

'Universal' curve of ionic conductivities in binary alkali silicate glasses*

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In the past 25 years, there has been an increasing interest in ionic-glass conductors, mainly motivated by the discovery of new glasses, attempts to produce new solid-state batteries, and the search for an 'universal' theory of iontransport in glassy materials. It is well-known that the ionic conductivity increases rapidly when a network glassformer is modified by the addition of an alkali metal. Despite considerable experimental and theoretical attempt, there is currently no consensus regarding the diffusion mechanism [1]. Numerous models have been proposed, and they vary from thermodynamics with principles in models for liquid electrolytes, such as the weak electrolyte model [2], to models based on solid state concepts such as the jump diffusion model [3], the strong electrolyte model [4], and the dynamic structure model [5].

Ionic conductivity σ in glass is a thermally activated process of mobile ions that overcome a potential barrier E_A , of the form:

$$\log \sigma = \log \sigma_0 - (\log e)E_A/k_B T \quad (1)$$

where σ_0 is the preexponential factor, k_B is the Boltzmann constant and T is the absolute temperature. Extensive studies have recently been made for obtaining an 'universal' equation from the standpoint of glass structure. For example, Doi [6] presented 17 different glasses (not specified) that follows an 'universal' conductivity rule. Swenson and Börjesson [7] proposed a common cubic scaling relation of σ with the expansion volumes of the networking-forming units in salt-doped and -undoped glasses. This fact suggested that the glass network expansion, which is related to the available free volume, is a key parameter in determining the increase of the high ionic conductivity in some types of fast ion-conducting glasses.

According to Adams and Swenson [8], the ion conduction should be determined by the ionic motion within an infinite pathway cluster. For various silver ion conducting glasses [9–10], it was found that the cubic root of the volume fraction F of infinite pathways for a fixed valence mismatch threshold is closely related to both the absolute conductivity and the activation energy of the conduction process as:

vation energy of the conduction process as:

$$\log \sigma T \propto \sqrt[3]{F} = \log \sigma'_0 - (\log e) E_A/k_B T \quad (2)$$

where σ'_0 is the preexponential factor (in K·S/cm).

More recently, Nascimento and Watanabe [11] verified this 'universal' finding in binary borate glasses, considering both Equations 1 and 2. This investigation focuses on ionic-silicate conductors with various types of mobile cations in different concentrations and structures.

Fig. 1 shows Arrhenius plots of σ for 95 binary alkali-silicate glasses, of form $x\text{A}_2\text{O} \cdot (1-x)\text{SiO}_2$ ($A = \text{Li, Na, K, Cs}$, x in wt.% from $x = 2.64$ – 79.33 , as indicated [12]), ranging from 10^{-1} S/cm to less than 10^{-20} S/cm between 20 and 400 °C. The range of activation energy E_A lie between 0.4 and 1.6 eV in all glasses studied. These data were compared with the 'universal' equation for $\sigma_0 = 50$ S/cm in Equation 1. This "universal" equation, following Doy's definition, appears in Fig. 1 as a dotted line.

The substitution of one kind of mobile ion by another affects the ionic conductivity in various ways, such as by modification of the glass structure. Looking at Fig. 1, it is remarkable to observe such a strong correlation between σ and E_A/T for so many different binary silicate glasses. It is interesting to note that the increase in the ionic conductivity with alkali content is almost entirely due to the fact that the activation energy E_A required for a cation jump decreases, as presented in Ref. [4]. Thus, the term σ_0 in Equation 1 is largely unaffected by alkali content.

The fact is that the σ -values for various binary alkali-silicate glasses lie along a single 'universal' curve. These σ -values, except for half a dozen cases, differ from each other by not larger than one order of magnitude. Note that for each sample, the σ -value differ by more than 20 orders of magnitude in the experimental $E_A/k_B T$ -values range. Also, is important to note the wide composition range involved. Therefore, if one measure σ at some temperature, it is possible to estimate E_A from Equation 1 considering $\sigma_0 = 50$ S/cm, and achieve a rough sketch of at different temperatures. Or,

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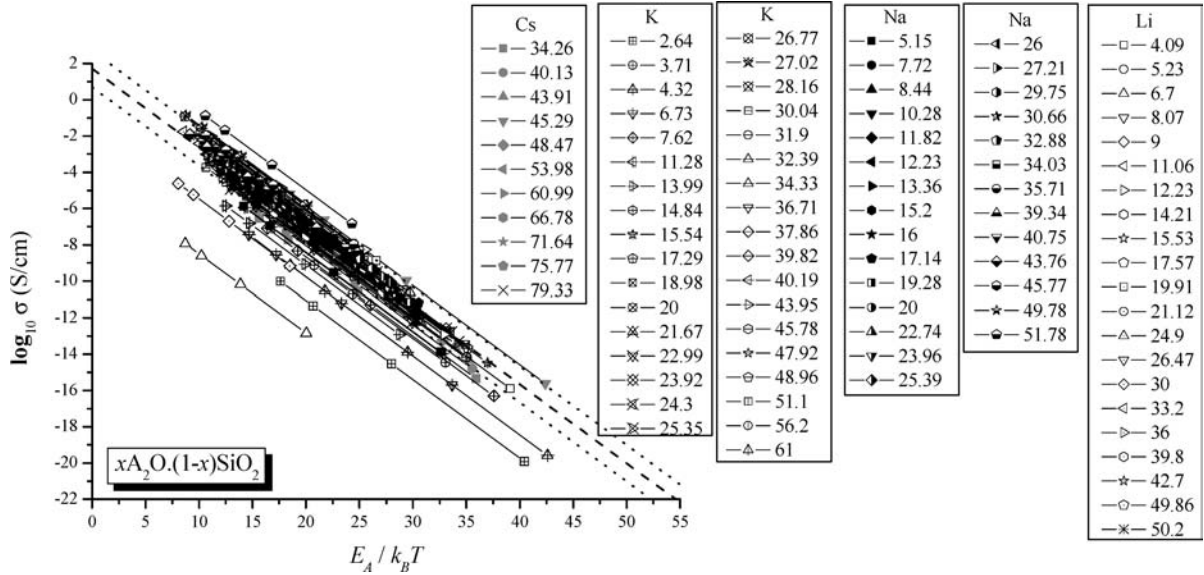


Figure 1 Arrhenius plots of ionic conductivities in 95 binary alkali-silicate glasses [12], of form $x\text{A}_2\text{O}\cdot(1-x)\text{SiO}_2$ ($\text{A} = \text{Li, Na, K, Cs}$, x in wt.%, as indicated). The dashed line is the ‘universal’ curve, Equation 1, with $\sigma_0 = 50$ S/cm, and the dotted lines correspond to one order of magnitude higher or lower than Equation 1.

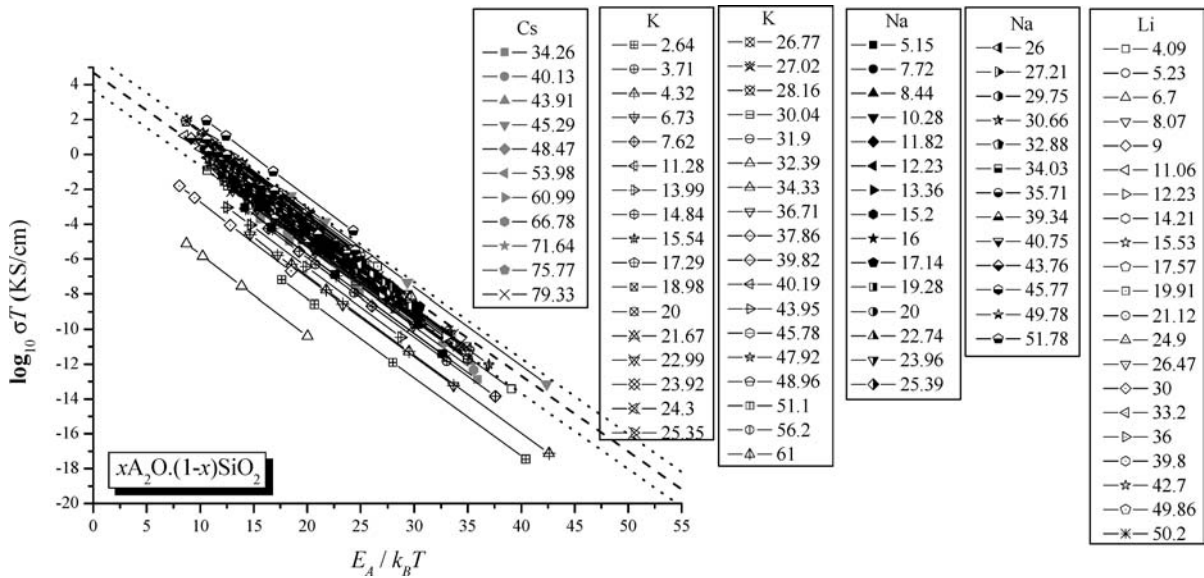


Figure 2 Arrhenius plots of ionic conductivities in 95 binary alkali silicate glasses [12], of form $x\text{A}_2\text{O}\cdot(1-x)\text{SiO}_2$ ($\text{A} = \text{Li, Na, K, Cs}$, x in wt.%, as indicated). The dashed line is the ‘universal’ curve, Equation 2, with $\sigma'_0 = 50\,000$ K.S/cm, and the dotted lines correspond to one order of magnitude higher or lower than Equation 2.

if E_A is obtained by some experimental or theoretical technique, ionic conductivity can be calculated.

Another “universal” curve is obtained using Equation 2, and it is shown in the Fig. 2. The preexponential factor has now the value $\sigma'_0 = 50\,000$ K.S/cm, which conform with the value of σ_0 in the Equation 1. Similar conclusions for Fig. 1 can be drawn here. The most important fact is that in Figs 1 and 2 the scattered data by glasses of different compositions are unified by the single ‘universal’ Equations 1 and 2. The fact that σ lies on these single ‘universal’ curves for many ion-conducting glasses means that σ is governed mainly by E_A .

However, the reason for the decrease of the activation energy with increasing alkali concentration is still not clear. The expansion of the glass framework and the introduction of the alkali ions into voids in the structure

forming narrow pathways would lead to two effects that lower the activation energy, and thus, promote the ionic conductivity. In terms of the AndersonStuart model [4], E_A may be written as $E_A = E_b + E_s$, where E_b is the binding energy term and E_s is the strain energy term. The binding energy is the average energy that a cation requires to leave its site, and E_s is the average kinetic energy that a cation needs to structurally distort the environment and to create a “doorway” through which it can diffuse to a new site. The cation induced expansion of the network structure would lead to a lowering of the strain energy part E_s of the activation energy and the formation of pathways, in which the cations may coordinate with oxygens of the network, leading to a lowering of E_b .

The relations expressed in Equations 1 and 2 have an important conclusion: no matter what is the ionic con-

ductor type, if one takes its conductivity $\log \sigma$ or $\log \sigma T$ and plots against $E_A/k_B T$, all systems will follow the same rule. In summary, there are *strong connections* between the microscopic structure and the ionic conductivity, this fact is based on the different types of composition in the alkali-silicate glasses presented. All these compositions fall into an identifiable pattern where conductivity is related to structure in the form expressed by the “pathway volumes” of Adams and Swenson [13]. Further studies on other binary alkali-oxide glasses as presented in Figs 1 and 2 that would refuse or recognize this ‘universal’ finding to gain further insight into the nature of ion dynamics in glass.

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