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Complex Impedance Studies of S-SEBS Block Polymer Proton-Conducting Membranes

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Water uptake, swelling, ^{1}H pulsed gradient spin-echo nuclear magnetic resonance (NMR) and variable temperature and pressure complex impedance/electrical conductivity studies have been carried out on sulfonated styrene /ethylene-butylene /styrene (S-SEBS) triblock polymer proton conducting membrane. All of the data show different characteristics above and below about 10 wt-% water. For example, the diffusion coefficients, D from NMR and D_σ calculated from conductivity data (which are the same to within experimental uncertainty), show different dependence on water above and below about 10 wt-% At high water content, the properties of S-SEBS are similar to those for Nafion 117, proton transport being similar to that in bulk water. For low water contents, however, the materials are different. For low water content S-SEBS, the variation of the conductivity with temperature is Arrhenius while that for Nafion 117 is not. The variation of the electrical conductivity with pressure gives rise to activation volumes on the order of 14 cm^3/mol while those for Nafion 117 are about four times larger. These results indicate that proton transport in low water content S-SEBS occurs via a thermally activated process (ion motion via energy barriers) which is consistent with the rigid side chains in that material.

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Complex Impedance Studies of S-SEBS Block Polymer Proton-Conducting Membranes

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Abstract--Water uptake, swelling, ^1H pulsed gradient spin-echo nuclear magnetic resonance (NMR) and variable temperature and pressure complex impedance/electrical conductivity studies have been carried out on sulfonated styrene /ethylene-butylene /styrene (S-SEBS) triblock polymer proton conducting membrane. All of the data show different characteristics above and below about 10 wt-% water. For example, the diffusion coefficients, D from NMR and D_σ calculated from conductivity data (which are the same to within experimental uncertainty), show different dependence on water above and below about 10 wt-%. At high water content, the properties of S-SEBS are similar to those for Nafion 117, proton transport being similar to that in bulk water. For low water contents, however, the materials are different. For low water content S-SEBS, the variation of the conductivity with temperature is Arrhenius while that for Nafion 117 is not. The variation of the electrical conductivity with pressure gives rise to activation volumes on the order of 14 cm^3/mol while those for Nafion 117 are about four times larger. These results indicate that proton transport in low water content S-SEBS occurs via a thermally activated process (ion motion via energy barriers) that is consistent with the more rigid side chains in that material.

Keywords: Electrical Conductivity, Polymer Electrolytes, Proton Conducting Membranes, Activation Volume, High Pressure

Chemical Compounds: sulfonated styrene /ethylene-butylene /styrene triblock polymer.

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INTRODUCTION

Sulfonated styrene /ethylene-butylene /styrene (S-SEBS) triblock polymer is of interest because it is a proton conductor. In fact, S-SEBS is employed by the Dais-Analytic Corporation as a low cost proton conductor for use in hydrogen fuel cells. As S-SEBS is a relatively new material, only a few papers describing the properties of this material have been reported [1,2]. However, S-SEBS is particularly interesting because of the structural differences between it and the widely studied Nafion or Dow materials [3-10]. The important differences are both the composition of the backbone, hydrocarbon vs. fluorocarbon, and nature of the sulfonate group, connected via a benzene ring vs. fluorocarbons.

In an attempt to learn more about S-SEBS, a variety of experiments have been carried out including complex impedance/electrical conductivity and ^1H pulsed gradient spin-echo nuclear magnetic resonance (NMR) studies. All studies are carried out at various water contents. In addition, the electrical conductivity studies were carried out over a range of temperatures and pressures. All results are compared with results for fluorocarbon-based proton conductors, some of which are reported for the first time.

EXPERIMENTAL DETAILS

All studies were carried out on S-SEBS manufactured by the Dais-Analytic Corporation. For the S-SEBS used in this work, approximately 60% of the styrene units were sulfonated. The material was on the order of 0.06 mm thick and was cut into strips approximately 1 cm wide by 3 cm long. Gold was sputtered onto the ends of the sample. All electrical measurements were carried out along the plane of the samples using the same geometry as that used previously for fluorocarbon-based materials [10].

The samples were dried for several weeks at room temperature and atmospheric pressure in a glove box with a water content of less than 1.0 ppm. The mass and dimensions of each sample were measured in situ. Next, the samples were placed in a chamber where the relative humidity was controlled by an ETS Model 514 Automatic Humidity Controller using an ETS 5612C Ultrasonic Humidification System. After allowing the samples to reach equilibrium, the mass and dimensions were again measured. The wt-% of water in the samples for the atmospheric pressure experiments was calculated by dividing the change in mass by the mass of the dry samples.

While the samples remained in the chamber, the audio frequency complex impedance of the samples, $Z^* = Z' - jZ''$, was measured using a CGA-83 Capacitance bridge, a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer or a 1255 Solartron High Frequency Response Analyzer connected to a Solartron 1296 Dielectric Interface. The high pressure electrical conductivity measurements for various water content materials and the conductivity as a function of temperature for a dry sample were carried out as described previously for Nafion materials [5,10].

The techniques used to carry out ^1H pulsed gradient spin-echo nuclear magnetic resonance experiments are given elsewhere [11].

RESULTS AND DISCUSSION

Water Uptake and Sample Volume *vs.* Water Content

The results for the water uptake of S-SEBS are shown in fig. 1 along with the results of similar experiments on Nafion 117. (The results for Nafion 117 have not been published previously.) The most important feature is that above about 10 wt-% water uptake (about 75% relative humidity) S-SEBS begins to take up water more rapidly i.e. above 10 wt-%, small increases in the relative humidity result in larger increases in the water uptake than for water contents below about 10 wt-%. It is also interesting that for all measured values of relative humidity S-SEBS absorbed a greater equilibrium wt-% water than Nafion 117 and the greater the relative humidity, the more substantial the difference in water absorption. Next, as shown in fig. 2, the membrane swells in approximately linear proportion to the wt. % water absorbed.

Electrical Conductivity *vs.* Water Content

The complex impedance diagrams for the S-SEBS membrane are similar to those observed for the various Nafions [10] and Dow materials [8]. In general, an impedance arc, attributable to the bulk electrical 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. The data were transformed to the electrical conductivity, σ, using techniques described elsewhere [10].

The results for the variation of the electrical conductivity with water content are shown in figs. 3a and 3b. For comparison, both figures include some previously published work for Nafion 117 [10]. The figure shows that, as expected, the electrical conductivity for S-SEBS decreases as the water content decreases. However, the dependence of the electrical conductivity of S-SEBS on water content differs from the fluorocarbon-based materials. As is apparent from fig. 3a, for water uptake values below about 10 wt-% the electrical conductivity of S-SEBS begins to decrease rapidly with decreasing water content and at low water content the electrical conductivity of S-SEBS is as much as an order of magnitude less than for Nafion 117. However, it is important to realize that S-SEBS has more sulfonate groups (per unit volume) than does Nafion 117. Consequently, for a given weight percent water uptake, S-SEBS has significantly fewer water molecules per sulfonate group than Nafion 117. This points out that at low water content the side chains have a significant influence on the electrical conductivity. Clearly, the effect of the side chains is to lower proton transport in S-SEBS as compared with Nafion 117. This is consistent with the nature of the side chains and what is known about Nafion 117 since the side chains in S-SEBS are more rigid than those in Nafion 117 and it is well known that at low water content electrical transport is controlled by the side chains [7,10]. An important additional consideration is that the basicity of the phenyl sulfonate group is S-SEBS is expected to be higher than that of the fluorosulfonate in Nafion, and thus at low water content hydronium ions and attendant water molecules in S-SEBS will be more tightly bound to sulfonate counterions [12].

The results in fig. 3a also show that for water contents greater than about 10 wt-% the electrical conductivity of S-SEBS is about the same as for Nafion 117. The interpretation is that for high water content in both materials, the electrical conductivity approaches that of bulk water. This interpretation has been given previously for Nafion 117 [7,10].

Fig. 3b is a plot of the electrical conductivity vs. λ, the number of waters per sulfonate. It is apparent that for values of λ less than about 2.5 the conductivities of S-SEBS and Nafion 117 are approximately the same. This is probably fortuitous reflecting the increased proton mobility in S-SEBS due to a greater amount of water. Interestingly, for values of λ greater than about 2.5 the conductivity of S-SEBS is larger than that for Nafion 117. This also probably just reflects the greater amount of water in the S-SEBS i.e. the approach to bulk water occurs at a smaller value of λ because of the greater water content.

Electrical Conductivity *vs.* Temperature (low water content)

The results for the electrical conductivity vs. temperature for dry S-SEBS are plotted in fig. 4. The results for various fluorocarbon-based materials are included for comparison. (The results for Nafion 117 are from ref. 4 and those for Dow 1000 have not been published previously.) It is clear that dry S-SEBS exhibits Arrhenius behavior. The activation enthalpy is 0.66eV. By contrast, Nafion 117 and Dow 1000 exhibit non-Arrhenius behavior. Again, the difference is attributed to the different side chains. Specifically, these results for the fluorocarbons represent strong evidence that proton transport in low water content fluorocarbon-based materials is due to segmental (presumably side-chain) motions [5,10]. That is reasonable since those side chains are flexible. Again, the side chains in S-SEBS are expected to be significantly less flexible than those in the fluorocarbon-based materials, and the counterion basicity is expected to be greater. Consequently, it is more likely that proton motion in S-SEBS will take place via motions of the host which are more vibrational in nature (thermally activated process of ions and energy barriers) and thus it is not surprising that Arrhenius behavior is observed.

Electrical Conductivity *vs.* Pressure

Plots of the electrical conductance vs. pressure are similar to those observed previously for Nafion 117 [10]. The pressure derivative of the conductance was converted to the pressure derivative of the electrical conductivity using the equations and estimated value of the compressibility, χ_T, given elsewhere [10]. Finally, the activation volume, ΔV, was calculated from the pressure variation of the electrical conductivity via:

$$\Delta V = -kT\,[d\ln\sigma/dp]_T. \qquad (1)$$

The results of the experiments and calculations are given in Table 1. Fig. 5 is a plot of ΔV vs. water content for S-SEBS.

At very low water content an activation volume of 13.7 cm^3/mole is observed. This is approximately one fourth of the value obtained for low water content Dow 1000 and Nafion 117 [8]. This trend is consistent with the interpretation given above for proton motion in these materials at low water contents. Specifically, the large values obtained for Dow and Nafion have been attributed to segmental motions in the electrical conductivity of these materials at low water content [8,10] since they are typical of those observed in traditional polymer electrolytes [13]. On the other hand, the small values observed in S-SEBS are typical of those observed for thermally activated ion motion such as those which occur in crystals [14]. Again, this is attributed to the relatively rigid side chains of S-SEBS.

As is also apparent from fig. 5, ΔV decreases as water content increases and, in fact, becomes negative at the highest water contents. This is similar to the results for Nafion and Dow materials [8,10]. The negative activation volumes represent evidence that proton transport in the highest water content materials is the same as that in bulk water since ΔV for water is negative [10].

Next, as shown in fig. 6, an interesting result is obtained when the activation volumes are plotted vs. the log of the electrical conductivity. There appears to be an approximately exponential relationship between the activation volume and the electrical conductivity, at least in the range of medium to low water content, for both S-SEBS and Nafion 117. The data for S-SEBS can be well represented by:

$$\sigma = (0.0118)\exp(-\Delta V/1.30) \qquad (2)$$

A similar result has been observed for a traditional ion-conducting polymer, poly(propylene glycol) containing $LiCF_3SO_3$ [14].

A qualitative explanation of this type of behavior based on free volume is given elsewhere [8,13]. In addition, a recent theory based on defect diffusion provides a quantitative explanation of the results [15]. Most importantly, it is apparent from fig. 6 that there is a significant difference between the behavior of Nafion and S-SEBS, the slope of the curve for S-SEBS being almost three times smaller. This is taken to be further proof of a difference in transport mechanism between the two systems, at least at low water contents.

NMR Results

The NMR results for the diffusion coefficient vs. water content are shown in Fig. 7 along with some new results for Nafion 117. Values for the diffusion coefficient, D_σ calculated from the Nernst-Einstein [16,17]:

$$\sigma = q^2 n D_\sigma/(k_B T) \qquad (3)$$

are also shown. In eq. (3), q is the charge per charge carrier, n is the number density of the charge carrier, k_B is the Boltzmann constant and T is the absolute temperature. As shown in fig. 7 the diffusion coefficients determined by the two methods at high water content are approximately the same and imply that the measured quantities are the result of the same physical effect. The results for Nafion 117 are different than the previously published results of

Zawodzinski and coworkers [18] who report a difference between values determined by NMR and conductivity as the water content increases. This difference was used to imply that proton transport by Grotthus hopping becomes increasingly significant as water content increases. In contrast to this, the current results imply that transport at high water content is by molecular diffusion [9].

However, for low water content S-SEBS, the value of D is larger than that for D_σ. This suggests that proton transport in S-SEBS does not occur via molecular diffusion at low water content. Again, this is consistent with the present interpretation.

CONCLUSIONS

Several types of data reported in the present paper indicate an abrupt change in the properties of S-SEBS when the water content exceeds about 10 wt-%. First, the rate of water uptake becomes more rapid as the relative humidity exceeds the value at which the water content is about 10 wt-%. Second, the rate of increase in the electrical conductivity with an increase in water content slows significantly. Third, the activation volume becomes negative. Fourth, the rate of change of the diffusion coefficient (as determined by electrical conductivity) with an increase in water content is much smaller. The implications of the abrupt change in the properties including a detailed discussion of the applicability of percolation are given elsewhere [19]. Next, the data indicate that at high water content, proton transport in S-SEBS is similar to that for bulk water which is that same as for Nafion 117. At low water content, the behavior of S-SEBS is different from Nafion in that it is a thermally activated process such as might be expected for ion motion via an energy barrier.

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Table I. Effect of pressure on the electrical conductivity for S-SEBS.

T (K)	σ (S/cm)	Water Content (wt-%)	λ	$\frac{d\ln G}{dp}$ (GPa)$^{-1}$	$\frac{\chi_T}{3}$ (GPa)$^{-1}$	$\frac{d\ln\sigma}{dp}$ (GPa)$^{-1}$	ΔV (cm^3/mol)
294.5	3.29×10^{-5}	0.5	0.09	-4.11	0.1	-4.01	9.8
295.5	4.47×10^{-4}	4.3	0.75	-5.33	0.1	-5.23	12.8
295.5	8.45×10^{-4}	5.8	1.01	-1.46	0.1	-1.36	3.3
295.5	6.20×10^{-4}	11.7	2.05	-0.64	0.1	-0.54	1.31
292.6	8.60×10^{-3}	13.6	2.38	+0.13	0.1	+0.23	-0.56
292.6	1.70×10^{-2}	18.6	3.25	+0.14	0.1	+0.24	-0.58

FIGURE CAPTIONS

Figure 1. Water content in wt-% vs. relative humidity at room temperature. The values for Nafion 117 are new and are represented by the open squares. The half-filled squares are the values for S-SEBS.

Figure 2. Percent volume change vs. water content in wt-% for S-SEBS at room temperature.

Figure 3. (a) Electrical conductivity vs. water content in wt-% at room temperature. (b) Electrical conductivity vs. λ, the number of water molecules per sulfonate, at room temperature. The values for Nafion 117 are from ref. 7 and are represented by the open squares. The half-filled squares are the values for S-SEBS.

Figure 4. Electrical conductivity vs. 1000 / T in K^{-1} for dry S-SEBS. The solid line is a best fit linear curve which corresponds to an activation enthalpy of 0.66 eV. The results for Nafion 117 are from ref. 4 and those for Dow 1000 are new.

Figure 5. Activation volume vs. water content in wt-% for S-SEBS at room temperature

Figure 6. Activation volume vs. electrical conductivity, σ, for S-SEBS and Nafion 117. The solids line represent best-fit exponentials.

Figure 7. Diffusion coefficient from ^1H NMR and electrical conductivity vs. water content in wt-% for S-SEBS and Nafion 117. The legend is the same as that for fig. 8.

Figure 8. Log_{10} of the diffusion coefficient vs. water content in wt-%.

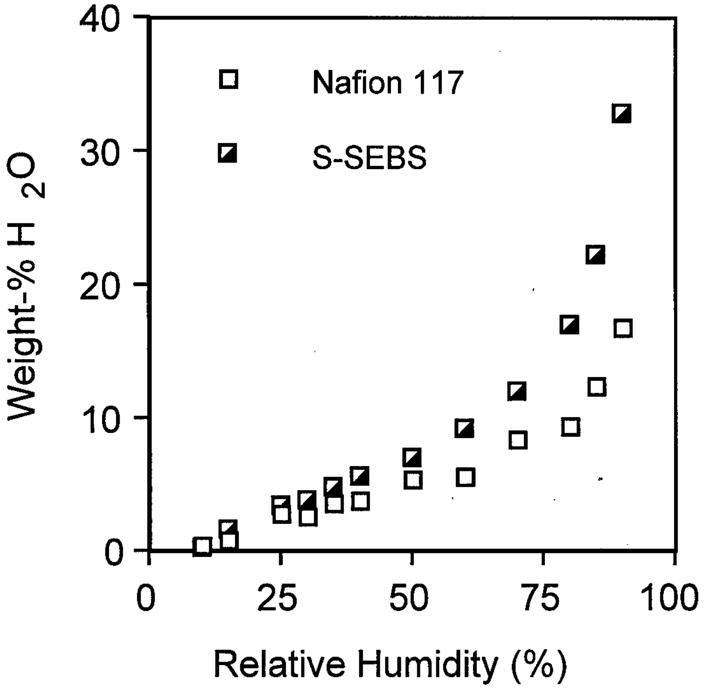

Figure 1
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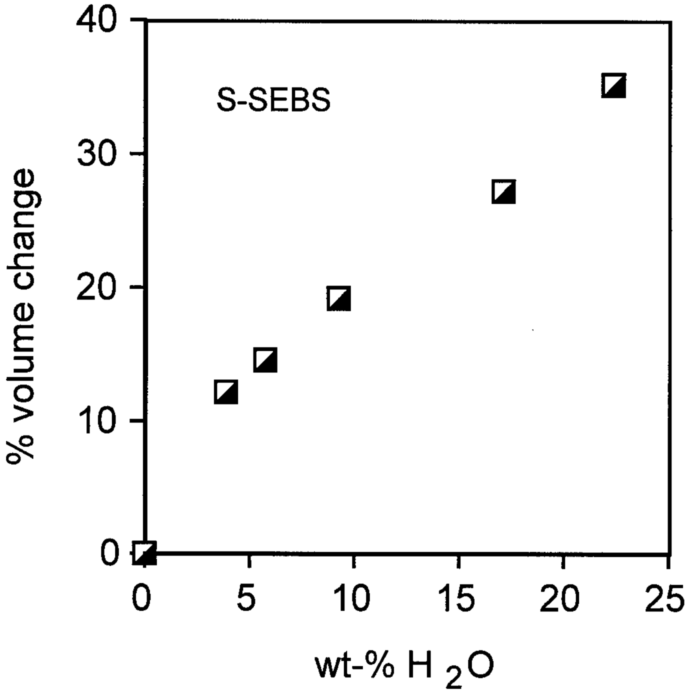

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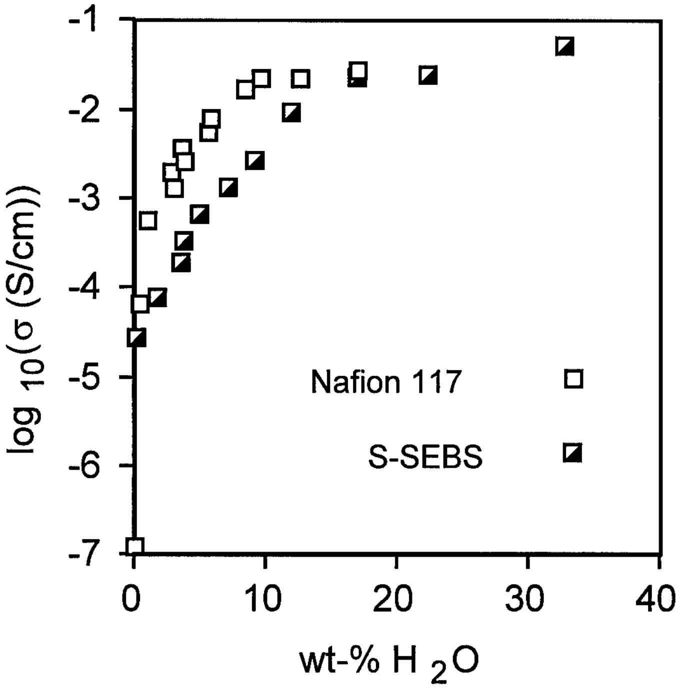

Figure 3a
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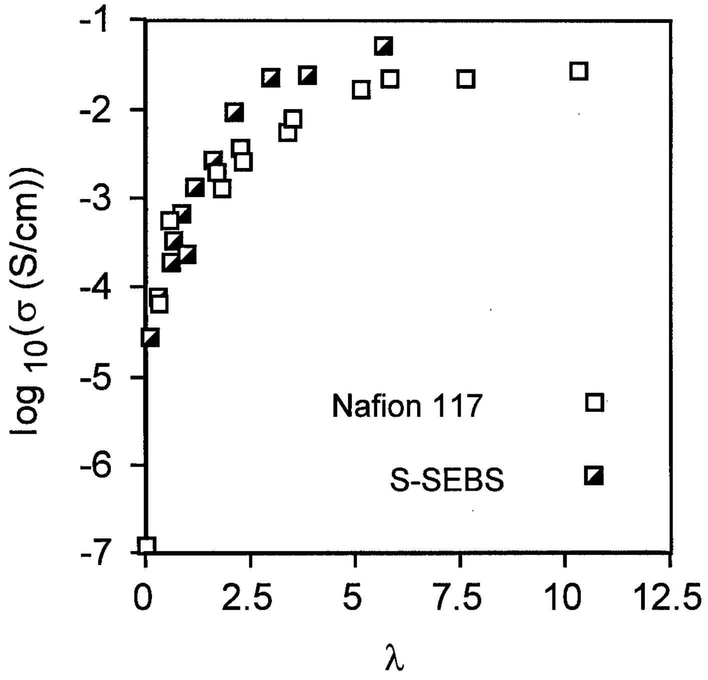

Figure 3b
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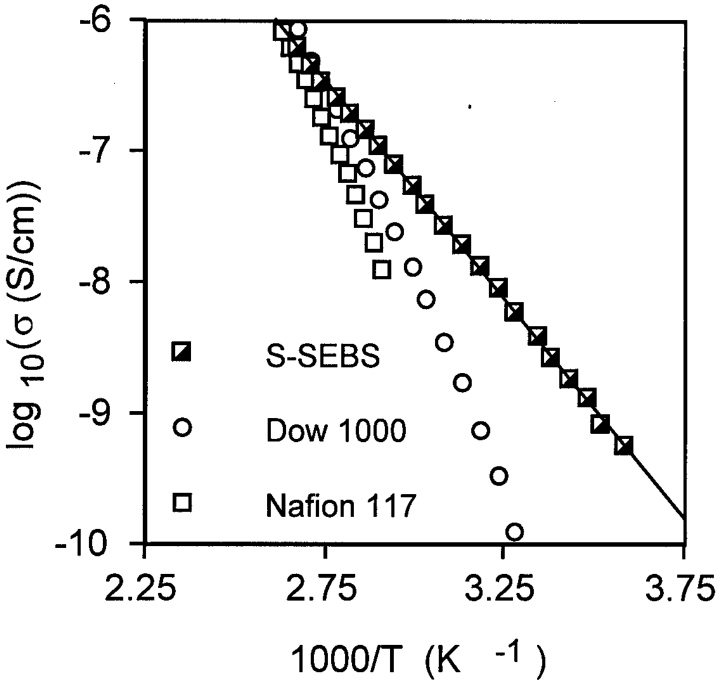

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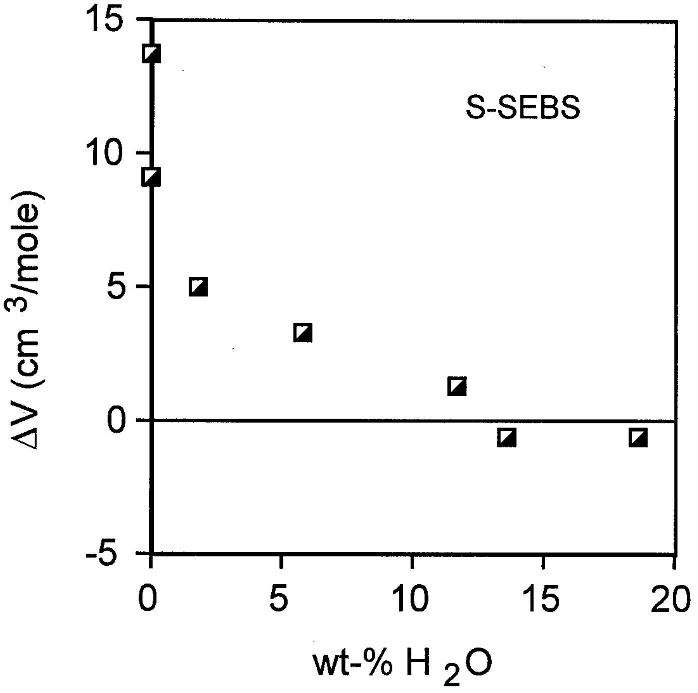

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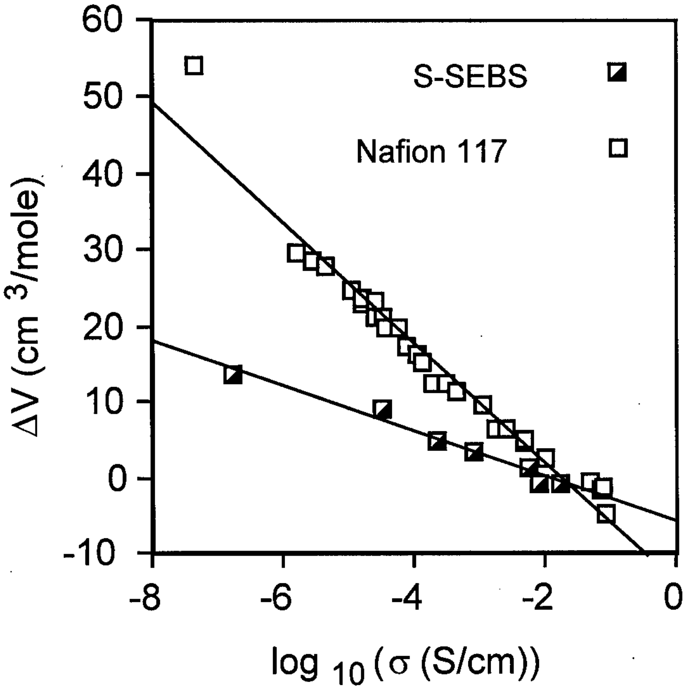

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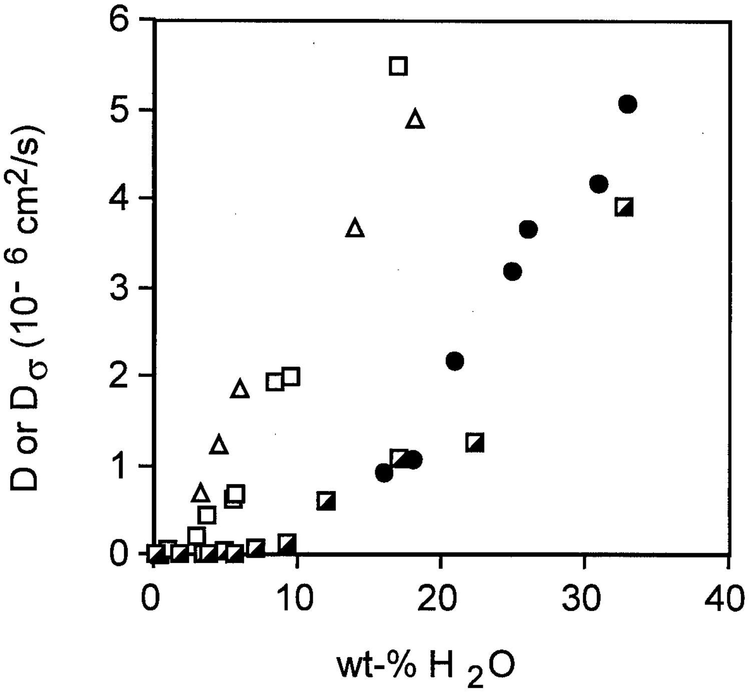

Figure 7
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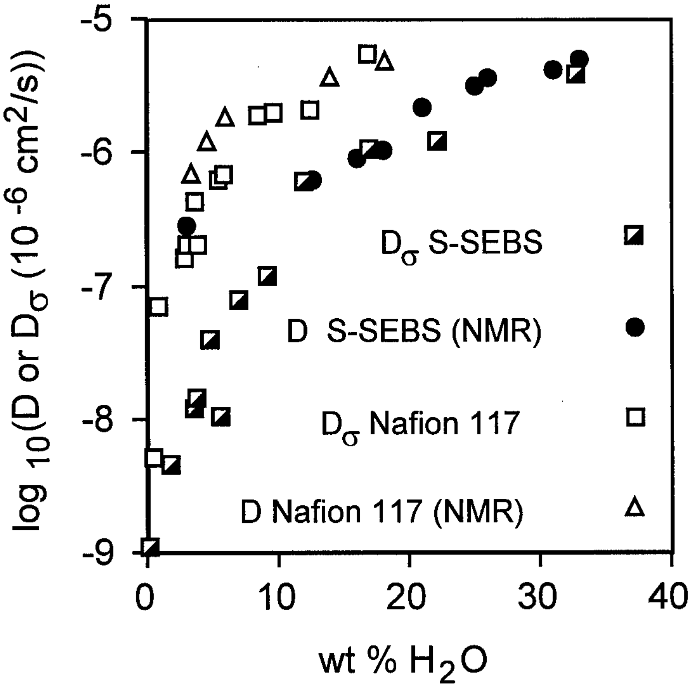

Figure 8
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