EFFECT OF PRESSURE ON CONDUCTIVITY IN POLY(ETHYLENE OXIDE) COMPLEXED WITH ALKALI METAL SALTS

by

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**Title**: Effect of Pressure on Conductivity in Poly(ethylene Oxide) Complexed with Alkali Metal Salts

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**Abstract**: Audio frequency complex admittance measurements at a number of temperatures have been performed on PEO complexed with various alkali metal perchlorates and thiocyanates at pressures up to 0.2 GPa. In general, the activation volumes tend to increase with the size of both the cation and anion. The trend is best explained if the ion transport mechanism involves both anions and cations. The results are in good agreement with the predictions of a dynamical diffusion theory with an attempt mode Gruneisen.
parameter appropriate for interchain vibrations. This implies that diffusion takes place via interstice-interstice hopping of the ions. Next, it is shown that free volume considerations lead to unreasonable results if \( T_0 \) is interpreted as the glass transition temperature. Finally, the effect of pressure on the activation volume is determined.
EFFECT OF PRESSURE ON CONDUCTIVITY IN POLY(ETHYLENE OXIDE) COMPLEXED WITH ALKALI METAL SALT

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Audio frequency complex admittance measurements at a number of temperatures have been performed on PEO complexed with various alkali metal perchlorates and thiocyanates at pressures up to 0.3 GPa. In general, the activation volumes tend to increase with the size of both the cation and anion. The trend is best explained if the ion transport mechanism involves both anion and cations. The results are in agreement with the predictions of a dynamical diffusion theory with an attempt mode Grunisen parameter appropriate for interchain vibrations. This implies that diffusion takes place via interte-interstice hopping of the ions. Next, it is shown that free volume considerations lead to unreasonable results if $T_0$ is interpreted as the glass transition temperature. Finally, the effect of pressure on the activation volume is determined.

1. INTRODUCTION

Ion conducting poly(ethylene oxide)(PEO) has been attracting a great deal of attention because of possible application as the electrolyte in solid state batteries. As the effect of pressure on the conductivity provides useful information concerning ion transport, such studies of PEO complexed with various salts were undertaken and the results are presented here.

2. EXPERIMENT AND RESULTS

Film of PEO (Polysciences, MW 5400) with various amounts of alkali metal perchlorates and thiocyanates were prepared as described elsewhere. As before, aluminum electrodes were evaporated onto the surfaces. One face had a central circular electrode of about 2 mm diameter while the other was about 10 mm in diameter. The samples were 0.5-0.5 mm thick. The configuration was chosen to be optimal for the apparatus used. Such a configuration does not readily yield absolute values of the conductivity at a high accuracy, however, since the primary goal of the present work is the relative change in conductance with pressure, this was considered to be a reasonable procedure.

The complex admittance measurements were made using a fully automated microprocessor controlled bridge constructed by one of the authors (CGA). The bridge operates at five audio frequencies from 100-10,000 Hz, and is as accurate as the best commercially available manual bridges (General Radio 1416, for example).

At the relatively low temperatures of the present work, it was found that there was usually very little difference between the 1,000 and 10,000 Hz values of conductance, even though the samples were rather thin. As pressure increased, however, the apparent conductance became lower for the lower frequencies. This effect can be seen in Figure 1 where the results for PEOg-NaClO$_4$ are shown. This is due to enhanced blocking electrode effects. However, this dispersion has little effect on the zero pressure slope, though the curvature is affected somewhat. In this paper, the 10,000 Hz data will be taken to represent the conductance of the sample.

Two different high pressure bombs were used, each with a design similar to that described elsewhere. The pressures were generated using

![Figure 1: $\ln(G/\text{ohm}^{-1})$ vs. P(GPa) for PEOg-NaClO$_4$ at 314.9 K. The data are: o-increasing pressure and x-decreasing pressure at 10,000 Hz; + increasing pressure and * decreasing pressure at 1,000 Hz. The solid line is the best fit curve for the 10,000 Hz data.](image-url)
Table 1: Various experimental and theoretical results related to the effect of pressure on the 
ionic conductivity in PEO complexed with alkali metal salts.

<table>
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<th>Conductance (10^-9 S cm^-1)</th>
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<td>-11.3</td>
<td>14.3</td>
<td>31.4</td>
<td>31.4</td>
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*Samples provided by R. Dagen and D. J. Shriver, Northwestern University

Both argon and nitrogen gases as well as

**Sphinesstic 22 oil.** The measurements of the pressure were made using a Heise 7 kbar Bourdon tube pressure gauge. In many cases, the data runs using either argon or nitrogen gas as the pressurising medium proved not to be entirely satisfactory. The samples frequently failed after one or two data runs, either by an apparent short circuit or by generating a voltage. Furthermore, the samples turned white during the pressure run. All the samples returned to their initial transparency after heating at 100°C in vacuum for a few hours.

Using the Sphinesstic 22 as the pressure fluid, however, the samples showed no such effects and the change in appearance of the samples is therefore attributed to dissolved gas in the samples. However, the dissolved gas had very little effect on the conductivity as can be seen in Figure 2 where the results for PEO-LiClO4 obtained using both gas and oil are shown.

Clearly, the effect of pressure on the conductivity is independent of the pressurising medium. Samples removed from the pressure bomb after a week of constant immersion in the Sphinesstic 22 were scrutinised for signs of swelling or chemical interaction but none showed any effects from the oil.

In interpreting the results, the equation:

\[
\ln G = \ln G_0 + ab + bp^2
\]

where \(G_0\), a, and b are constants, was best-fitted to the data. G is the conductance in \(-1\) and P is the pressure in GPa. The results of the best-fits are listed above in Table 1.
3. DISCUSSION

The data were used to calculate an activation volume associated with the conduction process. The activation volume is defined as:

\[ \gamma = \left( \frac{\partial v}{\partial \phi} \right)_P \]  

where \( \phi \) is the Gibbs energy. The problem is to determine the most appropriate method to associate the Gibbs energy with the ionic conductivity. The difficulty arises from the uncertainty as to whether the Arrhenius equation:

\[ \gamma = \gamma_0 \exp\left(-\frac{Q}{RT} \right) \]  

should be used to describe the conductivity. As will be shown below, the free volume expression leads to unreasonable results and thus the Arrhenius equation will be used.

3.1. Arrhenius Analysis

The assumption of Arrhenius behavior leads to an activation volume:

\[ \gamma = \gamma_0 \left[ \ln \frac{\lambda_0}{\lambda} + \frac{1}{2} \left( \frac{\Delta S}{R} \right) \right] \]  

where \( \Delta S \) is the entropy, \( \Delta S \) is given by \( \Delta S = h - \Delta S_0 \). Assuming that the electric field inside the sample is uniform:

\[ \gamma = \frac{A}{d} \left[ \ln \frac{\lambda_0}{\lambda} + \frac{1}{2} \left( \frac{\Delta S}{R} \right) \right] \]  

where \( A \) is the area of the electrode, and \( d \) is their separation, it follows that:

\[ \ln \frac{\lambda_0}{\lambda} = \frac{\Delta S}{R} + \frac{1}{2} \left( \frac{\Delta S}{R} \right) \]  

where \( \Delta S \) is the isothermal compressibility.

Further, assuming that the only pressure dependent terms in the pre-exponential are the attempt mode frequency, \( \gamma_0 \), the number of charge carriers per unit volume, \( n \), and the mean squared jump distance, \( r \), that is:

\[ \gamma_0 = C_0 n r^2 \]  

and also that the entropy is independent of pressure, Equation (5) becomes:

\[ \gamma = \gamma_0 \left[ \ln \frac{\lambda_0}{\lambda} - \frac{1}{2} \left( \frac{\Delta S}{R} \right) \right] \]  

In this expression, the attempt mode Grunenfelder parameter, \( \gamma_0 \) is given by:

\[ \gamma_0 = \frac{A}{d} \left[ \ln \frac{\lambda_0}{\lambda} - \frac{1}{2} \left( \frac{\Delta S}{R} \right) \right] \]  

The compressibility of pure H2O is 0.117(iGPa)\(^{-1} \) as reported by Ito.\(^6\) As values for complexed H2O do not appear to be available at present, this value will be used for the complexed material. Here, there is considerable ambiguity as to the appropriate value of \( \gamma_0 \). Bulk Grunenfelder constants for polars are on the order of \( 6 \times 10^{-13} \) while mode Grunenfelder constants range from \( 0.06 \) to about \( 0.27 \). However, the activation volume \( \gamma \), relatively insensitive to the value of \( \gamma_0 \), is for example, the correction factor in equation (11) \( \left( \frac{\gamma_0}{\gamma} \right) \) is about 0.2(iGPa)\(^{-1} \) which represent, a difference of about \( 1 \) in the activation volume.

In order to be internally consistent, dynamical diffusion theory will be used to evaluate \( \gamma_0 \). Specifically, it follows from Equation (11) that:

\[ \gamma_0 = A \]  

This equation has been used successfully in similar applications for ionic crystals.\(^2\) Insertion Equation (11) into Equation (8), the resulting equation becomes:

\[ \gamma = \gamma_0 \left[ \ln \frac{\lambda_0}{\lambda} - \frac{1}{2} \left( \frac{\Delta S}{R} \right) \right] \]  

The resultant values of the activation volumes are listed in the seventh column of Table 1.
unit, values of the free energy approximated by
the enthalpies determined from the slopes on the
in Figure 1 and 2.
There are several interesting features of these
results. The most important trend is that in
general the activation volume increases with
both the size of the cation and anion. For
example, v for PLE2CN is significantly
larger than that for PLE2Cl, which is oposed
variation for this result is that the
difference is due to the difference in size and
shape of the anions and that the anions are
mobile. That is, the tetrahedral perchlorate
ion requires more volume increase of the polymer
matrix than does the linear thiocyanate ion in
order for transport to take place. Also, it is
possible that a larger number of perchlorate
ions than thiocyanate ions may be mobile.
These considerations support the recent results of
Winton and Steele\textsuperscript{12} and Stenstrom and
Jacobson\textsuperscript{13} which imply that the anions are
mobile.
Of course, other explanations are possible. For
example, it is not necessary that the anions be
mobile. Their function may simply be to
decrease the free volume, which, in turn,
increase the activation volume for motion of
cations. However, the difference between PLO-
NaClO\textsubscript{4} and PLO-Cl\textsubscript{2}NaClO\textsubscript{4} seems to be too large to be
attributable to cation motion alone. Other
explanations may be associated with morphology
or degree of crystallinity. Experiments are
currently underway to ascertain the extent to
which such factors are influencing transport
processes.
Most trends shown by the remaining results are
also consistent with an argument based on ion
size, specifically, the activation volume for
PLO-Cl\textsubscript{2}NaClO\textsubscript{4} is larger than for PLE2Cl and
v for PLO2 CN, NaClO\textsubscript{4} is slightly smaller than for
PLO2 CN, NaClO\textsubscript{4}. The latter results are particularly
significant since electrical relaxation studies
show that there are severe local distortions of
the polymer chain in PLO-Cl\textsubscript{2}NaClO\textsubscript{4}. Finally, v
for PLO2 CN, LiClO\textsubscript{4} appears to be larger than for
PLO2 LiClO\textsubscript{4}, though the difference is not as
dramatic as for the sodium complex material.
The one clear exception to the rule of scaling
of v with ion size is that v for PLO2 LiSCN is
larger than for PLO2 CN, NaClO\textsubscript{4}. However, it
should be kept in mind that the LiSCN complexed
materials were prepared without taking great
care to exclude water and were, in fact,
synthesized using hydrated LiSCN.\textsuperscript{21}
Consequently, the PLO2 LiSCN results may be
anomalous as the role of the water has yet to
be determined.
Next, information concerning the transport
mechanism can be obtained from further
consideration of dynamical diffusion theory.
In particular, the values of \(v=1\) in Equation (1)
are necessary to predict the experimental values of
the activation volume are of interest. These
values of \(v=1\) have been calculated and are listed
Table 2. It is seen that the values are all
greater than 1.0. This implies that it is the
low frequency interchain vibrations of the
polymer which control the ionic motion. This is
because intrachain mode Gruneisen parameters are
usually much smaller, typically 0.000-0.5 while
interchain \(v\)'s are larger than 1.0 (Ref. 28).
The reason for this is simply that interchain
vibrations (chain-chain) are much more strongly
affected by pressure than intrachain vibrations
(motions within the chain). The difference is
enhanced by the smaller frequencies which appear in the denominator of the expression for \( \ell \). Consequently, the picture of ion motion in PIO suggested by the results of the present pressure work is that at high temperatures both anions and cations undergo "interstice-interstice" hopping via low frequency interchain vibrations. "Interstices" are taken to be the spaces between the polymer chains. The reason for choosing the "interstices" rather than the chains themselves as the normal sites for both anions and cations under low "interstice-interstice" hopping is that at high temperatures the ions reside on the chains, the effect of pressure should be to increase the conductivity since the chains would be closer together at elevated pressures. For "interstice-interstice" hopping, increased closeness of the chains should inhibit the motion thus decreasing the conductivity, as is observed experimentally.

As an alternative transport mechanism, the intrachain hopping process, is often discussed in conjunction with these materials, some comments here are appropriate. This process is ruled out by the large mode Gruneisen parameter as that transport mechanism would require interchain vibrations. However, chain-end bridging, which must be associated with an intrachain hopping process in real materials, would probably require interchain vibrations, and thus such a process might be consistent with the present results. However, the conclusion that the intrachain hopping process is not dominant in these materials is consistent with the recent results of Papke et al.**

### 3.2. Free Volume Analysis

The pressure results can also be used to comment on the free volume theory as represented by Equation (4). Papke et al.* have shown that the basis of a configurational entropy model (Equation (4)) can be derived in which:

\[
\frac{\Delta \mu^*}{R} = \frac{\mu^0}{k_B} T_0
\]

where \( k_B \) is a constant, \( \mu^* \) is a configurational entropy, and \( T_0 \) is a parameter usually associated with the glass transition temperature. In order to use Equation (4) to comment on the activation volume, the first step is to consider:

\[
\frac{\Delta \mu^*}{\mu^0} = \frac{1}{k_B} \left[ \frac{\ln \left( \frac{\mu^0}{\mu^*} \right)}{\Delta P} \right]
\]

assuming that \( \Delta \mu^* \) is independent of pressure. The two terms in Equation (14) are of approximately equal magnitude if \( T_0 \) is identified with the glass transition temperature since, for polymers in general, \( (\Delta T_0/\Delta P) \) is about 150 kbar \(^{-1}\) and for PIO, \( T_0 \approx 300\) kbar \(^{-1}\) and \( \mu^0 = 30 \) cm\(^3\)/mol. Using these numbers, both terms in parentheses are about 150 kbar \(^{-1}\). However, it is clear that the conductivity is very non-thermal, and that free volume theory is useful. Hence the interpretation of \( T_0 \) is unclear. An alternative interpretation is to attribute the difference in the activation volume to interferences by analogy with small crystals. In this case, association with the same and with each other (not pairwise) must be considered. Similar considerations have been suggested previously by Papke et al.* Additionally, the polymer is probably multishift and thus some of the curvatures may also be attributable to equilibration among the various phases.

### 3.3. Variation at \( \phi \) with Pressure

![Graph](image-url)

Figure 5: Activation volume vs. temperature calculated using Equation (15) and the values of the parameters given in the text.
Finally, a few comments will be made concerning the curvature of the ln(2) vs. pressure plots. The values of b in equation (1) range from about 2 to 20 (in units of cmHg). These values are not unphysical as can be seen from the following analysis.

Ignoring the correction term in equation (3), the "compressibility of the activation volume," \( \kappa \), can be calculated from:

\[
\kappa = \frac{1}{\gamma} \frac{1}{V} \frac{dV}{dV} = \frac{1}{N} \frac{dN}{dP}
\]

(16)

The results of the calculations are listed in Table 1. It is seen that the compressibility of the activation volume range from about 3 to 22. This agrees with the theoretical expectations 33-35 and the experimental results 26 in ionic crystals where the compressibility of the migration volume is found to be on the order of 5-15. The compressibility of the host lattice is.

B. V.V.

In summary, the effect of pressure on the ionic conductivity in all silicate perovskites and thiomolybdate complexed FETD has been measured. The primary results are as follows.

(a) The activation volume scales with the size of both the anion and cation. The simplest explanation of this is that both the anions and cations are mobile.

(b) The experimental values for the activation volume are in good agreement with the predictions of a donor-acceptor theory with an attempt made to measure parameter of about 2. This implies that the motion of the ions is controlled by inter-atomic vibrations transitioning into diffusive hopping of the ions.

(c) The donor and acceptor sites lead to a positive activation volume if it is interpreted at the glass transition temperature. Consequently, a negative curvature in the Arrhenius plots has better be interpreted in terms of relaxation of the ions which can be made with each other. In general, relaxation of a single system is a complex problem.

(d) The compressibility of the activation volume is found to be about an order of magnitude larger than the compressibility of the host lattice.

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REFERENCES

NOTE ADDED IN PROOF

After the completion of the work described above, two experiments were performed which extend and support the results reported above. First, careful differential scanning calorimeter (DSC) measurements were performed on all samples using a DuPont 990 DSC. The data for PEO4.5-NaClO4 and PEO4.5-NaSCN were extremely similar consisting of a weak, narrow melting at low temperatures (20-30°C), a strong, narrow melting at high temperatures (150-180°C), and a weak, broad endothermic event between these two peaks. This supports the comparison of these two materials at all temperatures. That data will be presented in detail elsewhere.

Second, the temperature range of the pressure measurements was extended to 350K for the two most important materials, PEO4.5-NaClO4 and PEO4.5-NaSCN. The results for PEO4.5-NaClO4 can be represented by:

\[ \ln(G(\eta^{-1})) = -7.9 - 10.2P + 4.6P^2 \]

and

\[ \ln(G(\eta^{-1})) = -8.0 - 7.3P \]

describes the data for PEO4.5-NaSCN. The latter material was a hot-pressed sample provided by Northwestern University while the former was a film prepared in our laboratory. These results lead to activation volumes of 30.2 and 22.0 cm³/mol, respectively. Once again, the activation volume for PEO4.5-NaClO4 is found to be much larger than for PEO4.5-NaSCN. Consequently, this extends and supports the arguments above concerning ion size effects on \( \gamma \) and the resultant conclusion concerning anion motion in these materials. Next, the activation volumes are smaller at 350K than at lower temperatures though not small enough to change any of the arguments presented above concerning the transport mechanism. That is, since \( \gamma_0 = 1.72 \) and 2.38(1.29) for these materials at 350K, these are still much larger than would be expected for intrachain mode gammas. Finally, it is noted that the extremely large decrease in \( \gamma \) (26.4 to 15.9 cm³/mol for 313 to 350K) as temperature increases which is reported by Chadwick, Strange, and Worboys for PEO4.5-NaSCN at this conference, is not reproduced in the present work. However, it is noted that the PEO4.5-NaSCN studied at 350K in the present
work was hot-pressed while that of Chadwick et al. was a film. Consequently, some of the difference may be due to the difference between the preparative techniques. In support of this, the PEO4.5-NaSCN films studied in the present work showed significant curvature while the hot-pressed samples did not. Further, the zero pressure slope for the hot-pressed sample is about 10% lower than for the film. In addition, the PEO4.5-NaClO4, which is a film, does exhibit a somewhat larger decrease in activation volume as temperature increases (38.5 to 30.2 cm³/mol for 310 to 350K) than does the hot-pressed PEO4.5-NaSCN. However, the decrease is still much smaller than that observed by Chadwick et al. Whatever the magnitude, it is clear that v does decrease with increasing temperature. Some decrease is expected since, as temperature increases and the polymer expands, the free volume increases and thus the activation volume should decrease. However, the decrease in activation volume appears to be too large to be explained by this effect. Rather, these results may represent evidence for an "association" process occurring in the polymer. In such a model, the large decrease in activation volume follows since at low temperatures there is a "volume of formation" for the associated ions in addition to a "motion volume." The activation volume then decreases because the "formation volume" decreases due to increased "dissociation" as temperature increases.
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