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High Pressure Studies of Hydrated Nafion Membranes:
Dielectric Relaxation and Deuteron NMR

by

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HIGH PRESSURE STUDIES OF HYDRATED NAFION MEMBRANES: DIELECTRIC RELAXATION AND DEUTERON NMR

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ABSTRACT

Audio frequency electrical conductivity/dielectric relaxation and nuclear magnetic resonance studies of Nafion-117 have been carried out at pressures up to 0.3 GPa (3 kbar). For some samples, the electrical conductivity exhibits dispersion typical of hopping conductivity in an amorphous material, $\sigma = \sigma_0 \omega^m$. The values of m are sample dependent and vary from about 0.55 to 0.75. In addition, the values of m are not strongly pressure sensitive. At a given frequency, the electrical conductivity tends to decrease as pressure increases and yield activation volumes on the order of 5 to 10 cm³/mol. The activation volume determined from the NMR spin-lattice relaxation time measurements are also sample dependent. The data shown correspond to an activation volume of about 8.6 cm³/mol.

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INTRODUCTION

Perfluorinated ion exchange membranes, such as Nafion, are currently the object of intense interest due to their potential use in fuel cells and other electrochemical applications. It is well known that the presence of water in these membranes greatly enhances proton transport and is therefore intimately linked with the proton exchange properties of this material. A number of studies have been directed at elucidating the role of water in proton transport and related work has examined the molecular diffusion of water through the membrane.¹⁻⁴ The properties of water in these membranes have been shown to differ significantly from those of bulk water.

In a recent paper,⁵ several of the authors have reported the results of vacuum/atmospheric pressure dielectric relaxation/electrical conductivity and nuclear magnetic resonance (NMR) studies of Nafion-117. That investigation yielded the interesting result that considerable anisotropy of the host polymer is evident in the angular-dependent NMR spectra despite the high mobility of molecular water. In addition, NMR and DR data characteristic of glassy water domains were also observed. Further work has revealed a previously unreported relaxation in dry Nafion-117.⁶

Previously, it has been shown that high pressure conductivity measurements have provided useful insights into conductivity mechanisms by yielding activation volumes. For example, in polymer electrolytes consisting of anhydrous amorphous complexes of alkali salt and polyether, activation volumes in excess of 20 cm³/mol were observed which are consistent with the generally accepted paradigm of ion motion being coupled to large segmental motions of the polymer host.^{7,8} In an attempt to further elucidate the role of water in the proton conductivity mechanism of Nafion 117, electrical conductivity and NMR studies

are being carried out at high pressure. Preliminary results from those studies are reported in the present work.

EXPERIMENTAL DETAILS

For the electrical measurements, gold electrodes were evaporated onto the faces of as-received samples in a two terminal configuration. The samples of NAFION 117 were then conditioned by exposing them to the atmosphere at about 50% relative humidity. Audio frequency values of capacitance, C , and conductance divided by the angular frequency, G/ω , were measured at various temperatures and pressures using techniques described elsewhere.⁹ The pressure fluid was Fluorinert (FC-77) Electronic Liquid.

The data were transformed to the apparent complex dielectric constant, $\epsilon^* = \epsilon' - j\epsilon''$. The procedure was to measure the area, A and the thickness, d , and calculate the value of the real part of the dielectric constant, ϵ' , at room temperature using the usual expression for the capacitance of a parallel plate capacitor:

$$C = \epsilon_0 \epsilon' A/d \quad (1)$$

It was then assumed that the relative change in the real part of the dielectric constant with both frequency and temperature is equal to the relative change in capacitance and hence the effects of thermal expansion have not been included. The imaginary part of the dielectric constant at any other frequency and temperature was then calculated using the definition:

$$\epsilon'' = \epsilon' G/\omega C \quad (2)$$

where ω is the angular frequency. Finally, the results were transformed to the electrical conductivity, σ , via:

$$\sigma = \epsilon_0 \epsilon'' \omega \quad (3)$$

Deuteron NMR measurements were performed at a Larmour frequency of 46 MHz. The sample, containing 5.7 wt% D₂O was enclosed in a polyurethane sheath and inserted into the radiofrequency coil contained within a stainless steel pressure bomb. The water content was determined by weight gain in D₂O vapor following vacuum drying. Spin-lattice relaxation times, T₁, were measured by inversion recovery.

RESULTS AND DISCUSSION

The variation of the electrical conductivity with frequency depends upon the water content. For example, some samples exhibit curvature in a log-log plot of conductivity vs. frequency. Other samples show a relaxation peak when the data are displayed in a semi-log plot of ϵ'' vs. frequency. Still others exhibit a power law dependence:

$$\sigma = \sigma_0 \omega^m. \quad (4)$$

As a comprehensive treatment of the frequency variation of the electrical properties of Nafion with various water contents is beyond the scope of the present paper, only the latter samples, those exhibiting the power law dependence, will be discussed. Typical results for the variation of the electrical conductivity for such

samples are shown in Figure 1. The deviation from a straight line in the log-log plot at the highest frequencies is attributed to a contribution from the relaxation behavior mentioned above. The relaxational behavior is associated with the glass transition of the aqueous domains or with space charge polarization.

A power law dependence for the electrical conductivity appears to have been first reported by Starkweather and Chang² and later studied extensively by Mauritz and co-workers.^{3,4} In order to directly compare the results with those workers, the results were transformed to ϵ'' via Equation (3) which yields

$$\epsilon'' = \sigma_0 \omega^{m-1} / \epsilon_0 \quad (5)$$

and Mauritz writes:

$$\epsilon'' = A \omega^{-n} \quad (6)$$

so that $n=1-m$ and $A=\sigma_0/\epsilon_0$. A log-log plot of ϵ'' vs. frequency is shown in Figure 2. Best-fit values of n and m at various pressures are listed in Table 1. The value of $m = 0.75$ is typical of hopping conductivity, albeit electronic, in amorphous semiconductors.^{10,11} This indirect result, which is indicative of amorphous structure, is especially interesting in light of the previous direct observation by NMR of amorphous D₂O in 10 wt% of D₂O in Nafion 117.⁵

As is apparent from Figure 3, the power law dependence of the electrical conductivity is also observed at high pressures. The resultant values of the exponents are also listed in Table 1. The exponent m does not change much as pressure increases. This is reasonable since the effect of pressure on a random distribution will also result in a random distribution i.e. a small change in each energy barrier will result in essentially the same distribution of barriers.

An attempt was made to study the variation of electrical conductivity at various frequencies vs. pressure. However, it was found that the conductivity varied with time. This was attributed to changing water content in the sample. This is plausible since for the present experiment the sample is in contact with the pressure fluid. However, it is clear from a comparison for Figures 1 and 3 that the electrical conductivity decreases as pressure increases. Because of the drift of the conductivity with time, the value of the change in the conductivity with pressure which can be calculated from those figures is not an accurate measure of the decrease of conductivity with pressure. In fact, experiments to date show that the variation is somewhat larger leading to activation volumes of about 5 to 10 cm³/mol as calculated from:

$$V_{\text{act}} = -kT d(\ln \sigma)/dP. \quad (7)$$

Further work is underway both to eliminate the variation of the conductivity with time and to more completely characterize the electrical properties of Nafion under high pressure.

Figure 4 displays deuteron T_1 measurements as a function of pressure for Nafion 117 containing 5.7 wt% D₂O at 295 K. Previous ²H T_1 measurements have determined the presence of a T_1 minimum at 205 K.⁵ Therefore the effect on T_1 of increasing pressure is similar to that of decreasing temperature (i.e. 295 K is on the high-T side of the T_1 minimum). One can also describe this process in terms of an activation volume as described above for conductivity. In this case

$$V_{\text{act}} = -kT d(\ln T_1)/dP \quad (8)$$

which, from the data in Figure 6, yields an activation volume of about 8.6 cm³/mole. Again, it was found that the NMR results varied from sample to sample. Further work is underway to more completely describe this system.

This activation volume is small compared with that observed in polymer electrolytes.^{7,8} One possible explanation is that the ion transport mechanism is different. In ion conducting polymers, ion transport is usually associated with large scale segmental motions of the polymer chain, hence the large activation volumes. However, another possible reason for small activation volumes in hydrated Nafion is that the mobile ions are extremely small, namely protons or associated ions. Consequently, further work is necessary in order to understand the reason for the relatively small activation volumes in Nafion.

CONCLUSIONS

In summary, several results have been obtained by studying the pressure variation of dielectric relaxation/electrical conductivity and nuclear magnetic resonance. First, the power law dependence of the electrical conductivity for some samples has been confirmed and quantified. Second, it is found that the electrical conductivity decreases with pressure. Those results lead to activation volumes of on the order of 5-10 cm³/mol. Finally, NMR T₁ measurements have been carried out on a sample which yield an activation volume of about 8.6 cm³/mol.

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Table 1. Best-fit exponent in Equation (4).

Pressure (GPa)	m	n
0.0001	0.711	0.298
0.01	0.730	0.270
0.075	0.744	0.256
0.15	0.750	0.250
0.225	0.747	0.253
0.246	0.745	0.255
0.3	0.746	0.254

FIGURE CAPTIONS

Figure 1. Electrical conductivity vs frequency at 295K and atmospheric pressure for Nafion 117 conditioned at about 50% relative humidity. The solid line has been best-fit to the first 9 datum points.

Figure 2. Imaginary part of the dielectric constant vs. frequency at 295K and atmospheric pressure for Nafion 117 conditioned at about 50% relative humidity. The solid line has been best-fit to the first 9 datum points.

Figure 3. Electrical conductivity vs. frequency at 295K and 0.3 GPa (3000 bars) for Nafion 117 conditioned at about 50% relative humidity. The solid line has been best-fit to the first 9 datum points.

Figure 4. NMR spin-lattice relaxation times, T_1 , vs. pressure at 295K for Nafion 177 containing 5.7 wt% D_2O .

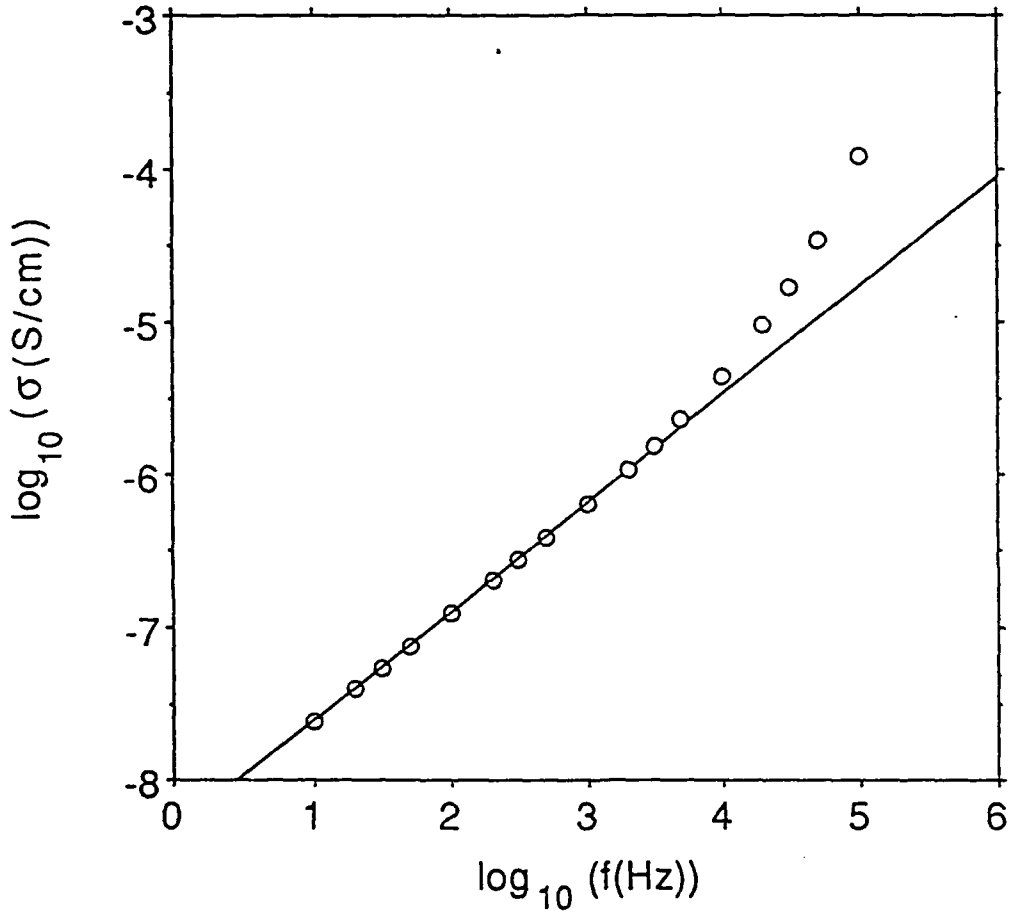


Figure 1
Dependence of

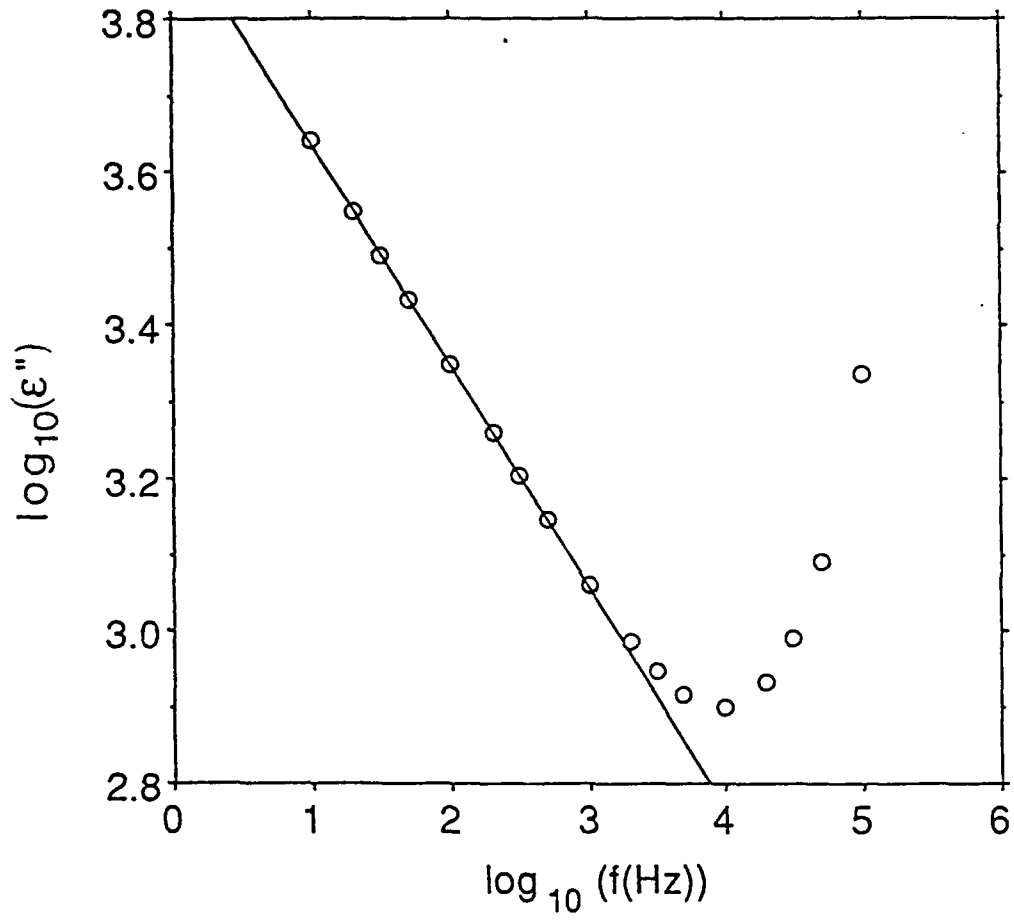
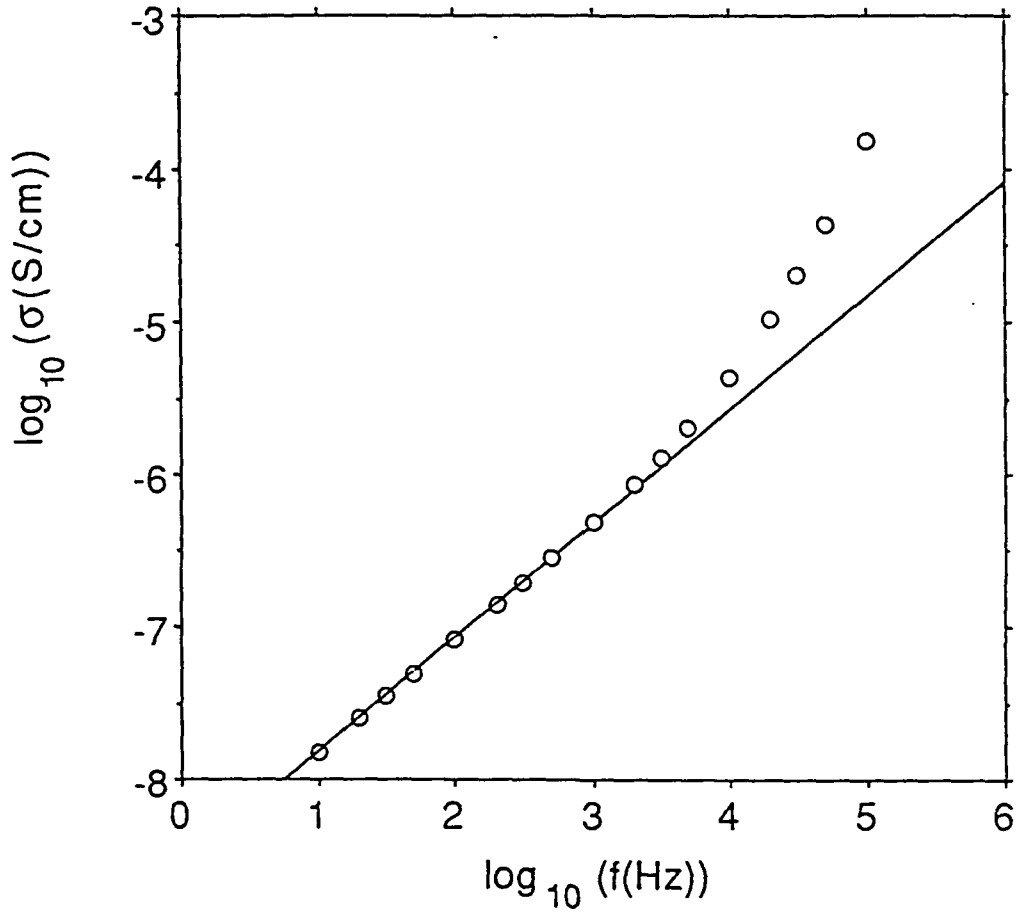
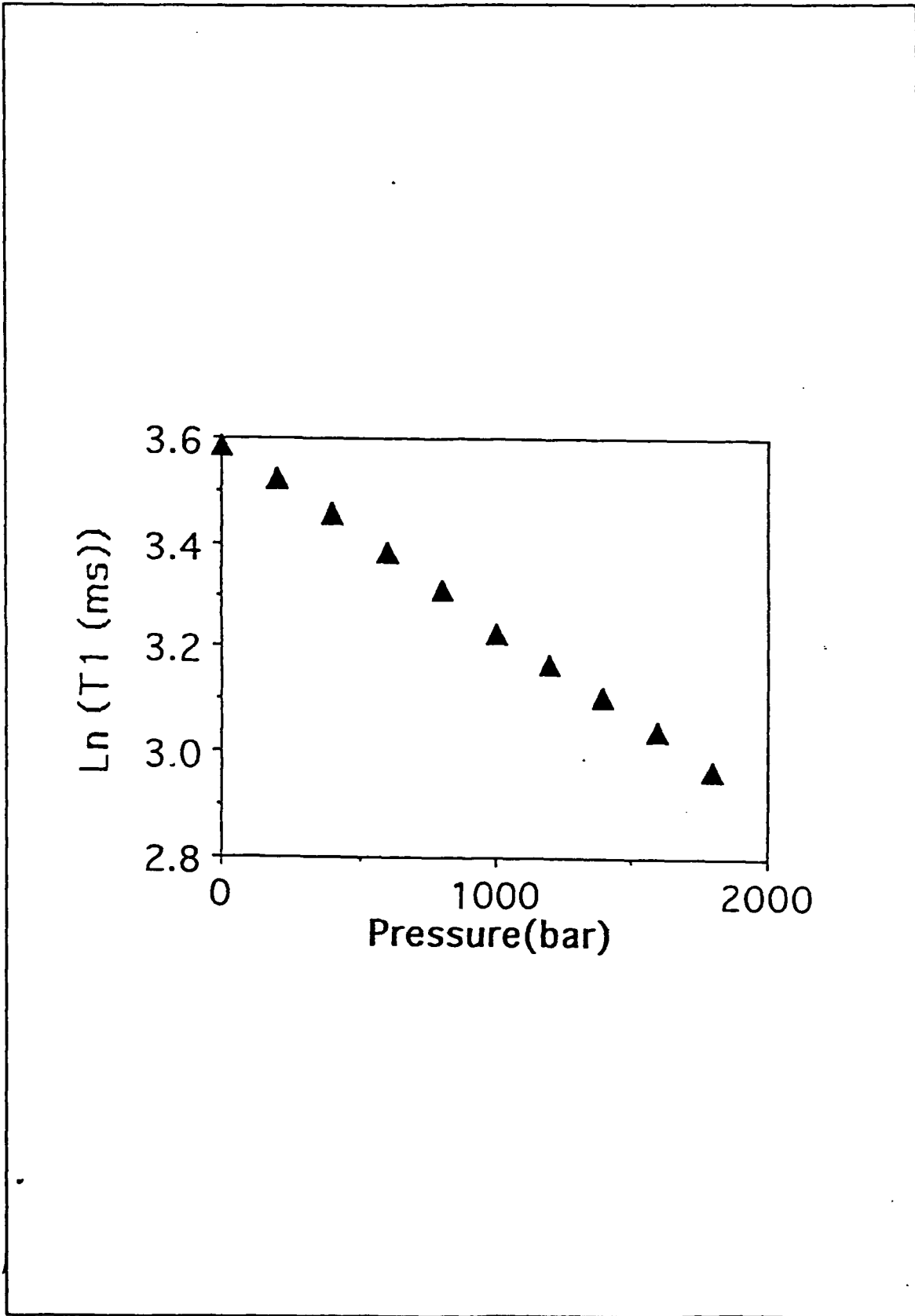


Figure 2





Non-metal Figure 4