Microscopic and thermodynamic interpretations of experimental data on ionic conductivity in lithium silicate glasses

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Experimental data from the literature on electrical conductivity are reviewed for 43 glass compositions in the $x\text{Li}_2\text{O}-(1-x)\text{SiO}_2$ system (0.05<x<0.67). The data are presented herein as a function of temperature and in isothermal plots as a function of the $\text{Li}_2\text{O}$ molar ratio, $x$. Below the glass transition temperature, $T_g$, the experimental ionic conductivity of all the compositions follows an Arrhenius law, $\sigma=\sigma_0 \exp(-E_a/RT)$. The large quantity of experimental data minimizes the experimental inaccuracy in glass composition and conductivity measurements, thus allowing for accurate estimates of the mean values of the pre-exponential term ($\sigma_0$) of the Arrhenius expression and the activation energy ($E_a$), as well as a precise assessment of the variations in electrical conductivity and activation energy with the molar ratio, $x$. The value of the pre-exponential term and the variation of isothermal conductivity and activation energy with $x$ are then interpreted by reference to general concepts for ionic transport in solids, and to the so-called weak electrolyte theory. The Anderson & Stuart model is employed to estimate the absolute values of activation energy. The association of the intrinsic cationic pair model and the weak electrolyte theory provides a good description of the variations in electrical conductivity and activation energy as a function of the $\text{Li}_2\text{O}$ molar ratio. The Anderson & Stuart model leads to consistent absolute values of activation energy only if an arbitrarily chosen value of jump distance is employed in the corresponding expression.

1. Introduction

Inorganic glasses are among the oldest known solid electrolytes since Warburg, more than a century ago, proved the existence of Na+ ionic conductivity by sodium transfer through a glass membrane. (1) Like the Thuringer glass used by Warburg, most oxide-based glasses are purely cationic conductive, the highest conductivities resulting from the migration of singly charged cations like Li+, Na+ or Ag+. In a simple binary glass, composed of a glass former and a glass modifier, the ionic conductivity depends strongly on the modifier concentration; in fact, it is currently observed that an increase in the mobile cation concentration by a factor of two increases the room temperature conductivity by one or two orders of magnitude. This quasi-exponential dependence of ionic conductivity on concentration is the main characteristic of glassy electrolytes. The corresponding interpretations remain an open question, as noted in previous review articles.(2,3)

Below their glass transition temperature, the experimental ionic conductivity for all glasses is currently found to obey an Arrhenius law

$$\sigma = \sigma_0 \exp(-E_a/RT)$$

where $\sigma_0$ is the so-called pre-exponential term, $E_a$ is the activation energy for electrical conduction, and $R$ and $T$ represent, respectively, the gas constant and the absolute temperature. This relationship links the two measured experimental parameters, $\sigma$ and $T$, without any hypothesis related to a specific model.

For simple glass forming systems, the literature reports numerous d.c. or a.c. conductivity data. This is the case particularly for glasses in the binary system $x\text{Li}_2\text{O}-(1-x)\text{SiO}_2$, for which we have found literature data on 43 compositions in the 0.05<x<0.67 range presented in a single Arrhenius plot. From this representation, the characteristic parameters of the Arrhenius expression, i.e. the pre-exponential term and the activation energy of conduction, were calculated and are presented as a function of the molar fraction, x. Isothermal conductivity data were interpolated from the Arrhenius expression and are also presented as a function of the molar ratio, x. This large amount of experimental data allowed us to minimize the experimental inaccuracy of glass composition and conductivity measurements.

The variation in ionic conductivity, pre-exponential
term and activation energy could thus be examined and accurately determined. In a first approach, we will extend the ionic crystal defect theory to glasses, which allows an accurate value of the pre-exponential term to be calculated. The variations in ionic conductivity, pre-exponential terms and activation energies as a function of the modifier concentration are interpreted using a thermodynamic approach, the so-called weak electrolyte model. In addition, experimental values of activation energy and its variation with $x$ are compared to calculated values using the model proposed by Anderson & Stuart.

2. Conductivity data and their dependence on temperature and on the molar ratio, $x$

2.1. Experimental conditions and glass homogeneity

Experimental procedures of glass synthesis are detailed in Refs. 7–21. Most syntheses have been carried out in platinum crucibles at temperatures of 1400°C to 1550°C, depending on the glass composition, followed by air quenching.

Most of the glasses thus obtained appeared homogeneous. However, Charles found visual evidence of phase separation in glasses with $x$ below 0.15 and also studied the influence of such phase separation on the electrical properties.

In fact, phase separation has already been investigated in the $x$Li$_2$O–(1–$x$)SiO$_2$ binary system and a large miscibility gap was found below the liquidus curve. This miscibility gap, at 500°C, extends from pure silica to $x$=0.33. However, the limits between the spinodal domain, in which the phase separation is instantaneous, and the domain in which the phase separation is governed by nucleation and growth, are not exactly known. Two amorphous phases have already been found experimentally in glasses of this system subjected to lengthy heat treatments. In this case, it seems that one phase would approximate the lithium disilicate composition and the other one would consist of silica containing a very small amount of Li$_2$O.

Electrical measurements were performed by d.c. or a.c. techniques using gold, platinum, silver or graphite electrodes. With a high alkali content, the samples were hygroscopic and measurements were taken in dry nitrogen/argon atmospheres or using a three-point guard ring configuration.

2.2. Conductivity as a function of temperature

In all the lithium silicate glasses ($x$=0.05 to 0.67) investigated here, the conductivity was found to obey an Arrhenius behaviour, according to Equation (1), within the measured temperature range. This behaviour is illustrated in Figure 1, where the points indicate experimental data and the lines follow the data. Electrical conductivity ranged from $10^{-1}$ Scm$^{-1}$ to $10^{-19}$ Scm$^{-1}$. We limited from room temperature to 400°C the collected or extrapolated data except for the highest conductive composition, $x$=0.67.

The data of Figure 1 are represented in Figure 2 as a “scaling curve”. In fact, if the conductivity data are plotted against $E_a/RT$, ($E_a$ calculated from the slope of the straight lines in Figure 1), all the straight lines

![Figure 1. Arrhenius plot of ionic conductivity for 43 glass compositions in the binary system xLi$_2$O.(1–x)SiO$_2$ measured between –50°C and 400°C](image)
have the same slope. Differences in conductivity are thus due to the pre-exponential term $\sigma_0$, as observed in previous works on alkali oxide systems.\textsuperscript{(25–28)} Extrapolation to infinite temperature yields $\log\sigma_0$ with a mean value of $2\pm1.5$.

2.3. Pre-exponential term variation versus Li$_2$O content

Figure 3 represents the pre-exponential terms, $\log\sigma_0$, obtained from the linear regression of the experimental data in Figure 1 as a function of $x$ for the 43 compositions investigated. Despite some data scatter, a continuous and monotonic increase with $x$ is evidenced. The superimposed solid line represents the behaviour of $\log\sigma_0$ with $x$, deduced from a thermodynamic model as discussed later herein under Section 3.2.

2.4. Isothermal conductivity variation versus Li$_2$O content conductivity

Isothermal conductivity at 20 and 300°C, represented in Figure 4 as a function of $x$, shows good agreement and continuity between different authors. For $0.1 \leq x \leq 0.67$, the ionic conductivity increases monotonically by four orders of magnitude at 20°C and two orders of magnitude at 300°C. A very important decrease in ionic conductivity with $x$ for $x<0.1$ is observed. The points in Figure 4 represent values

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Figure 3. Variations of $\log\sigma_0$ as a function of $x$ for the 43 glassy lithium silicates investigated. The superimposed solid line represents the variation calculated from the weak electrolyte model discussed under Section 3.2.}
\end{figure}
Figure 4. Isothermal conductivity at 20 and 300°C as a function of x. Symbols represent values interpolated from the data in Figure 1. Solid lines represent the variation in conductivity calculated from the thermodynamic model presented in Section 3.2 (Equation (11)). Note that this model does not give absolute conductivity values, and solid lines are adjusted to the experimental data by translation along the y-axis.

2.5 Activation energy variation versus Li2O content

Figure 5 shows the activation energies calculated from the slopes of the straight lines in Figure 1. As can be seen, \( E_a \) smoothly decreases from 0.65 to 0.50 eV when \( x \) increases from 0.1 to 0.67, with little dispersion of the experimental data. A sharp increase is observed for \( x < 0.1 \), and \( E_a \) reaches 1.25 eV for \( x = 0.05 \). The same graph shows superimposed values of \( E_a \) calculated from the Anderson–Stuart model, as discussed later herein. Also superimposed is the variation in activation energy calculated according to the weak electrolyte approach, as discussed in Section 3.2.

3. Theoretical approaches and comparison with experimental data

3.1. Charge carriers in glass: interpretation of the Arrhenius behaviour based on the defect theory in crystals

In ionic crystals, ions are trapped in well defined cationic sites. Statistically, due to thermal vibrations, some of these ions escape from their normal site to access, for instance, an interstitial position, thus leaving a normal site vacant. Both vacant site and interstitially trapped ion have an associated negative or positive electrical charge.

The idea of charged defects as charge carriers was extended to glassy electrolytes by various authors. According to this description, a normal site in an oxide-based glass is an alkali cation electrostatically trapped near a nonbridging oxygen, while an interstitial defect is a cationic pair composed of two alkali cations sharing the same nonbridging oxygen. A Haven ratio between 0.3 and 0.6, which is usually found for oxide mineral glasses, suggests that ionic transport is expected to occur by the migration of such a cationic pair from one nonbridging oxygen to another rather than by a simple vacancy mechanism. These effective charge carriers can also be seen as sites of higher energy than the normal sites, as suggested by Martin & Angell.

Since the energy required to escape from a normal position is expected to be much higher than the mean thermal energy, \( RT \), the concentration of such positively charged defects, \( n_+ \), is very low compared to the number \( n \) of ions in their normal positions. In this case, only a small fraction of the cations escape temporarily from their stable cationic site and participate in the conductivity. Nevertheless, on a time scale far exceeding the instantaneous charge carriers’ lifetime, all alkali cations participate in ionic transport.

Calling \( \Delta G \) the free energy required to form an interstitial–vacancy pair, the concentration of cationic pairs, \( n_+ \), can be expressed by

\[
n_+ = n \exp\left(\frac{-\Delta G}{2RT}\right)
\]

where \( \mu_+ \) is the attempt frequency of cation in the ionic pair, \( \lambda \) is the jump distance to a neighbouring position, while \( F, R, \) and \( T \) have their usual meanings. An expression can thus be proposed for the cationic conductivity

\[
\sigma = \frac{n \mu_+ \exp\left(\frac{-\Delta G_m}{RT}\right)}{6RT}
\]

or, after separation of the enthalpic and entropic terms

\[
\sigma = \frac{n \mu_+ \exp\left(\frac{\Delta H_m}{2RT} + \frac{\Delta S_m}{R}\right)}{6RT}
\]

Formally, the pre-exponential term of Equation (3b) is temperature dependent, justifying the alterna-
tive representation of experimental data using \( \log \sigma T \) as a function of reciprocal temperature. Nevertheless, the exponential term is more sensitive to temperature, reducing this relationship to the experimentally observed Arrhenius law, Equation (1), by identification of the experimental value of \( E_A \) to

\[
E_A = \Delta H_i / 2 + \Delta H_m
\]

(4)

and the pre-exponential term, \( \sigma_0 \), to

\[
\sigma_0 = n F^2 \lambda^2 v_0 \exp \left( \frac{\Delta S_i / 2 + \Delta S_m}{R} \right)
\]

(5)

In a first approximation, the pre-exponential term, \( \sigma_0 \), can be estimated if the entropic terms in Equation (5) are considered negligible. This assumption is likely in glasses since the local order is not affected by the formation and migration of charge carriers. Since the average jump distance, \( \lambda \), between two cationic sites can be estimated from the concentration \( n \) of mobile cations (\( \lambda = \sqrt{1/n^*} \), and \( n^*/N_A \) \( N_A \) is Avogadro's number), the pre-exponential term can be written as

\[
\sigma_0 = \frac{F^2 \lambda^2 v_0}{6RT} \sqrt{n^*}
\]

If \( n^* \) is expressed in \( \text{ions/cm}^3 \), \( \sigma_0 \) is given in \( \text{S/cm} \). Thus, a numerical estimation based on \( v_0 = 10^{13} \text{Hz} \), \( n^* = 10^{23} \text{ions/cm}^3 \) and \( T=500 \text{K} \) yields \( \log \sigma_0 = 2 \), which is close to the values depicted in Figures 2 and 3.

Equations (4) and (5) provide a good interpretation of the Arrhenius behaviour of ionic transport in ionic crystals and glasses. Nevertheless, in the case of glasses, these equations do not allow the variations of \( E_A \) or \( \sigma_0 \) to be predicted as a function of the modifier concentration, \( x \), since the entropic and enthalpic terms are not expressed as a function of \( x \). To account for these variations, a complementary approach related to the dependence of the enthalpic and entropic terms on \( x \) is needed to explain the major variations observed in the ionic conductivity of glasses according to the modifier concentration. This complementary approach presented below derives from the thermodynamics of electrolytic solutions.

Note that, regarding Equation (3b), it is also possible to discuss the value of a temperature independent pre-exponential term \( \sigma = n F^2 \lambda^2 v_0 / 6 R \), if the data are represented in the form of \( \log \sigma T \) as a function of the reciprocal of absolute temperature \( 1/T \), leading to an activation energy \( E_A = E_0 + RT \).

However, we have not used the \( \log \sigma T \) plot since most of the available published data used in this work are presented as \( \log \sigma \) as a function of \( 1/T \).

Nevertheless, in an Arrhenius representation of conductivity data in a limited temperature range, typically from 300 to 700 K as represented in Figure 1, the variations in \( \log \sigma_0 \) with temperature remain small. The choice of 300 K to calculate an estimated mean value for \( \log \sigma_0 \) as done above, is based on the fact that 300 K is a mean temperature at which conductivity measurements are done.

Concerning the experimental variations of \( \log \sigma_0 \) with composition as shown in Figure 3 they can be related to the variations of \( \log A \) by a simple translation of \( 1/2.3 + \log 500 = 3.1 \).

However, the behaviour and the curve shape of both \( \log \sigma_0 \) and \( \log A \) as a function of the \( \text{Li}_2\text{O} \) molar ratio, \( x \), will remain the same.

A similar remark can be made concerning the values of the determined activation energy \( E_A \) which
would differ by about $3 \times 10^{-2}$ eV in the two representations and whose variations as a function of composition, as shown in Figure 5, would be the same.

### 3.2. Ravaine–Souquet model ('weak electrolyte theory'): interpretation of the variation in ionic conductivity as a function of the modifier concentration, $x$

#### 3.2.1. Charge carrier thermodynamics

Ravaine & Souquet\(^{(4,5)}\) extended the concept of weak electrolyte solutions to glassy electrolytes to interpret the major variations observed in ionic conductivity as a function of alkali ion concentrations.

According to the classic approaches to ionic transport in glasses\(^{(30,34)}\) all the cations migrate simultaneously. Since it is observed experimentally that the increase in conductivity is several orders of magnitude greater than the corresponding change in the cation concentration, it can be assumed that the cation mobility increases substantially. Nevertheless, this assumption cannot be justified from a structural point of view, since the terms in the mobility expression (Equation (2b)) are not significantly affected by the alkali oxide content. Therefore, Ravaine & Souquet have proposed a simplifying hypothesis so that, in a first approximation, the charge carrier mobility, $\mu_c$, can be considered independent of the cation concentration. The large variation in ionic conductivity with $x$ would thus be the result of the large variations in charge carrier concentrations.

To justify this assumption, the weak electrolyte model\(^{(45)}\) assumes that the number of instantaneous charge carriers does not correspond to all the alkali cations present in the glass, but is the result of the partial dissociation of the modifier or “solute” in a solvent of low dielectric constant, which, in the present case, are Li$_2$O and vitreous SiO$_2$, respectively. Thus, the following equilibrium takes place

$$\text{Li}_2\text{O} \rightleftharpoons \text{Li}^+ + \text{LiO}^- \quad (6a)$$

The dissociated species Li$^+$ and LiO$^-$ may be identified, respectively, as a lithium cation in an interstitial pair and its vacant site, as previously described by the defect theory extended to glasses.\(^{(31)}\)

To this dissociation equilibrium is associated a dissociation constant, $K = \exp(-\Delta G_f^0/RT)$ in which $\Delta G_f^0$ is the standard dissociation free energy of Li$_2$O. For high values of $\Delta G_f^0$, $K$ is very low and the number of effective charge carriers is far below the total number of lithium ions. In this case, the number of effective charge carriers is an exponential function of the partial free energy $\Delta G_{\text{Li}_2\text{O}}$ and can be written as

$$n_c = n \exp \left( -\frac{\Delta G_f^0 + \Delta \tilde{G}_{\text{Li}_2\text{O}}}{2RT} \right) \quad (6b)$$

where $\Delta \tilde{G}_{\text{Li}_2\text{O}}$ is the difference in the partial free energy of Li$_2$O in the reference state and in the studied composition. The factor 2 in the exponent means that, as in the case of ionic crystals, the dissociation process generates two charged species, a charge carrier and its vacant site, both in the same concentration. The total free energy necessary for charge carrier formation, $\Delta G_f^0 - \Delta \tilde{G}_{\text{Li}_2\text{O}}$, may be identified as the free energy $\Delta G_f^0$ required to form an interstitial–vacancy pair, as previously described in Section 3.1.

Finally, since the mobility term is considered constant, the variation in ionic conductivity according to $x$ should follow the variation in the partial free energy of lithium oxide, according to

$$\log \sigma = \log n_c = \frac{\Delta G_{\text{Li}_2\text{O}}}{2RT} \quad (7)$$

This correlation can be evidenced by measuring the ionic conductivity and partial free energy of lithium oxide using thermodynamic measurements. However, to the best of our knowledge, results of thermodynamic and electrical conductivity measurements carried out on the same glass composition and under the same experimental conditions have been reported only for sodium silicate glasses\(^{(4)}\) and silver phosphate glasses.\(^{(35)}\) Because of this lack of thermodynamic data, we will estimate the dependence of $\Delta G_{\text{Li}_2\text{O}}$ on $x$ by employing a thermodynamic model derived from the lattice gas model, as currently used for thermodynamics of intercalation compounds.\(^{(36)}\)

The dissolution of the network modifier, in the present case Li$_2$O, in silica involves a chemical reaction in which each molecule of Li$_2$O reacts with a bridging oxygen, according to

$$\text{Si} - \text{O} - \text{Si} + \text{Li}_2\text{O} \rightarrow \text{Si} - \text{O}^– \quad \text{Li}^+ \quad \text{Si} - \text{O} – \text{Si} \quad (8)$$

This reaction is highly exothermic, in the order of several hundred kilojoules\(^{(37)}\) and, with high silica contents ($0 < x < 2/3$), all the Li$_2$O molecules are consumed. For $x > 2/3$, all the bridging oxygens react with a Li$_2$O molecule and the mixtures do not form a glass; these latter compositions will therefore be excluded.

According to the lattice gas model, for compositions with $0 < x < 2/3$, the entropic term representative of the distribution of the broken oxygen bridges in the silicate network can be written as

$$\Delta \tilde{S}_{\text{Li}_2\text{O}} = -R \log \left( \frac{\text{number of broken Si–O–Si bridges}}{\text{number of remaining Si–O–Si bridges}} \right) \quad (9)$$

or as a function of $x$

$$\Delta \tilde{S}_{\text{Li}_2\text{O}} = -R \log \left( \frac{x}{2 - 3x} \right) \quad (9)$$

Note that this expression defines the Li$_2$O standard state for $x = 1/2$ since, for this value, $\Delta \tilde{S}_{\text{Li}_2\text{O}} = 0$.

Taking into account an enthalpic term representative of the interactions between the dissolved Li$_2$O molecules, the partial free energy of Li$_2$O becomes
\[ \Delta G_{\text{Li}_2O} = \Delta H_{\text{Li}_2O} - T \Delta S_{\text{Li}_2O} = h \left( x - \frac{1}{2} \right) + RT \log \frac{x}{2 - 3x} \]  

in which the enthalpic term is reasonably estimated as proportional to the concentration \( x \) of \( \text{Li}_2O \) molecules in the glass. The factor \( x - 1/2 \) allows the reference state to be maintained as \( x=1/2 \). Note that this dependence of \( \Delta G_{\text{Li}_2O} \) on \( x \) is similar to the one derived from a quasi-chemical model proposed earlier by Ravaine et al.\(^{(5)}\) and Pradel et al.\(^{(6)}\)

The dependence of \( \Delta G_{\text{Li}_2O} \) and consequently, the dependence of the number of charge carriers on \( x \) is due to both the entropic and enthalpic terms. Using Equations (7) and (10), the important isothermal variations in ionic conductivity as a function of \( x \) are finally represented by the relationship

\[ \log \sigma = \frac{\Delta G_{\text{Li}_2O}}{2RT} = \frac{h}{2RT} \left( x - \frac{1}{2} \right) + \frac{1}{2} \log \frac{x}{2 - 3x} \]  

(11)

The enthalpic parameter \( h \) can be determined by fitting the variation of \( \Delta G_{\text{Li}_2O}/2RT \), calculated by Equation (11), to the isothermal lithium conductivity as a function of \( x \) obtained from experimental data.

This estimate can also be made by adjusting the experimental variation in activation energy with \( x \), since the global activation energy obeys the relation

\[ E_\text{RS} = \text{constant} - \frac{h}{2} (x - \frac{1}{2}) \]  

(12)

which includes the migration and dissociation enthalpies in the constant term.

### 3.2.2. Comparison with experimental data

(a) The pre-exponential term \( \sigma_0 \)

According to Equation (5), the configurational entropic term of Equation (10) should be included in the pre-exponential term of conductivity in Equation (5) to take into account the modifications introduced by an increase in the \( \text{Li}_2O \) concentration. Therefore, a more accurate expression for the pre-exponential term is

\[ \log \sigma_0 = \log n - \frac{F^2 k^2 \varepsilon_0}{6RT} + \frac{1}{2} \log \frac{x}{2 - 3x} \]  

(13)

Taking a value of 2 for the first term as estimated in Section 3.1, the evolving numerical values of \( \log \sigma_0 \) calculated from Equation (13) are superimposed on the experimental data in Figure 4. The fit can be considered satisfactory, especially because it quantitatively justifies the experimental increase in \( \log \sigma_0 \) as a function of \( x \).

(b) Isothermal conductivity and activation energy variation versus \( \text{Li}_2O \) content

Figure 4 shows the best fit of Equation (11) to experimental conductivity data at 20 and 300°C, which resulted in an enthalpic \( h \) parameter of 27 kJ/mol (0.28 eV). A positive value of \( h \) means that, the chemical reaction, Equation (8), is less and less exothermic as more \( \text{Li}_2O \) is added to the glass structure. The low value of \( h \) (27 kJ/mol compared to hundreds of kJ for the initial reaction\(^{(37)}\)) shows that the entropic term is predominant in Equation (11). The fit to experimental data is satisfactory for \( x>0.1 \). Although the proposed model foresees a sharp drop in electrical conductivity at low concentrations of alkali ions, the experimental drop begins at \( x=0.1 \), a somewhat higher value than that predicted by Equation (11), whatever \( h \) value is chosen.

This model does not allow an absolute value to be calculated for the activation energy, since absolute values for the mobility terms (\( \mu_i \), \( \Delta G_i^f \), and \( \Delta G_{\text{Li}_2O} \) are not known. Therefore, only variations in activation energy with composition can be estimated through the parameter \( h \) in Equation (12). Using the estimated \( h=0.28 \) eV, the expected decrease in \( E_a \) should be 0.06 eV between \( x=0.1 \) and \( x=0.5 \), which is comparable to the variations reported in Figure 5 in this compositional range.

However, the very large increase in activation energy (and the corresponding decrease in electrical conductivity) observed for \( x<0.1 \) cannot be explained by this model, probably because a phase separation occurs, as observed by Charles.\(^{(8)}\) In this domain, the glass is no longer homogeneous, consisting instead of droplets of a lithia-rich phase dispersed in a matrix of relatively pure amorphous silica. The ionic displacement would thus be limited by the difficult migration of lithium cations through this matrix. Nevertheless, the collected data for \( x>0.1 \) show a rather monotonic increase in conductivity and in the pre-exponential term, and a decrease in activation energy which would be more compatible with a homogeneous glass structure. This experimental behaviour does not corroborate the idea proposed by Charles\(^{(8)}\) that glasses from \( x=0.15 \) to \( x=0.4 \) would be composed of a highly conductive phase of nearly constant and continuous composition (\( x=0.33 \)). If this were the case, the pre-exponential term and activation energy would have constant values in this compositional range.

### 3.3. The Anderson–Stuart model

#### 3.3.1. Basic assumptions

This model\(^{(40)}\) is restricted to an estimation of the activation energy for ionic migration using classic electrostatic and elasticity theories and proposes that the activation energy for conduction, \( E_{\text{AS}} \), is composed of two terms, an electrostatic energy, \( E_{\text{es}} \) and a strain energy, \( E_{\text{str}} \), required to move an ion from one site to another. Few attempts have been made to extend this approach to quantitatively interpret major variations in the activation energy with composition.\(^{(39,40)}\) The basic idea is that an ion makes a simple hop from one site to another, passing through a ‘doorway’ that opens to the size of the ion as it
crosses through. This model assumes the presence of a large number of available cationic sites and is more similar to a vacancy mechanism rather than to the interstitial pair model developed in Sections 3.1 and 3.2. Moreover, it does not distinguish between bridging and nonbridging oxygen, since the proposed equations assume that all the constituents of the glass are in their ionic form. The two contributions to the activation energy are reduced to

\[ E^{\text{AS}} = E_{\text{a}} + E_{\text{s}} \]  

(14)

or

\[ E^{\text{AS}} = \frac{2z_{M}z_{O}e^{2}}{4\pi\varepsilon_{0}E_{\text{r}}} \left( \frac{1}{r_{\text{M}} + r_{\text{O}}} - \frac{1}{\lambda/2} \right) + 4\pi\varepsilon_{0}G_{\text{r}} \left( r_{\text{M}} - r_{\text{O}} \right)^{2} \]  

(15)

where \( z_{M} \) and \( z_{O} \) are the charges of the mobile ion \( M \) and the fixed counterion, in the present case, alkali and oxygen, respectively, with \( z_{M}=1 \) and \( z_{O}=2 \). The first term represents the maximum electrostatic barrier between two sites, while the second term expresses the strain energy necessary to open the doorway to the size of the ion; \( r_{\text{M}} \) and \( r_{\text{O}} \) are the corresponding alkali and oxygen ionic radii, \( \varepsilon_{r} \) is the dielectric permittivity of vacuum, \( \varepsilon_{r} \) is the relative dielectric permittivity of the medium, \( \lambda \) is the effective radius of the (unopened) doorway, and \( G \) is the shear modulus. Anderson & Stuart assumed that the Madelung constant, which should be included in the electrostatic term, is near unity due to the low density structure of glasses.

The parameters necessary to calculate \( E_{\text{a}} \) and \( E_{\text{s}} \) are the jump distance \( l \) between two equivalent cationic sites, the ionic radii, the shear modulus \( G \) and the relative dielectric permittivity \( \varepsilon_{r} \). In their original paper, Anderson & Stuart supposed, for all alkali silicate systems, an average jump distance of 7 Å (the lattice constant of cristobalite) and a constant value for the systems, an average jump distance of 7 Å (the lattice constant of cristobalite) and a constant value for the corresponding alkali and oxygen ionic radii, \( \varepsilon_{r} \) is the dielectric permittivity of vacuum, \( \varepsilon_{r} \) is the relative dielectric permittivity of the medium, \( \lambda \) is the effective radius of the (unopened) doorway, and \( G \) is the shear modulus. Anderson & Stuart assumed that the Madelung constant, which should be included in the electrostatic term, is near unity due to the low density structure of glasses.

\[ E^{\text{AS}} = \frac{2z_{M}z_{O}e^{2}}{4\pi\varepsilon_{0}E_{\text{r}}} \left( \frac{1}{r_{\text{M}} + r_{\text{O}}} - \frac{1}{\lambda/2} \right) + 4\pi\varepsilon_{0}G_{\text{r}} \left( r_{\text{M}} - r_{\text{O}} \right)^{2} \]  

(15)

The concept of charged point defects, initially developed to interpret ionic transport in crystals, is extended to glasses in which positive charge carriers would be formed by a cationic pair, i.e. two alkali cations sharing the same nonbridging oxygen. This model justifies the Arrhenius behaviour of conductivity with temperature, \( \sigma = \sigma_{0} \exp(-E_{\text{A}}/RT) \), where the pre-exponential term, \( \sigma_{0} \), and activation energy \( E_{\text{A}} \) are both a function of \( x \).

The microscopic model is then completed by a thermodynamic approach developed by Ravaine & Souquet. Basically, this model considers the glasses as the dominant factor in the transport of charge carriers.
as an electrolytic solution of Li₂O in the solvent SiO₂. The partial dissociation of Li₂O in this low dielectric solvent produces the positive charge carriers, which correspond to the abovementioned cationic pair. According to the dissociation equilibria of weak electrolytes, their concentration is a function of the Li₂O partial free energy, G_{Li₂O}, which can be estimated as a function of x by a thermodynamic model (lattice gas model) applied to xLi₂O-(1-x)SiO₂ glasses. Assuming the mobility of the charge carriers is independent of x, this model allows one to interpret quantitatively the variations of σ0 and activation energy, E_a, as a function of x for x>0.1. For x<0.1, the proposed model does not allow for an accurate fit to the experimental data, probably because phase separation occurs in this compositional range. This model does not allow for assessments of absolute values of the activation energy.

An attempt to estimate the values of E_a as a function of x was made here using the Anderson–Stuart equation which, in the case of lithium cations, is reduced to the electrostatic term. An estimation using experimental variations of the dielectric constant with x, but an arbitrary and constant jump distance, gives an approximation to experimental values of activation energy. The microscopic jump mechanism underpinning this model is more likely due to a vacancy displacement, which does not agree with the cationic pair model. Improvements of the Anderson–Stuart model should consider a more realistic description of the glass structure.

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