

Correlation between the Activation Energies for Ionic Conductivity for Short and Long Time Scales and the Kohlrausch Stretching Parameter β for Ionically Conducting Solids and Melts

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The temperature dependence of the dc conductivity σ of most glass-forming and crystalline ionic conductors is Arrhenius with constant activation energy, E_σ , at sufficiently low temperatures or conductivity levels. However, σ becomes non-Arrhenius at high temperatures or conductivity levels. We have found that the product, βE_σ , of the Kohlrausch stretching exponent for the conductivity relaxation, β , and the dc conductivity activation energy in the Arrhenius regime is approximately the same as the high temperature apparent activation energy, E_a , of σ at the temperature where σ reaches the high level of $1 \Omega^{-1} \text{cm}^{-1}$ and the conductivity relaxation time τ_σ is of the order of 1 psec. [S0031-9007(97)05200-9]

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Conductivity relaxation due to mobile ions in glasses, ceramics, molten salts, and solid electrolytes [1–4] is a subject of great interest to chemists, physicists, and materials scientists. What makes the phenomenon so difficult to describe is the complex structure of some of these materials (e.g., glasses) within which the ions diffuse and the necessity to take into consideration the effects of interaction and correlation between the ions on the diffusion process. It is difficult to come up with a microscopic theory of conductivity relaxation, although some advances have been made in recent times using models which are based on the interactions between the ions [5–8]. Conductivity relaxation and the dynamics of ion transport in glass are still very much a semiempirical science. As in any such case, well established phenomenologies such as robust correlations between experimentally observed quantities are important for the development of the field. These correlations help to achieve an improved understanding of the basic mechanism of ionic transport through the eventual development of a correct microscopic theory.

In this Letter we report a very general quantitative correlation between two activation energies, the product, βE_σ , and E_a . Here β is the Kohlrausch stretching exponent of the ionic conductivity relaxation [1,2,4,5,9] (to be defined later) and E_σ the constant activation energy of the ionic dc conductivity σ at lower temperatures throughout which σ has the Arrhenius dependence, $\exp(-E_\sigma/kT)$. At high temperatures and high conductivity levels, σ no longer follows the Arrhenius temperature dependence. E_a is the asymptotic high temperature apparent conductivity activation energy, $-Rd \ln \sigma/d(1/T)$ with R being the ideal gas constant, at the temperature where the mean electric field

or conductivity relaxation time [1,4,9],

$$\langle \tau_\sigma \rangle = \epsilon_0 \epsilon_\infty / \sigma, \quad (1)$$

has reached short times of the order of 1 psec. In Eq. (1), $\epsilon_0 = 8.854 \times 10^{-14} \text{F/cm}$ is the permittivity of free space and ϵ_∞ is the high frequency dielectric constant. Note that since ϵ_∞ is only very weakly temperature dependent, the activation energies E_σ and E_a and the corresponding activation energies [$=Rd \ln \langle \tau_\sigma \rangle / d(1/T)$] for $\langle \tau_\sigma \rangle$ are virtually identical. For glasses, ϵ_∞ usually lies in the range 4–20. For $\epsilon_\infty = 10$,

$$\langle \tau_\sigma \rangle = \frac{8.9 \times 10^{-13}}{\sigma} \text{ s}, \quad (2)$$

where σ is measured in $\Omega^{-1} \text{cm}^{-1}$, so that $\langle \tau_\sigma \rangle$ is about 1 ps when σ reaches the high conductivity level of about $1 \Omega^{-1} \text{cm}^{-1}$. Since E_a is an important quantity in this work, we define it explicitly by

$$E_a = [-Rd \ln \sigma / d(1/T)]_{\sigma=1 \Omega^{-1} \text{cm}^{-1}}. \quad (3)$$

Specifically, in crystalline ionic conductors where there is no change in structure throughout the entire temperature range, we find βE_σ is almost the same as E_a . In glass-forming ionic conductors, the structure has to change because both β and E_σ are from measurements in the glassy state and E_a is from the high temperature melt data. Even so, we still find that generally βE_σ is no more than about 20% larger than E_a . The correlation holds for most glass-forming ionic conductors with any value of the decoupling index $R_i(T_g)$, which is defined as the ratio [1,4] $\langle \tau_s(T_g) \rangle / \langle \tau_\sigma(T_g) \rangle$ at the glass transition temperature T_g . Here $\langle \tau_s \rangle$ is the viscosity or shear stress relaxation time which usually [4] has the value of 20 s at T_g . From the

relation between σ and $\langle\tau_\sigma\rangle$ given by Eq. (1), it is clear that $R_\tau(T_g)$ is another indicator of the conductivity level at T_g . The correlation is also valid in crystalline fast ionic conductors. Although the undertaking that leads to these findings is motivated by the predictions of the coupling model [5,6,10,11], which anticipates such a correlation in glass-forming or crystalline ionic conductors, we would like the correlation described here to be considered on its own weight, independent of any theory.

The conductivity relaxation in glassy [1,2,4,5(a),5(c), 8–19] and even in crystalline [5(b),8,20,21] ionic conductors is generally a highly nonexponential process. In the complex electric modulus representation of the conductivity relaxation by Macedo and co-workers [1,4,9,14], the conductivity dispersion is related to a nonexponential conductivity relaxation function, $\phi(t)$, in the time domain. $\phi(t)$ is well described by the stretched exponential function [1,2,4,9–15],

$$\phi(t) = \exp[-(t/\tau_\sigma)^\beta], \quad (4)$$

where the stretching exponent β lies within the bounds $0 < \beta \leq 1$. From (4) it follows that $\langle\tau_\sigma\rangle = \beta^{-1}\Gamma(\beta^{-1})\tau_\sigma$ where Γ is the gamma function. This relation together with Eq. (1) indicates that $\langle\tau_\sigma\rangle$, τ_σ , and σ all have the same temperature dependence as long as β is not strongly temperature dependent. The electric modulus and the stretched exponential function have been used to characterize the nonexponentiality of conductivity and nuclear spin lattice relaxation [1,2,15–17]. Experimentally, it is found that β increases with decreasing interaction between the ions, as realized by decreasing the concentration of ions [1,12]. Other properties of β also indicate that its complement, $n = 1 - \beta$, is a measure of the effect the many-body interactions between ions have on the motion of the ions [1,2].

Crystalline ionic conductors can attain high conductivity, such that $\langle\tau_\sigma\rangle$ is approaching the time scale of picoseconds, without phase or structural changes by raising the temperature. This is the case for Na β -alumina [5(b)], RbAg₄I₅ [8], and yttria stabilized zirconia, (Y₂O₃)_x(ZrO₂)_{1-x} [20,21]. In the present consideration we shall exclude any crystalline ionic conductor where there are additional complications, such as the ordering of ions as temperature is lowered in Na β'' -alumina. Such a complication makes an extraneous contribution to the low temperature activation energy, which understandably will undermine the correlation.

The route to such short $\langle\tau_\sigma\rangle$ values can vary in glassy ionic conductors depending on the magnitude of the conductivity at T_g or, equivalently, the value of $R_\tau(T_g)$. For some fast glassy ionic conductors with $R_\tau(T_g) \geq 10^{13}$, it is possible for $\langle\tau_\sigma\rangle$ to reach the picosecond time scale by raising the temperature without leaving the glassy state [1,22]. We shall henceforth refer to these materials as glassy superionic conductors. However, most measurements of σ of glassy superionic conductors have not

been carried out at high enough temperatures that $\langle\tau_\sigma\rangle$ estimated by Eqs. (1) or (2) has reached the picosecond time range [22]. Such measurements require high temperatures that approach T_g which the experimentalists try to avoid in order to keep the glassy structure unchanged. The data of Ag₂S-B₂S₃-SiS₂ glasses collected in Ref. [22] are good examples of this situation. The onset of deviation from Arrhenius behavior and the decrease of the apparent activation enthalpy in the glass well below T_g are clearly evident [22] and explained [5(c),7(b)]. However, because the σ measured does not exceed $10^{-2} \Omega^{-1} \text{cm}^{-1}$, these data do not permit an unambiguous determination of E_a defined by Eq. (3) and hence cannot be included into our present consideration. In poorer glassy ionic conductors with $R_\tau(T_g) \ll 10^{13}$, for $\langle\tau_\sigma\rangle$ to attain a picosecond time scale by raising temperature, the materials have no choice but to go across the glass-liquid boundary [1,4,10,18,19,23–31] at T_g . In general, the temperature dependence of σ in the liquid state is non-Arrhenius. The apparent activation energy defined by $E_{\text{app}}(T) = -Rd \ln \sigma / d(1/T)$ decreases with increasing temperature. The decrease of $E_{\text{app}}(T)$ becomes less rapid with increasing T . Usually when σ approaches a high conductivity level of the order of $1 \Omega^{-1} \text{cm}^{-1}$ the variation of $E_{\text{app}}(T)$ with T becomes small and an approximately constant asymptotic high temperature activation energy, E_a , can be obtained from the experimental data. The examples we have taken from the family of glassy ionic conductors are those in which conductivity measurements have been carried out above T_g up to temperatures where σ is of the order of or slightly less than $1 \Omega^{-1} \text{cm}^{-1}$, to permit an estimate of E_a . Since we are interested in showing the correlation between the product βE_σ and E_a , our choice of data is further limited to those ionic conductors on which the frequency dependence of the conductivity has been measured at lower temperatures in the glassy state and analyzed in the electric modulus representation to obtain both β and E_σ .

The parameters β , E_σ , and E_a we use to show the correlation

$$\beta E_\sigma \approx E_a \quad \text{or} \quad \beta E_\sigma / E_a \approx 1 \quad (5)$$

are given in Table I. It can be seen by inspection that the product βE_σ is generally slightly larger than E_a , but by no more than about 20%. The results from the crystalline ionic conductors are also included at the end of Table I. The thermodynamic variables such as the specific volume or density undergo significant changes with the large temperature change involved in going from the glassy state to the high temperature melt. Therefore, it is remarkable that the two quantities βE_σ and E_a are so close to each other for a wide variety of glassy ionic conductors for which $R_\tau(T_g)$ varies over 11 orders of magnitude. The only exception to our finding that $\beta E_\sigma \approx E_a$ is the fused salt 0.4Ca(NO₃)₂-0.6KNO₃ (CKN), for which $\beta E_\sigma / E_a = 3.0$. The main difference between CKN and

TABLE I. Ionic transport and conductivity relaxation parameters. For the glass-forming melts β and E_σ were obtained in the glassy state from conductivity relaxation measurements, while the activation energies, E_a , were obtained from the high temperature melt dc conductivity data by Eq. (3). The activation energies E_a^{glass} from neutron scattering or high frequency microwave and far infrared conductivity data were obtained within the glassy state. All activation energies are in units of kJ/mol.

Glass-forming ionic conductors	β	E_σ	βE_σ	E_a	E_a^{glass}	$\log_{10} R_\tau(T_g)$	$\frac{\beta E_\sigma}{E_a}$	Refs.
LiCl · 7H ₂ O	0.46	34	15.6	14.4		0.48	1.08	[8,28,34,35]
0.4Ca(NO ₃) ₂ · 0.6K(NO ₃)	0.74	100	74.0	25		3.5	2.96	[4,36]
CdF ₂ -LiF-AlF ₃ -PbF ₂	0.77	109	83.9	68.4		7.1	1.23	[27]
ZBLAN20	0.68	85	57.8	50		8.5	1.16	[18]
ZBLAN10	0.66	79	52.1	46		8.9	1.13	[18]
ZBLA	0.61	72	43.9	36		9.7	1.22	[18]
(Li ₂ O) · 3(B ₂ O ₃)	0.52	84	43.7	40		10.9	1.09	[23,24]
(Na ₂ O) · 3(SiO ₂)	0.55	64	35.2	33.5		10.6	1.05	[25,26]
0.56Li ₂ O · 0.45LiBr · B ₂ O ₃	0.44	47.1	20.7		21.1		0.98 ^a	[29]
AgPO ₃	0.66	49.5	32.7	28.5		9.9	1.14	[19]
(AgI) _{0.1} · (AgPO ₃) _{0.9}	0.59	43	25.4	22.5		10.0	1.13	[19]
(AgI) _{0.2} · (AgPO ₃) _{0.8}	0.57	39.5	22.5	19.8		10.5	1.14	[19]
(AgI) _{0.3} · (AgPO ₃) _{0.7}	0.54	32.9	17.8	15.6		10.8	1.14	[19]
(AgI) _{0.4} · (AgPO ₃) _{0.6}	0.51	32.0	16.3	13.3		11.1	1.23	[19]
(AgI) _{0.5} · (AgPO ₃) _{0.5}	0.48	26.9	12.9	10.1	8.7	11.5	1.27	[19,31]
(AgI) _{0.6} · (AgPO ₃) _{0.4}	0.48	26.9	12.9	7.9		11.9	1.29	[19]
(AgI) _{0.7} · (Ag ₂ MoO ₄) _{0.3}	0.44	19.3	8.5	9.0		11.4	0.95	[37]
(Ag ₂ S) _{0.5} (GeS ₂) _{0.5}	0.45	32.8	14.8		14.5		1.02 ^a	[32,33]
Crystalline conductors								
Na β -Al ₂ O ₃	0.5	13.4 ^b	6.7	6.8 ^c	6.74		0.99	[5(b),38]
RbAg ₄ I ₅	0.47 ^d	9.8 ^c	4.6		4.2 ^c		1.09 ^a	[8]
(Y ₂ O ₃) _{0.095} (ZrO ₂) _{0.905}	0.43	111.9	48.2	48.2			1	[21,39–42]

^aCalculated from the ratio $\beta E_\sigma/E_a^{\text{glass}}$.

^bAt 300 K.

^cObtained by plotting $\log_{10} \sigma$ against $1/T$.

^dEstimated from $\log_{10} \sigma$ versus $\log_{10} f$ data.

the other ionic conductors in Table I is that CKN is composed entirely of small, simple ions (Ca²⁺, K⁺, and NO₃⁻). This is in contrast to the other glasses and melts in which some complexity persists even at high temperatures, e.g., large anions such as ZrF₈⁻⁴ in ZBLA, ZBLAN10, and ZBLAN20 melts and hydrated Li⁺ and Cl⁻ ions in the LiCl · 7H₂O melt.

As stated earlier, the importance of the $\beta E_\sigma \approx E_a$ correlation in Table I should be judged by its own worth. Any theoretical model needs to be evaluated for consistency with this correlation. In the context of the coupling model [2,5,6,10,16], the product βE_σ is identified with the true microscopic energy barrier E_a^{glass} opposing ion migration in the glassy state. There are independent methods for obtaining E_a^{glass} of fast glassy ionic conductors without leaving the glassy state by carrying out isothermal ac conductivity measurements [2,29,30] in the high frequency range ($>10^{11}$ Hz) or neutron time of flight measurements of ionic diffusion constants [2,31–33]. These techniques measure ionic motion at times shorter than the crossover time t_c (≈ 2 ps) from independent motion to cooperative motion in the coupling model [5,6,10,11,33]. In fact, high frequency conductivity data in glassy [29] and crystalline [5(b),8,30] ionic conductors have shown a frequency independent conductivity plateau, σ_0 , corresponding to the independent ionic motion. Only at suf-

ficiently high temperatures σ_0 is found to be thermally activated [5(b),8,29,30] and its activation energy gives directly E_a^{glass} , the energy barrier for independent ionic motion. The relation

$$E_a^{\text{glass}} = \beta E_\sigma \quad (6)$$

between the three experimental quantities (all obtained in the glassy state for glassy ionic conductors) is found to hold true for the ionic conductors for which neutron scattering or high frequency conductivity data are available. The values of E_a^{glass} determined for a few of these ionic conductors are entered into one of the columns of Table I. Let us recall that E_a is the activation energy of the dc conductivity at high temperatures when $\langle \tau_\sigma \rangle$ has attained the picosecond time scale. Since $\langle \tau_\sigma \rangle \leq t_c$ in this case, it follows as a consequence of the coupling model that even the dc conductivity is due to the independent motion of the ions and E_a is the true energy barrier. If there is no change in structure in raising the temperature to satisfy the condition $\langle \tau_\sigma \rangle \leq t_c$, as in the case of the few crystalline ionic conductors in Table I, then E_a is the same as $E_a^{\text{glass}} = \beta E_\sigma$. On the other hand, for all of the glass-forming ionic conductors in Table I in which the condition $\langle \tau_\sigma \rangle \leq t_c$ is satisfied only after the structure has been changed from the glass to the melt by raising the temperature, the two quantities E_a and

$E_a^{\text{glass}} = \beta E_\sigma$ are not expected to be exactly equal. This is because E_a and $E_a^{\text{glass}} = \beta E_\sigma$ are the true microscopic energy barriers for independent ionic motion in the melt and in the glass, respectively. The density of the melt is lower than the glass, and from this fact we may infer that E_a should be somewhat smaller than βE_σ , consistent with the trend found in Table I. The alkali silicate glasses are known to have smaller changes in density in going from the glassy state to the melt [25] than do the ZrF₄-based fluoride glasses [18]. For Na₂O-(3.17)SiO₂, the density ρ is equal [25] to 2.392 g/cm³ at $T = T_g = 480^\circ\text{C}$ and 2.230 g/cm³ at $T = 1300^\circ\text{C}$ when σ is near $1 \Omega^{-1} \text{cm}^{-1}$, i.e., a density change of 6.8%. On the other hand, the corresponding density changes are 12.0%, 15.4%, 14.2%, and 12.8%, respectively, for the four fluoride glasses CdF₂-LiF-AlF₃-PbF₂, ZBLAN20, ZBLAN10, and ZBLA. It is interesting to find in Table I that the ratio $\beta E_\sigma/E_a$ is closer to unity for the Na₂O-3SiO₂ glass, which has a smaller density change, than for the fluoride glasses.

Finally, it is worth noting that models for thermally activated hopping over energy barriers can be valid only if $E_a \gg RT$. The E_a values for melts given in Table I all exceed the values of RT at the temperatures at which they were evaluated by factors of roughly 2 or greater.

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