LIMIT OF APPLICATION OF THE NON-ARRHENIUS EXPONENTIAL BEHAVIOUR TO DESCRIBE IONIC CONDUCTION IN SOLIDS

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Resumen

En este trabajo reportamos un modelo fenomenológico para comportamientos no Arrhenius de la dependencia con la temperatura de la conductividad iónica (expresada en una escala logarítmica, $log(\sigma)$) en electrolitos sólidos, basado en una función algebraica fraccionaria del inverso de la temperatura (T^{-1}). En particular, el modelo describe bien tanto aquellos sistemas que exhiben un decaimiento exponencial en el comportamiento de $log(\sigma)$ en términos de *1000/T*, como aquellos que tienen una tendencia a un comportamiento de Arrhenius, esto es, ellos están en el límite entre el comportamiento de Arrhenius y el comportamiento exponencial decreciente cuando se grafica $log(\sigma)$ versus *1000/T*. El modelo da cuenta de la variación con la temperatura de la energía de activación por los diferentes efectos de relajación en el transporte iónico en estado sólido.

Palabras Claves: *Conductividad iónica, comportamiento de Arrhenius y no-Arrhenius*

Abstract

In this work we report a phenomenological model for non-Arrhenius behavior of the temperature dependence of the ionic conductivity (expressed in a logarithmic scale, $log(\sigma)$) in solids electrolytes, based on a fractional algebraic function of the inverse temperature (T^{-1}). In particularly, the model describes well either those systems that exhibit an exponential decrease behavior of $log(\sigma)$ versus *1000/T*, or those that have a tendency to the Arrhenius behavior, that is, they are in the limit between the Arrhenius and the decrease exponential behavior of $log(\sigma)$ in terms of *1000/T*. The model accounts the observed variation with temperature of the activation energy due to different effects of electrical relaxations in solid state ionics.

Keywords*:* Ionic conductivity, Arrhenius and non-Arrhenius behavior

1. INTRODUCTION

Different from electronic conduction, ionic conduction in ionic solids is closely related to a particular structural characteristic of crystals known as a substantial sublattice disorder. The large ionic conductivity is due to a mass motion of a large number of diffusing ions in this sublattice and the presence of passageways in its structure for the charge carriers. Thus, the factors that influence the solid state conductivity are the concentration of charge carriers, availability of vacant-accessible sites which is controlled by the density of defects in the crystal and an open crystal structure resulting in passageways for ion migration, from its normal lattice position to another site. An energy barrier for hopping called the "activation energy" describes the accomplishment of this process. The activation energy is a phenomenological quantity associated to single particle hops. Cooperative motion of the ions is also essential, such that an ion out of equilibrium position moves though the lattice without changing its configurational entropy. This explanation of the experimental activation energy from dc-conductivity measurements requires that the "particle" hopping has a low energy barrier [1].

A general expression for the ionic conductivity is

$$\sigma = \sum_i n_i \cdot q_i \cdot \mu_i \qquad (1)$$

where n_i, q_i and μ_i are the concentration, charge and mobility, respectively, of the *i*th moving species [2]. This equation is however difficult to use since it is often impossible to get an estimate of the number of different carriers charge in the system.

In an attempt to describe the ionic conductivity, several models have been developed, among which the one based on the random walk approach, it is described by an Arrhenius equation. It determines a linear relationship between $log(\sigma)$ and the inverse of temperature. The problem is then to generalize the random walk approach to systems which include large cooperative effects. Those conductivity that do not meet this linearity are known as *non-Arrhenius behaviors* of the ionic conductivity. One of the models proposed to describe non-Arrhenius behaviors in polymer electrolytes is the VTF model (Vogel-Tamman-Fulcher) [3-5]. This is an empirical relationship originally developed to describe the viscosity of supercooled liquids and where the "pseudoenergy" of activation, determined in this model, is associated with the barrier energy that the charge carriers need to overcome to move into the substance [6]. Our research team is currently interested in developing an equation based on exponential terms that adjust non-Arrhenius temperature dependence of the ionic conductivity, observed mainly on AgI-based electrolytes. We have found that systems such as that with composition (1-*x*)(NaI+4AgI) – *x*(Al_2O_3) for $x = 0.1$, 0.2 and 0.3 show an exponential decrease of $log(\sigma)$ in terms of *1000/T* described by:

$$\log(\sigma) = \exp\left[\frac{-\left(\frac{1000}{T} - k_1\right)}{k_2}\right] + C_1 \qquad (2)$$

where k_1, k_2 y C are fitting parameters [7].

2. LIMIT BETWEEN THE EXPONENTIAL AND THE ARRHENIUS EXPRESSIONS: MOTIVATION

The temperature dependence of the ionic conductivity for the three concentration ($x = 0.1$, 0.2 and 0.3) show very particular behavior (see Fig. 1), quite different from one to another. For $x = 0.1$ (Fig. (a)), we note that all the data points are described well by the same function, independently of frequency. That is, in the tested frequency range (20Hz - 1MHz), the temperature dependence of the activation energies, $d(log\sigma)/d(T\text{-}1)$, for all curves at fixed frequency, are identical. However, for $x = 0.2$ and 0.3 (Figs. 1 (a) and (b)) the fitting functions to

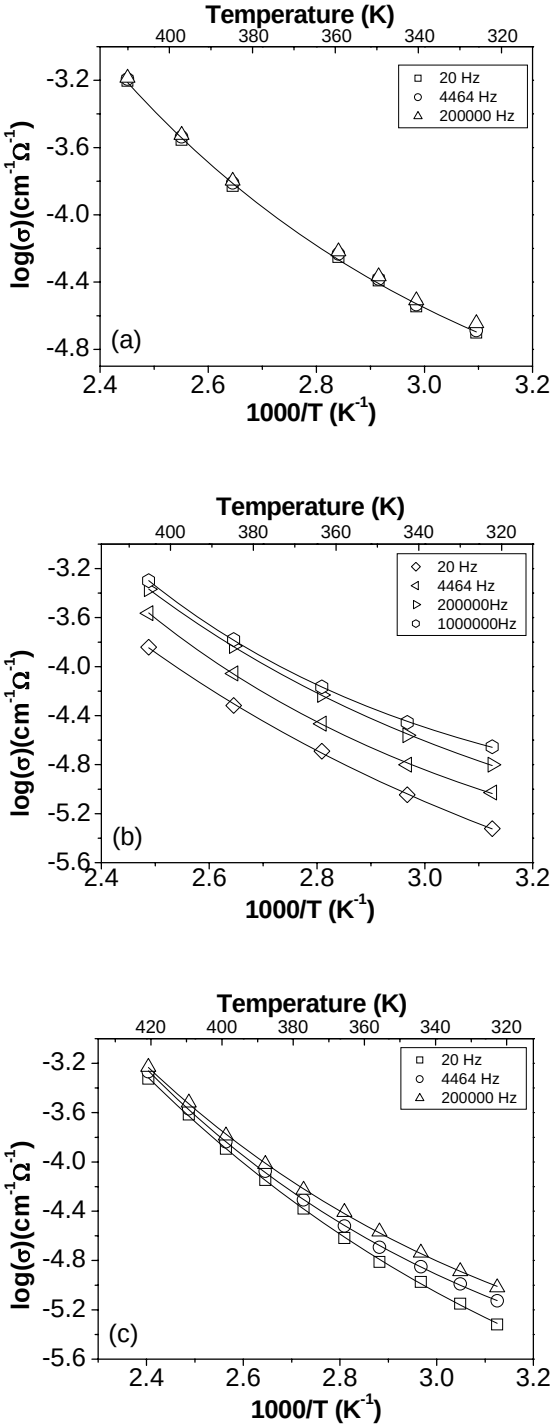


Figure 1. Experimental conductivity data in Arrhenius plots and fitting curves using an exponential function for the conductivity as a function of *1000/T* (Eq. 2) at different frequencies between 20 Hz and 1MHz of the system (1-*x*)(NaI+4AgI)-*x*(Al_2O_3): (a) $x = 0.1$, (b) $x = 0.2$ and (c) $x = 0.3$.

the data points are no longer identical, showing a frequency dependence of the conductivity at a given temperature.

One way to find the explanation of the observed behavior as a function temperature and frequency is by looking at the electrical response of the moving ions as a function of frequency at constant temperature, and then selecting the identical regimes of ionic transport in the whole spectra. It is important to point out that the measuring cell is a two-electrodes configuration Pt/sample/Pt in which the two main contributions to the impedance of the cell are from the sample's bulk electrical response that dominate at higher frequencies or lower temperatures and the grain boundaries effects at the sample-electrode interface that dominate at lower frequencies or higher temperatures.

By plotting the conductivity data at a frequency where the electrical response obeys the same regime, that is, at a frequency where all the isotherms (when plotted as a function of frequency) exhibit the same variation, then a linear behavior in the Arrhenius plot is observed. However, at certain frequencies, as that shown if Fig. 2, if it is analyzed in detail, a small curvature is apparent, characteristic of an decreasing exponential function. So, at this limiting case, ¿which will be the best fitting function to the conductivity data?. To solve this dilemma, we wish to present here a study of these two functions when they approach to each other as a limiting case of electrical response of the moving-ion subsystem in solid ionic conductors.

3. EXPERIMENTAL METHODS

The different samples with composition $(1\text{-}x)(NaI+4AgI)–x(Al_2O_3)$ (x = 0.1, 0.2 and 0.3) were prepared from previously grown polycrystalline samples of NaI-4AgI and nanoparticles of Al_2O_3 (grain size 565.3 Å) The composites were prepared by thoroughly mixing the component in an agate mortar and then heated for 1 hour at 120°C. The polycrystalline samples of NaI-4AgI were grown by solving casting methods. Ultrapure powders of AgI and NaI (Aldrich) with a molar fraction of 4:1 were dissolved in HI (57% aqueous solution) at 48°C under a dry atmosphere. After 3 weeks of solvent evaporation under these conditions, small crystals with the given composition were grown. Acetone was used as solvent to clean the crystals before mixing them with the nanoceramic powder.

The electrical characterization of the samples was done by impedance spectroscopy (IS) [8] using a two electrode configuration Pt/sample/Pt and a home-built temperature and atmosphere controlled cell for measurements. The electrode-electrolyte contact surface (A) and the distance between electrodes (d) were measured using a micrometer. No corrections for thermal expansion of the cell were carried out. The measurements were carried out with a computer controlled LCR meter in the frequency range of 20Hz-1.0 MHz, in the isothermal or in the heating cooling modes at temperatures between $320 \leq T \leq 412$K under a dry N_2 atmosphere. To carry out the impedance measurements cylindrical pellets of 1 mm thickness and 6 mm in diameter were prepared by uniaxial pressure of about 2 tons/cm^2. From the impedance data, $Z(\omega)=Z'(\omega)-iZ''(\omega)$ **(**where $\omega = 2\pi f$ / Hz is the angular frequency, $i = (-1)^{1/2}$, the real part of the electrical conductivity, $\sigma'(\omega) = (d/A)(Z'/(Z'^2+Z''^2)$, was obtained.

4. RESULTS AND DISCUSSION

The figure 2 evidence a peculiar behavior: the tendency of the data seem to follow a straight line, but when realized a lineal fit of the data, we see how the tendency of the point decrease, following a curve which can be described with an decrease exponential function, developed by Rodriguez *et al.* [7]. We can talk that the tendency of these points are in a boundary or *limit* between the model proposed by Arrhenius and the decrease exponential function. From the Arrhenius equation we can interpret the conductivity as:

$$\log(\sigma) = \frac{-E_a \log(e)}{1000k}\left(\frac{1000}{T}\right) + \log(\sigma_0) \qquad (3)$$

where e = *2.71828182…*), k is the Boltzmann's constant and σ_0 is the preexponential factor. On the other hand, the conductivity of the system using the decrease exponential function is expressed using equation (2). In the limit between these two functions, the values of $\log(\sigma)$, as shown in Figure 2, are very similar. Thus, in this limit, equating the right-hand sides of equations (2) and (3) and solving for E_a, we obtain

$$E_a \lim \approx \frac{-kT}{\log(e)}\left\{\exp\left[\frac{-\left(\frac{1000}{T}-k_1\right)}{k_2}\right]+\eta\right\} \qquad (4)$$

where $\eta = C_1 - \log(\sigma_0)$ the calculated activation energy by $E_a lim$. Considering that the activation energy in an Arrhenius plot of the ionic conductivity can be calculated from the slope $d(\log(\sigma))/d(T^{-1})$ [5] which we identified as $E_a exp$, using the expression (2), we have

$$E_a \exp = \frac{1000k}{k_2 \log(e)} \exp\left[\frac{-\left(\frac{1000}{T} - k_1\right)}{k_2}\right] \qquad (5)$$

Figure 3 represents the temperature dependence of the activation energies $E_a lim$ and $E_a exp$. It is noted that $E_a lim$ is approximately constant, while $E_a exp$ change linearly with temperature. Since the values of $E_a exp$ were calculated from the fitting of the conductivity data to the exponential function, we might perform a rotation transformation to carry $E_a lim$ values to those of $E_a exp$. This was achieved by a rotation around a point very close to the intersection of the two lines by an angle ϕ and changing the temperature scale to $1000kT$.

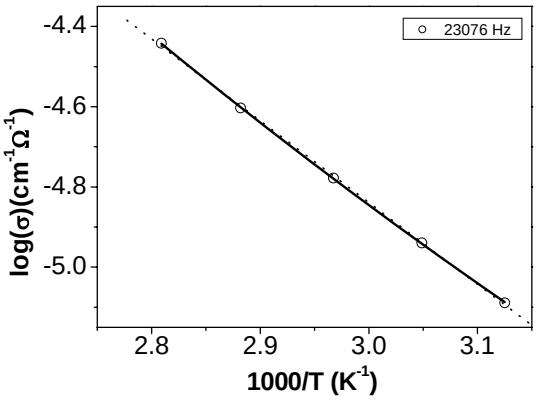


Figure 2. Logσ versus $1000/T$ for x = 0.3 at the frequency of 23076 Hz where the ionic conduction obeys the same mechanism in the temperature range between 320 K and 360 K. The dotted line represents the fitting to the Arrhenius equation (3) while the solid line is the fitting to the exponential expression (2).

It is important to point out performing the rotation with the energy scale for the T-axis shown in Figure 4, then the angle ϕ will be related to the slope m_{exp} obtained by linear regression fitting of the points belonging to the plot $E_a exp$ vs. $1000kT$ function, by $\phi \approx \pi + m_{exp}$ [7]

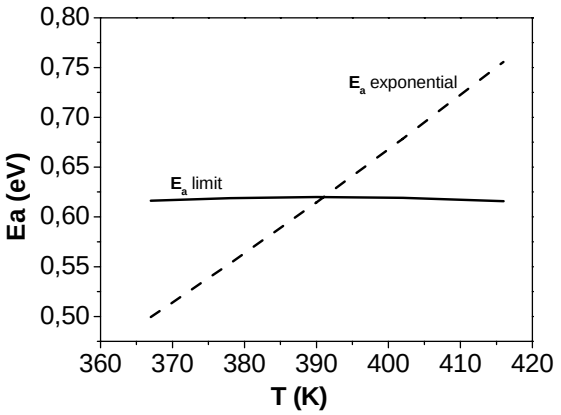


Figure 3. Temperature dependence of $E_a lim$ (solid line) and $E_a exp$ (dashed line) as calculated from the expressions (4) and (5), respectively. The conductivity data corresponds to sample with concentration x = 0.3 at the frequency of 300000Hz, and in the temperature range between 367 K and 416 K.

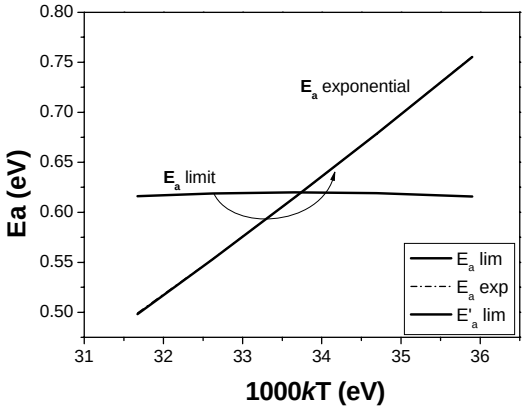


Figure 4. The same as Fig. 3 but scaling the temperature axis to $1000kT$ and including the rotated $E_a lim$ by an angle ϕ (dashed line).

Performing the rotation transformation on $E_a lim$, we obtain:

$$\begin{aligned} E_a^{'} \lim &= -1000kT\sin(\phi) + E_a \lim \cos(\phi) + A \\ &= -1000kT\sin(\phi) + \\ &\left[\frac{-kT}{\log(e)}\left\{\exp\left[\frac{-\left(\frac{1000}{T} - k_1\right)}{k_2}\right] + \eta\right\}\right]\cos(\phi) \\ &+ A \end{aligned} \qquad (6)$$

where $E'_a lim$ is the rotated function of $E_a lim$ and A is a adjusting parameter that account for the best chosen center of rotation. We notice that, for certain values of ϕ y A, $E'_a lim \approx E_a exp$, then, by equating expressions (5) and (6), and using equation (2), we obtain

$$\log(\sigma) = \frac{a\left(\frac{1000}{T}\right) + b}{\frac{1000}{T} + c} \qquad (7)$$

where

$$a = (Ak_2 \log(e))/(1000k) + C_1 \qquad (8a)$$

$$b = -k_2(1000\log(e)\cdot\sin(\phi) - \log(\sigma_0)\cdot\cos(\phi) \qquad (8b)$$

$$c = k_2\cdot\cos(\phi) \qquad (8c)$$

which is a fractional algebraic function of the variable *1000/T*

5. APPLICATION FRACTIONAL ALGEBRAIC FUNCTION TO THE CONDUCTIVITY DATA OF THE (1-*x*)(NaI+4AgI) – *x*(Al_2O_3) SYSTEM.

Figure 5 shows the Arrhenius plots of the temperature dependence of the conductivity data for the x = 0.2 composite at various frequencies. These frequency values correspond to temperature region (between 320K and 416K) where the ionic transport obeys the same mechanism. These Arrhenius plots show the limit of application of the two fitting function, i.e., the Arrhenius and exponential ones.

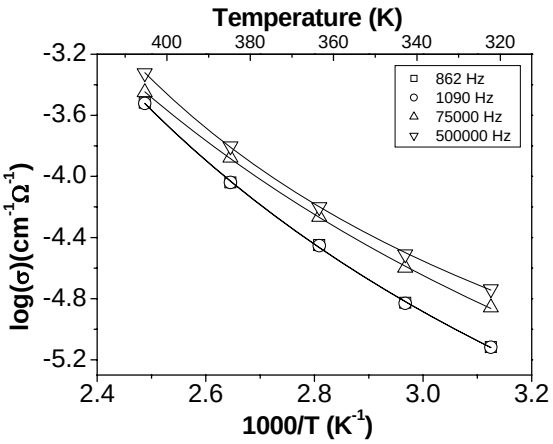


Figure 5. Arrhenius plots of the temperature dependence of the conductivity data for the x=0.2 composite at various frequencies. The continuous lines are the fitting curves to rational function (13).

Table 1. Fitting parameters (*a*, *b*, *c*) to the Arrhenius plots for the temperature dependence of the conductivity data for the x=0.2 composite at various frequencies, according to the fractional equation (7).

	Fitting values			*Calculated values*		
Freq. (Hz)	a	b (K^{-1})	c (K^{-1})	a	b (K^{-1})	c (K^{-1})
862	-8.9	16.9	-1.0	-9.1	17.1	-0.9
1090	-9.0	16.9	-1.0	-9.1	17.1	-0.9
75000	-8.9	15.9	-0.7	-9.0	16.3	-0.7
500000	-7.2	14.2	-1.4	-7.7	14.7	-1.0

In these cases, our proposed fractional algebraic function (eq. 7) is used to fit that data curves. Table 1 shows the best fitting parameter values (*a*, *b* and *c*). Table 1 also shows the calculated values of these parameters using the expressions (8a), (8b) and (8c) showing wood agreement with those obtained by fitting. Thus, we are presenting a new approach to analyze ionic conductivity data as a function of temperature for those transport processes in which the Arrhenius behavior is not quite evident.

6. CONCLUSIONS

On analyzing the ionic conductivity of the highly dispersive ionic conductors as those based on AgI, it is frequently found that when presenting the data as Arrhenius plots, the temperature dependence of $d(\log\sigma)/d(T^{-1})$ is not constant as a function of temperature. In these case, we previously found a good fitting to the data points by using an exponential-type function [7]. Moreover, we have shown in this work, that when both the Arrhenius and the exponential-type function are in the limit of their applications, then a fractional algebraic function is a good alternative to describe the observed behavior of the conductivity data.

7. ACKNOWLEDGEMENTS

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