

## ANDERSON-STUART MODEL OF IONIC CONDUCTORS IN Na<sub>2</sub>O-SiO<sub>2</sub> GLASSES

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### ABSTRACT

Glasses based on sodium silicates [xNa<sub>2</sub>O-(1-x)SiO<sub>2</sub>] with  $x = 30, 35, 40, 45$  and 50 mole%, have been prepared. These materials were investigated mainly by direct conductivity and Impedance Spectroscopy techniques for electrical characterization below  $T_g$ . In this work we discuss our data obtained by these conductivity measurements and comparison between the data obtained and those published hitherto. A modified Anderson and Stuart model has been used to describe the variation of activation energy with sodium concentration in Na<sub>2</sub>O-SiO<sub>2</sub> system. The agreement between calculated and experimental activation energies is discussed in the light of assumptions used in calculations.

**Keywords:** Glass; Ionic Conduction; Anderson-Stuart Model; Activation Energy

### 1 - INTRODUCTION

In simple alkali silicate glasses, the conductivity increases with the increment of the concentration of alkalis [1, 2]. Less certain, however, is the form of the compositional dependence of the activation energy for conduction.

Most of structural changes are based on the assumption that as the alkali is added to a silica network, a progressive breakdown of the three-dimensional network occurs with the rupture of the Si–O bonds. Others [1] have tried to correlate the variation of activation energy and conductivity with the onset of phase separation.

Several models to calculate the activation energy for conduction in glass have been proposed, among which that proposed by Anderson and Stuart (A-S) [3] is perhaps the most directly related to physical parameters such as the radius of the ion, the elastic module, etc. The model is, however, a highly approximate one, and as presented does not describe the variation of the activation energy with experimental parameters data, just calculated ones.

For this system only Hakim and Uhlmann [4] had proposed modifications on A-S model.

The present paper will report on the conductivities and activation energies of glasses in Na<sub>2</sub>O-SiO<sub>2</sub> system, with another proposals to activation energy with composition and new experimental parameters data.

### 2 - EXPERIMENTAL

Glass samples were prepared by melting together SiO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> of reagent grade purity. Batches of about 80g were melted at 1200-1400°C in a SiC furnace (constructed for this purpose) in air on Pt-10%Rh crucibles, from 2-4h.

The samples were examined by optical microscopy (Jenapol Carl Zeiss) and found to be free of observable strains, bubbles or inclusions. Chemical analysis of a few randomly selected samples indicated a deviation from

batch composition of less than 1 mol% in Na<sub>2</sub>O-SiO<sub>2</sub> for the high alkali glasses.

Specimens used for DC and AC measurements were squared in cross section, about 10mm×10mm×1mm thick. They were prepared by hand grinding with slurry of water (or kerosene for the high alkali samples), and SiC 600-800-1000 meshes. For final polishing very fine alumina powder (Buehler) was used. In all cases, electrodes were applied with silver paint (PC-200, Joint Metal).

Conductivity DC measurements were carried out in a constant temperature zone ( $\pm 1^\circ\text{C}$ ) using an ECIL JR temperature controller connected to vertical wire-wound tube furnace, specially prepared for this purpose, with windings running in opposite directions to eliminate fields due to heating current. The electrodes were spring-loaded Ni rods, with springs located outside furnace to assure good contact between sample and electrode. Current measurements were made using a Keithley 610C electrometer ( $10^{-1}$ - $10^{-11}$ A range), and 100mV Lambda tension source.

AC measurements were carried out in another furnace, using silver paint and Pt electrodes, a HP 4192A (5Hz-13MHz) impedance analyzer with 100-200mV tension applied, and ZView 1.5 free-program for analysis. Both measurements were made in air atmosphere, with type K thermocouples placed close to the electrodes, and systems calibrated.

Electrical conductivities of glasses were measured at various temperatures, from room temperature up to 50°C below  $T_g$  (when applicable), and all samples were kept in a desiccator between measurements. More details could be found elsewhere [5].

### 3 - RESULTS

For all glass compositions studied within the measured temperature range, the conductivity was found to obey

Hasch-Hinrichsen relation  $\sigma = \sigma_0 \exp(-E_A / R_c T)$  (with an excellent agreement using AC), where  $\sigma$  is the conductivity,  $R_c$  the gas constant, and  $E_A$  is the activation energy. Examples of this behaviour are shown in Figs. 1-2. Linear fits showed *chi*-squares  $\chi^2 \approx 0.02$  and  $\chi^2 \approx 0.001$  for measurements from DC and AC data, respectively.

Sodium silicate glass showed increased conductivity (Fig. 1) with the increment of sodium concentration, but one could note that there is some scatter from linear curves.

This difficulty comes from DC measurements, mainly electrode influence and non-uniformity (at constant voltage).

Sodium silicate glass on AC measurements showed better fit on straight lines than in DC measurements, as expected (Fig. 2). In this case electrode influence could be separated on fitting Nyquist (or Cole-Cole)  $Z_{real}(\omega) \times Z_{imaginary}(\omega)$  diagram.

Many experimental works on conductivity have been published over years [1-2, 4-5 and 7-28], basically searching highest conductivity values or presenting theories that apply better in one than another system. However, there is a disparity between experimental data on similar glasses from different authors. In many works one could see omissions over simple characteristics as kind and electrode influence, surface preparation and conditions,

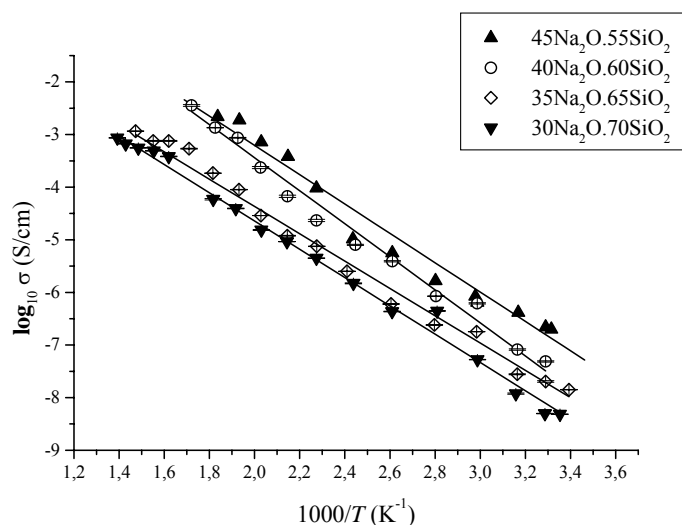


Fig. 1. DC measurements as function of temperature for four different sodium silicate glasses.

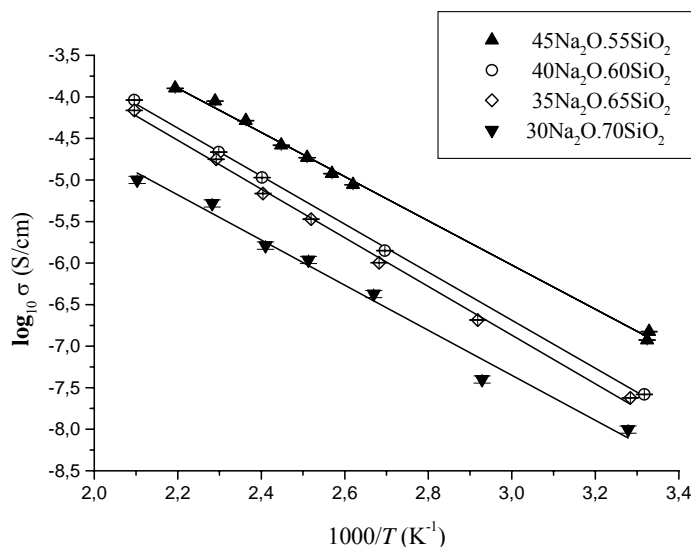


Fig. 2. AC measurements as function of temperature for four different sodium silicate glasses.

heat treatments, phases involved, etc. Table 1 follows these examples.

The chief purpose to measure conductivity from DC and AC modes was to note the influence on these two

experiments on results. *DC* mode is more easy and frequent experimental procedure. Many authors had presented data on this simple experiment, against the more precise *AC* mode.

It was expected that conductivity followed Jonsher's Law  $\sigma(\omega) = \sigma_0 + A\omega^n$  [39], where  $\sigma_0$ ,  $A$  and  $n$  are constants, and  $\omega$  is the frequency, with  $\sigma(\omega=0) = \sigma_0$ , a value close to *DC* experiments.

Comparison of activation energy between *DC* and *AC* measurements data and literature are presented on Table 1.

Results presented on Table 1 show relative distribution data on same compositions glasses. Besides disparity on some results, one could found a general agreement on each case. Better results frequently come from impedance (*AC*) measurements, but good data could still exist measuring on *DC* mode, taking some precautions. From a statistical point of view, it is interesting to use all data available to assess general behaviour.

#### 4 - DISCUSSION

The calculated activation energies differ more significantly in some cases. This scatter implies in different experimental procedures. For glasses with low alkali content, the conductivities at low temperatures are lower than  $10^{-10}$  (ohm-cm)<sup>-1</sup>, approaching the limit of available measuring apparatus. At high alkali content, the samples are hygroscopic, and special precautions on preparation procedures must be taken.

Observed differences in the activation energies seem likely, therefore, to be associated with differences in the chemical and/or structural states of the glass samples and in some cases to differences in the experimental methods employed. For example, differences in melting and annealing procedures, sample preparation techniques, and water content could affect results. In Na<sub>2</sub>O-SiO<sub>2</sub> composition system, a further difference arises from the effect related of phase separation on electrical properties [1].

Table 1 - Activation energies from *DC* and *AC* mode conductivities of some sodium glasses (in eV, with uncertainties in brackets corresponding to final digits) [1-2, 4-5 and 7-28].

Glass	Activation Energy <i>DC</i>	Activation Energy <i>AC</i>	Activation Energy Literature Data
50Na <sub>2</sub> O-50SiO <sub>2</sub>	0.596(94)	-	0.544 (Zhitkyarvichyute) 0.705 (Pernice) 0.481 (Vargin)
45Na <sub>2</sub> O-55SiO <sub>2</sub>	0.553(26)	0.5278(92)	0.526 (Mazurin) 0.614 (Otto) 0.538 (Charles)
40Na <sub>2</sub> O-60SiO <sub>2</sub>	0.622(30)	0.582(13)	0.603 (Bansal) 0.541 (Lapp) 0.516 (Mazurin) 0.601 (Otto) 0.398 (Petrovskii) 0.544 (Martinsen)
35Na <sub>2</sub> O-65SiO <sub>2</sub>	0.515(18)	0.582(13)	0.629 (Bansal) 0.653 (Seddon) 0.605 (Otto) 0.648 (Hunter)
30Na <sub>2</sub> O-70SiO <sub>2</sub>	0.533(10)	0.538(29)	0.663 (Bansal) 0.633 (Evstropiev) 0.631 (Mazurin) 0.527 (Vakhrameev) 0.626 (Otto) 0.587 (Petrovskii) 0.679 (Wakabayashi) 0.573 (Namikawa) 0.629 (Charles) 0.690 (Hakim) 0.718 (Boricheva) 0.635 (Unuma)

Despite differences in the activation energies observed by different investigators, a number of common trends are seen in those data. Perhaps most important is the decrease in activation energy with increasing sodium concentration.

It is interesting, therefore, to see whether such behaviour can be predicted from a model proposed by Anderson and Stuart [3, 4]. In this 'classical' model, the

activation energy for conduction may be divided in two parts (Eq. 1): the *electrostatic binding energy* of the original site  $E_b$ , and the *strain energy*,  $E_s$ , required to move an ion from one site to another.

The basic idea is that an ion (in this case Na<sup>+</sup>) makes a simple jump from one site to another, and passes through a 'doorway' which opens as it passes through, where cations

sites require only the presence of non-bridging oxygens (Eq. 2).

$$E_A(\sigma) = E_b + E_s \quad (1)$$

$$E_A(\sigma) = \frac{\beta z z_0 e^2}{\gamma(r_{Na} - r_O)} + 4\pi G r_D (r_{Na} - r_D)^2 \quad (2)$$

where  $z$  and  $z_0$  are the charges on the mobile ion and the fixed counterion – in this case sodium and oxygen with ionic radii  $r_{Na}$  and  $r_O$  respectively,  $e$  is the electronic charge, and  $r_D$  is the effective radius of the (unopened) doorway.

The parameters of interest in the A-S model are the elastic modulus ( $G$ ), a ‘Madelung’ constant ( $\beta$ ), which depends on how far apart the ions are, and a covalence parameter ( $\gamma$ ), which indicates the degree of charge neutralization between the ion and its immediate neighbours.

In their original paper, Anderson and Stuart assumed that this covalence parameter was equal to a typical value of the dielectric constant ( $\gamma = \epsilon' \approx 7$ ).

Two considerations are proposed here: *a*) One is related with shear modulus  $G$ . Data available decreases slightly with increasing  $Na_2O$  mole% concentration, confirming what was just calculated (in really estimated) in [3], and presented on Fig. 3. *b*) Indeed the covalence parameter  $\gamma$  (still calculated by [3]) showed a small increase with increasing  $Na_2O$  mole% concentration if one considers its magnitude close to permittivity.

It was not possible to find something related to  $\gamma$ , only the experimental permittivity  $\epsilon'$ , that showed similar behaviour and values, respectively (see Fig. 4).

At least, we consider  $\beta$  as done by Anderson and Stuart:

$$\beta = \frac{2.1 - r_{Na}}{3.5} \quad (3)$$

where  $r_{Na}$  is in angstrom unity.

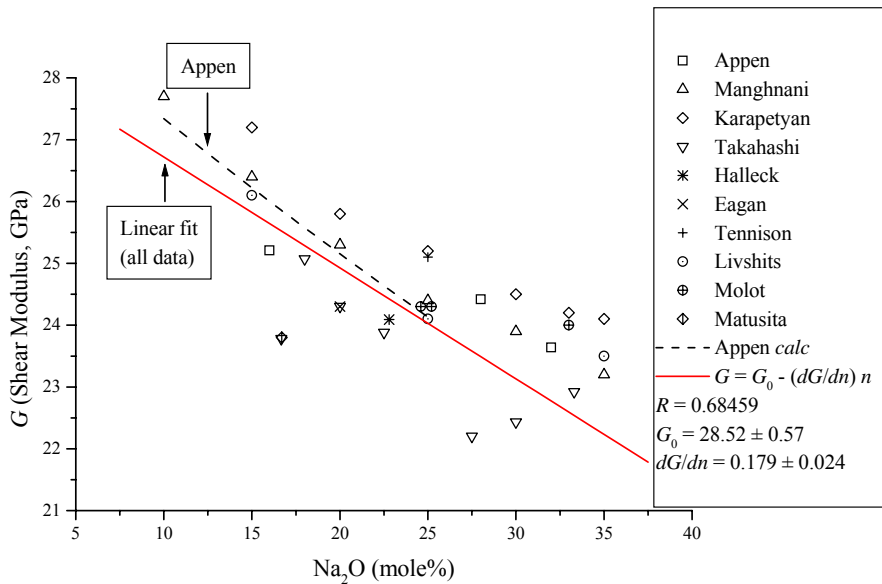


Fig. 3. Shear modulus of  $Na_2O-SiO_2$  system versus  $Na_2O$  composition [29-38]. Fit of shear modulus of all data available followed Appen’s calculations (dashed line).

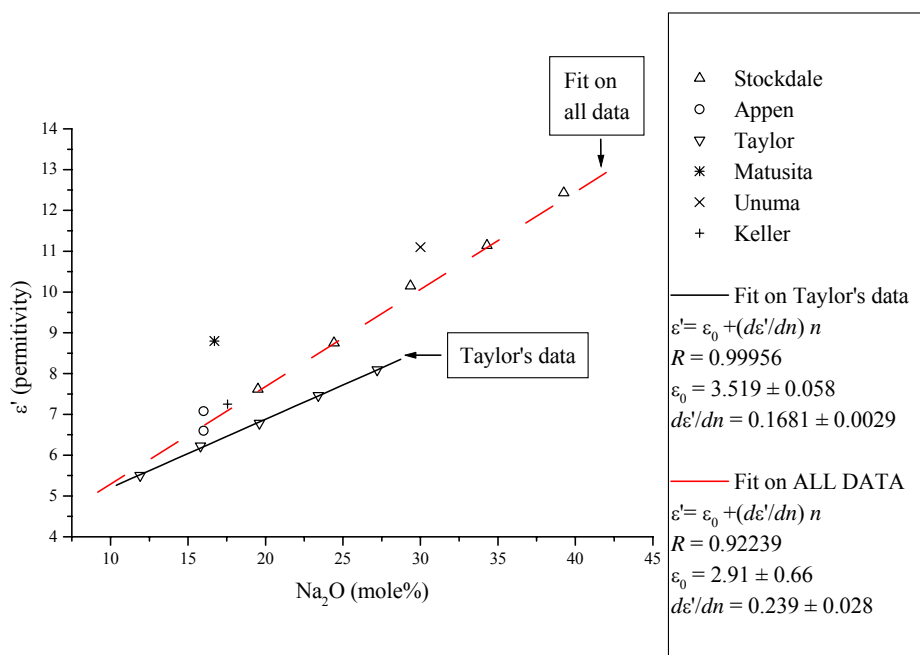


Fig. 4. Permittivity values of Na<sub>2</sub>O-SiO<sub>2</sub> system versus Na<sub>2</sub>O composition [40-44]. Fits on all data (dashed line) and just with Taylor's data (full line, that was considered on Anderson-Stuart Model).

Hakim and Uhlmann proposed a modification on A-S model. On estimating the change in strain energy with concentration and type of alkali, they assumed that  $r_D$  varies as  $\Delta r_D/r_D = 1/3(\Delta V/V_0)$ , where  $V_0$  is the molar volume of SiO<sub>2</sub>, and  $\Delta$  denotes the change in the respective quantities on addition of the alkali. Here there are suggested two analysis suppositions: *i*) fixed  $r_D$ , as suggested by A-S theory; *ii*)  $\Delta r_D/r_D = 1/3\Delta n/n_0$ , where  $n_0$  is SiO<sub>2</sub> mole% concentration. In this fit  $r_D$  had a value of 0.6 Å with 18Na<sub>2</sub>O-82SiO<sub>2</sub> mole% composition, following suggestion of Anderson and Stuart [3]; and one could find  $r_D$  versus composition to vary from 0.37 Å <  $r_D$  < 0.72 Å (the minimum  $r_D$  value is near that used by Hakim and Uhlmann [4], the maximum  $r_D$  value close to used by Anderson and Stuart [3]). It is recognized that these assumptions of a similitude of form may provide an inadequate description of the change in  $r_D$  with alkali concentration, but it seems to represent only a degree of approximation.

On the fit, was used a Levenberg-Marquardt non-linear fit. This algorithm minimizes  $\chi^2$  by performing a series of iterations on the parameter values. In order to do this, the fitting program internally calculates partial derivatives for all the values of the input variables, which were computed numerically.

Variation of activation energy with Na<sub>2</sub>O mole% composition is shown in Fig. 5. Despite differences in the activation energies observed by different investigators, including different experimental procedures, a number of common trends are seen on these data. Perhaps most important is the decrease in activation energy with increasing concentration of alkali. In fact, results obtained on  $r_{Na}$  and  $r_O$  are close to presented in [3], of 0.95 Å and

1.4 Å, respectively. The relatively high uncertainty values in  $E_A$  could be related to data distribution, from various investigators and techniques used, but one could assess that Hakim and Uhlmann [4] and Haven and Verkerk [29] data at low Na<sub>2</sub>O mole% concentration could not be acceptable. A-S model using experimental  $G$  and  $\gamma$  values is good for finding close values, but not at low (superestimated) Na<sub>2</sub>O mole% concentrations.

It may be noticed that with increasing Na<sub>2</sub>O content the molar volume decreases [4] highlighting the fact that more and more nonbridging oxygens are formed in the network. Close experimental values of  $G$  and  $\gamma$  were found by comparing with A-S theoretical values. It is important to note that these values from [3] were calculated ones, and those in the present work are resulted from experiments. Results also have shown that  $E_b$  is higher than  $E_s$ , as presented by Anderson and Stuart [3]. It is interesting to note that  $E_b$  dependence with Na<sub>2</sub>O content is related to 'covalence parameter'  $\gamma$ , which increases with increasing sodium concentration.

Values of permittivity  $\epsilon'$  presented by Taylor [42] are close to A-S prediction for  $\gamma$ . The major difference between suppositions *i* and *ii* and A-S theoretical values is firstly related to  $\gamma$ . 'Doorway' radius  $r_D$  has a secondary importance.

A-S theory could be seen in Fig. 5 adjusting very well data from different authors. Its prediction power is very good, besides the fact that this theory only includes two terms,  $E_b$  and  $E_s$ , and just few considerations.

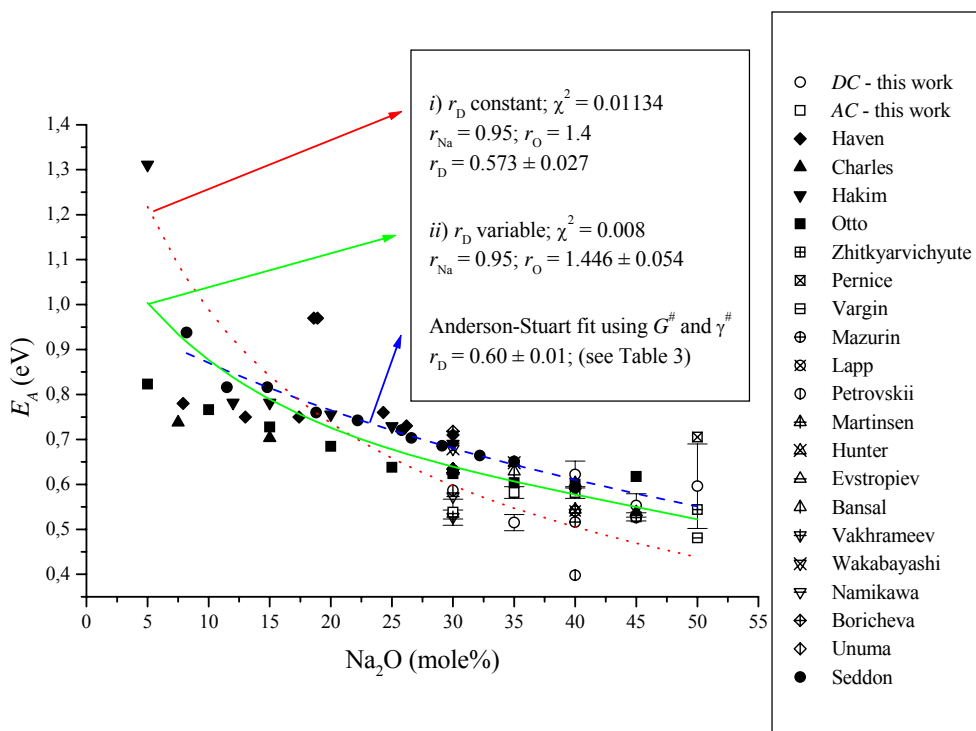


Fig. 5. Non-linear fit on activation energies (various authors) of  $\text{Na}_2\text{O-SiO}_2$  system and this work (DC and AC mode) versus  $\text{Na}_2\text{O}$  concentration considering hypothesis *i* ( $r_D$  constant, dotted line) and *ii* ( $r_D$  variable, full line). In the first case were fixed radii values as done by A-S ( $r_{\text{Na}}=0.95\text{\AA}$  and  $r_{\text{O}}=1.4\text{\AA}$ ). In the second case oxygen radius fitted was  $r_{\text{O}}=(1.446\pm 0.054)\text{\AA}$  with  $r_{\text{Na}}=0.95\text{\AA}$  fixed. On suppositions *i* and *ii* were used  $G$  considering all data and  $\gamma$  only from Taylor's experimental values (Fig. 4). Finally we considered A-S calculated parameters  $G^\#$  and  $\gamma^\#$  (dashed line, see Table 1 in reference [3]) and presented together with all  $E_A$  data available.

## 5 - CONCLUSIONS

New data on conductivities and activation energies concentrations on sodium silicates  $[x\text{Na}_2\text{O}\cdot(1-x)\text{SiO}_2]$  with  $x = 30, 35, 40, 45$  and  $50$  mol% were presented. Besides considerable discrepancies on DC and AC values from experimental data, those could be compared between and with another data from literature.

A modified Anderson-Stuart model for sodium-silica glass system has been used to describe the variation of the activation energy against composition, with reasonable results. It is interesting that some simple considerations with aid of classical theories about ionic crystals and elasticity could improve reasonable accordance.

For the first time considerations on experimental shear modulus  $G$ , a better estimative of 'covalence' parameter  $\gamma$  and two considerations ( $r_D$  constant and near variable) with sodium composition presented good fits on experimental data available.

Covalence parameter  $\gamma$  should be replaced by permittivity  $\epsilon'$  and presented more influence on fitting than  $G$ .

## 6 - ACKNOWLEDGEMENTS

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