

The determination of the activation energy of a relaxational process from thermally stimulated depolarisation currents (TSDC) data: an illustration with the β -relaxation of maltitol

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Received 6 July 2004; received in revised form 27 July 2004; accepted 30 July 2004

Available online 16 September 2004

Abstract

Three different and independent procedures to obtain the activation energy of a motional process from thermally stimulated depolarisation currents (TSDC) data are reported. One of the procedures requires a single thermal sampling (TS) experiment: the activation energy is calculated from the temperature dependence of the relaxation time associated with this TS peak. The other two procedures are based on the influence of the heating rate on the features of the TS peak namely, on the temperature location T_m and on the intensity of the maximum $I(T_m)$ of the peak. The illustration with the case of an elementary component of the β -relaxation of maltitol shows that the values of the activation energy provided by these procedures are in good mutual agreement. The fact that the TSDC technique provides different and independent procedures to obtain the kinetic parameters of a motional process is a unique feature in the context of the experimental techniques most often used to study molecular mobility.

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Keywords: Molecular mobility; Secondary relaxation; Heating rate; Relaxation time

1. Introduction

The technique of thermally stimulated depolarisation currents (TSDC) has been widely used to study the kinetics of slow relaxations in solids [1–4]. The experimental output of a TSDC experiment is the depolarisation current intensity as a function of temperature. Since, the depolarisation current density (current intensity per unit area $J(T)$) is the rate of decreasing of the polarisation, we have

$$J(T) = \frac{I(T)}{A} = -\frac{dP(T)}{dt} \quad (1)$$

where $I(T)$ is the current intensity at temperature T (or at time t) of the constant rate heating ramp (depolarisation step), $P(T)$ is the remaining polarisation at temperature T (or at time t)

and A is the effective area of the electrodes. The analysis of the TSDC results is based on the Debye relaxation concept. In this context, the assumption is that, at each temperature of the linear heating ramp, the decay of the polarisation with time is a first-order rate process. For an elementary single motional process, we can thus write:

$$\frac{dP(T)}{dt} = -\frac{P(T)}{\tau(T)} \quad (2)$$

where $P(T) = P(t)$ is the polarisation at temperature T (at time t) of the heating ramp and $\tau(T)$ is a temperature-dependent relaxation time, characteristic of the elementary mode of motion under consideration. Combining Eqs. (1) and (2), it comes out that

$$J(T) = \frac{P(T)}{\tau(T)} \quad (3)$$

An important feature of the TSDC technique is that it allows the study of elementary or single relaxational processes

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using the so-called thermal sampling (TS) procedure. The importance of Eq. (3) is that it allows the calculation of the temperature-dependent relaxation time of a single relaxation process from the experimental result of the corresponding TS experiment. As the temperature rises linearly with time in the depolarisation step, temperature and time are related by $T = T_0 + rt$, where T_0 (the so-called freezing temperature) is the temperature at the beginning of the heating ramp (at $t = 0$) and r is the heating rate. In this context, the remaining polarisation at temperature T , $P(T)$, is given by

$$P(T) = \frac{1}{r} \int_T^\infty J(T') dT' = \frac{1}{r} \int_T^{T_f} J(T') dT' \quad (4)$$

where T_f is a temperature well above the temperature of the maximum of the TS peak, where the sample is already completely depolarised. The temperature-dependent relaxation time associated with a given mode of motion can thus be calculated from:

$$\tau(T) = \frac{1/r \int_T^{T_f} J(T') dT'}{J(T)} = \frac{1/r \int_T^{T_f} I(T') dT'}{I(T)} \quad (5)$$

where $I(T)$ is as noted before, the depolarisation current intensity measured in the heating ramp of the TS experiment. The capability of directly calculating the relaxation time from the results of a single TS experiment constitutes an essential quantitative feature of the TSDC technique and that is why thermally stimulated depolarisation currents is an experimental technique that provides important information on molecular mobility in solids, i.e. on the kinetics of relaxational processes and the distribution of relaxation times.

In the present work, we will report and compare different procedures to determine activation energies from TSDC data and we will illustrate with the case of a TS component of the β -relaxation of maltitol. The only justification for the choice of this substance is that we wanted to illustrate with a glass former that was the recent object of mobility studies [3,5]. The β -relaxation was taken for simplicity. The methodology presented in this work has been applied to other kinds of mobility in a different system with similar results [6]. The fact that the TSDC technique provides different and independent procedures to obtain the kinetic parameters of a motional process is not a finding of the present work and a review of these procedures can be found in classical textbooks [7,8]. However, this important feature of this experimental technique seems to be forgotten in the recent literature dealing with the TSDC technique. One of the objectives of this work is precisely to provide the users of the technique the possibility of getting a better comprehension on the obtained results, and a valuable tool to test their self-consistency and validity.

2. Experimental

Maltitol (4-*o*- α -D-glucopyranosyl-D-glucitol) was an Aldrich product, cat. no. 86,206-1, 98% purity and was

used without further purification. The melting temperature is 150 °C and the glass transition temperature is 45 °C (at 4 °C min⁻¹). Maltitol in the glassy state was prepared without difficulty, since this substance is easily supercooled (low tendency to crystallize on cooling) and the glass transition temperature is above room temperature.

Thermally stimulated depolarisation current experiments were carried out with a TSC/RMA 9000 spectrometer (Thermold Partners, Stamford, CT, USA) covering the temperature range between -170 and +400 °C. Several references explaining the physical background of TSDC is available [7–9] that can be useful for the reader not familiar with this experimental technique. Moreover, several recently published papers [3,4] can be helpful to explain the experimental procedures used in TSDC, and the physical meaning of the data provided by this technique.

3. Results and discussion

The methods for evaluating the activation parameters from thermally stimulated techniques are numerous and have been reviewed [7]. In the present work, we will just use those that lead to more reliable values of the activation energy.

3.1. Activation energy from the temperature-dependent relaxation time of a single process

If the temperature-dependent relaxation time of a single relaxation process is calculated from Eq. (5), the activation energy can be determined from the definition:

$$E_a(T) = R \left(\frac{d \ln \tau(T)}{d(1/T)} \right)_T \quad (6)$$

The most usual procedure to obtain activation energies from TSDC data consists in equating the slope of the representation of $\ln \tau(T)$ as a function of $1/T$ to E_a/R . If the temperature dependence of the relaxation time is described by the Arrhenius equation, the activation energy is a constant, independent of temperature. Fig. 1(a) shows a peak that is the result of a thermal sampling experiment on the β -relaxation of maltitol, while Fig. 1(b) shows the corresponding representation of $\ln \tau(T)$ as a function of $1/T$. The linearity of the representation in Fig. 1(b) indicates an Arrhenius behaviour, and the linear fitting of points allowed the determination of the activation energy $E_a = 36.4 \text{ kJ mol}^{-1}$.

3.2. Activation energy from the heating rate dependence of the features of a thermal sampling peak

Several features of a TSDC peak are influenced by the experimental heating rate. Firstly, the temperature of maximum intensity T_m , i.e. the location of the peak in the temperature axis shifts to higher temperatures as the heating rate increases. Secondly, the area of the peak increases with increasing heat-

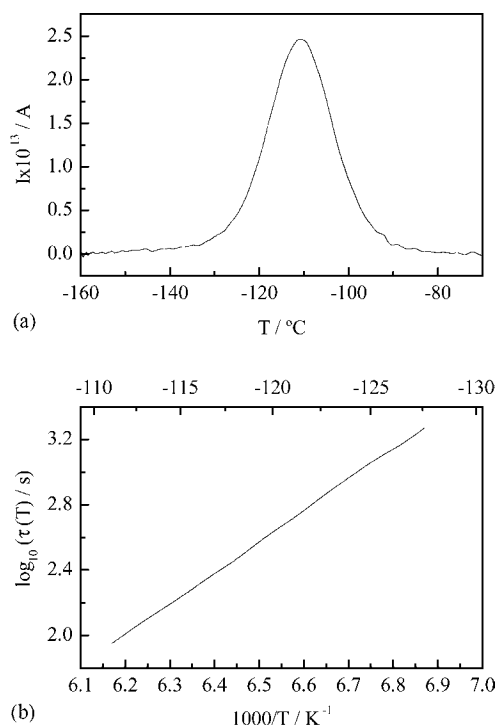


Fig. 1. (a) Thermal sampling (TS) component of the β -relaxation of maltitol. The experimental conditions were: polarisation temperature $T_P = -115^\circ\text{C}$; strength of the polarising electric field $E = 500\text{ V/mm}$; polarisation time $t_p = 5\text{ min}$; width of the polarisation window $\Delta T = 2^\circ\text{C}$ and heating rate $r = 4^\circ\text{C min}^{-1}$. (b) Line of $\ln \tau$ as a function of $1/T$ for the peak in (a).

ing rate. The area L under an experimental TS peak can be expressed as:

$$L = \int_{T_0}^{T_f} I(T') dT' = A \int_{T_0}^{T_f} J(T') dT' \quad (7)$$

where T_0 is a temperature well below the temperature of the maximum of the TS peak where the intensity of the depolarisation current is negligibly small and T_f is a temperature well above the temperature of the maximum of the TS peak, where the sample is already completely depolarised. In Eq. (7), as in Eq. (1), A is the effective area of the electrode system. Taking Eq. (4) into account, the relationship between the area L of a TS peak and the total polarisation P_0 , of the sample at the beginning of the heating ramp is

$$P_0 = \frac{L}{Ar} \quad (8)$$

In a series of experiments designed to study the effect of the heating rate, the total polarisation P_0 of the sample at the beginning of the heating ramp is the same in all experiments, since the previous electric and thermal treatments are identical for all the experiments. Eq. (8) shows that the area under the TS peak increases linearly with increasing heating rate. At the same time, the intensity of the maximum $I(T_m)$, increases as the heating rate increases. In the following we will analyse from a quantitative point of view, how these features of a TS peak depend on the heating rate.

3.2.1. The effect of the heating rate on the location T_m of a TS peak

In order to show the relationship that exists between the heating rate r , of the TS experiment and the location T_m , of the obtained peak, let us briefly discuss some particular features of a TS peak. Taking the derivative of Eq. (3), and taking Eq. (2) into account, gives

$$\frac{dJ(T)}{dT} = \left[-\frac{1}{r} - \frac{d\tau(T)}{dT} \right] \frac{P(T)}{\tau^2(T)} \quad (9)$$

From Eq. (9) we conclude that, at the maximum of the TS peak ($T = T_m$), we have

$$\left[\frac{d\tau(T)}{dT} \right]_{T=T_m} = -\frac{1}{r} \quad (10)$$

Eq. (10) is a fundamental equation of the TSDC technique. It indicates that at the temperature of maximum intensity of a TS peak T_m , there is a crossing between the time scale of the relaxation process defined by the temperature derivative of the relaxation time and the time scale of the TS experiment, defined by the reciprocal of the heating rate, i.e. by $dt/dT = 1/r$. In fact, the temperature dependence of the relaxation time is such that it decreases as the temperature increases. If $T < T_m$, the rate of decreasing of the relaxation time with temperature is in modulus, higher than $1/r$, while if $T > T_m$, it is lower than $1/r$. At $T = T_m$, the two time scales are equal [10].

If the temperature dependence of the relaxation time is described by the Arrhenius equation, Eq. (10) becomes:

$$\tau(T_m) = \frac{RT_m^2}{rE_a} \quad (11)$$

where T_m is the temperature of maximum intensity of the TS peak, $\tau(T_m)$ is the relaxation time of the process at that temperature. Writing the Arrhenius equation at T_m , taking Eq. (11) into account, and rearranging it comes out:

$$\ln \frac{T_m^2}{r} = \frac{E_a}{R} \times \frac{1}{T_m} + \ln \frac{E_a \tau_0}{R} = \frac{E_a}{R} \times \frac{1}{T_m} + a \quad (12)$$

where $a = \ln(E_a \tau_0/R)$ is a constant and E_a is the Arrhenius activation energy. According to Eq. (12), a linear relationship is expected between $\ln(T_m^2/r)$ and $1/T_m$, with a slope equal to E_a/R . Given that the area under the TS peak increases linearly with increasing heating rate (Eq. (8)), a linear relationship between $\ln(T_m^2/L(T_m))$ and $1/T_m$ is also expected, with a slope equal to E_a/R . Fig. 2 shows the results of a series of thermal sampling experiments, similar to that shown in Fig. 1(a), where the depolarisation peak was recorded at different heating rates. Table 1 shows some of the features of the peaks, namely the temperature location T_m , the intensity of the maximum $I(T_m)$ and the area $L(T_m)$.

Fig. 3, on the other hand, shows the representation of $\ln(T_m^2/r)$ as a function of $1/T_m$. The straight-line in Fig. 3 is the result of the linear fitting of the experimental points,

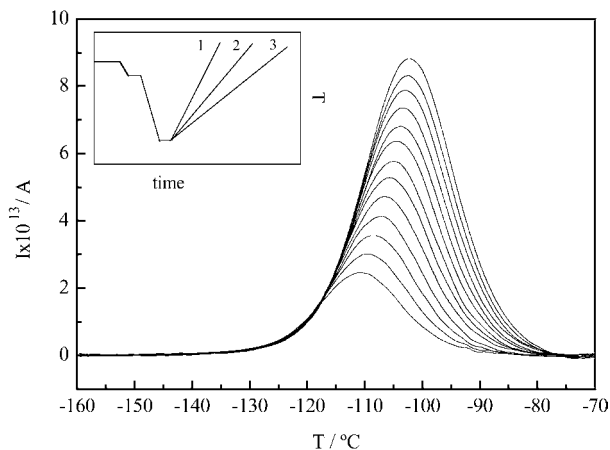


Fig. 2. Thermally sampled component of the β -relaxation of maltitol (the same as in Fig. 1(a)) obtained with different heating rates. The heating rates were from $r = 4 \text{ }^\circ\text{C min}^{-1}$ up to $r = 16 \text{ }^\circ\text{C min}^{-1}$, with intervals of $1 \text{ }^\circ\text{C}$. The other experimental conditions are similar to those reported in Fig. 1. The insert schematically shows the experimental procedure used in the TS experiment. The thicker lines correspond to the experimental steps where the electric field is applied. The lines 1, 2 and 3 correspond to the depolarisation step (the linear heating ramp) carried out at different heating rates with decreasing rate from 1 to 3.

and from its slope the value of $E_a = 33.6 \text{ kJ mol}^{-1}$ was obtained.

This value is in reasonable agreement with that previously reported, obtained from the temperature dependence of the relaxation time of a TS peak obtained with a heating rate of $4 \text{ }^\circ\text{C min}^{-1}$.

It is to be underlined that the influence of T_m^2 in the variation of the left hand side of Eq. (12) is relatively small compared with the influence of the heating rate (namely if the activation energy is low), so that it can be written as:

$$\ln r = -\frac{E_a}{R} \times \frac{1}{T_m} + \text{cte.} \quad (13)$$

Table 1

Some features of the TS component of the β -relaxation of maltitol obtained with $T_p = -115 \text{ }^\circ\text{C}$ and a thermal window of $\Delta T = 2 \text{ }^\circ\text{C}$ recorded at different heating rates r

$r \text{ (}^\circ\text{C min}^{-1}\text{)}$	$T_m \text{ (}^\circ\text{C)}$	$I(T_m) A$	$L(T_m) A \text{ (}^\circ\text{C)}$
4	-110.90	2.46×10^{-13}	4.82×10^{-12}
5	-109.51	3.02×10^{-13}	5.86×10^{-12}
6	-108.66	3.57×10^{-13}	6.77×10^{-12}
7	-107.16	4.14×10^{-13}	7.93×10^{-12}
8	-106.56	4.72×10^{-13}	9.39×10^{-12}
9	-105.70	5.28×10^{-13}	1.04×10^{-11}
10	-105.00	5.77×10^{-13}	1.13×10^{-11}
11	-104.48	6.37×10^{-13}	1.27×10^{-11}
12	-103.81	6.81×10^{-13}	1.35×10^{-11}
13	-103.46	7.36×10^{-13}	1.48×10^{-11}
14	-102.88	7.88×10^{-13}	1.59×10^{-11}
15	-102.50	8.31×10^{-13}	1.69×10^{-11}
16	-102.22	8.82×10^{-13}	1.81×10^{-11}

The tabulated features are: temperature location of the peak T_m , intensity of the maximum $I(T_m)$, area of the experimental peak $L(T_m)$.

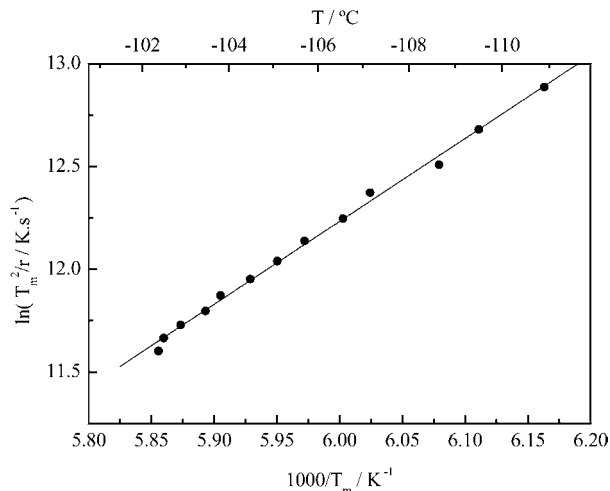


Fig. 3. Representation of $\ln(T_m^2/r)$ as a function of $1/T_m$, for the series of experiments with different heating rates (TS peak with $T_p = -115 \text{ }^\circ\text{C}$). The straight-line is the result of the fitting of the points corresponding to heating rates from 4 to $16 \text{ }^\circ\text{C/min}$.

An equation similar to Eq. (13) is used to determine the activation energy of the structural relaxation from differential scanning calorimetry data [11]. Again, taking into account Eq. (8), we expect also a linear relationship between $\ln L(T_m)$ and $1/T_m$, with a slope equal to $-E_a/R$.

3.2.2. The effect of the heating rate on both the maximum intensity $I(T_m)$ and the location T_m , of a TS peak

As reported before, and clearly shown in Fig. 2, the effect of the heating rate on the features of a TSDC peak is such that the intensity of the maximum $I(T_m)$, increases as the heating rate increases and at the same time, the temperature of maximum intensity T_m , i.e. the location of the peak, shifts to higher temperatures. From the basic equations that constitute the background of the TSDC technique, it can be shown that the increase in $I(T_m)$ and the increase in T_m are related each other in such a way that $\ln I(T_m)$ shows a linear dependence on $1/T_m$, with a slope equal to $-E_a/R$. We have thus:

$$\ln I(T_m) = -\frac{E_a}{RT_m} + \text{constant.} \quad (14)$$

We decided to present the justification of Eq. (14) at the end in Appendix A, in order to lighten the text. Eq. (14) is thus at the origin of another procedure to calculate the activation energy from TSDC data [7]. Fig. 4 shows the representation of $\ln I(T_m)$ as a function of $1/T_m$ for the experiments presented in Fig. 2.

Once again, the straight-line in Fig. 4 is the result of the linear fitting of the experimental points. The linear dependence is confirmed and the activation energy obtained from the slope is $E_a = 33.4 \text{ kJ mol}^{-1}$. The results previously reported suggest the following comments: (1) the values that have been obtained from the different procedures based on TSDC data were 36.4, 33.6 and 33.4 kJ mol^{-1} , showing a very good mutual agreement. (2) Both Eqs. (12) and (14) are

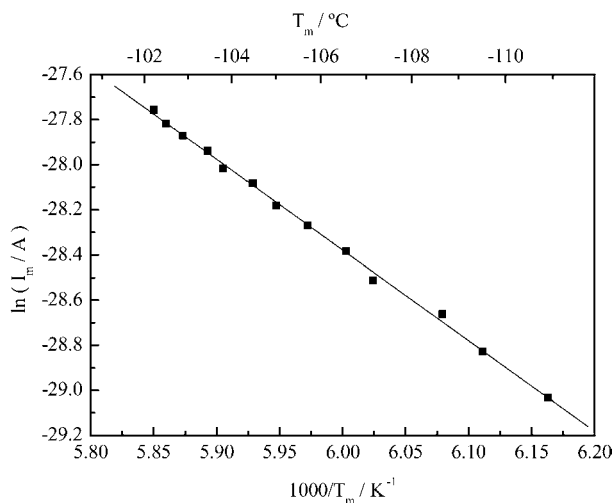


Fig. 4. Representation of $\ln I(T_m)$ as a function of $1/T_m$, for the series of experiments with different heating rates (TS peak with $T_p = -115$ °C). The straight-line is the result of the fitting of the points corresponding to heating rates from 4 to 16 °C/min.

based on the assumption that the relaxation time shows an Arrhenius temperature dependence. Since, this is generally a very good assumption for the individual components of the β -relaxation, we conclude that the proposed procedures are very adequate to the study of the kinetics of the secondary relaxations.

4. Conclusions

Three different procedures based on TSDC data were used in order to determine the activation energy associated to a single relaxational component of the β -relaxation of multi-tol. The obtained values were 36.4, 33.6 and 33.4 kJ mol^{-1} , showing a very good mutual agreement. The TSDC technique thus appears as a very helpful technique to study molecular mobility. On the other hand, the simultaneous use of the different procedures TSDC offers to determine the activation energy provides a self-consistency test for the validity of the obtained results. Furthermore, the fact that the TSDC technique provides different and independent procedures to obtain the kinetic parameters of a motional process is a unique feature in the context of the experimental techniques most often used to study molecular mobility.

Acknowledgements

N.T. Correia acknowledges a post-doctoral grant from the Fundação para a Ciência e Tecnologia. Supported by a franco-portuguese cooperation protocol (GRICES/CNRS) is also gratefully acknowledged.

Appendix A. Relationship between the increasing of the intensity of the maximum $I(T_m)$ and the shift of the peak location T_m to higher temperatures with increasing heating rate

The Debye hypothesis for the decay of the polarisation along the TSDC heating ramp (Eq. (2)) leads to:

$$P(T) = P_0 \exp \left[-\frac{1}{r} \int_{T_0}^T \frac{dT'}{\tau(T')} \right] \quad (\text{A.1})$$

where P_0 is the total polarisation of the sample at the beginning of the depolarisation step (heating ramp), and $P(T)$ the polarisation that remains at temperature T of the heating ramp.

Combining Eqs. (3) and (A.1), the depolarisation current density is given by:

$$J(T) = -r \frac{dP(T)}{dT} = \frac{P_0}{\tau(T)} \exp \left[-\frac{1}{r} \int_{T_0}^T \frac{dT'}{\tau(T')} \right] \quad (\text{A.2})$$

If the temperature dependence of the relaxation time is described by the Arrhenius equation, we will have

$$J(T) = \frac{P_0}{\tau_0} \exp \left(-\frac{E_a}{RT} \right) \exp \left[-\frac{1}{r\tau_0} \int_{T_0}^T \exp \left(-\frac{E_a}{RT'} \right) dT' \right] \quad (\text{A.3})$$

If the quantity inside the square brackets is named $S(T)$,

$$S(T) = \frac{1}{r\tau_0} \int_{T_0}^T \exp \left(-\frac{E_a}{RT'} \right) dT' \quad (\text{A.4})$$

Eq. (A.3) can be rewritten as

$$J(T) = \frac{P_0}{\tau_0} \exp \left(-\frac{E_a}{RT} \right) \exp[-S(T)] \quad (\text{A.5})$$

and at the temperature of the maximum,

$$\ln J(T_m) = \ln \frac{P_0}{\tau_0} - \frac{E_a}{RT_m} - S(T_m) \quad (\text{A.6})$$

Combining Eqs. (12) and (A.4), the function S can be written as

$$S(z_m) = -z_m^2 \exp(z_m) \int_{z_0}^{z_m} z^{-2} \exp(-z) dz \quad (\text{A.7})$$

where $z = E_a/RT$, and $z_0 = E_a/RT_0$ is taken at a temperature T_0 , well below the temperature of the maximum of the TS peak T_m , where the intensity of the depolarisation current is negligibly small (where the polarisation is P_0). The graphical representation of $S(z_m)$ as a function of z_m is presented in Fig. 5(a). It can be concluded from Fig. 5(a) that $S(z_m)$ is an increasing function of z_m and is very slightly dependent on z_m (i.e. on T_m) if $z_m = E_a/RT_m \geq 60$. For the TS peaks in the glass transition region, the quantity E_a/RT_m has in general values much higher than 60 and consequently, $S(T_m)$ behaves as a constant. It is thus expected from Eq. (A.6) that $\ln J(T_m)$ shows a linear dependence on $1/T_m$, with a slope equal to $-E_a/R$, as indicated in Eq. (14) (remember that the current

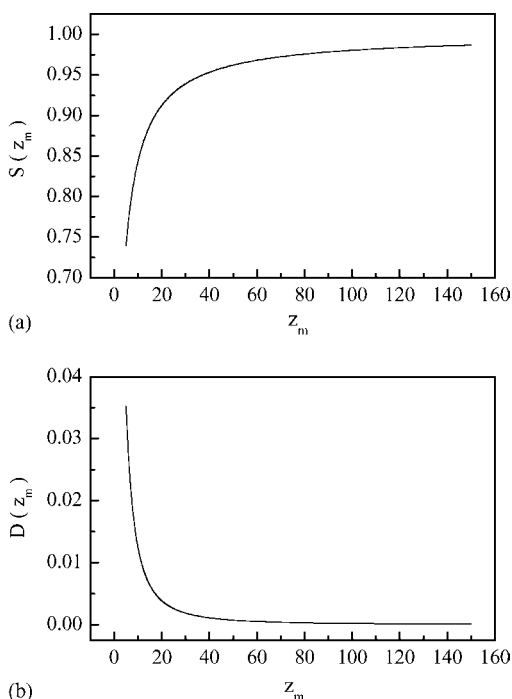


Fig. 5. (a) Representation of $S(z_m)$ as a function of z_m . (b) Representation of $D(z_m) = dS(z_m)/dz_m$ as a function of z_m . When $z_m \geq 60$, the function nearly behaves as a constant and the values of the function $D(z_m)$ are negligible so that the activation energy can be directly obtained from the slope of the plot shown in Fig. 4.

intensity $I(T)$ and the current density $J(T)$, are related by Eq. (1).

From Eq. (A.6) we have

$$\frac{d \ln J(T_m)}{d 1/T_m} = -\frac{E_a}{R} - \frac{d S(T_m)}{d 1/T_m} = -\frac{E_a}{R} \left(1 + \frac{dS(z_m)}{d z_m} \right) \quad (\text{A.8})$$

Fig. 5(b) displays the representation of $D(z_m) = dS(z_m)/dz_m$ as a function of z_m , showing that it decreases by positive values with increasing z_m . When $z_m \geq 60$, the values of the function $D(z_m)$ are negligible, so that the activation energy can be directly obtained from the slope of the plot shown in Fig. 4 (see Eqs. (A.6) and (A.8)). In the case of the β -

relaxation of maltitol considered in the present work, however, we have $z_m \sim 26$, that is a low value compared to 60. However, the value of $D(z_m)$ is ~ 0.0024 , indicating that, even in this unfavourable situation, the error in the determination of the activation energy from the slope of Fig. 4 is no more than 0.3% (see Eq. (A.8)).

We can conclude that the fitting based on Eq. (14) can be used to determine the activation energy of a motional process in practically all the situations, which are found in mobility studies using the TSDC technique.

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