Abstract

Kinetic data for structural relaxation in silver iodomolybdates at the glass transition temperature ($T_g$) are obtained by high-pressure differential scanning calorimetry (HP-DSC) and are compared with activation energies ($E_A$) and volumes ($V_A$) obtained earlier from conductivities below $T_g$. The results are fitted to an empirical equation, $E_A = MV_A$, and displayed in the form of a master plot of $E_A$ versus $V_A$, an approach previously applied to strongly coupled systems, including polymer electrolytes and molten salts above their glass transition temperatures. The parameter, $M$ emerges as a localised modulus, expressive of interatomic forces within the medium, linking together $E_{A,s}, V_{A,s}$ and $E_{A,\sigma}, V_{A,\sigma}$, the ‘apparent’ activation parameters for structural relaxation and ionic conductivity, respectively. Ion transport is distinguished from structural relaxation in the iodomolybdate system by the much smaller $V_A$ and $E_A$ values. However, remarkably close agreement emerges between the ‘process parameters’, $M$,
and $M_\sigma$, both falling near to 8 GPa, thus establishing a quantitative link between ion transport and structural relaxation in this highly decoupled system. This new $E_A$ versus $V_A$ master plot may provide a sound basis for forming a unified approach to ion transport in polymers and glasses.

Key words: ion transport; structural relaxation; polymers; glasses; high-pressure differential scanning calorimetry (HP-DSC); coupling phenomena

**Introduction**

Angell and his coworkers\textsuperscript{1-4} have distinguished between ion transport in polymer electrolytes and glasses, by identifying ionic motions in the former that are *coupled* to viscous flow and where electrochemical applications are possible only above the glass transition temperature $T_g$, and those in glasses that are *decoupled* from viscous flow and where cation mobility is significant at and below $T_g$.

The distinctive behaviour\textsuperscript{2,3} of decoupled systems is shown schematically in Figure 1. The graph consists of two curves relating respectively to the relaxation times for structural reorganisation (essentially viscous flow) and electric field decay (caused by ion transport) plotted ‘Arrhenius style’ with $\log_{10}(\tau/s)$ given as a function of $T_g/T$. The curves are notably non-Arrhenius in shape, the curvature clearly seen in the molten region ($T_g/T < 1$) being a feature of many ‘fragile’ systems including the silver iodomolybdates being investigated in the present study. The key features of this graph are the kinks observed in both curves at $T_g/T=1$ (i.e. at the glass transition) and the way the curves increasingly diverge from left to right, i.e. with decreasing temperature.
Figure 1. A schematic of a $T_g$-reduced Arrhenius plot of shear (mechanical/structural mode, $\tau_s$) and conductivity (electrical mode, $\tau_\sigma$) relaxation times, representative of a fast-ion conducting glass, as seen for example in the AgI-AgCl-CsCl system. (See Figure 1 in ref. 2 and Figure 4 in ref. 3). $R_\tau$ is the decoupling index as defined in the text.

The $\log_{10}(\tau/s)$ values in the upper curve rise from a very low value of approximately –13 at the high temperature extreme to a value of approximately 2.0 (corresponding to $\tau=100$ s) at $T_g$. The lower curve shows the much smaller variation that is found in the electrical modes, where the characteristic relaxation time (defined in terms either of the maximum in the electric modulus spectrum or by a crossover frequency in the conductivity spectrum) reaches a much lower value, close to –10 at the glass transition temperature. On this basis, Angell followed Moynihan and others$^{5,6}$ in defining a decoupling index, $R_\tau$, as the ratio of structural to conductivity relaxation times at $T_g$ such that $R_\tau=\tau_s/\tau_\sigma$ (being
ca.10^{12} in this case). Such large decoupling indices are a characteristic feature of the whole class of ion conducting glasses [see ref 7 for a comprehensive review of this topic].

By way of contrast, the curve for log(τ/σ) will follow much closer to the line for log(τ/σ) in the case of a coupled system. In fact, Torell and Angell\textsuperscript{3} have indicated that $R_c$ could be even less than 1 in the case of a typical, poly(alkylene oxide) electrolyte, as a result of ionic association. The values of $R_c$ thus differ by many orders of magnitude in coupled and decoupled systems. The question arises as to whether it is possible to establish a common approach which embraces the differing patterns of behaviour in coupled and decoupled electrolytes, and ultimately to develop coherent strategies for optimising their conductivity behaviour.\textsuperscript{8}

The approach we are adopting here relies on integrating information obtained from variable pressure and variable temperature experiments, and focuses on the concept of activation as distinct from free volume. We refer to a recent Letter\textsuperscript{9}, in which some of us have analysed the behaviour of several salt-in-polymer electrolytes and of molten calcium potassium nitrate (CKN) [see also ref 10]. These are predominantly coupled systems, where the activation energies (and volumes) were found to be strongly temperature dependent.\textsuperscript{9,10} Accordingly, we have defined ‘apparent’ or ‘instantaneous’ activation parameters, $E_{A,\sigma}(T)$ and $V_{A,\sigma}(T)$ by:

\begin{equation}
E_{A,\sigma}(T) = - R \left( \frac{\partial \ln \sigma}{\partial T} \right)_P
\end{equation}

and

\begin{equation}
V_{A,\sigma}(T) = - RT \left( \frac{\partial \ln \sigma}{\partial P} \right)_T
\end{equation}

Here, $\sigma$ is the d.c. conductivity, and $R, T$ and $P$ have their usual meanings.
In the case of polymer electrolytes based on poly(ethylene oxide), for example, $V_A$ varies from 20 to 40 cm$^3$ mol$^{-1}$ in the range of measurement, and $E_A$ from 45 up to 90 kJ mol$^{-1}$. These changes in the activation energies and volumes, indicated by $\Delta$, have been related to each other by the empirical formula:

$$\Delta E_{A,\sigma}(T) = M_\sigma \Delta V_{A,\sigma}(T)$$

(3)

Thus, ‘master plots’ of $\Delta E_{A,\sigma}(T)$ versus $\Delta V_{A,\sigma}(T)$ emerged as respectable straight lines, which suggests that $M_\sigma$ remains substantially constant over the actual range of measurements (about 100 K in all these cases). We described $M_\sigma$ as a kind of ‘modulus of elasticity’, strongly influenced by intermolecular forces, with values varying from 1.3 GPa in the case of liquid poly(propylene oxide) to 5.0 GPa for molten CKN. We might make the reasonable assumption that these $M$-values would approximate to those that would be obtained from measurements of structural relaxation, because of the strong coupling that exists in these systems. The corresponding log$(\tau_{\sigma}/s)$ and log$(\tau_{\sigma}/s)$ curves would deviate therefore much less from each other than those shown in Figure 1. The question arises as to what happens if the same master-plot approach is applied to decoupled systems. This is the principal object of the present investigation.

Using high-pressure differential scanning calorimetry (HP-DSC), we have studied the structural relaxations occurring in a silver iodomolybdate glass-forming system of molar composition: 50AgI:25Ag$_2$O:25MoO$_3$. In these experiments, the glass is formed by controlled cooling, until the point is reached where the structural relaxations associated with the decreasing enthalpy of the melt cannot keep pace with the cooling rate. The system then drops out of internal equilibrium at a “fictive” temperature, $T_f$, which may be understood as the temperature at which the glass would appear to be in equilibrium if removed instantaneously to that temperature. The value of $T_f$, so defined, may be
determined by standard procedures, essentially involving the study of heat capacity changes occurring during a subsequent reheat cycle. To make a comparison with activated conductivity behaviour, we need to find out how $T_f$ varies with both cooling rate and pressure.

The comparison with activation parameters derived from conductivity data is in this case not entirely straightforward. Thus, we may note that even below $T_g$ these glasses exhibit some curvature in the Arrhenius plots. This curvature was first reported in the closely related silver iodoarsenate system, and has since been observed in many other (usually highly) conducting glasses, and has been the subject of much discussion. The effect in the silver iodomolybdate (as in the iodoarsenate) glasses is to see the emergence of lower activation energies (around 20 kJ mol$^{-1}$) for conductivity data obtained in the region between $T_g$ and room temperature, where indeed the variable pressure conductivity measurements had previously been made, than are needed to fit sub-ambient conductivity data (around 23.0 kJ mol$^{-1}$).

To show how the comparisons are made, we begin by introducing two more activation parameters, defined in analogous fashion to those appearing in Equations 1 and 2:

$$E_{A,s} = -R \left( \frac{\partial \ln |q|}{\partial T_f} \right)_P$$  

and

$$V_{A,s} = -RT_f \left( \frac{\partial \ln |q|}{\partial P} \right)_{T_f}$$

Here, $T_f$ is the fictive temperature of a glass formed by cooling at rate $q$, and the subscript $s$ indicates structural relaxation. If we now refer to the mathematical equality:
\[-(\partial z/\partial y)_x = (\partial z/\partial x)_y (\partial x/\partial y)_z\]

and put \(z = \ln q, \ y = P\) and \(x = T_f\), this gives \(V_{A,s}/RT\) as the term on the left hand side, \(E_{A,s}/RT_f^2\) as the first term on the right hand side, and \((\partial T/\partial P)_q\), the dependence of the fictive temperature on pressure at constant cooling rate, as the second term on the right hand side. The relationship between \(E_{A,s}\) and \(V_{A,s}\) can then be written as:

\[
E_{A,s} = T_f (\partial P/\partial T_f)_q \cdot V_{A,s}
\]

(6)

and we have a newly defined ‘process modulus’ for structural relaxation in the glass given by:

\[
M_s = E_{A,s}/V_{A,s} = T_f (\partial P/\partial T_f)_q = (\partial P/\partial \ln T_f)_q
\]

(7)

Note that the “\(\Delta\)-symbols” shown in Equation 3 are now omitted from Equation 7 and in all our subsequent discussions of the \(E_{A,\sigma}\) and \(V_{A,\sigma}\) values for this glass. The temperature dependence of these activation parameters is not our primary concern. One may also note the unconstrained plots of \(E_{A,\sigma}(T)\) versus \(\Delta E_{A,\sigma}(T)\) given for the first time in ref [9] and shown again in Figure 6 of this paper pass quite close to the the origin (where \(E_{A,\sigma}(T) = V_{A,\sigma}(T) = 0\)) indicating that to a good approximation \(M_\sigma \approx E_{A,\sigma}/V_{A,\sigma}\) even in polymer electrolytes. Note also that in the HP-DSC experiments, \(E_{A,s}\) and \(M_s\) values are determined directly by experiment, and that \(V_{A,s}\) is calculated indirectly via Equation 7.

We take activation energies and activation volumes for Ag\(^+\) ion conductivity in the silver iodomolybdate glasses, \(E_{A,\sigma}\) and \(V_{A,\sigma}\), directly from the literature\(^ {23-25}\) and use ratios of these to calculate the corresponding values of \(M_\sigma\). Linear plots of \(RT\ln\sigma\) versus \(P\) provide values of \(V_{A,\sigma}\) directly, while the lack of evidence for hysteresis indicates the absence of structural relaxation (densification) occurring during the period of measurement, as would be expected for measurements performed some 40 K below
Tg, i.e. well to the right of the kinks appearing at Tg in Figure 1. We are thus able to determine separately the ‘activation parameters’ for hopping processes occurring in less than 1 nanosecond in this highly conducting glass, and then to compare them with corresponding data for structural relaxations occurring at Tg requiring more than 100 seconds for completion.

We can thus compare ‘fast’ and ‘slow’ processes occurring within the same system, and construct a new master plot of E_A versus V_A, which includes the conductivity data for strongly coupled systems discussed in ref [9], together with the relevant relaxation data for the strongly decoupled iodomolybdate system. On this basis, we are able to outline a unified approach to ion transport, which in principle should be applicable to a wide range of coupled and decoupled amorphous electrolytes.

**Experimental Techniques**

The samples of AgI-Ag_2O-MoO_3 glass were taken from those prepared in the molar ratio 50:25:25 for an earlier study.\(^2^6\)

The design, operation and calibration of our HP-DSC system are fully described in a recent publication.\(^2^7\) It is essentially based on a power-compensated DSC (Pyris Diamond DSC from Perkin-Elmer) equipped with an autoclave that can be pressurised by means of a hand-operated spindle pump from 50 MPa to 500 MPa using silicone oil as the pressurising medium. It may be operated in a temperature range from 293 K to 573 K at pressures from 0.1 MPa to 500 MPa and with various heating and cooling rates (from 0.5 K min\(^{-1}\) to 50 K min\(^{-1}\)).

HP-DSC experiments were performed using a single sample of about 12 mg ground to a powder and sealed in an aluminium crucible. This sample was subjected to various thermal cycles, each at constant pressure in the range from 50 MPa to 400 MPa. After applying the chosen pressure, each thermal cycle
involved heating the glass from 308 K to 383 K (chosen to be above $T_g$ at all pressures) at 10 K min$^{-1}$, in order to erase the previous thermal history (aging), cooling the sample at a constant rate within the range from -5 to -50 K min$^{-1}$ to 308 K (in the asymptotic glassy state), and then immediately reheating at a single rate of 10 K min$^{-1}$ from 308 K to 383 K. Repeat scans following cooling of the sample to below $T_g$ were sufficiently reproducible to confirm that no significant crystallization had taken place at the higher temperatures.

The values of $E_{A,\sigma}$ and $V_{A,\sigma}$, which are used in this paper and are shown in Table 1, include data taken directly from references 23 and 24. These data correspond to high pressure experiments performed some years ago at the former EPSRC High Pressure Facility, located then in the STL laboratories in Harlow, UK. These data refer exclusively to measurements made at ambient temperatures and above, using a fixed-frequency (2 kHz) $ac$ bridge. No corrections were made for electrode effects. We considered any errors inherent in this procedure to be relatively small, and largely self-cancelling when the $E_{A,\sigma}$ and $V_{A,\sigma}$ values were calculated.

**Results**

Figure 2 shows typical HP-DSC curves obtained by reheating the sample from 308 K to 383 K at a single heating rate of 10 K min$^{-1}$ under pressure (here about 250 MPa) following cooling of the sample at various rates (from 50 K min$^{-1}$ to 5 K min$^{-1}$). Only parts of the complete scans are shown so as to separate the curves more clearly. It should also be noted that the baseline has been subtracted from the curves, which also have been arbitrarily shifted by a small amount in the $y$-direction for clarity. From these heating scans, the fictive temperature, $T_f$, of the glass cooled under pressure is determined using the “equal area” method$^{12,13}$ shown in the inset of Figure 2, where the shaded area equals the area under the experimental curve. The fictive temperatures are corrected for various factors associated with the operation of the HP-DSC.$^{27}$
Figure 2. HP-DSC scans obtained from 308 K to 383 K at 10 K min\(^{-1}\) on a 50\%AgI-25\%Ag\(_2\)O-25\%MoO\(_3\) sample of 12.24 mg under pressure (about 250 MPa) following cooling of the sample at various rates (solid line: 50 K min\(^{-1}\); long-dashed line: 40 K min\(^{-1}\); medium-dashed line: 30 K min\(^{-1}\); short-dashed line: 20 K min\(^{-1}\); dotted line: 10 K min\(^{-1}\); dash-dotted line: 5 K min\(^{-1}\)). Inset shows the “equal area” method\(^{12,13}\) used to determine the fictive temperature, \(T_f\), from the HP-DSC scan of the 50\%AgI-25\%Ag\(_2\)O-25\%MoO\(_3\) glass cooled at 5 K min\(^{-1}\) under pressure (about 250 MPa). \(T^*\) is a temperature in the equilibrium liquid, while \(T'\) is a temperature in the asymptotic glassy region.

The apparent activation energy, \(E_{A,s}\), for each pressure, is then determined from the variation of \(T_f\) with the cooling rate or, more exactly, from the slope of \(\ln|q_c|\) vs \([1/T_f]\)\(^{12,14}\) (see Figure 3). Since the variation of fictive temperature with cooling rate is small, the reliable evaluation of \(E_{A,s}\) is difficult, and there is appreciable scatter when different data sets are being compared. The value reported in Table 1 is an average value of \(E_{A,s}\) from the values obtained for different pressures. The dashed line in Figure 3 clearly shows, however, the strong effect of pressure on the fictive temperature. This effect is more clearly seen in Figure 4 which shows HP-DSC curves obtained by first cooling the sample at 50 K min\(^{-1}\)
under various pressures, followed by reheating the sample from 308 K to 383 K at a single heating rate of 10 K min\(^{-1}\) under each selected pressure.

Figure 3. Plot of \(\ln(\text{cooling rate})\) versus reciprocal fictive temperature, \(T_f\), obtained for various pressures (filled circles: 56 MPa; open circles: 106 MPa; filled triangles down: 157 MPa; open triangles up: 207 MPa; filled squares: 257 MPa; open squares: 306 MPa; filled diamonds: 357 MPa; open diamonds: 413 MPa) and a heating rate of 10 K min\(^{-1}\). The full lines represent a least-squares fit to each set of data. The dashed line is shown to guide the eye to the strong effect of pressure on \(T_f\) for one cooling rate.
Figure 4. HP-DSC scans obtained from 308 K to 383 K at 10 K min$^{-1}$ of 12.24 mg of the same glass as in Figure 2, following cooling/heating cycles under different pressures (about 50 MPa: bottom solid line; 100 MPa: long-dashed line; 150 MPa: medium-dashed line; 200 MPa: short-dashed line; 250 MPa: dotted line; 300 MPa: dash-dotted line; 350 MPa: dash-double dotted line; 400 MPa: top solid line), and using constant cooling and heating rates, 50 K min$^{-1}$ and 10 K min$^{-1}$, respectively.

Both onset and peak temperatures, and hence $T_f$, clearly increase in Figure 4 with increasing pressure. It should be noted that only parts of the complete scans are shown here to separate the curves more clearly, and that the curves have been arbitrarily shifted by a small amount in the $y$-direction for clarity. The variation of $T_f$ with pressure at constant cooling rate is much greater than that of $T_f$ with cooling rate for a given pressure. This important difference is emphasised in Figure 5, where in accordance with Equation 7 the variations of pressure with the natural logarithm of the fictive temperature are plotted for four different cooling rates. The slopes of the regression lines obtained are very similar, and come to 7.39 MPa, 7.20 MPa, 7.16 MPa and 6.89 MPa for cooling rates of 50 K min$^{-1}$, 20 K min$^{-1}$, 10 K min$^{-1}$ and 5 K min$^{-1}$, respectively. These form a set of separately-determined values for the required modulus, $M_s$, which taken together average out at 7.2 GPa.
**Figure 5.** Plot of pressure versus ln(Tf/K), obtained from HP-DSC heating curves using various pressure values (from 50 MPa to 400 MPa) during cooling/heating cycles using constant cooling [50 K min\(^{-1}\) (filled circles), 20 K min\(^{-1}\) (open squares), 10 K min\(^{-1}\) (filled triangles up) and 5 K min\(^{-1}\) (filled triangles down)] and heating (10 K min\(^{-1}\)) rates. The full lines represent least-squares fits to the data for each cooling rate.

**Discussion**

Table 1 reveals obvious differences and similarities between the parameters for structural relaxation and ion transport for one composition within the silver iodomolybdate system. The most obvious differences are the much larger values of \(E_{A,s}\) and \(V_{A,s}\) compared with \(E_{A,\sigma}\) and \(V_{A,\sigma}\): namely, 1250 kJ mol\(^{-1}\) as compared with 20.0 kJ mol\(^{-1}\), and 174 cm\(^3\) mol\(^{-1}\) as compared with 2.38 cm\(^3\) mol\(^{-1}\). The most striking similarity is the closeness of the \(M_s\) and \(M_\sigma\) values: which are 7.2 GPa and 8.4 (the average of 8.7 and 8.1) GPa, respectively. Table 1 also includes conductivity-based data for a glass close to the composition 55AgI:22.5Ag\(_2\)O:22.5MoO\(_3\), taken from the literature.\(^{25}\) The value of \(M_\sigma = 7.5\) GPa is remarkably close to the \(M_s\) value, which we have now derived from the HP-DSC data.
Table 1. Activation parameters and moduli for structural relaxation and ion transport for a silver iodomolybdate glass: a average values from this work; b from Figure 5 and Table 2 in ref 23; c from Tables 2 and 1 in ref 24; d from ref 25 for a glass with composition 55AgI:22.5Ag2O:22.5MoO3. It should be noted that $V_{A,\sigma}$ values from refs 23 and 24 refer to measurements made at ambient temperature.

<table>
<thead>
<tr>
<th>Structural relaxation</th>
<th>Ionic conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{A,s}$/kJ mol$^{-1}$</td>
<td>$M_s$/GPa</td>
</tr>
<tr>
<td>1250$^a$</td>
<td>7.2$^a$</td>
</tr>
</tbody>
</table>

In order to put these numbers into perspective, we recall that the activation volumes for ionic conductivity found in single-cation glasses are normally similar in magnitude to the actual sizes of the mobile ions. In effect, the activation volume, $V_{A,\sigma}$, relates directly to the activated hop and may be thought of as the volume required either to open up doorways between sites or to open up the intended ‘target sites’ to the incoming cations. At first sight, this is a clear vindication of the concept of decoupling. No additional relaxation of the network is apparently required – certainly, for the ‘fast hops’ that appear to dominate the charge transport process in highly conducting single-cation glasses. In fact, the observed value of $V_{A,\sigma}$ of 2.38 cm$^3$ mol$^{-1}$ is somewhat smaller than the expected volume of the Ag$^+$ ion. We can compare this value with that of $V_{A,\sigma} = 5.0$ cm$^3$ mol$^{-1}$ obtained for Ag$^+$-ion conductivity in an AgPO$_3$ glass, and much the same value calculated from a standard value of the ionic radius. As we shall see shortly, the ‘smallness’ of $V_{A,\sigma}$ contributes significantly to the exceptionally low value of $E_{A,\sigma}$, and hence to the correspondingly high room temperature conductivities found in this and other AgI-doped glasses (approaching $10^{-2}$ S cm$^{-1}$ at ambient).

The much larger $V_{A,s}$ value obtained by HP-DSC is to be expected since it indicates the much larger disturbances that occur within the glass during structural relaxation close to and within the glass transition. That the two ‘process-defined moduli’, $M_s$ and $M_\sigma$, are virtually the same implies that...
activation energies increase simply in proportion to activation volumes. This in turn leads to much slower rates of structural relaxation compared with ion hopping, and hence to the large decoupling indices that are observed experimentally.

Perhaps the really remarkable result is the virtual identity of the $M_s$ and $M_\sigma$ values. This new finding poses the question of what *shared* property of the system is being sensed by these two process parameters. We have already indicated that for polymer electrolytes the $M_\sigma$ values show no obvious temperature dependence. This ‘independence’ is maintained despite significant changes occurring in the medium range order, involving for example the presence of tiny cavities that increase in size with increasing temperature, and which have been indicated by positron annihilation lifetime spectroscopy (PALS).\textsuperscript{11} The local moduli as defined here differ from conventional bulk or shear moduli that are *material* parameters and usually decrease with increasing temperature.\textsuperscript{9}

Furthermore, we find that the moduli quoted here for the silver iodomolybdate system are significantly smaller than the published values\textsuperscript{25,35} of the bulk modulus, $K \approx 22$ GPa, obtained by two different methods (changes in sample dimensions and ultrasound velocity, respectively) for a glass of very similar chemical composition (the 55AgI:22.5Ag$_2$O:22.5MoO$_3$ glass referred to in Table 1). We are led, therefore, to conclude that the process moduli are independent of medium (and clearly long range) structural features, and must be much more local in their origins. Such a conclusion is consistent with the magnitude of the activation volumes involved in both ion hopping and structural relaxation. In the latter case, a simple calculation shows that if $V_A$ represents a *local dilatation* from 0.5 to 0.6 nm taking place in some identifiable ‘sphere of interaction’, the molar activation volume would be 230 cm$^3$, which is close to the $V_{A,s}$ value determined in this study by HP-DSC. We suggest, therefore, that the quantities $M_s$ and $M_\sigma$ refer to the properties of localised regions where ‘action is in progress’, and that this is the crucial difference distinguishing the process moduli as defined here from the more familiar elastic constants defining the properties of the bulk material.
We note, also, the remarkable simplicity of Equation 3, which provides a basis for discussing
variations in conductivity without apparently being dependent upon any details of the transport
mechanism. These ‘details’ will obviously include the actual mechanism of conduction\textsuperscript{28-31} and the
existence or otherwise of pre-existing pathways for ion migration.\textsuperscript{36-45} The implied unimportance of any
‘long-range’ structural features supports the idea that the conduction pathways in glass exist as a result
of ionic motions, rather than the other way round. This conclusion is very much in the spirit of the
‘updated’ dynamic structure model of Bunde et al.,\textsuperscript{44} and applied in recent discussions of the variations
in activation volume in mixed-cation glasses\textsuperscript{29,30} and in a detailed analysis of the pressure dependence
of correlation effects\textsuperscript{31} in sodium and rubidium borate glasses.

We may note here that the ‘classical’ theory of Anderson and Stuart [see ref 7] gives $E_{A,\sigma}$ as the sum
of two terms: one relates to the electrostatic energy ($E_b$) which binds an ion to its site, and the other to
an elastic strain energy ($E_s$) which must be overcome to allow the ion to move through a doorway into
its new site. It appears, in the approach being adopted here, that both process moduli, $M_s$ and $M_{\sigma}$, somehow combine the contributions from electrostatic and elastic forces within a single parameter. However, we hesitate to assume that this is a general result.

Certainly, a number of special factors are operating here. Of these, the most obvious is the presence of
AgI, a partially covalent salt which imparts high Ag$^+$-ion conductivity to crystalline and glassy
electrolytes.\textsuperscript{7} This effect relates to the ability of Ag$^+$ ions to move readily into sites of differing
coordination number,\textsuperscript{45} and to charge-neutralisation effects between Ag$^+$ and I$^-$ ions, which serve to
reduce electrostatic repulsions between neighbouring Ag$^+$ ions. This latter effect could indeed be
responsible for allowing Ag$^+$ ions to approach each other more closely than a fully ionic model would
suggest, and could account for the smaller activation volumes for Ag$^+$ ion transport observed in the AgI-
doped glasses. It is the combination of a small $M$-parameter (much smaller than the bulk modulus as
already discussed) with a small activation volume (only half the ionic volume) that imparts the exceptionally high conductivities to these glasses at room temperature.

However, the value $M$ could itself be an important indicator of glass behaviour, closely related to the rigidity, or inversely to the flexibility of the glass structure. In a recent paper, Novita et al.\textsuperscript{46} have found evidence for changes occurring in the analogous AgPO\textsubscript{3}-AgI system: moving from what they term “stressed rigid”, through “unstressed rigid”, to “floppy” (i.e flexible) phases with progressively increasing AgI content. The silver iodomolybdate glass studied here will certainly satisfy the requirements for similar matrix flexibility to the AgI-rich phosphate glasses. Thus, there is no network structure present (the molybdate entities exist as discrete molecular anions), and the high concentration of Ag\textsuperscript{+} and I\textsuperscript{−} ions will tend to soften any alternative structures which may form in this glass.

In this context, it is worth recalling an earlier study of a wider range of silver iodomolybdate glasses by conventional DSC.\textsuperscript{26} These experiments were directed towards determining the variations with AgI content of the $\alpha$-parameter in the Tool-Narayanaswamy-Moynihan equation.\textsuperscript{12,47}

$$\tau = \tau_0 \exp[\alpha E_A/RT + (1-\alpha) E_A/RT_f]\quad (8)$$

which describes the dependence of the retardation (or relaxation) times for enthalpy relaxation in the glassy state. It involves the actual temperature $T$, and the fictive temperature $T_f$, $\tau_0$ which is the value of $\tau$ at infinitely high temperature, and $E_A$, the activation energy for enthalpy relaxation in the equilibrium system. Here $\alpha$ partitions the relative contributions of temperature and stucture (identified by $T_f$) to the enthalpic (or structural) relaxation times occurring in the glass, and can have any value between 0 and 1. In the glassy state, where $T_f$ remains constant and $\alpha$ is less than 1, the measured activation energy ($\alpha E_A$) is less than the value of $E_A$ in the equilibrium liquid. This change is clearly seen in Figure 1, and applies
apparently to both structural and electrical relaxations. The kinks in the Arrhenius plots seen at $T_g$ will, however, become less pronounced the closer $x$ approaches to unity.

The parameter, $x$, may thus be regarded as a measure of the *continuity* in behaviour between molten and glassy states. We found earlier$^{26}$ that $x$ actually increases with increasing mole fraction of AgI in the silver iodomolybdate glasses. Such an increase would normally be associated with the increasing ‘strength’ and network character in the melt. It is hard to see, however, how such arguments could apply in this system when the concentration of AgI is increasing, since AgI is hardly likely to impart network character. More probably, we think, the increasing degree of continuity between melt and glass behaviour is associated with the increasing flexibility (i.e. decreasing $M$-parameter) of the glassy matrix.

Key features of the foregoing discussion are summarised in Figure 6, which brings together a ‘master plot’ of $E_A$ versus $V_A$ for several coupled systems including selected polymer electrolytes and molten calcium potassium nitrate (CKN) taken from ref 9, and are based on variable-pressure variable-temperature data taken from the relevant literature$^{48-51}$ and for the silver iodomolybdate glass. As in ref 9, the lines drawn through the data points for the polymer electrolytes and for molten CKN are not constrained to pass through the origin, and their slopes correspond directly to moduli calculated from Equation 3. The new line for this silver iodomolybdate glass has a slope of 7.8 GPa (an average of the $M_s$ and $M_\sigma$ values), and passes through the origin in accordance with Equation 7.
Figure 6. Activation energy versus activation volume ‘master plots’ for different polymer electrolyte systems: PPO-Na(CF$_3$SO$_3$)$_2$ and PPO-Li(CF$_3$SO$_3$)$_2$ ($\bullet$); PEO-LiClO$_4$ ($\bullet$); 2Ca(NO$_3$)$_2$:3KNO$_3$ (CKN) molten salt ($\bullet$); silver iodomolybdate glasses from this work ($\bullet$); and a sodium aluminoborate glass ($\bullet$). The inset shows the same variations, but on restricted $E_A$ and $V_A$ scales, omitting the data point for structural relaxation in the silver iodomolybdate glass. The slope of the full line referring to the silver iodomolybdate glass is $M = 7.8$ GPa while the dotted lines represent a least-squares fit to the data obtained on the other systems.

The main graph in Figure 6 enables a direct comparison to be made between parameters for structural relaxation in the iodomolybdate glass with the parameters obtained for the coupled systems. The more obvious difference to emerge between the iodomolybdate and the other systems is the much larger $V_{A,s}$ value – a difference attributable to the fact that the HP-DSC measurements are made at the glass transition temperature, while the conductivity data were obtained far above it in the case of both the
polymer electrolytes and molten CKN. The inset allows a corresponding comparison to be made between the parameters for electrical relaxation in the iodomolybdate glass and those in the strongly coupled systems. Here, the main difference to emerge is the much smaller $V_{A,\sigma}$ value for the glass, an observation directly related to decoupling in the iodomolybdate system. There is also a single data point, included for comparison, for ion conductivity in a sodium aluminoborate glass.\textsuperscript{29} This system also exhibits a small value of $V_{A,\sigma}$.

Certain crystalline solid electrolytes such as the the high temperature $\alpha$-form of AgI and those in the family of $\beta$-aluminas, based on the composition Na$_2$O:9Al$_2$O$_3$, have been excluded from Figure 6 even though they have somewhat disordered structures and exhibit very high cationic conductivities. All these materials show finite, positive activation energies. However, $V_{A,\sigma}$ takes negative values in $\alpha$-AgI\textsuperscript{52} and in the Li form of $\beta$-alumina (prepared by ion exchange)\textsuperscript{53} while the value of $V_{A,\sigma}$ is essentially equal to zero for Na $\beta$-alumina. It makes little sense to include data points on the master plot that fall either in the in the left-hand quadrant or on the $y$-axis, which would imply that $M$ may either take negative values or become infinite.

On the other hand, the behaviour of \textit{amorphous} systems does make good sense when displayed in Figure 6. Thus matrix flexibility is clearly revealed in this figure, in the sense that it increases with clockwise rotation about the origin. Thus, all the polymer electrolytes are characterised by relatively weak intermolecular forces, and, since measurements are usually made somewhat above $T_g$, they tend towards the upper limit of flexibility found in amorphous electrolytes. The behaviour of the sodium aluminoborate glass is that of a much more rigid system, arising from the presence of a strong and largely continuous network structure, containing four-fold coordinated B and Al atoms [see ref 29 and papers cited therein].
However, the main significance of Figure 6 is that it unites two fundamentally different patterns of behaviour. Thus, whereas in the polymer electrolytes the spread of data points arises from the effect of temperature on the activation parameters, the separation of the two points for the iodomolybdate glass indicates instead the *decoupling* of Ag⁺-ion motions from relaxations occurring in the host matrix. The separation between these two points along the horizontal axis (with $V_A$ values of 2.38 and 174 cm³ mol⁻¹, respectively) corresponds in Figure 1 to the vertical distance at $T_g$ between two separate curves. In Figure 6, we see that points falling on a single straight line suffice to demonstrate the degree of decoupling.

Finally, we note that Figure 6 also includes data for the glass-forming molten salt, calcium potassium nitrate (CKN). Recently, Singh et al.⁵⁴ have discussed the links that will exist between frequency-dependent ionic conductivities and the corresponding frequency-dependent fluidities in this system. Their theoretical treatment involves the idea¹⁰,⁵⁵ that all dynamic properties in the melt can be related to the same *microscopic* processes (or elementary steps) occurring at very short times, i.e. of the order of picoseconds. Such an argument, which is implicit also in Ngai’s coupling concept [see refs 21 and 36], seems to be entirely reasonable in that system, since ion transport and structural relaxations in CKN are known to be strongly coupled – especially in the higher-temperature, moderately fluid region well above $T_g$, where the variable-pressure data⁵¹ used in constructing this master plot were obtained. What Figure 6 shows, and for the first time, is that this argument can now be extended to *decoupled systems*. Thus, the extension of the silver iodomolybdate line, from 2.38 right out to 174 cm³ mol⁻¹, corresponds to an effective stretching along the *time scale* from hundreds of picoseconds up to hundreds of seconds. The linearity of this plot (there are three points including the origin) shows that the same interatomic forces are active across a huge spectrum of relaxation times. This makes sense only insofar as the long time behaviour is determined by what happens at short times.
A unified treatment of ion transport in glassy and polymeric materials is presented here, which is based on a simple approach involving activation energies and activation volumes for ion transport and those obtained by high-pressure DSC for structural relaxation at \( T_g \). The remarkable agreement between two ‘process’ moduli for silver iodomolybdate glass, defined here by the equations \( M_\sigma = E_{A,\sigma} V_{A,\sigma} \) and \( M_s = E_{A,s} V_{A,s} \), points to the involvement of very similar intermolecular forces in ion migration and structural relaxation in a highly-conducting \( \text{Ag}^+ \)-ion containing glass. The implication of this new result is that a sharp distinction can no longer be drawn between the behaviour of ions in strongly coupled and decoupled systems, suggesting that \textit{elementary} processes occurring at short times and involving short-range interactions, control both ‘fast’ and ‘slow’ processes in these materials.

We also suggest that master plots of \( E_{A,\sigma} \) versus \( V_{A,\sigma} \), and \( E_{A,s} \) versus \( V_{A,s} \), may provide a useful way of classifying electrolytes and for understanding their differing behaviours. Thus, if amorphous polymer electrolytes are to find important applications in energy storage devices, they will do so despite the large and varying activation volumes (ranging from 20 to nearly 100 cm\(^3\) mol\(^{-1}\)) because their \( M \)-values are small. Alkali aluminoborate glasses on the other hand may find electrochemical applications (for example in thin film devices), despite having much larger \( M \)-values (ca. 20 GPa), because the activation volumes for \( \text{Na}^+ \) (and \( \text{Li}^+ \)) ion transport will be so much smaller (3.3 cm\(^3\) mol\(^{-1}\) or less). The silver iodomolybdate glass that has been discussed in detail in this paper would score on both counts, since both \( V_{A,\sigma} \) and \( M_\sigma \) values are small. Electrochemical applications of this glass [see for example ref 56] would certainly not be limited by its very respectable \( \text{Ag}^+ \)-ion conductivity.

Acknowledgements

The authors thank the UK Engineering and Physical Sciences Research Council (EPSRC) for financial support (GR/S74614/01) and Dr. Amanda Pappin for supplying the glass.
References and Notes


[22] K. Funke (Univ. of Münster, Germany) has indicated in a private communication that the onset of curvature in sub-$T_g$ Arrhenius plots may be a natural consequence of the disappearance of the dispersion in the conductivity spectrum.


[34] Tables of ionic radii can be found in many standard texts. Typically, \( r(\text{Ag}^+) = 126 \text{ pm} \), from which the (molar) ionic volume is readily calculated.


