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# ON THE LINEARIZATION OF THE FREE-VOLUME LAWS IN THE SOLID POLYMER ELECTROLYTES FIELD

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**Abstract**—Linearization methods are proposed to get easily the three coefficients of either the VTF or the WLF law, without making hypotheses or approximations on any of the coefficients. These methods allow to derive a system of three equations, the three unknowns of which are the desired coefficients. Standard errors on the coefficients are also easily determined. These methods have been applied to experimental data picked in the literature and results discussed.

## INTRODUCTION

The conductivity of many solid polymer electrolytes displays a thermal behavior which can be often described using a free-volume law such as the VTF or the formally equivalent WLF law [1, 2], provided the morphology of the polymer is amorphous. The relevant points and conditions of applications of this free-volume concept to solid polymer electrolytes have been discussed by Ratner [3] and it is important to check if conductivities of the investigated materials really follow these laws.

Nevertheless, when reading papers dealing with the temperature dependence of such solid electrolytes, it seems a "VTF-type" profile, based on the only shape of the conductivity curve, is taken as a sufficient condition for displaying a free-volume behavior, without indicating any numerical value for the parameters of the laws, although they are important if taking into account thermodynamic considerations.

Fitting the VTF or WLF laws requires to find the sets of three coefficients, namely $A$, $B$, $T_0$ or $c_1^0$, $C_2^0$, $\sigma_0$ in the following equations:

$$\sigma = A \cdot T^{-1/2} \cdot \exp(-B/(T - T_0)) \quad (1)$$

$$\log(\sigma/\sigma_0) = c_1^0(T - T_R)/(c_2^0 + T - T_R). \quad (2)$$

Iterative methods can be used, but they generally spend some calculation time, although the new generations of personal computers allow to dispense with this aspect. In many papers, it is claimed a non-linear least squares minimization procedure was used, but there is no details about the method, so that it cannot be reused. Approximations of hypotheses (usually on $T_0$ or $\sigma_0$) allow to give a numerical value for one of the three coefficients and the question becomes to find only two parameters, that can be done using a graphical method, but this solution is not quite satisfactory for mind.

We propose here a simple linearization method of both VTF and WLF laws allowing to derive a system of three equations, the three unknowns of which are the sought coefficients. The validity of the linearization methods can be checked by comparing the calculated conductivity with the experimental one. It must be underlined that this mathematical method does not depend on any physical model, so that the numerical values of the parameters are the consequence of the only accuracy of the measurements and temperature range.

It must be kept in mind that many curves can be smoothed from a mathematical model with three fitting parameters and the challenge is to keep a physical meaning for each of them or to explain the reason for this numerical value. To overcome this drawback, standard errors on the parameters can be used to appreciate the validity of the free-volume theory for the investigated sample.

## RESULTS AND DISCUSSION

### *(a) The VTF law*

According to equation (1), the three parameters to be determined are respectively $A$, $B$ and $T_0$. $A$ is connected to the number of charge carriers. According to the Adams–Gibbs model [4], $B$ is a constant, the value of which is connected to the segmental motion of the polymer chains whereas the product $B \cdot R$ (R is the gas constant) is often considered as a pseudo activation energy; $T_0$ is an equilibrium glass transition temperature (the Vogel temperature) for which the system remains in one of configurations of lowest permissible energy and is generally around 50° below the glass transition temperature (see the Appendix).

It must be noted that a simpler relationship is sometimes applied in the form (1′)

$$\sigma = \sigma_0 \exp(-B/(T - T_0)) \quad (1')$$

where $\sigma_0$, $B$, $T_0$ are taken as empirical constants, although $\sigma_0$ contains a $T^{-1/2}$ term, due to the thermal velocity of the chain segments. If considering a small temperature interval, $\sigma_0$ can be taken as a constant and the form (1′) is obviously easier to linearize.

Some approximations have been reported: $T_0$ was taken as 210 K, because this value was reported to

be optimum for a fully amorphous PEO-based solid electrolyte [5], but this argument is rather questionable since functionalization or modification of the polymer backbone by grafted chains may alter in a noticeable way the viscoelastic properties, so that 210 K cannot be taken as a "universal" value. $T_0$ can also be taken as $T_0 = T_g - 50$, with $T_g$ experimentally determined by calorimetric experiments. Using $T_g$ determined by DSC as $T_0$ was also discussed [6, 7]. Some authors used dynamic methods for determining the glass transition temperature, but it must be kept in mind, the $T_{gs}$ measured by DSC measurements are slightly smaller than those obtained by dynamic methods. No such assumptions were taken into account by Chabagno [8] who proposed an iterative procedure to have the best straight line by plotting $\{\mathrm{Ln}(\sigma T^{1/2}/A)\}^{-1}$ vs $(T - T_0)$.

The linearization method we propose here affords to derive the three parameters $A$, $B$ and $T_0$ from the experimental data, without any hypothesis about $T_0$. The logarithmic form of equation (1) can be written as

$$\mathrm{Ln}\,\sigma + 0.5\,\mathrm{Ln}\,T = \mathrm{Ln}\,A - B/(T - T_0).$$

Let $x = \mathrm{Ln}\,\sigma + 0.5\,\mathrm{Ln}\,T$ and $C = T_0\,\mathrm{Ln}\,A + B$. Then

$$T\,\mathrm{Ln}\,A + xT_0 - C = xT. \tag{3}$$

Equation (3) may be applied to each of the $n$ experimental data pairs $(T_i, x_i)$. In addition, each set of data is independent, so that a system of three equations may be written:

$$\begin{cases} \mathrm{Ln}\,A \sum T_i^2 + T_0 \sum x_i T_i - C \sum T_i = \sum x_i T_i^2 \\ \mathrm{Ln}\,A \sum T_i x_i + T_0 \sum x_i^2 - C \sum x_i = \sum T_i x_i^2 \\ \mathrm{Ln}\,A \sum T_i + T_0 \sum x_i - nC = \sum x_i T_i \end{cases} \tag{4}$$

Solving this system yields the desired parameters. Some examples will be given in the third part of this paper. The convenient method to solve this system is the matriciel calculus which allows to deduce further the variance-covariance matrix to get the standard errors (Appendix 2).

*(b) The WLF law*

In the WLF law, both coefficients $c_1^0$ and $c_2^0$ are calculated with respect to a reference temperature $T_R$ for which the conductivity is $\sigma_0$. $c_1^0$ and $c_2^0$ depend both on the temperature and are connected to the free-volume fraction $f_0$ and its thermic expansion coefficient $\alpha$.

$$c_1^0 = 1/2.3 f_0.$$
$$c_0^2 = f_0/\alpha$$

If choosing $T_R$ and its related conductivity $\sigma_0$, both coefficients $c_1^0$ and $c_2^0$ can be determined using a graphical method [7, 8] by plotting $[\log(\sigma/\sigma_0)]$ vs $(T - T_R)^{-1}$. It is here assumed that any error can influence the value of $\sigma_0$. Nevertheless, this method fails if $T$ is chosen too close from $T_R$, so that the conductivity data around the reference temperature cannot be taken into account. Another way consists in choosing a reference temperature far away from the experimental temperature range, calculating both $c_1^0$ and $c_2^0$ at this reference temperature and then at the desired temperature from the relations exposed in the appendix.

The best method consists in deriving simultaneously the three parameters $c_1^0$, $c_2^0$ and $\sigma_0$ from the experimental data for any reference temperature. Let $x = T - T_R$, $A = c_1^0 + \log \sigma_0$ and $B = c_2^0 \log \sigma_0$.

Equation (2) can be rewritten as

$$c_2^0 \log \sigma - Ax - B = -x \log \sigma. \tag{2'}$$

Equation (2′) may be applied to each of the $n$ experimental data pairs $(T_i, x_i)$ so that the following system can be used to calculate the three parameters $c_1^0$, $c_2^0$, $\log \sigma_0$.

$$\begin{cases} -c_2^0 \sum \log \sigma_i + A \sum x_i + nB = \sum x_i \log \sigma_i \\ -c_2^0 \sum x_i \log \sigma_i + A \sum x_i^2 + B \sum x_i = \sum \log \sigma_i x_i^2 \\ -c_2^0 \sum (\log \sigma_i)^2 + A \sum x_i \log \sigma_i + B \sum \log \sigma_i = \sum x_i (\log \sigma_i)^2 \end{cases} \tag{5}$$

*(c) Examples and discussion*

(1) The first example is dealing with a set of experimental data reported by Chabagno [8], from which the numerical values of the VTF parameters have been extracted using the linearization procedures and reported in Table 1 with the related standard errors. The VTF parameters are $A = 2.69$, $T_0 = 257$ K, $B = 888$ K ($B \cdot R = 0.076$ eV), to compare with the values reported by Chabagno after his iterative procedure, namely $A = 2.57$, $T_0 = 258$ K, $B \cdot R = 0.0757$ eV. Figure 1 depicts the conductivity curve drawing from the above values of the parameters and reports the experimental points. The WLF parameters are $c_1^0 = 4.33$ and $c_2^0 = 84.66$ for a reference temperature $T_R = 70°$. As expected, using either the VTF or the WLF procedure gives the same calculated values for the conductivity.

(2) The following example is making use of the conductivity data reported by Le Nest *et al.* [9] for a polyurethanne network containing 12% $LiClO_4$. Choosing a reference temperature $T_R = 339$ K, the authors determined the values of WLF coefficients using a graphical method and found $c_1^0 = 2$ and $c_2^0 = 160$. Our second procedure gives $c_1^0 = 2.17$ and $c_2^0 = 172.34$ for the same reference temperature. The values of the three parameters of the VTF were also derived and reported in Table 1. These latter

Table 1. Numerical values and standard errors of the three coefficients of the VTF procedure

| Sample | $T$ (K) | Ln $A$ | $B$ (K) |
|---|---|---|---|
| Chabagno[a] | 256 *(7.2)* | 0.99 *(0.61)* | 932 *(117)* |
| Chabagno[b] | 258 | 0.94 | 881 |
| Le Nest | 160 *(4.8)* | 0.278 *(0.14)* | 975 *(51)* |
| Giles[a] | 221 *(3.3)* | −0.97 *(0.20)* | 654 *(48)* |
| Giles[c] | 229 | −1.45 | 554 |

[a]Values found from our VTF procedure.
[b]Values found from the iterative procedure [8].
[c]Values for the onset of the glass transition temperature for the parent polymer [7].
The standard errors are in italics.

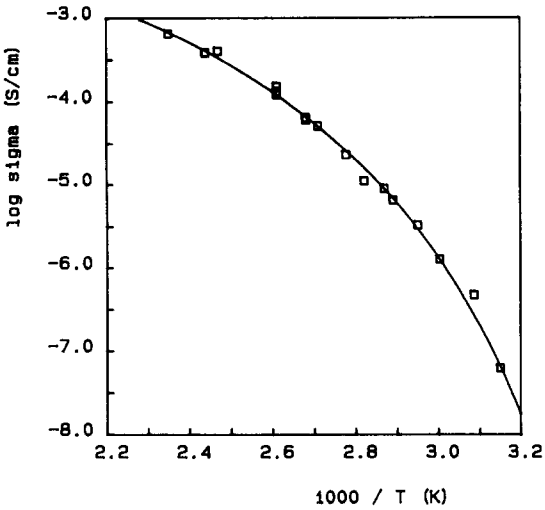


Fig. 1. Experimental data reported by Chabagno [8] (□) and the fitting curve after using the VTF procedure. The three coefficients are reported in the text.

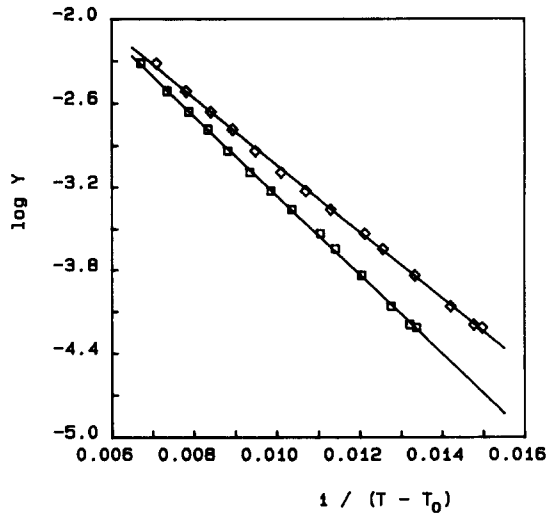


Fig. 3. "Linear" treatment of experimental data reported by Giles [7] with two values for $T_0$: 221 K (□) and 229 (◇). $Y = \sigma T^{1/2}$. Both curves can be qualified as excellent straight lines. The best fitting is chosen by taking into account the error function $S$.

values were used to draw the conductivity curve shown in Fig. 2.

(3) With networks of poly(ethylene glycol)s cross-linked by chlorophosphates, Giles [7] took $T_0$ as the temperature for the onset of the glass transition for the parent polymer (229 K) and used the linear form of equation (1):

$$\log \sigma T^{1/2} = \log A - B/(T - T_0).$$

Plotting $\log \sigma T^{1/2}$ vs $(T - T_0)^{-1}$ must give a straight line. Using Gile's data [the Fig. 3 in Ref. (7)], we found a value of 221 K for $T_0$. The other coefficients are reported in Table 1. Nevertheless, as shown in Fig. 3, using the above linear form gives excellent straight lines whatever the value of $T_0$ (221 K as well as 229 K). Furthermore, it may be seen on Fig. 4 that the fitting curves are quite superimposable within the range of experimental data. The accuracy of the results can be compared using the error function $S$ defined as

$$S = \left[\sum (Y_{\text{exp}} - Y_{\text{th}})^2\right]^{1/2} \tag{6}$$

where the subscripts exp and th refer to the experimental and theoretical values of the conductivity respectively. The $Y_{\text{th}}$ were calculated using the equation (1) with the extracted coefficients. Our procedure leads to an $S$ value equal to 0.050, lower than that of Giles ($S = 0.058$). It may easily be seen that the $S$ value found by our procedure is the

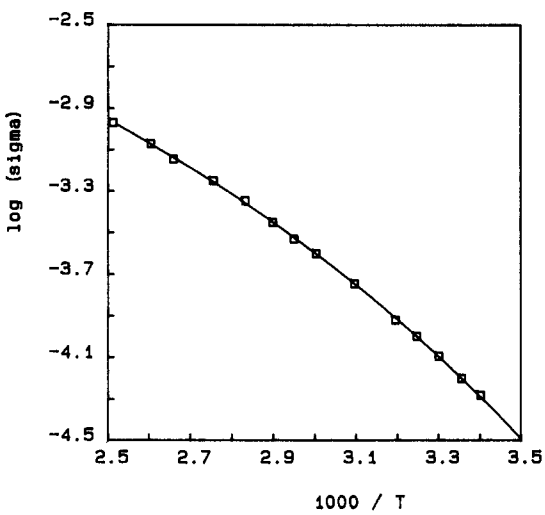


Fig. 2. Experimental data reported by Le Nest [9] (□) and the fitting curve. The coefficients are reported in Table 1.

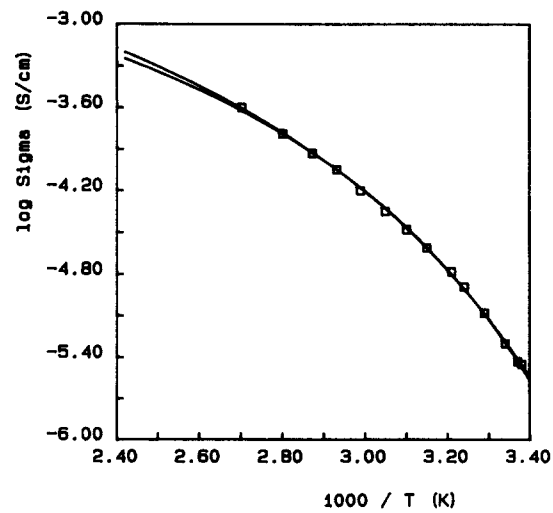


Fig. 4. Experimental data reported by Giles [7] (□) and both fitting curves using the two sets of VTF coefficients. These curves cannot be distinguished from each other.

Table 2

| Sample | $T$ (K) | Ln $A$ | $B$ (K) |
|---|---|---|---|
| ESP34 (100%) | 242 *(4)* | −1.748 *(0.29)* | 450 *(59)* |
| ESP32 (60%) | 268 *(7)* | −5.765 *(0.56)* | 164 *(135)* |
| ESP31 (40%) | 259 *(10)* | −4.227 *(0.60)* | 210 *(160)* |
| ESP41 (100%) | 219 *(36)* | −1.202 *(3.35)* | 795 *(645)* |
| ESP40 (80%) | 229 *(13)* | −0.64 *(1.17)* | 714 *(226)* |
| ESP26 (23%) | 234 *(12)* | 1.963 *(1.62)* | 934 *(234)* |

The triblock copolymer is polybutadiene in ESP 31, 32, 34 and polyisoprene in ESP 26, 40 41. The % in parenthesis is the amount of triblock copolymer in the mixture of polymers. In italics are the standard errors.

minimum one: any other $T_0$ will give a higher value for $S$.

Finally, both WLF coefficients have been found to be 2.94 and 89.45 for $c_1^0$ and $c_2^0$ respectively for a reference termperature equal to 313 K.

(4) As the last example, Table 2 reports the VTF parameters extracted from the thermal behaviour of the conductivity of some poly(ethylene oxide)–polydiene–poly(ethylene oxide) triblock copolymers synthesized by anionic way and mixed with poly(ethylene oxide) and $LiClO_4$ [10]. The polydiene is either a polybutadiene ($M_n = 32000$, ethylene oxide molar fraction $F_{EO} = 0.71$) or a polyisoprene ($M_n = 4600$, $F_{EO} = 0.80$). Also reported are the standard errors on the parameters. Figure 5 displays the conductivity curves for both of them. Although a good agreement between the experimental and calculated data is observed, the physical meaning of these parameters may be questionable in view of the standard errors: The values of $T_0$ obtained for the solid polymer electrolytes based on the polybutadiene are very high for an equilibrium glass transition temperature. On the other hand, the standard errors on the preexponential factor for SPE based on the polyisoprene appear quite disproportioned. It could be concluded the volume-free theory is not the good one to describe the conductivity behavior of such solid electrolytes, since these materials are more or less phase-segregated and

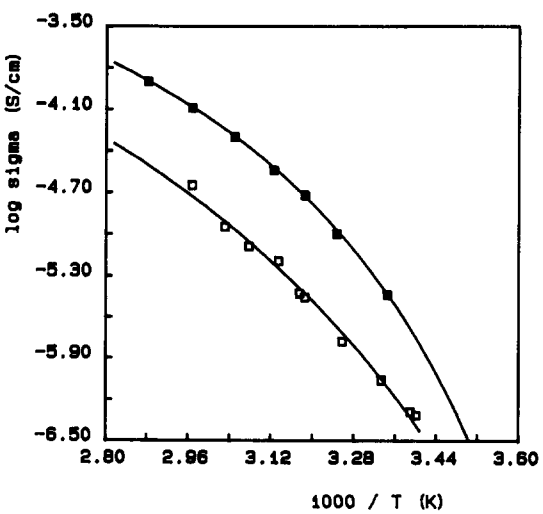


Fig. 5. Conductivity curves for both ESP 34 (■) and ESP 41 (□).

Table 3. Determination of WLF parameters related to the given examples, for a reference temperature taken as $T_0 + 50$, with $T_0$ previously derived from the linearization of the VTF law

| Sample | Ref. | $T_0 + 50$ | $c_1^0$ | $c_2^0$(K) | $f_0$ | $\alpha\ 10^3$ |
|---|---|---|---|---|---|---|
| Chabagno | [8] | 307 | 3.04 | 48.66 | 0.143 | 2.94 |
| Le Nest | [9] | 210 | 1.24 | 43.54 | 0.350 | 8.00 |
| Giles | [7] | 271[a] | 5.51 | 47.79 | 0.079 | 1.65 |
| | | 279[c] | 4.74 | 55.5 | | |

[a] and [c], same comments as in Table 1.

the "amorphous material" condition is not really fulfilled.

Another interesting exercise is to derive the WLF coefficients values for a reference temperature $T_R$ taken as $T_0 + 50$, with $T_0$ previously determined from the VTF linearization method. This reference temperature would be close from the glass transition temperature and "universal" values for $c_1^0$ and $c_2^0$ could be expected. These coefficients values are reported in Table 3. The $c_2^0$ values are close to 50, while the $c_1^0$ values remain rather scattered.

Finally, the free-volume fraction $f_0$ and its thermic expansion coefficient $\alpha$ can be calculated from the WLF coefficients. The values of the thermic coefficient are in the range $1.3\ 10^{-3}$–$8.0\ 10^{-3}$, (Table 3) which is above the value generally used in the viscoelastic properties of polymers ($\alpha = 4.8\ 10^{-4}\,deg^{-1}$).

In conclusion, linearization methods can be used to get easily the three coefficients of either the VTF or the WLF law, without making hypotheses or approximations on one of the coefficients. Nevertheless, it has clearly be shown that many sets of linearization coefficients could be found which gave a good fitting of the experimental data. Therefore, other considerations, based for example on the physical meaning or merely on the common sense can be proposed to choose the best set of coefficients. Furthermore, the validity of free-volume theories to describe the thermal behaviour of the conductivities can be checked by considering the standard errors.

## APPENDIX 1

Williams, Landel and Ferry defined a ratio $a_T$ of any relaxation time at temperature $T$ to its value at an arbitrary reference temperature $T_R$. This ratio was shown to depend on the temperature according to the well known WLF equation [2]:

$$\log a_T = -c_1^0(T - T_R)/(c_2^0 + T - T_R). \quad \text{(A1)}$$

The values of both coefficients $c_1^0$ and $c_2^0$ depend on the reference temperature. They can be calculated at any other temperature according to

$$c_1^0 = c_1^1 \cdot c_2^1/(c_2^1 + T_R - T_1) \quad \text{(A2)}$$

$$c_2^0 = c_2^1 + T_R - T_1 \quad \text{(A3)}$$

and then

$$c_1^0 \cdot c_2^0 = c_1^1 \cdot c_2^1. \quad \text{(A4)}$$

Equation (A3) can also be written as

$$T_R - c_2^0 = T_1 - c_2^1 = T_0 \quad \text{(A5)}$$

where $T_0$, often called Vogel temperature, is a fixed temperature for which $\log a_T$ becomes infinite.

Using the glass transition temperature $T_g$ as the reference temperature affords to obtain "universal" values of $c_1^g$ and $c_2^g$, estimated to be 17.44 and 51.6, respectively, so that

$$T_0 = T_g - c_2^g = T_g - 51.6. \quad \text{(A6)}$$

## APPENDIX 2

*Standard Errors for the Parameters*

Matrices provide a convenient method to solve the systems of linear equations. Furthermore, the variance–covariance matrix can be decuded to get the standard errors [11]. In matrix notations, the system (4) can be written as

$$\mathbf{X}\theta = \mathbf{Y}$$

where $\mathbf{X}$ and $\mathbf{Y}$ are respectively a $3 \times 3$ matrix and a vector of coefficients. $\theta$ is the vector containing the parameters to be estimated. Then

$$\theta = \mathbf{X}^{-1}\mathbf{Y}.$$

Notice that both $\mathbf{X}$ and $\mathbf{X}^{-1}$ are diagonale matrices. The variance–covariance matrix for the parameters is

$$\mathbf{V} = \mathbf{X}^{-1}\sigma^2$$

$\sigma^2$ is the error variance and can be substituted by the estimate $s^2 = S_r/(n-p)$. $S_r$ is the residual sum of squares $\Sigma (Y_{exp} - Y_{th})^2$, $n$ is the number of data and $p$ is the number of estimated parameters, here $p = 3$.

The square root of the variances, located on the diagonale of $\mathbf{V}$, gives the standard errors.

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