

## Activation Energy–Activation Volume Master Plots for Ion Transport Behavior in Polymer Electrolytes and Supercooled Molten Salts

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We demonstrate the use of activation energy versus activation volume “master plots” to explore ion transport in typical fragile glass forming systems exhibiting non-Arrhenius behavior. These systems include solvent-free salt complexes in poly(ethylene oxide) (PEO) and low molecular weight poly(propylene oxide) (PPO) and molten  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$  (CKN). Plots showing variations in apparent activation energy  $E_A$  versus apparent activation volume  $V_A$  are straight lines with slopes given by  $M = \Delta E_A / \Delta V_A$ . A simple ion transport mechanism is described where the rate determining step involves a dilatation (expressed as  $V_A$ ) around microscopic cavities and a corresponding work of expansion ( $E_A$ ). The slopes of the master plots  $M$  are equated to internal elastic moduli, which vary from 1.1 GPa for liquid PPO to 5.0 GPa for molten CKN on account of differing intermolecular forces in these materials.

## Introduction

We explore the use of master plots to show the dependence of apparent activation energy on apparent activation volume for ion-transport processes in glass-forming systems exhibiting non-Arrhenius behavior, usually in the range some 50 to 150 K above their glass transition temperatures. The systems under study include the classical solvent-free complexes of salts dissolved in poly(ethylene oxide) (or PEO)<sup>1</sup> and low-molecular-weight poly(propylene oxide) (or PPO)<sup>2</sup> and molten  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$  (or CKN),<sup>3</sup> data being collected in temperature ranges where both conductivity and viscous flow are usually described by the empirical Vogel–Tamann–Fulcher (VTF) equation.<sup>1–9</sup> These materials have been selected because crystallization is readily suppressed, and their low-temperature conductivity behavior may be considered as typical of a diverse group of materials commonly encountered at the interface between solid-state and liquid-state ionics.

The temperature-dependent or “instantaneous” activation energies and corresponding volumes<sup>10–16</sup> are obtained from variable-pressure variable-temperature (VPVT) data (see refs 1 and 15 for practical details), from the equations

$$E_A = -R \left( \frac{\partial \ln \sigma}{\partial T^{-1}} \right)_P \quad (1)$$

and

$$V_A = -RT \left( \frac{\partial \ln \sigma}{\partial P} \right)_T \quad (2)$$

where  $\sigma$  is the dc conductivity, and  $R$ ,  $T$ , and  $P$  are the universal gas constant, Kelvin temperature, and hydrostatic pressure, respectively.

The “low-pressure”  $V_A$  values are determined directly at selected temperatures from graphs of  $\ln \sigma$  versus  $P$ . For convenience, the corresponding instantaneous values of  $E_A$  are obtained from a fit (see also ref 5 for an alternative formulation of non-Arrhenius behavior) to the empirical VTF equation:

$$\sigma = A \exp \left( \frac{-B}{T - T_0} \right) \quad (3)$$

where  $A$  and  $B$  are empirical fitting parameters and  $T_0$  is a zero mobility temperature, by differentiating eq 3 with respect to  $1/T$  to obtain

$$E_A = BR \left( \frac{T}{T - T_0} \right)^2 \quad (4)$$

Equation 4 shows values of  $E_A$  decreasing continuously with increasing temperature, a point that is indicative of the fragile nature<sup>6</sup> of these materials.

There are already reports in the literature<sup>1,2</sup> that  $V_A$  decreases with increasing temperature. To account for this, Fontanella<sup>2</sup> has suggested that  $V_A$  is an additional volume, over and above that normally available to an ion, that is required when it moves. The available volume ( $V_{\text{avail}}$ ) (often referred to as the free volume) may itself be both temperature and pressure dependent. Thus the total volume required for transport,  $V_{\text{tot}}$ , is written as the sum of two volumes:

$$V_{\text{tot}} = V_{\text{avail}} + V_A \quad (5)$$

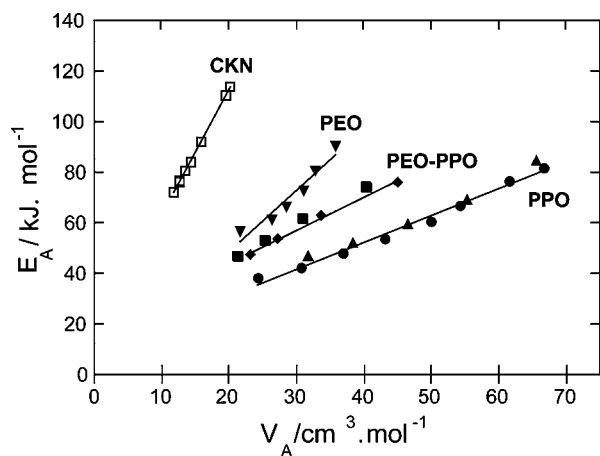
The conclusion is that the way  $V_A$  changes with temperature (or indeed pressure) may be attributed to changes in  $V_{\text{avail}}$ . The

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**Figure 1.** Activation energy versus activation volume master plots for three polymer electrolyte systems (see text), where different symbols refer to different salts: ( $\blacktriangledown$ )  $\text{LiClO}_4$ ; ( $\bullet$ )  $\text{Li}(\text{CF}_3\text{SO}_3)$ ; ( $\blacksquare$ )  $\text{Mg}(\text{ClO}_4)_2$ ; ( $\blacklozenge$ )  $\text{NaPF}_6$ ; and ( $\blacktriangle$ )  $\text{Na}(\text{CF}_3\text{SO}_3)$ . ( $\square$ ) is the fragile molten salt  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$  (CKN). Note that moving along the lines from right to left corresponds to moving toward higher temperatures.

question we seek to answer in this letter is how far such changes in  $V_A$  influence the observed changes in  $E_A$ .

## Results and Discussion

A very strong connection between  $E_A$  and  $V_A$  is revealed in Figure 1. The plots of  $E_A$  versus  $V_A$  summarize the behavior of a range of polymer electrolytes, including a purely anion conducting  $\text{Mg}(\text{ClO}_4)_2$ -doped material and more conventional mixed anionic–cationic conductors containing the salts  $\text{LiClO}_4$ ,  $\text{Li}(\text{CF}_3\text{SO}_3)$ ,  $\text{Na}(\text{CF}_3\text{SO}_3)$ , and  $\text{NaPF}_6$ . The  $E_A$  and  $V_A$  data (measured from 300 to 370 K) were obtained in our laboratories for the amorphous O:Li = 6:1 ratio complex of  $\text{LiClO}_4$  in PEO, and for similar complexes of  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{NaPF}_6$  in the cross-linked copolymer of ethylene oxide and propylene oxide.<sup>16</sup> Data for lithium and sodium triflates ( $\text{LiCF}_3\text{SO}_3$  and  $\text{NaCF}_3\text{SO}_3$ ) in low-molecular weight poly(propylene oxide) (PPO)<sup>2</sup> and for molten CKN were also taken from the literature.<sup>3</sup>

A very simple result emerges. All the data, regardless of the mobile cations involved, lie on three separate straight lines for the three amorphous polymers. There is another straight line for molten CKN. We refer to these four lines as the master plots for these systems. Extrapolation of the plots toward zero  $V_A$  corresponds to progressively increasing the temperature. Although these lines pass fairly close to the origin, they have not been constrained to do so. We prefer to say that over the temperature ranges studied the changes in  $E_A$  are directly proportional to changes in  $V_A$ .

To our knowledge, there is no existing theory that can explain the existence of such master plots, nor to account for the strong variations seen from system to system. We note, however, that the slope of each plot (given here by the symbol  $M$ ) will have clearly defined units and that this will provide a clue as to the overall significance of the plots. Thus, if the activation volumes are expressed in  $\text{m}^3 \cdot \text{mol}^{-1}$ , and activation energies in  $\text{J} \cdot \text{mol}^{-1}$ , the slopes must be in Pascals (Pa). These are units either of pressure or of an elastic modulus. The slopes are, respectively, PEO  $M = 2.4$  GPa; EO–PO copolymer  $M = 1.3$  GPa; PPO  $M = 1.1$  GPa; and molten CKN  $M = 5.0$  GPa. The question now is to decide what property of these systems is represented by the  $M$  parameters.

Here, we make use of published thermodynamic data. Pressure–volume–temperature (PVT) studies for amorphous

PEO<sup>17</sup> and liquid PPO<sup>2</sup> provide us with isotropic compressibilities (in  $\text{Pa}^{-1}$ ) at different temperatures, the reciprocals of these being the bulk moduli ( $K$ ). For PEO at its melting point of 340 K, the modulus  $K$  is 3.3 GPa, decreasing to 2.8 GPa by 390 K. The corresponding bulk moduli for the low molecular weight PPO are somewhat smaller, decreasing from 2.8 GPa at 300 K to 2.2 GPa at 370 K. Thus, although the moduli,  $K$ , are of the same order of magnitude as the slopes,  $M$ , they are clearly larger (being some 25% larger for PEO and 100% for PPO.) Nevertheless, the similarity in the magnitudes of  $K$  and  $M$  clearly suggest that  $M$  also represents some kind of “material constant”, and that it is probably a measure of the elastic forces operating within the host materials that are called into play by ion transport.

Accordingly, we have chosen to express the observed changes in apparent activation energy  $\Delta E_A$  in terms of changes in apparent activation volume  $\Delta V_A$ , by a very simple equation

$$\Delta E_A = M \cdot \Delta V_A \quad (6)$$

Here  $E_A$  and  $V_A$  are the limiting low-pressure activation parameters and  $M$  is the new modulus of elasticity. The key point is that while  $V_A$  and  $E_A$  vary with temperature,  $M$  does not.

To understand better what  $M$  may represent, it is useful to know more about the distribution of available (free) volume in these systems. Relevant information comes from recent positron annihilation lifetime spectroscopy (PALS) studies.<sup>16,18,19</sup> Pas et al.<sup>16</sup> have adopted the simple procedure of adding cavity volumes derived from ortho-positronium (o-Ps) lifetimes to activation volumes obtained via eq 3 for the same salt complexes in copolymers of ethylene oxide and propylene oxide that are shown in Figure 1. They obtained numerical values of  $V_{\text{tot}}$ , as defined in eq 5, that are close to  $115 \text{ cm}^3 \text{ mol}^{-1}$  (ca. 190 cubic Angstrom units per cavity). This volume, which would be equivalent to three or four ethylene oxide units, would be available for some cooperative process that is responsible both for ion transport and viscous flow in these materials. Since the cavities increase in size with increasing temperature<sup>8,16,18</sup> while activation volumes correspondingly decrease, one is led to the conclusion that ion transport and viscous flow processes are facilitated by the presence of these cavities, and that this assistance depends in some way on the deformability of such cavities.

Some years ago, MacKenzie<sup>19</sup> considered the somewhat analogous situation of porous materials subjected to externally applied hydrostatic pressures. He showed that the ease with which the holes may collapse during compression depends on both bulk and shear moduli appropriate to the hole-free material. In other words, the compressibility of such composite materials is itself a “composite” quantity, containing contributions from compressibility and shear compliances (i.e., from  $1/K$  and  $1/G$ , respectively) of the continuous phase.

Since one knows that the shear modulus of soft materials is strongly frequency dependent (being much smaller at lower frequencies than at higher ones), it follows that at lower frequencies the shear compliance of the continuous phase will make an increasingly dominant contribution to the measured compressibility of a porous material. So in polymer electrolytes, where the continuous phase is viscoelastic in nature and microscopic cavities are present, the measured compressibility becomes temperature dependent, as indeed is observed experimentally.<sup>2,17</sup> So, the fact that  $M$  is temperature independent implies that  $M$  is some kind of high frequency modulus,

indicative of elastic responses to stresses generated within the material at very short times.

These arguments lead us toward a very simple picture of the transport mechanism, where the motion of a mobile ion (usually an anion in a polymer electrolyte,<sup>20</sup> but it could be a  $K^+$  ion in molten CKN) initiates the displacement of material into a nearby cavity leading to an expansion in its immediate vicinity. The activation volume  $V_A$  measures the extent of this dilatation, and  $E_A$  is the work done against the relevant modulus of elasticity,  $M$ .

Recent studies in Funke's group based on broadband conductivity spectroscopy in fragile liquids such as molten CKN [see refs 5, 21, and 22] reveal important differences in mechanism between these systems and solid electrolytes where a hopping mechanism prevails. Thus, in the melts showing fragile behavior, the mobile ions do not hop into preexisting sites, so "successful" ionic displacements (i.e., those contributing to the dc conductivities) must always involve appropriate "site building" rearrangements (or structural relaxations) within the host matrix. We suggest, in light of the information derived from variable pressure and from PALS experiments and from conductivity spectroscopy, that these site-building activities begin very quickly after an ion has moved (after 1 picosecond, say) and that they involve local displacements of material (ions or neutral particles) into a cavity in the immediate vicinity of the moving ion. The modulus  $M$  indicates the strength of the intermolecular forces that oppose such displacements.

We note here that the parameter  $M$  increases with increasing intermolecular attraction within the host media, i.e., in the order PPO < PEO < PPO-PEO < CKN. Thus, on moving from salt complexes in PPO through to those in the PPO-PEO composite to PEO, and finally to the molten CKN, one first replaces weaker by stronger van der Waals interactions as alkane groups give way to polar ether groups, and finally the van der Waals forces are then replaced by ionic interactions. Thus,  $M$  measures the cohesive energy density. One can speculate that the increased modulus, as reported here for PEO as compared with PPO electrolytes, may also indicate an increased degree of salt dissociation in the former polymer and the related formation of additional ionic cross-links between neighboring polymer chains, as a consequence of the better solvating power of the poly(ethylene oxide)<sup>23</sup> as compared with its poly(propylene oxide) analogue.

It is interesting also to compare this present treatment of fragile liquids with the Anderson-Stuart (A-S) model<sup>24</sup> that has long been applied to ion hopping processes in glasses, which by contrast obey the normal Arrhenius law.<sup>25</sup> According to the A-S and to later models,<sup>25-29</sup> ions hop into sites that are already present in the glass structure. The measured (dc) activation energy contains a significant contribution from the elastic energy required either to open up doorways between sites or, as has been suggested more recently,<sup>26-29</sup> to open up the preexisting "target sites" for ions to enter. The relevance to the present discussion is that, in the A-S model, the contribution that network dilatation makes to  $E_A$  also depends on the elastic modulus of the glassy material.

If we take data obtained recently for a sodium aluminoborate glass system<sup>26</sup> and calculate the ratio  $E_A/V_A$  for a glass of composition 0.45 Na<sub>2</sub>O: 0.55 (0.87 B<sub>2</sub>O<sub>3</sub>:0.13 Al<sub>2</sub>O<sub>3</sub>), we obtain a value of  $M = E_A/V_A = (60 \times 10^3 \text{ J mol}^{-1}/3 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) = 20 \text{ GPa}$ . Two points about this calculation are worth noting. First, the value of  $V_A$  obtained ( $3 \text{ cm}^3 \text{ mol}^{-1}$ ) is much smaller than the values obtained so far for fragile liquids (see Figure 1), and indeed it corresponds very closely to the size of a sodium

ion. The reason for this lower value is that ion hopping in glass proceeds without the need for "site building" (this has already occurred in the molten glass<sup>29</sup>), and so ion hopping processes become entirely decoupled from viscous flow processes.<sup>30</sup> Second, we may note that the apparent modulus ( $M$ ) obtained directly from the ratio of  $E_A$  to  $V_A$  is of the same order of magnitude as many of the elastic moduli quoted in the literature for inorganic glasses. This coincidence suggests that expansion effects are significant in glassy materials, even though electrostatic effects are in some cases thought to be more important.<sup>24,25</sup>

## Conclusions and Further Work

We have now established a clear link between apparent activation energies and corresponding activation volumes for ion transport in fragile systems that typically show non-Arrhenius behavior. The fact that this link holds good for both classical polymer electrolytes (where ions are dispersed within a polymer matrix) and for anhydrous (i.e., entirely solvent-free) molten salts, suggests that this may be a very widespread pattern of behavior.

We argue that the existence of the  $E_A$  versus  $V_A$  master plots may be attributed to a very simple transport mechanism involving mobile ions that initiate localized displacements of material into small cavities, which, in turn, necessitates dilatation of the surrounding matrix. The activation volume  $V_A$  measures this dilatation, and  $E_A$  expresses the work required, first in moving material into the cavities and then in bringing about the required expansion.

Looking to the future, it seems that the parameter  $M$ , which may be derived directly from the master plots, will emerge as a useful tool for comparing different kinds of ionic conductor, especially those based on hard and soft materials. In future papers, for example, we will explore the application of  $E_A/V_A$  plots to various kinds of structured polymer electrolytes, including side-chain liquid-crystal polyethers,<sup>31,32</sup> where decoupled ion transport has been reported as occurring at or below  $T_g$ , and where the possibility of a hopping mechanism being operative in a polymer electrolyte is currently receiving more detailed attention.

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