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High Pressure NMR and Electrical Conductivity Studies of
Acid Form *NAFION* Membranes

by

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**HIGH PRESSURE NMR AND ELECTRICAL CONDUCTIVITY STUDIES IN
ACID FORM NAFION MEMBRANES**

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ABSTRACT

The effect of high pressure on the electrical conductivity and proton, deuteron and ^{17}O NMR in acid form NAFION-117 conditioned at various levels of relative humidity has been determined. NMR measurements of T_1 were carried out as a function of pressure up to 0.25 GPa. The complex impedance studies were made along the plane of the film at frequencies from 10 to 10^8 Hz at room temperature and pressures up to 0.3 GPa. The electrical conductivity and proton and deuteron NMR measurements show that the activation volume for materials containing greater than about 3 water molecules per sulfonate is 2 to 3 cm^3/mol and larger values are found as the amount of water decreases. The implications of these results are discussed. The ^{17}O NMR results are unexplained at the present time.

INTRODUCTION

Temperature and pressure are the thermodynamic variables which determine the state of a system. In some cases they are complementary variables, while in others, pressure is the essential variable. Understanding of ion transport processes in polymers can be greatly assisted by employing pressure as the dynamic variable. The activation volume associated with ionic and molecular motion, which is a measure of the volume change of the material as the ions or molecules pass from an equilibrium position to a saddle point, can be derived directly from the pressure data. As discussed later, such motion could include both translation and rotation. Whether both motions are included, of course, depends upon the type of measurement. Consequently, it is clear that such information is of use in any attempt to understand an electrically conducting system.

Because of their possible application in methanol fuel cells, the electrical conductivity of ion exchange membranes such as NAFION is of current interest. One type of experiment which does not appear to have been carried out to date is the effect of high pressure on the conductivity. Some preliminary results were described generally in a previous work [1], however, as has been pointed out elsewhere [2], those data were actually measurements of interfacial effects and do not represent the effect of pressure on the bulk conductivity. In the former work [1], a preliminary report of the effect of high pressure on NMR measurements also was given. In the present paper, further NMR measurements and the first detailed results of the effect of pressure on the electrical conductivity are presented.

EXPERIMENTAL DETAILS

All studies were carried out on NAFION 117 supplied by E. I. DuPont de Nemours. The material was approximately 0.18 mm thick. For the NMR measurements, 1 cm strips of film were cut into short pieces or rolled into cylinders and placed into open-ended glass tubes, and then exposed to various relative humidities to obtain the desired water content. This was done by suspending the sample above the surface of appropriate aqueous salt solutions (saturated) in sealed bottles. For example, pure water, NaCl and KNO_2 yield approximately 100%, 75% and 45% relative humidity, respectively at 25°C. Samples were prepared with distilled water for proton NMR, and D_2O (Aldrich) and 20% ^{17}O H_2O (ICN) were used for the deuteron and ^{17}O NMR measurements. For all samples, the water uptake was measured by weighing. In cases where comparison was possible, the water uptake was found to be very close to that observed by Zawodzinski et al [3,4]. In order to maintain the water content, the NMR measurements were carried out on samples wrapped in teflon.

A Novex broadband NMR spectrometer was utilized. Larmor frequencies were 46 MHz and 42 MHz for ^2H and ^{17}O , respectively, at high magnetic field, and 42 MHz for ^1H at lower field. A probe was constructed specifically for use at high pressure up to 0.25 GPa. Typical dimensions of the solenoidal rf-coil were 7.5 mm in diameter and 13.5 mm in length. The coil assembly was housed in a stainless steel cylindrical pressure bomb fitted with a double electrical feed-through for the coil leads. Earlier designs utilizing only a single feed-through, with the pressure bomb serving as electrical ground, are usually less reliable because of stray capacitance that varies strongly with applied pressure. Elevated hydrostatic pressure was achieved with an Enerpac 11-4000 manual pump; hydrogen-free

Fluorinert FC-77 (3M) was employed as the pressure transmitting fluid. Pressures were monitored with a Heise 12 inch gauge, and the samples were wrapped in teflon tape to prevent intrusion of the Fluorinert into the film. A secondary benefit of the teflon wrapping is to maintain the water content of the samples. All measurements were made at 24°C. Spin-lattice relaxation (T_1) measurements were made using an inversion recovery pulse sequence.

For the electrical conductivity studies, the sample was pretreated as described previously and the measurements were made along the length of the thin film for reasons described elsewhere [2]. A strip of NAFION approximately 4 cm long and 1 cm wide was cut. 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 [2].

For one set of high pressure measurements, the sample was allowed to equilibrate in the atmosphere (approximately 50% relative humidity). For a second set of measurements, a different sample was conditioned at 25% relative humidity. In each case, the sample was then clamped onto the closure plug of the high pressure vessel used previously to measure the effect of high pressure on the electrical conductivity of ion conducting polymers [5]. The vessel was then closed and pressurized using a hydrocarbon pressure fluid, Spinesstic 22. A hydrocarbon pressure fluid was chosen because it is known that a similar material, teflon, swells much less when immersed in fluids which do not contain fluorine [6].

The equivalent parallel capacitance and resistance of the sample were then determined using both a CGA-83 Capacitance bridge (10-10⁵ Hz) and a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer. For the present

measurements, the Impedance Probe was used with the Hewlett Packard instrument which has a frequency range of $10^4 - 10^8$ Hz. All data were then transformed to the complex impedance, $Z^* = Z' - jZ''$.

RESULTS AND DISCUSSION

Electrical Conductivity

Typical results for the electrical studies of NAFION are shown in Figure 1 in the form of a complex impedance diagram. It is clear that for the present material, the electrical resistance is sufficiently high that an impedance arc is observed at the highest frequencies. In addition, the electrode and interface effects are observed at the lowest frequencies. However, it is noted that the data from the two regions do not overlap even though there are common frequencies. This is attributed to the different measurement techniques used by the instruments. Specifically, the measurements made using the CGA-83 Capacitance bridge are true three terminal measurements which means that virtually all capacitance to ground is discarded. This is particularly important in the case of a high pressure vessel because there is a large capacitance to ground at the electrical feedthrough, for example. Some of these capacitances will impact the measurements made using the Hewlett Packard 4194A Impedance/Gain-Phase Analyzer which is a two terminal instrument beyond the Impedance Probe. In support of this conclusion, there was overlap of similar data taken in an atmospheric pressure cell designed to eliminate stray capacitances [2]. However, the important feature is that both instruments yield essentially the same value of resistance for the sample. This is clear since it is apparent from Figure 1 that both the impedance arc and the low frequency data intersect the real axis at approximately the same position. The low frequency data, which are

dominated by electrode and interface effects, will not be considered further in the present paper.

The high frequency data were analyzed by best-fitting a Cole-Cole expression [7]:

$$Z^* = \frac{Z_0}{[1 + (i\omega\tau_0)^{1-\alpha}]} \quad (1)$$

to the data where Z_0 , τ_0 and α are fitting parameters. Typical results are shown by the solid line in Figure 1. The data exhibit a slightly depressed semicircular arc similar to that seen in ion conducting polymers, for example [5]. In fact, the Cole-Cole parameter, α , is about 0.016. This is very close to the value of 0 expected for a single relaxation time process and is consistent with the observation by various groups [2,8] that the electrical conductivity is attributable to a simple, frequency independent conductivity mechanism.

The bulk resistance, R , was obtained from the intercept of the Cole-Cole arc with the Z' axis. The conductance, $G=1/R$, was calculated from the intercept and transformed to the electrical conductivity, σ , via:

$$\sigma = GA/\ell . \quad (2)$$

where A is the area of the sample and ℓ is the length. For lack of a bulk modulus or compressibility, the approximation was made that the dimensions of the sample do not change upon application of pressure. The effects of this approximation are discussed below.

The results for the variation of the electrical conductivity with pressure are shown in Figure 2. The data shown are for decreasing pressure. Upon

increasing pressure a small offset was found, but the slope remains essentially the same. The slope of the data was determined and used to calculate an activation volume via:

$$\Delta V = -kT (d \ln \sigma / dp)_T. \quad (3)$$

A room temperature value of $\Delta V = 2.9 \pm 0.1 \text{ cm}^3/\text{mol}$ was obtained, where the uncertainty is estimated on the basis of the reproducibility of the data. The slope and hence activation volume are somewhat smaller than this because of the omission of the compressibility, χ_T . Specifically, the correction factor to the slope is given by:

$$\left(\frac{d \ln \sigma}{dp} \right)_T = \left(\frac{d \ln G}{dp} \right)_T + \frac{\chi_T}{3}. \quad (4)$$

On the basis of typical polymer compressibilities, the slope and hence activation volume may be too large by as much as 10%.

The intercept is also significant since it approximately gives the atmospheric pressure value for the electrical conductivity. That value was found to be $0.0080 (\Omega\text{-cm})^{-1}$. This value is almost an order of magnitude lower than the value found for NAFION conditioned at 100% relative humidity [2-4,9] and is important because it represents the most reliable of measure of the water content of the sample. Because of the steps required to load the pressure vessel and because the sample was directly in contact with the pressure fluid, direct weighing of the sample was not carried out. Rather, an in situ estimate of the amount of water in the sample was obtained using the results of Zawodzinski et al. [3,4] for the variation of electrical conductivity with water content. On the basis

of their work, the present sample contains approximately three water molecules per sulfonate.

A data run was also carried out on NAFION conditioned at 25% relative humidity. The sample was immediately immersed in the pressure fluid after removal from the relative humidity chamber. The sample exhibited an atmospheric pressure electrical conductivity of $0.0019 (\Omega\text{-cm})^{-1}$ which, on the basis of the work of Zawodzinski et al. [3,4], implies that the sample contains approximately two water molecules per sulfonate. While the actual amount of water is somewhat uncertain, it is clear that the second sample contains less water than the first sample since each was processed in the same manner.

The variation of the electrical conductivity with pressure for the sample treated at 25% relative humidity was extremely reproducible from cycle to cycle and the data yielded an activation volume of $\Delta V = 6.9 \pm 0.1 \text{ cm}^3/\text{mol}$ which is larger than the value for the sample containing more water. As shown below, an increase in the activation volume as the amount of water decreases is also observed using NMR techniques.

The values found for the activation volume are extremely small compared with those in typical solvent-free polymer electrolytes [5]. As the value represents the dilatation of the material due to the diffusing species, one interpretation is that the diffusing species is very small. This is, of course, consistent with the fact that protons are involved in the conduction process in NAFION. However, care must be taken in the interpretation of the activation volume because the host matrix also affects the activation volume. For example, in the case of ion conducting polymers the activation volumes are much larger than the ions involved in the transport [5]. The large value in that case was attributed to the host polymer in that large scale segmental motions are involved in the transport and it is those which are strongly affected by pressure. Certainly, the small

values of the activation volume show that there is little similarity in the transport mechanism for NAFION containing a significant amount of water and traditional ion conducting polymers. This comes as no surprise, however, it emphasizes that care must be taken in the interpretation of the activation volume and that further studies of the variation of the electrical conductivity with pressure, both experimental and theoretical, are necessary.

Nuclear Magnetic Resonance

T_1 data were recorded as the pressure was first increased, then decreased, and increased again. Except for the ^{17}O results, only minor variations as a function of pressure history were noted. All results shown correspond to the middle stage of the cycle, i.e. pressure decreasing from the maximum value of 0.25 GPa. Figure 3 displays the proton NMR results for two samples, containing 9.8 and 18 wt% H_2O (corresponding to roughly 5 and 10 water molecules, respectively, per sulfonate [3,4]). Activation volumes can be extracted from the data in a manner similar to that described for the conductivity measurements. In particular:

$$\Delta V = -kT [\text{dln}(T_1)/\text{dp}]_T. \quad (5)$$

The T_1 results yield $\Delta V = 2.7$ and 2.0 (both ± 0.2) cm^3 /mole for the lower and higher water content samples, respectively. Deuteron T_1 data for samples with water content 6, 12 and 22 wt% are plotted in Figure 4. The results are $\Delta V = 4.6 \pm 0.3$, 2.8 ± 0.7 and 2.6 ± 0.3 cm^3 /mol, respectively. The calculated activation volumes for the proton and deuteron T_1 's are in surprisingly good agreement with each other and with the conductivity results. Moreover, the trend of increasing activation volume with decreasing water content is maintained in all of the

measurements. However, as shown in Figure 5, the ^{17}O T_1 pressure dependence is considerably different from the proton and deuteron results. In particular, following a fairly steep drop in T_1 for both the 12 and 22 wt% samples as pressure is increased to about 0.1 GPa, T_1 remains relatively constant. The situation just described and observed (but not shown) corresponds to the initial application of pressure, increasing from ambient. The data in Figure 5, however, were recorded during the decreasing portion of the pressure cycle, for consistency with the proton and deuteron measurements conditions. Furthermore, the slopes of the pressure dependencies up to 0.1 GPa reflect a higher activation volume for the sample with higher water content, which is opposite to the trends observed in the proton and deuteron NMR and conductivity measurements.

That the proton and deuteron results should yield similar activation volumes is not obvious because their relaxation mechanisms are significantly different. In liquid water, protons relax by magnetic dipole-dipole interactions, which are primarily *intermolecular* in nature, while deuterons (and for that matter ^{17}O , discussion of which is momentarily deferred) relax through the electric quadrupole interaction which is primarily *intramolecular* in nature [10]. Thus, relaxation measurements of protons are sensitive to translation while deuteron and ^{17}O relaxations are sensitive to rotation. However, in liquids there can be significant coupling between rotational and translational motion [11]. In acidic solutions proton transport and molecular rotation are also correlated [12]. The reasonably close agreement between the proton and deuteron NMR and conductivity results implies that the electrical transport process in NAFION is correlated with water molecular rotation. The trend of increasing activation volume with decreasing water content is consistent with a rotational proton transfer mechanism between adjacent water molecules, and with the well-known result that the electrical conductivity increases with increasing water content.

Proton, deuteron and ^{17}O T_1 's in pure water have a very weak pressure dependence over the range studied in this work, i.e. the activation volume associated with the relaxation is very small [13]. Therefore, another way the proton and deuteron results can be understood is that increasing the water content is effectively an approach toward bulk water behavior. Of course, comparison with results for acidic solutions, if they were available, would be more appropriate. Nevertheless, because pressure effects on NAFION containing water are so much larger than on bulk water, these results could shed light on the nature of the interaction between water molecules and the host polymer matrix.

Interpretation of the ^{17}O NMR results remains problematic at this time. The two essential differences between ^2H and ^{17}O NMR are the much stronger quadrupole coupling in the latter (by about a factor of 30) and, in the context of this investigation, the fact that deuteron NMR probes both water molecules and the mobile charge while ^{17}O probes only the water molecules. Given these differences, the behavior shown in Figure 5 is still, however, not presently understood.

CONCLUSIONS

In summary, then, the effect of high pressure on the electrical conductivity and proton, deuteron and ^{17}O NMR in acid form NAFION-117 conditioned at various levels of relative humidity has been measured. The electrical conductivity and proton and deuteron NMR measurements show that the activation volume for materials containing significant amounts of water is about 2 to 3 cm^3/mol and larger values are found as the amount of water decreases. The small values of the activation volume are generally consistent with the usual picture of electrical transport via small ions. Finally, the good agreement between the electrical conductivity and proton and deuteron NMR measurements suggests that the transport process may be correlated with water molecular rotation. The ^{17}O NMR results are anomalous and unexplained at the present time.

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FIGURE CAPTIONS

Figure 1. Complex impedance diagrams at two pressures for NAFION-117 containing some water. The triangles for which dotted lines connect the datum points were obtained using a CGA-83 Capacitance bridge. The frequencies are 10 Hz to 10^5 Hz from right to left. The circles were obtained using a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer. The frequencies are 10^4 Hz to 10^8 Hz from right to left. The solid line represents the best-fit Cole-Cole representation (Equation 1).

Figure 2. Electrical conductivity vs. pressure at room temperature (about 298 K) and various pressures for NAFION 117 conditioned in atmosphere. The circles are the results of complex impedance analysis from the Hewlett Packard 4194A Impedance/Gain-Phase Analyzer. Also shown is the best-fit straight line.

Figure 3. Pressure dependence of proton T_1 in NAFION-117, with two different water contents at 24°C. The solid circles are 9.8% H_2O and the triangles are 18% H_2O .

Figure 4. Pressure dependence of deuteron T_1 in NAFION-117, with two different water contents at 24°C. The solid circles are 6% D_2O , the open triangles are 12% D_2O and the solid triangles are 22% D_2O .

Figure 5. Pressure dependence of oxygen-17 T_1 in NAFION-117, with two different water contents at 24°C. The solid circles are 12% $H_2^{17}O$ and the triangles are 22% $H_2^{17}O$.

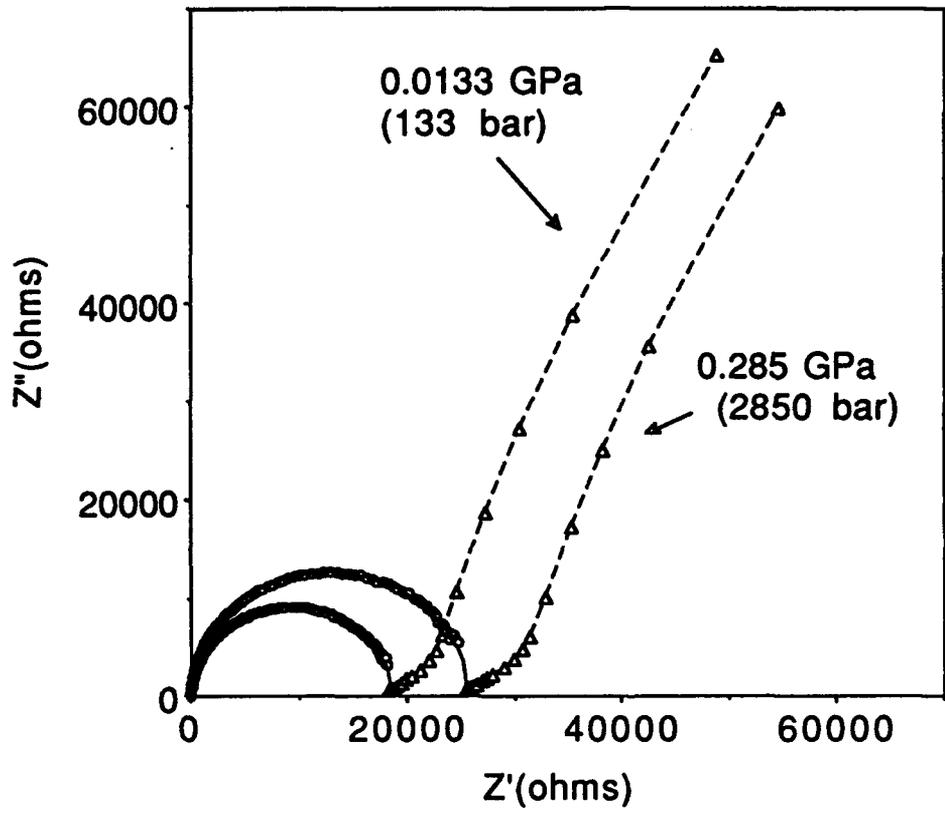


Figure 1

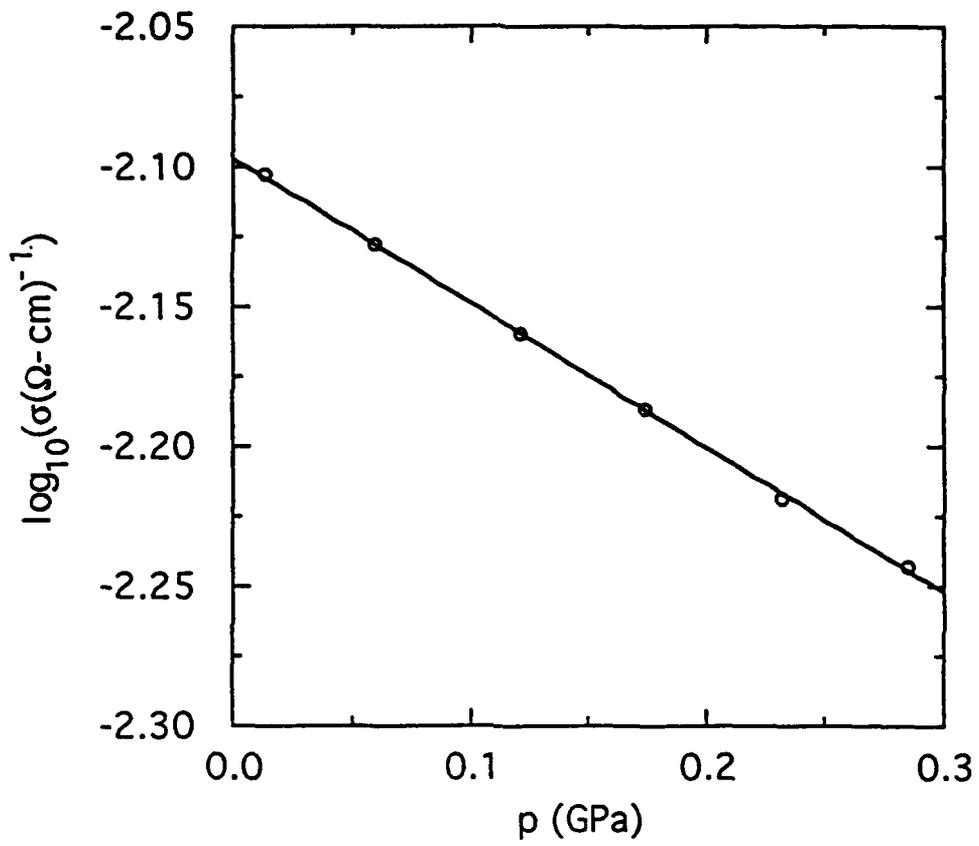


Figure 2

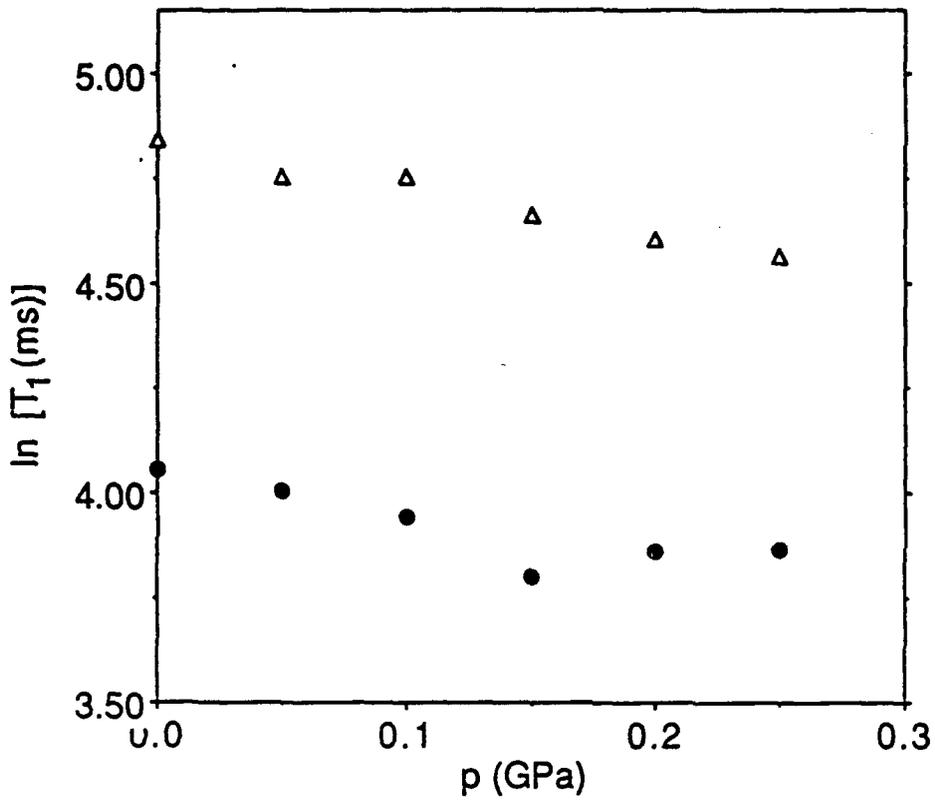


Figure 3

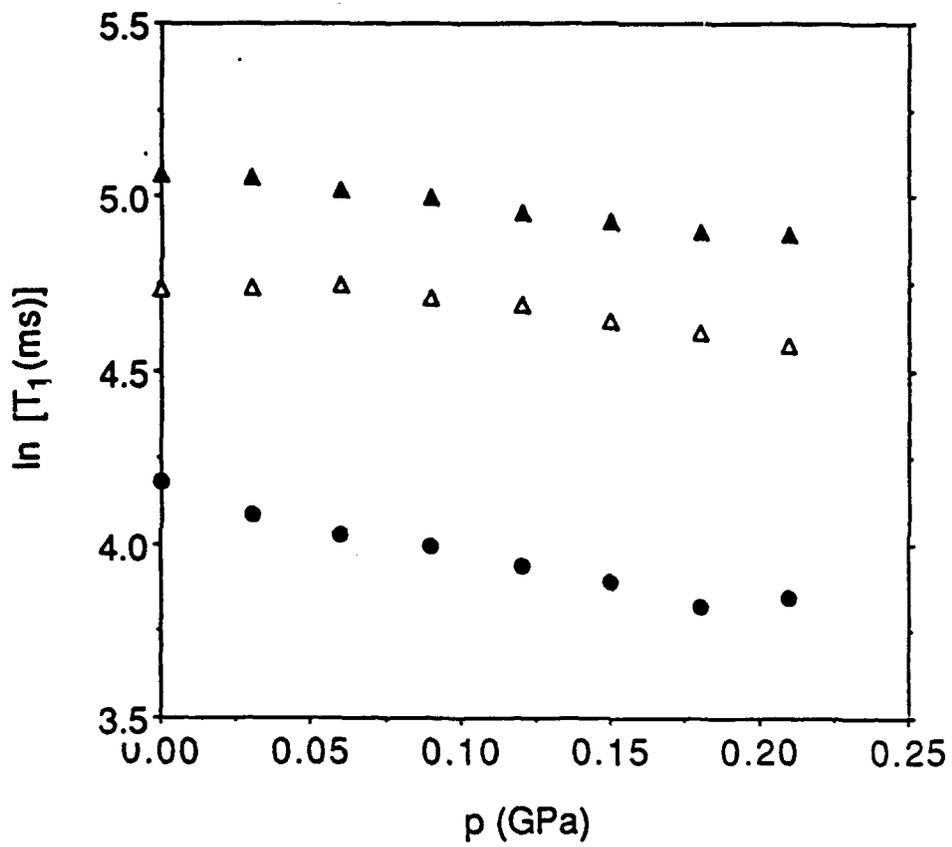


Figure 4

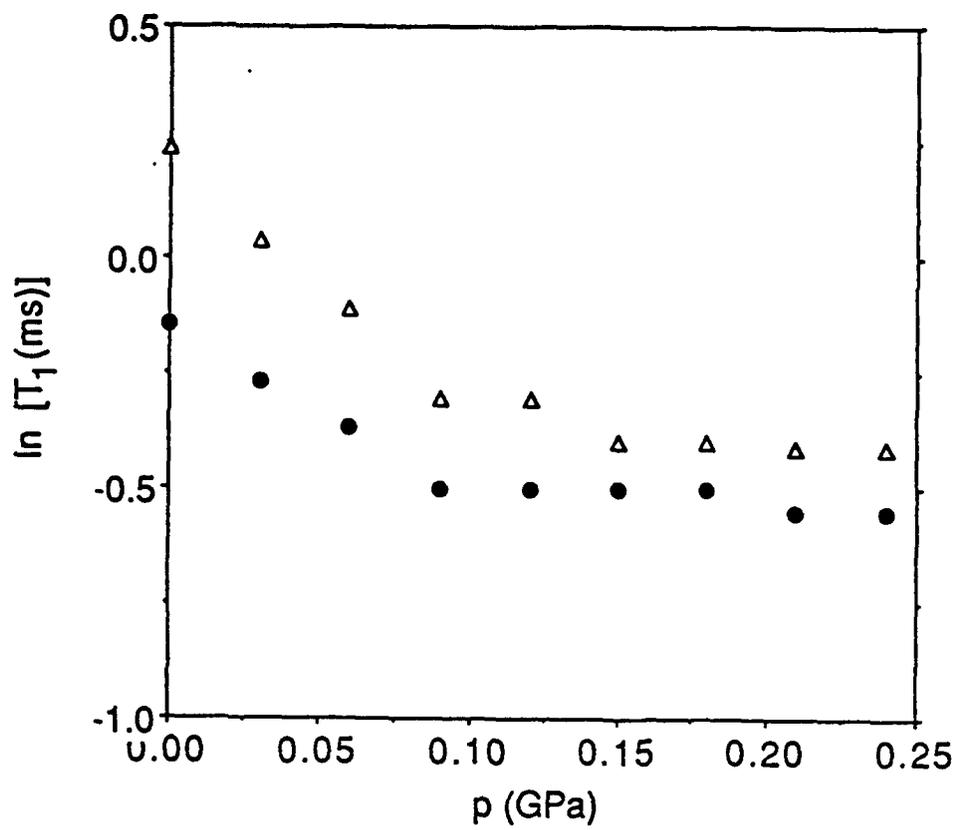


Figure 5