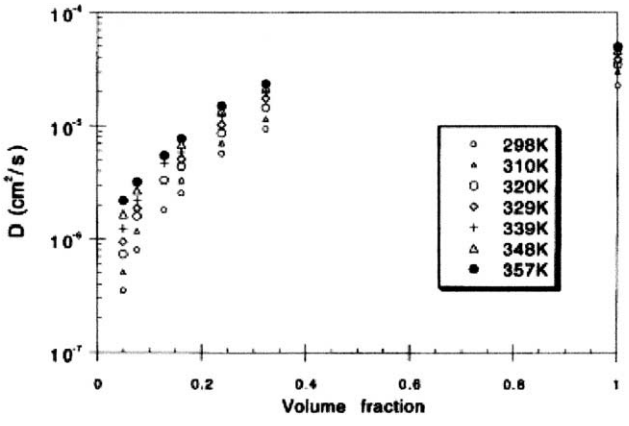

Fig. 1. The self-diffusion constants, D (cm^2/s), for water in Nafion as a function of concentration at a series of temperatures.

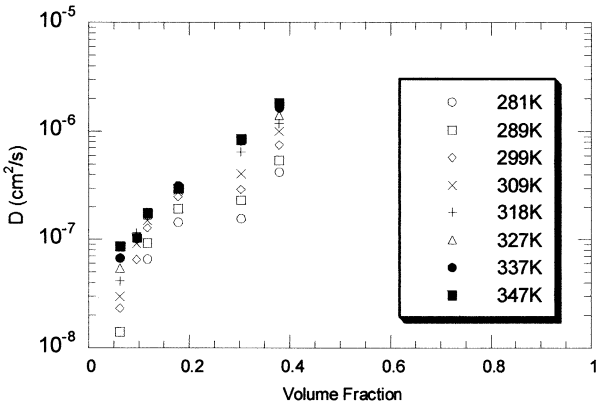

Fig. 2. The self-diffusion constants, D (cm^2/s), for ethanol as a function of concentration in Nafion at a series of temperatures.

where f_p is the fractional free volume of the polymer, f_s is the fractional free volume of the solvent, B_d is the minimum hole size needed to allow the molecule in question to undergo displacement, and ϕ_s is the volume fraction of the penetrant.

In the case of a two phase system such as Nafion where the penetrant is present mainly in only one phase, the volume fraction of the penetrant will be calculated based on only that fraction of the Nafion volume which is accessible to the penetrant. To a first approximation the accessible volume for either water or ethanol would be the volume of the pendant group phase, $V_{pendant}$. This view of the swelling process in Nafion was used in the interpretation of the fluorine-19 spin diffusion study of morphology and it led to a consistent view of the changes upon the addition of a penetrant and also indicated important differences between water and ethanol.

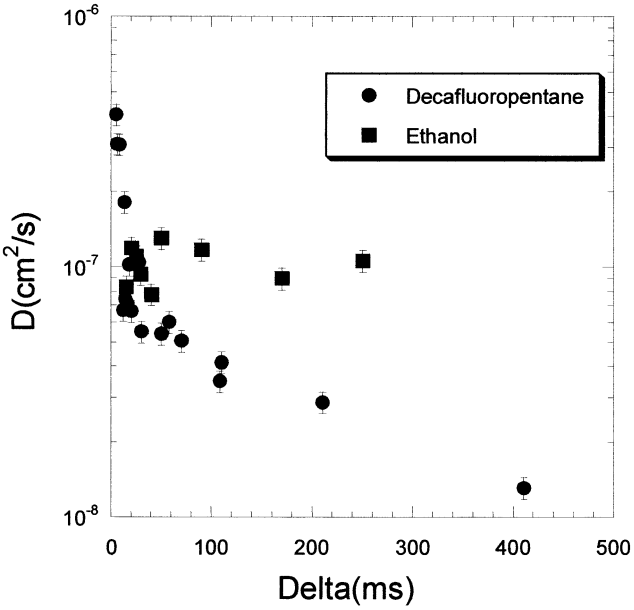

Fig. 3. The apparent self-diffusion constant as a function of Δ, the time during which diffusion is measured, for ethanol and decafluoropentane (CF3CHFCHFCF2CF3) in Nafion.

Table 1
Concentration of water in Nafion for diffusion measurements

Weight fraction	Volume fraction	ϕ_s
0.0253	0.0494	0.148
0.0394	0.0758	0.215
0.0685	0.1282	0.329
0.0876	0.1611	0.390
0.1312	0.2320	0.502
0.1570	0.2390	0.511
0.1929	0.3234	0.614

Table 2
Free volume parameters for water in Nafion

T (K)	D_0 (cm^2/s)	f_p/B_d	f_s/B_d
298	4.46×10^{-8}	0.089	0.222
310	6.26×10^{-8}	0.091	0.225
320	1.14×10^{-7}	0.093	0.220
329	1.25×10^{-7}	0.091	0.211
339	1.92×10^{-7}	0.096	0.222
348	2.50×10^{-7}	0.098	0.225
357	3.27×10^{-7}	0.101	0.230

For dry Nafion the pendant group domain will be considered to have a volume fraction corresponding to the weight of the pendant group, 363, divided by the equivalent weight of 1250. For the swollen Nafion, the volume associated with a weight of pendant chain is calculated assuming a density of 2.0 g/cm^3.

$$\phi_s = (V_{solvent})/(V_{solvent} + V_{pendant}). \quad (2)$$

Table 1 lists the weight fraction water, volume fraction water considering the total weight of Nafion and the parameter ϕ_s as defined above.

Fig. 4 displays sample fits of the diffusion data for water as a function of the concentration variable ϕ_s using Eqs. (1) and (2) at a series of temperatures. The parameters of the fit are D_0, f_p/B_d and f_s/B_d and the resulting values of these parameters are shown in Table 2.

The same procedure can be applied to the concentration dependence of the self-diffusion constants for ethanol in Nafion. First the concentration parameters for the ethanol measurements are listed in Table 3.

A free volume fit of the concentration dependence is then performed using ϕ_s as the relevant variable. The parameters of the fit are listed in Table 4 and sample fits are shown in Fig. 5. It should be pointed out that the free volume description is not nearly as suitable for ethanol as it is for water. There is considerably more scatter and suitable parameters are only obtained for the intermediate temperatures shown in Table 4. At low concentrations and low temperatures the error in the D determination is high. At the higher temperatures the dependence of D on ϕ_s is relatively flat. As will be discussed later, it is likely that these complications are associated with the large morphological changes induced in Nafion by the addition of ethanol [12]. For a limited range of temperatures, a Fujita free volume description can be applied which will at least allow for a comparison of the parameters with those obtained for water.

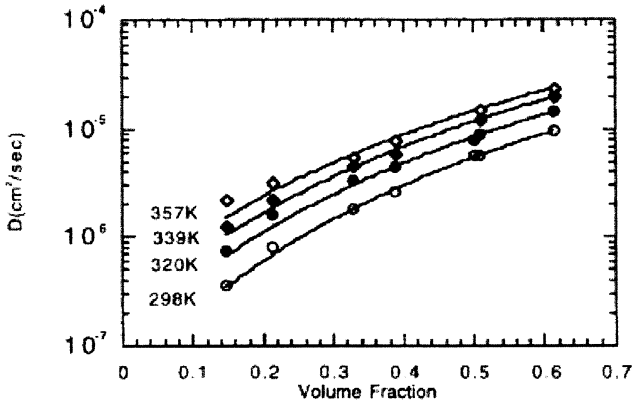

Fig. 4. Fits of the water diffusion data as a function of the concentration variable ϕ_s to the Fujita free volume theory using Eqs. (1) and (2) at a series of temperatures.

Table 3
Concentration of ethanol in Nafion for diffusion measurements

Weight fraction	Volume fraction	ϕ_s
0.0259	0.062	0.181
0.0400	0.095	0.258
0.0500	0.116	0.305
0.0800	0.178	0.420
0.1476	0.302	0.599
0.1952	0.378	0.680

The temperature dependence of the self-diffusion constants at a given concentration can be analyzed using the following form of the WLF equation [10]

$$\ln\left(\frac{DT_0}{D_0T}\right) = \frac{(\alpha(\phi_s)/B_d)(T-T_0)}{(f(\phi_s)/B_d)((f(\phi_s)/B_d) + (\alpha(\phi_s)/B_d)(T-T_0))}, \quad (3)$$

where $f(\phi_s)$ is the fractional free volume of the solution, $\alpha(\phi_s)$ is the fractional free volume expansion factor and T_0 is the reference temperature. The diffusion constants plotted as a function of temperature and the corresponding fits according to Eq. (3) are shown in Fig. 6 for water with the parameters of the fit given in Table 5.

In the case of the ethanol data, the leveling off of D at higher temperatures affects all of the WLF fits and a consistent

Table 4
Free volume parameters for ethanol in Nafion

T (K)	D_0 (cm^2/s)	f_p/B_d	f_s/B_d
299	1.3×10^{-10}	0.09	0.53
309	4.8×10^{-11}	0.08	0.61
318	2.3×10^{-10}	0.09	0.55
327	6.4×10^{-9}	0.09	0.19

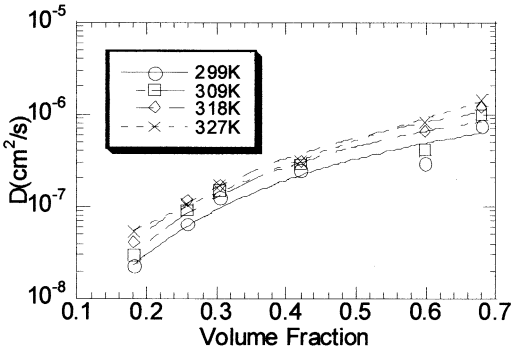

Fig. 5. Fits of the ethanol diffusion data as a function of the concentration variable ϕ_s to the Fujita free volume theory using Eqs. (1) and (2) at a series of temperatures.

progressive fit of all the compositions is not possible. Again this is ascribed to the greater morphological changes, which occur with the ethanol relative to the water behavior. The best data which could be described by WLF consequently occur at the lower concentrations and for example at 2.59 wt% ethanol ($\phi_s = 0.181$) a good fit to the WLF Eq. (3) is obtained with $\alpha(\phi_s)/B_d = 0.008$ and $f(\phi_s)/B_d = 0.42$. This fit is shown in Fig. 7.

The diffusion data as a function of diffusion time, Δ, in Fig. 3 show contrasting behavior for ethanol relative to

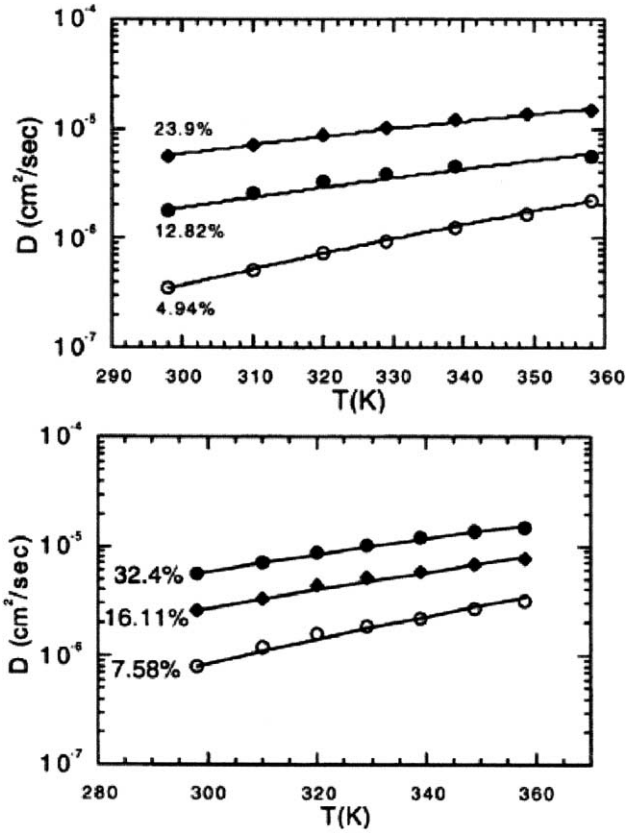

Fig. 6. The temperature dependence of the water self-diffusion constants in Nafion at various concentrations. The lines represent fits to the WLF Eq. (3) [10].

Table 5
WLF parameters for water in Nafion

ϕ_s	$f(\phi_s)/B_d$	$\alpha(\phi_s)/B_d$
0.148	0.0752	1.78×10^{-4}
0.215	0.122	3.52×10^{-4}
0.329	0.137	3.60×10^{-4}
0.390	0.171	5.55×10^{-4}
0.511	0.218	7.70×10^{-4}
0.614	0.279	1.27×10^{-3}

decafluoropentane. The independence of the ethanol diffusion constant on time suggests that there is no evidence for tortuosity or restricted diffusion on the length scale of microns. In other words at the concentration measured and over the length scale probed, ethanol has an unimpeded pathway for transport through Nafion. This can be interpreted to indicate that the region occupied by the pendant groups forms a continuous phase for transport of hydrogen bonding solvents. On the other hand the data for $CF_3CHFCHFCF_2CF_3$ shows the apparent D decreasing more than an order of magnitude. This is clearly indicative of the penetrant encountering barriers on a length scale of microns. A plot of the product of the apparent diffusion constant times the diffusion time Δ shown in Fig. 8 increases to a plateau value of about 5×10^{-9} cm^2. This is characteristic of restricted diffusion [19] as opposed to tortuous diffusion. In the case of tortuous diffusion, the apparent diffusion constant itself reaches a plateau at large Δ and the product of D with Δ monotonically increases. Thus the data for decafluoropentane in Nafion has the dependence on diffusion time, which is typical of restricted diffusion. The distance over which diffusion is unimpeded can be estimated based on simple models for restricted diffusion [19]. If a spherical geometry is assumed, the relationship is

$$D\Delta = a^2/5, \tag{4}$$

where a is the radius over which diffusion is unrestricted. Application of Eq. (4) leads to a value for a of 1.6 μm.

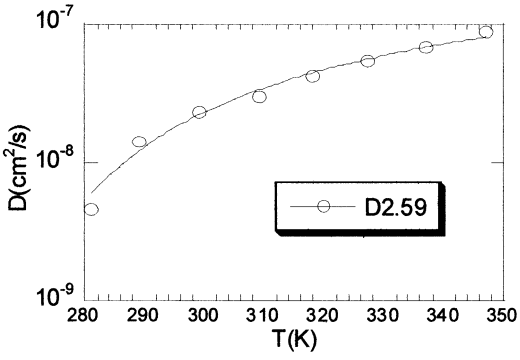

Fig. 7. The temperature dependence of the ethanol self-diffusion constants in Nafion at 2.59 wt% concentration. The line represents a fit to the WLF Eq. (3) [10].

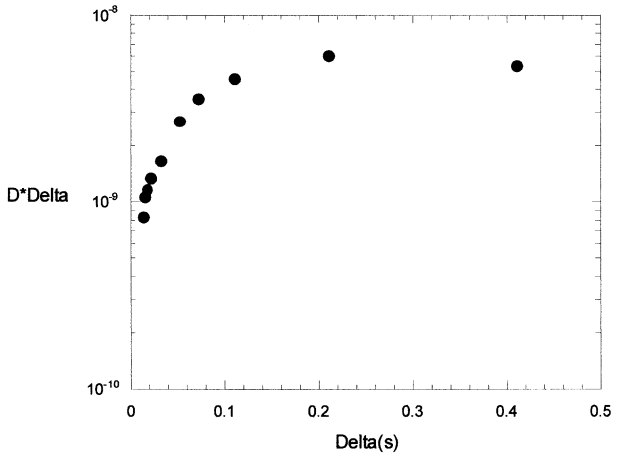

Fig. 8. The product $D \times \Delta$ versus Δ for decafluoropentante in Nafion.

5. Discussion

For water a Fujita type free volume analysis considering only the pendant group domain as accessible to the penetrant appears to yield a reasonable description of the experimental data leading to normal free volume parameters. The free volume parameter associated with the polymer f_p/B_d is about 0.09 to 0.10 For comparison a study of the diffusion of toluene in poly(isobutylene) was made by pulse field gradient NMR and a similar analysis was performed as a function of concentration and temperature. Of course in that case all the polymer volume is considered as accessible and there are no strong interactions between solvent molecules or between solvent molecules and functional groups on the polymer. For poly(isobutylene), f_p/B_d varied from 0.09 to 0.14 over a temperature range comparable to this study of Nafion. Thus considering the diffusion of water in Nafion to be controlled by polymer chain dynamics (free volume) leads to sensible parameters in spite of the potential for effects such as hydrogen bonding and ionization to complicate matters. Similarly, the free solvent volume parameter f_s has typical values as well; about 0.22. These are again much like the values determined for organic solvents in largely hydrocarbon based polymers. The values of D_0 in Table 2 should not be taken too seriously. These correspond to an extrapolation to zero concentration of water and the pendant group phase is glassy at the temperatures studied in the absence of water.

In the case of ethanol for the limited concentration range analyzed with free volume theory, the values of f_p/B_d are similar to that for water, about 0.08 to 0.09 while the result for f_s is 0.2 to 0.6 for ethanol. The somewhat larger values obtained for f_s for ethanol again reflect the complications in the ethanol system which result from the much greater uptake and the potential morphological changes arising from the increased domain swelling in this case. Also the values for D_0 become very small. The value of f_s and D_0 are both somewhat unreasonable probably because the effect of the large morphological changes is incorporated into the free volume fits. Thus while it might be surprising that the self-diffusion constant of water in Nafion can be plausibly discussed in the context of free volume theory, there is no such surprise for the ethanol data.

If the polymer fractional free volume parameters determined from the concentration dependence of self-diffusion for water are plotted as a function of temperature as shown in Fig. 9, and then fitted to an equation of the form

$$f_p(T) = f_p(T_0) + \alpha_p(T - T_0), \tag{5}$$

where α_p is the thermal expansion coefficient for the polymer, a value of 9.1×10^{-5} is obtained for α_p when water is the solvent. This value is again of reasonable magnitude. Likewise, the value for the solvent thermal expansion coefficient can be determined and for water the value is 1.7×10^{-4}.

All of the free volume analyses performed and discussed here are based on water and ethanol only accessing the pendant group domain. The volume of the pendant group domain was determined by the weight fraction of the polymer that is pendant group. This approach was used because the morphological interpretation of swelling based on fluorine-19 spin diffusion led to reasonable results using this assumption and no assumption of geometrical shape was required. However one might use one of the typical cluster pictures. For instance, the original cluster model of Gierke and Hsu [11] calculates the diameter of a cluster to be 3.88 nm with a Bragg spacing of 4.55 nm. For purposes of discussion, they employ a simple cubic lattice to array the clusters. One can calculate the volume fraction of the system that is clusters to be 0.32. This was for the same equivalent weight Nafion as studied here at a weight fraction water of 0.15. If the volume fraction is calculated following the approach employed to interpret the NMR data, which assumes that the volume fraction is that of water plus the pendant group, then this becomes a volume fraction of 0.48. Essentially the difference leading to the two estimates of the accessible volume fraction is that the Gierke and Hsu model only includes the SO_3^- group in the cluster while the whole

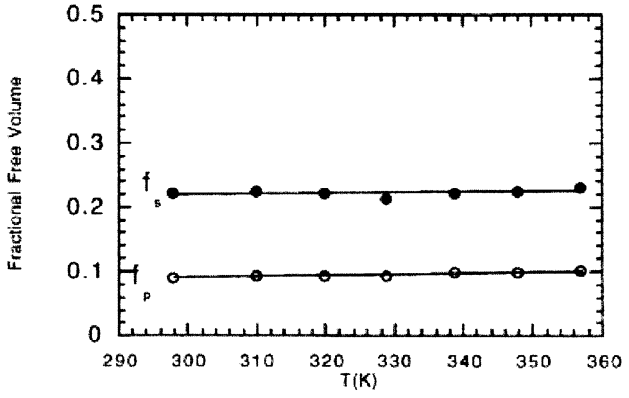

Fig. 9. The fractional free volume parameters as a function of temperature according to Eq. (4) for the water in Nafion.

pendant group is included in the accessible volume in the interpretation of the NMR data. Other interpretations [15] consider the water itself to be the cluster in the interpretation of SAXS and small angle neutron scattering (SANS) and the accessible volume fraction is just the volume fraction of water. If none of the Nafion is assumed to be in the cluster or only a little of the Nafion is in the cluster (just the SO_3^- groups), then a fit of the diffusion data as a function of concentration using Fujita free volume equations does not lead to reasonable free volume parameters. To get reasonable free volume parameters one must assume that 30 to 40% of the Nafion is in the cluster which is roughly the fraction of the system which is pendant group. Of course some of the polymer must be in the cluster to have a free volume type dependence since it assumes that segmental motion of a piece of the polymer controls the friction experienced by the penetrant.

A large accessible volume fraction is also consistent with lack of any evidence of tortuosity in the pulse field gradient diffusion measurements which is observed by us for ethanol (Fig. 3) and by others [8] for water. Of course the possible fractal character of the domain through which diffusion proceeds can also affect the apparent level of tortuosity. The method used here to estimate the accessible volume fraction is simplistic and should not be regarded as precise. It is arbitrary to include the pendant group but not the part of the backbone to which the pendant group is attached. There is likely to be disorder in the sense that in some cases some backbone units are in the accessible domain and in some cases perhaps only the ionizable group is in the accessible domain.

Also ethanol appears to plasticize Nafion more readily producing larger domains. Perhaps a different choice of the fraction of the polymer to be considered in the accessible domain should be made for ethanol. However such refinements cannot be made quantitatively without a better rationale for the definition of accessible volume.

The behavior of the decafluoropentane diffusion has further morphological implications. Namely, the phase that it accesses, the perfluoroethylenic backbone, or more specifically the amorphous component of it, consists of poorly interconnected regions, which lead to the apparent existence of restricted diffusion. Since this is the majority domain, at first glance it is difficult to understand poor interconnectedness. However, in the morphological study accompanying this report, only half of the perfluoroethylenic domain is mobile at temperatures above the glass transition for this type of unit and thus appears to be amorphous. This conclusion was reached based on the analysis of the fluorine-19 line shapes in swollen and unswollen Nafion. It was proposed that the immobile component should be associated with ordered regions, which are crystalline or nearly crystalline. Such crystalline regions are inaccessible to large penetrant molecules such as the decafluoropentane. The level of crystallinty is generally considered to be lower than fifty per cent as determined by diffraction experiments. Since the perfluoroethylenic regions are only several nanometers in thickness, there may be crystalline type order but it may be too small to diffract and thus appear crystalline in X-ray experiments. The NMR line shape data used mobility to define amorphous and more ordered regions so a larger level of order could result because small or less perfectly ordered regions would still be considered ordered in the NMR case. If half of the perfluoroethylenic regions are inacessible to penetrant, then the prospect of restricted diffusion is more reasonable. It was also noted in preliminary permeability measurements that the decafluoropentane shows very slow transport although it was soluble [20].

Table 6
Activation energy values

ϕ_s	ΔH_D (kJ/mole)	E_D (kJ/mole)
0.148	26.9	23.2
0.215	19.8	17.5
0.329	19.1	14.1
0.390	16.4	14.0
0.511	14.6	11.9
0.614	13.9	12.0

The WLF parameters listed in Table 5 for water are again plausible values at least qualitatively consistent with the Fujita fitting based on concentration. An activation energy can be calculated from the WLF parameters using the relationship

$$E_D = \frac{R(298)^2(\alpha(\phi_s)/B_D)}{(f^2(\phi_s)/B_D^2)} \quad (6)$$

The resulting values of E_D are given in Table 6. One could also assume an Arrhenius temperature dependence and analyze the self-diffusion constants as a function of temperature using the equation

$$D = D_0 \exp\left(-\frac{\Delta H_D}{RT}\right) \quad (7)$$

Values of H_D are also included in Table 6.

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References

[1] Eisenberg A, Yeager H, editors. Perfluorinated ionomer membranes. ACS symposium series 180. Washington DC: American Chemical Society, 1982.
[2] Yeager HL, Steck A. J Electrochem Soc 1981;128:1880.
[3] Verbrugge MW, Hill RF. J Electrochem Soc 1990;137:893.
[4] Pelligrino J, Kang YS. J Membrane Sci 1995;99:163.
[5] Morris DR, Sun X. J Appl Polym Sci 1993;50:1445.

[6] Yosida H, Miura Y. J Membrane Sci 1992;68:1.
[7] Rivin D, Kendrick CE, Gibson PW, Schnieder NS. Polymer 2001;42:623.
[8] Zawodzinski Jr TA, Neeman M, Sillerud LO, Gottesfeld S. J Phys Chem 1991;95:6040.
[9] Fujita H. Fortschr Hochpolym-Forsch Bd 1961;3:S. 1.
[10] Ferry JD. Viscoelastic properties of polymers. 3rd ed. New York: Wiley, 1980.
[11] Bandis A, Inglefield PT, Jones AA, Wen W-Y. J Polym Sci Polym Phys 1995;33:1495.
[12] Meresi G, Wang Y, Inglefield PT, Jones AA, submitted for publication.
[13] Chomakova-Haefke M, Nyffenegger R, Schmidt E. Appl Phys A 1994;59:151.
[14] Tant MR, Mauritz KA, Wilkes GL, editors. Ionomers. London: Blackie Academic and Professional, 1997.
[15] Gebel G, Lambard J. Macromolecules 1997;30:7914.
[16] Eisenberg A, Hird B, Moore RB. Macromolecules 1990;23:4098.
[17] Mitra PP, Sen PN, Schwatrz LM, LeDoussal P. Phys Rev Letts 1992;68:3555.
[18] Junker F, Veeman WS. Chem Phys Letts 1999;305:39.
[19] Callaghan PT. Principles of nuclear magnetic resonance microscopy. New York: Oxford University Press, 1991.
[20] Schnieder N, Rivin D, private communication.