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The Activation Energy at T_g and the Fragility Index of Indomethacin, Predicted from the Influence of the Heating Rate on the Temperature Position and on the Intensity of Thermally Stimulated Depolarization Current Peak

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Purpose. The purpose of this study was to estimate the activation energy at the glass transition temperature (and the fragility index) of amorphous indomethacin from the influence of heating rate on the features of the relaxation peaks obtained by thermally stimulated depolarization currents (TSDC) and to compare the obtained results with those obtained by other procedures based on TSDC data.

Methods. The glass transition temperature region of amorphous indomethacin was characterized at different heating rates by TSDC in a way similar to that used to determine the kinetics of the glass transition relaxation by differential scanning calorimetry. The features of a thermal sampled TSDC peak, namely the temperature location and the intensity, depend on the heating rate.

Results. The activation energy for structural relaxation (directly related to glass fragility) was estimated from the heating rate dependence of the TSDC peak location, T_m, and of the maximum intensity of the TSDC peak, $I(T_m)$.

Conclusions. The methods for determining the activation energy for structural relaxation and fragility of indomethacin from TSDC data obtained with different heating rates were compared with other procedures previously proposed. TSDC, which is not a very familiar technique in the community of pharmaceutical scientists, proved to be a very convenient technique to study molecular mobility and to determine the fragility index in glass-forming systems. The value of ~60 appears as a reasonable value of the fragility index of indomethacin.

KEY WORDS: molecular mobility; glass transition; fragility; TSDC, thermally stimulated depolarisation currents.

INTRODUCTION

The significance of the amorphous state in pharmaceutical systems has been underlined in relatively recent works (1,2). The time scales of molecular motions are necessary to effectively characterize the properties of amorphous pharmaceutical solids (3,4). The fragility index of a glass-forming liquid is a central parameter in glassy state physics that reflects the stability of the structure (short- and intermediate-range order) to thermally induced transformations (5,6). Several experimental techniques allow the determination of the fragility index of a glass-forming system. Among them we may enumerate dielectric relaxation spectroscopy (DRS) (7), conventional differential scanning calorimetry (DSC) (8), as well as modulated temperature differential scanning calorimetry (9), and thermally stimulated depolarization currents (TSDC) (10). The molecular mobility in indomethacin has been studied by several experimental techniques (11–13), which allowed the determination of the fragility index from the experimental data. However, the very large scattering of the values of the fragility index reported in the literature suggested us a new analysis of the problem. In fact, a value $m = 76.7$ is reported, obtained from the heating rate dependence of the calorimetric glass transition temperature (12). A quite different value, $m = 67$, is obtained from the parameters of the Vogel–Fulcher–Tamann equation obtained by fitting the dielectric relaxation data in the frequency range from 10 to 10^5 Hz (12). On the other hand, $m = 81$ is the value of the fragility that came out from the parameters of the Vogel–Fulcher–Tamann equation obtained by fitting recent dielectric relaxation data in a wider frequency range from 10^{-3} to 10^5 Hz (13). Finally, $m = 64$ is the value that was very recently obtained from TSDC data (14).

In the present work, we tried to enlighten the problem of determining the fragility index of indomethacin. To do so, we used two procedures based on TSDC data, different from those previously used, to calculate fragility. These procedures are based on the effect of the heating rate on the temperature of maximum intensity, on the area, and on the intensity of the maximum of the thermal sampling (TS) peaks. With this work we hope to complement a TSDC study of indomethacin recently published in this journal (14), where we emphasized the advantages of this experimental technique to study molecular mobility in pharmaceutical solids.

MATERIALS AND METHODS

Indomethacin (1-[4-chlorobenzoyl]-5-methoxi-2-methyl-indole-3-acetic acid), from Sigma (St. Louis, MO, USA; catalog number I-7378, lot 77H18461), with a melting point at 157°C = 430.15 K obtained by DSC and it was used without further purification. Its calorimetric glass transition temperature is reported to be $T_g = 42°\text{C}$ (315.2 K) for a heating rate of 0.0166667 K.s^{-1} (15).

TSDC experiments were performed with a TSC/RMA 9000 spectrometer (TherMold Partners, Stanford, CT, USA) covering the temperature range between 100 and 670 K. The results from two types of TSDC experiments are described in this report. Global TSDC allows the full distribution of relaxation processes in the vicinity of T_g to be observed. Thermal sampling TSDC, TS-TSDC, allows a narrowly distributed component of the distribution to be isolated. Several references explaining the physical background of TSDC are available (16,17), which can be useful for the reader not familiar with this experimental technique. Moreover, an article recently published in this journal (14) can be helpful in explaining the experimental procedures used in TSDC and the physical meaning of the data provided by this technique.

The configuration of the cell is a parallel plate capacitor with an effective area of ≈38 mm^2. The melting point of indium was used to calibrate the instrument at different linear

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rates, from −20 K · min^{-1} = −0.333333 K · s^{-1} to +20 K · min^{-1} = +0.333333 K · s^{-1}. The software of the instrument provides a calibration method that produces a specific data file (extension *.CAL). When the calibration file is loaded into the Analysis software application, the software recognizes this file and allows the calibration of the instrument.

The motional process that was considered in the present work is the thermal sampled component with higher intensity in the glass transition region of indomethacin. The essential experimental conditions were: intensity of the polarizing electric field, E = 200 V.mm^{-1}; polarization time, t_P = 60 s; polarization temperature, T_P = 37°C = 310.15 K; width of the polarization window, ΔT = 1 K; "freezing" temperature, T_0 = −10°C = 263.15 K. This thermal sampled motional component was obtained with different heating rates, from r = 0.05 K · s^{-1} up to r = 0.316667 K · s^{-1}, with intervals of 2 K. As shown in Figure 1 and explained in the text, the position of the peak shifts to higher temperature as heating rate increases and, at the same time, the intensity (and the area) of the peaks increases.

RESULTS AND DISCUSSION

The fragility index, m, of a substance was defined as the slope of the $\log_{10}\tau(T)$ vs. T_g/T line at the glass transition temperature, i.e., at $T = T_g$ (6,18):

$$m = \left[\frac{d\log_{10}\tau(T)}{d(T_g/T)}\right]_{T=T_g} \tag{1}$$

where τ is the structural relaxation time that slows down on cooling to 100 s at T_g. Equation (1) can be expressed in terms of the temperature dependent apparent activation energy, E_a, as follows:

$$m = \frac{1}{2.303}\left[\frac{E_a(T_g)}{RT_g}\right] \tag{2}$$

Any experimental technique that allows the determination of the temperature dependence of the relaxation time of a motional process from the rough experimental data is thus useful for obtaining the fragility index of a glass-forming system. For example, if the temperature dependence of the relaxation time in the vicinity of T_g is determined by DRS and the experimental data are fitted with a Vogel type equation:

$$\tau = \tau_0 \exp\frac{DT_0}{T - T_0}, \tag{3}$$

where τ_0, D and T_0 are constants, the fragility index can be obtained as

$$m = \frac{DT_0T_g}{2.303(T_g - T_0)^2}. \tag{4}$$

The methods for evaluating the activation parameters from thermally stimulated techniques are numerous and have been reviewed (17). In the present work, we will just use those that lead to more reliable values of the activation energy and of the fragility. A procedure to determine the fragility index of a glass former from TSDC data was recently proposed (10,19). To use this method it is necessary to identify the thermal sampling component (the TS peak) with highest intensity in the glass transition region. This TS-TSDC peak corresponds to a narrowly distributed mode of motion which is characterized by a temperature dependent relaxation time, $\tau(T)$, and by a given location in the temperature axis, T_M, the temperature of maximum intensity of the peak. The TSDC fragility index, m, was thus defined as

$$m = \left(\frac{d\log_{10}\tau(T)}{d(T_M/T)}\right)_{T=T_M} \tag{5}$$

or, alternatively,

$$m = \frac{1}{2.303}\left[\frac{E_a(T_M)}{RT_M}\right] \tag{6}$$

where $E_a(T_M)$ is the activation energy at T_M of the peak of maximum intensity in the glass transition region. The temperature of the maximum of the TS peak with maximum intensity in the glass transition region of indomethacin (the glass transition temperature provided by TSDC) was found to be T_M = 42.3°C = 315.5 K, and the activation enthalpy at T_M was $E_a(T_M)$ = 386 kJ · mol^{-1}, so that the TSDC fragility of indomethacin was m = 64 (14).

In the present work, we will explore two other procedures that allow the determination of the fragility index of a glass former from TSDC data. These procedures are based on the influence of the heating rate of the depolarization step on the experimental output, i.e., on the features of the experimental TSDC peak. As will be shown later, as the heating rate increases, the intensity of the maximum, I_m, (and the area, L) of the TS peak increase, and the temperature of maximum intensity, T_m, i.e., the location of the peak, shifts to higher temperatures.

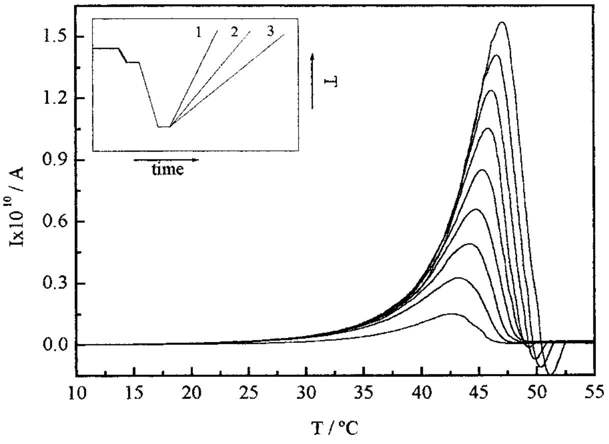

Fig. 1. Thermal sampled component with higher intensity in the glass transition region of indomethacin obtained with different heating rates. The experimental conditions were: intensity of the polarizing electric field, E = 200 V.mm^{-1}; polarization time, t_P = 60 s, polarization temperature, T_P = 310.15 K; width of the polarization window, ΔT = 1 K; "freezing" temperature, T_0 = 263.15 K. The heating rates were from r = 0.05 K · s^{-1} up to r = 0.3166667 K · s^{-1}, with intervals of 2 K. The position of the peak shifts to higher temperature as heating rate increases. The inset in the figure schematically shows the experimental procedure used in the TS experiment. The thicker lines correspond to the experimental steps where the electric field is applied. Lines 1, 2, and 3 correspond to the depolarization step (the linear heating ramp) conducted at different heating rates, with decreasing rate from 1 to 3.

Influence of the Heating Rate on the Temperature of Maximum Intensity

The experimental output of a TSDC experiment is the depolarization current intensity as a function of temperature. Because the depolarization current density (current intensity per unit area) is the rate of decreasing of the polarization, we have the following:

$$J(T)=\frac{I(T)}{A}=-\frac{dP\,(T)}{dt} \tag{7}$$

where $J(T)$ is the current density at temperature T (or at time t) of the constant rate heating ramp (depolarization step), $P(T)$ is the remaining polarization at temperature T (or at time t), and A is the effective area of the electrodes. As the temperature rises linearly with time in the depolarization step, we have $T = T_0 + r.t$, where T_0 is the temperature at the beginning of the heating ramp (the so-called freezing temperature of the TSDC experiment), and r is the heating rate. Equation (7) can thus be written as follows:

$$J(T)=-r\frac{dP(T)}{dT} \tag{8}$$

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 polarization with time is a first-order rate process. For an elementary, single motional process, we can thus write:

$$\frac{dP(T)}{dt}=-\frac{P(T)}{\tau(T)} \tag{9}$$

where $P(T)$ is the polarization at temperature T (or at time t), and $\tau(T)$ is a temperature-dependent relaxation time, characteristic of the elementary mode of motion under consideration. As seen before, because the TSDC experiments are performed with linear heating rates, Eq. (9) can be expressed in terms of the temperature and the heating rate as follows:

$$\frac{dP(T)}{dt}=-\frac{1}{r}\frac{P(T)}{\tau(T)}. \tag{10}$$

Combining Eqs. (8) and (10), it comes out that

$$J(T)=\frac{P(T)}{\tau(T)}. \tag{11}$$

The position of a TS-TSDC peak (the temperature of maximum intensity, $T_{\rm m}$) will vary with heating rate. It can be shown, from these fundamental equations of the TSDC technique, that a linear relationship between $ln\ (T_{\rm m}^2/r)$ and $1/T_{\rm m}$ is expected, with a slope equal to $E_{\rm a}/R$:

$$\ln\frac{T_{\rm m}^2}{r}=\frac{E_{\rm a}}{R}\cdot\frac{1}{T_{\rm m}}+a \tag{12}$$

where a is a constant and $E_{\rm a}$ is the Arrhenius activation energy. The justification for Eq. (12) is given in Appendix A. Equation (12) is at the origin of the procedure that allows the determination of the activation energy of a TS peak from the effect of the heating rate on the temperature, $T_{\rm m}$, of maximum intensity of the peak (17). This procedure is formally similar to that used for predicting the activation energy at T_g from the influence of the heating rate on the temperature position of the DSC signature of the glass transition (20).

Figure 1 shows the results of a series of TS experiments with different heating rates, carried out on indomethacin. The peaks shown in Fig. 1 correspond to the TS component of higher intensity in the glass transition region that was obtained with a polarization temperature $T_{\rm P}$ = 310.15 K. It was this TS peak that allowed the determination of the value m = 64 for indomethacin (14) according to Eqs. (5) and (6). Figure 2 shows the representation of the temperature of maximum intensity, $T_{\rm m}$, of the TS peak obtained with $T_{\rm P}$ = 310.15 K (full squares), as a function of the heating rate, r.

The same kind of representation of the evolution of $T_{\rm m}$ as a function of the heating rate is also shown in Fig. 2 for the global glass transition peak of indomethacin (full circles). Reference 14 can be useful in this context to recall the difference between a global TSDC experiment and a partial polarization or TS experiment. Finally, Fig. 3 shows the representation of $ln\ (T_{\rm m}^2/r)$ as a function of $1/T_{\rm m}$, for the two series of experiments presented in Fig. 2.

The observation of Figs. 2 and 3 deserves some comments. First, from Fig. 2, it can be seen that the temperature position of the global peak (full circles) is slightly lower, about one degree lower, than that of the TS peak (full squares). This is a consequence of the thermal sampling (or partial polarization) procedure that allows the freezing of a narrower distribution of activation energies (the relative contribution of higher activation energy modes is higher in the TS peak of higher intensity, when compared with the global peak). Second, from Fig. 3 it can be observed that the slope (i.e., activation energy) of the straight line defined by the full circles (global experiments) is slightly smaller than that of the straight line defined by the full squares (higher TS peak intensity, $T_{\rm P}$ = 310.15 K). This is also a consequence of thermal sampling: the contribution of the relaxation modes with lower activation energy is stronger in the case of the global peak.

Third, the peak position, $T_{\rm M}$, of the TS peak with highest peak intensity in the glass transition region thus appears as a better definition of the glass transition temperature than the temperature of maximum intensity of the glass transition global peak. This problem was discussed previously in some detail (14), and it was shown, in this context, that $T_{\rm M}$ appears as a very convenient scaling temperature.

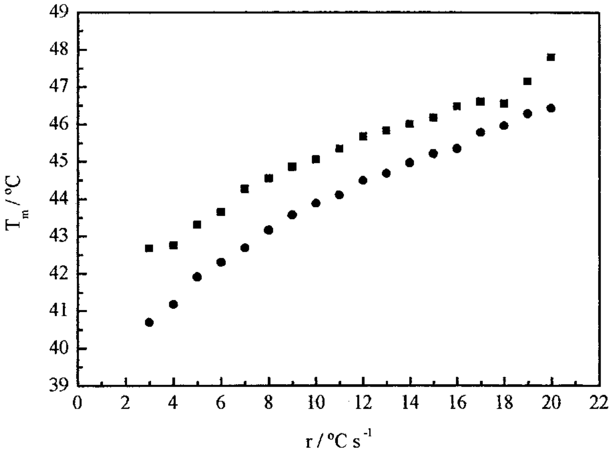

Fig. 2. Representation as a function of the heating rate r, of the temperature location, $T_{\rm m}$, of the TS component with $T_{\rm P}$ = 310.15 K (full squares), and of the global glass transition peak (full circles).

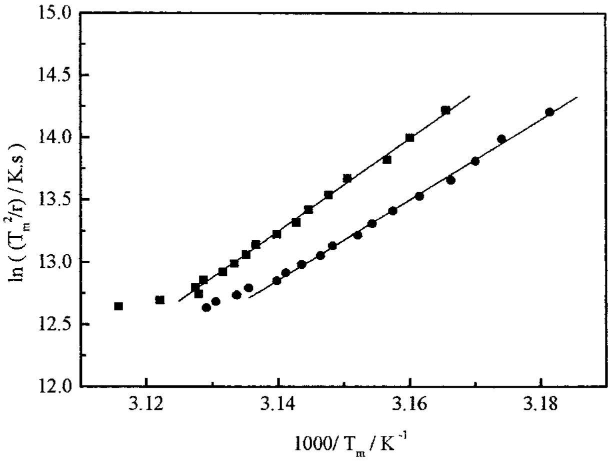

Fig. 3. Representation of *ln* (T_m^2/r) as a function of l/T_m, for the two series of experiments presented in Fig. 2. The straight lines are the result of the fitting of the points corresponding to heating rates from 0.066667 to 0.266664 K · s^{-1}.

To calculate the fragility index, that is defined as the slope of the representation of $\log_{10} \tau$ as a function of $1/T$ line at the glass transition temperature [Eq. (1)], we need to find the activation energy at the glass transition temperature [Eq. (2)]. As pointed out before and discussed elsewhere (10,14), the glass transition temperature provided by the TSDC technique is the temperature of maximum intensity, T_M, of the TS peak with highest intensity in the glass transition region. To calculate the fragility index, we thus need to find the activation energy at T_M [Eq. (6)], which can be obtained from the influence of the heating rate on T_M.

In the linear regression analysis of the TSDC data, we will consider only the data relative to the TS component with T_P = 310.15 K (peaks in Fig. 1, squares in Fig. 3). Furthermore, we will neglect the points corresponding to heating rates higher than 16°C · min^{-1} = 0.26667 K · s^{-1} where some scatter is observed probably caused by loss of thermal equilibrium of the polarization during depolarization at those high heating rates. The activation energy obtained from the linear fitting of the data for the TS component in Fig. 3 (T_P = 310.15 K) is 309 kJ · mol^{-1}. The fragility index calculated using Eq. (6) with T_M = 315.15 K is m = 51.

Influence of the Heating Rate on the Intensity of the Maximum of the TS Peaks

As reported previously, the effect of the heating rate on the features of a TSDC peak is such that, as the heating rate increases, the magnitude of the peak intensity, $I(T_m)$, increases, and the peak position, 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 shift in T_m are related each other in such a way that *ln* $I(T_m)$ shows a linear dependence on l/T_m with a slope equal to $-E_a/R$. We have thus (see Appendix B):

$$\ln I(T_m) = -\frac{E_a}{RT_m} + \text{const.} \tag{13}$$

Equation (13) is thus at the origin of another procedure to calculate the activation energy from TSDC data (17).

Figure 4 shows the representation of *ln* $I(T_m)$ as a function of l/T_m, for the TS peaks shown in Fig. 1 (squares), together with the results obtained for the global peak (circles).

The straight lines are the result of the fitting of the points corresponding to heating rates from 4 to 16°C/min. The activation energy for the TS component (T_P = 37°C) is 379 kJ · mol^{-1} and, considering T_g = 42°C, the fragility index of indomethacin is found to be m = 63 by this method.

The values obtained for the TSDC fragility index of indomethacin are thus m = 51 [E_a determined using Eq. (12)] and m = 63 [E_a determined using Eq. (13)]. These values satisfactory agree with m = 64 obtained by a different procedure also based on TSDC data (14). Let us briefly comment on the difference between the results obtained by the different procedures. First, let us note that, for a fragile glass former, the polarization of the sample at the beginning of the heating ramp of a TS experiment with T_P in the glass transition temperature range corresponds to a distribution of molecular motions, and not to a single motion (10). This is obviously the case for the TS peak with highest intensity in the glass transition region. Because the TS peak is distributed, the heating rate can influence the depolarization process so that the location and the shape of the peak are determined by a multitude of factors. Otherwise stated, parameters that define the shape of the peak (as the intensity of the maximum, and the half-width) and its temperature of maximum intensity, may vary with the heating rate in a rather complex way. Note that Eqs. (12) and (13) are both based on the hypothesis that the relaxation time displays an Arrhenius temperature dependence and that, as mentioned, this is not strictly the case for the TS peaks in the glass transition region of fragile systems, as is the case of indomethacin. Moreover, we need to recall that the activation energy of this mode of motion is high, implying that the shift of the peak's location occurs in a narrow temperature interval. This fact naturally leads to a relatively high uncertainty of the result. Finally, recall that the procedure that leads to the value of m = 64 is based on the results of a single TS experiment performed with a heating rate of 4°C/min (14), but that it is not built on the assumption

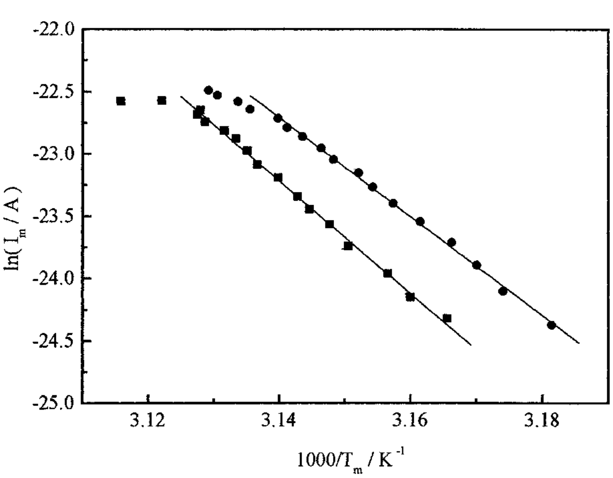

Fig. 4. Representation of ln $I(T_m)$ as a function of l/T_m, for the two series of experiments presented in Fig. 2. The straight lines are the result of the fitting of the points corresponding to heating rates from 0.066667 to 0.266667 K · s^{-1}.

of the Arrhenius temperature dependence of the relaxation time.

In synthesis, the technique of TSDC appears as an excellent technique to determine the activation energy at T_g and the fragility index of a glass forming system. First, because it provides an unambiguous transition temperature (T_M), which is very easy to determine. In fact, the choice of the calorimetric glass transition temperature presents some ambiguity because it can be chosen in different ways (onset, midpoint of the heat capacity change, etc), which is not the case for the glass transition temperature provided by the TSDC technique. We emphasize this point being aware of the fact that the glass transition is a phenomenon that occurs in a transformation temperature range and cannot thus be characterized by a single temperature provided by TSDC or DSC. Moreover, the determination of the calorimetric glass transition temperature (determination of the onset temperature of a step, or sigmoidal, signal) is much more subjected to uncertainties than the determination of the temperature of the maximum of a narrow and well-shaped peak as always is the TS peak of higher intensity of the glass transition. Finally, the TSDC technique offers three different and independent procedures to determine the activation energy at T_g and the fragility index of a glass former so that the simultaneous use of these procedures provides a self-consistency test for the validity of the result.

CONCLUSIONS

Three different procedures were used to estimate fragility from TSDC data. The application of each of these three procedures implies the experimental identification of the thermal sampling component of the glass transition with highest intensity. This TS peak shows its maximum intensity at a temperature, T_M, which can be considered as the glass transition temperature provided by the TSDC technique. All the three TSDC procedures to estimate the fragility index are based on the determination of the activation energy at T_M. In the case of indomethacin, these procedures yielded to the fragility values $m = 64$, 51, and 63. The previous discussion suggests that a value of $m \sim 60$ is probably a reasonable value of the fragility of indomethacin.

We conclude that TSDC appears as a convenient technique to determine the activation energy of motional processes in solids and namely the activation energy for structural relaxation (and thus the fragility index) in glass forming systems.

APPENDIX A: THE EFFECT OF THE HEATING RATE ON THE LOCATION, T_m, (TEMPERATURE OF MAXIMUM INTENSITY) OF A TS PEAK

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. The derivative of Eq. (11) gives

$$\frac{dJ(T)}{dT} = \left[\frac{dP(T)}{dT}\frac{1}{\tau(T)} - \frac{P(T)}{\tau^2(T)}\frac{d\tau(T)}{dT}\right]. \qquad \text{(A.1)}$$

or, taking Eq. (10) into account,

$$\frac{dJ(T)}{dT} = \left[-\frac{1}{r} - \frac{d\tau(T)}{dT}\right]\frac{P(T)}{\tau^2(T)}. \qquad \text{(A.2)}$$

From Eq. (A.2) we conclude that, at the maximum of the TS peak ($T = T_m$), we have

$$\left[\frac{d\tau(T)}{dT}\right]_{T=T_m} = -\frac{1}{r}. \qquad \text{(A.3)}$$

Equation (A.3) 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 $dt/dT = l/r$. 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 l/r, whereas if $T > T_m$, it is lower than l/r. At $T = T_m$, the two time scales are equal (21).

If the temperature dependence of the relaxation time is described by the Arrhenius equation:

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{RT}\right) \qquad \text{(A.4)}$$

Equation (A.3) becomes:

$$\tau(T_m) = \frac{RT_m^2}{rE_a} \qquad \text{(A.5)}$$

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 Eq. (A.4) at T_m, and taking (A.5) into account, it comes out as follows:

$$\tau(T_m) = \tau_0 \exp\left(\frac{E_a}{RT_m}\right) = \frac{RT_m^2}{rE_a} \qquad \text{(A.6)}$$

or, rearranging, we have

$$\ln\frac{T_m^2}{r} = \ln\frac{E_a\tau_0}{R} + \frac{E_a}{R}\frac{1}{T_m} \qquad \text{(A.7)}$$

As we wished to show, according to Eq. (A.7) a linear relationship is expected between $ln\ (T_m^2/r)$ and l/T_m, with a slope equal to E_a/R, as expressed by Eq. (12). It is to be underlined that the influence of T_m^2 in the variation of the left-hand side of Eq. (12) [or Eq. (A.7)] is often negligible compared with the influence of the heating rate, so that it can be written as:

$$\ln r = -\frac{E_a}{R}\cdot\frac{1}{T_m} + cte \qquad \text{(A.8)}$$

APPENDIX B: THE EFFECT OF THE HEATING RATE ON BOTH THE MAXIMUM INTENSITY, I(T_m), AND THE LOCATION, T_m, (TEMPERATURE OF MAXIMUM INTENSITY) OF A TS PEAK

The Debye hypothesis for the decay of the polarization along the TSDC heating ramp [Eq. (10)] leads to the following:

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

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

Combining Eqs. (8) and (B.1), the depolarization current density is given by the following

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

If the temperature dependence of the relaxation time is described by the Arrhenius equation [Eq. (A.4)], we will have the following:

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

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

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

Equation (B.3) can be rewritten as follows:

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

and, at the temperature of the maximum,

$$J(T_m) = \frac{P_0}{\tau_0}\exp\left(-\frac{E_a}{RT_m}\right)\exp[-S(T_m)] \tag{B.6}$$

or

$$\ln J(T_m) = \ln\frac{P_0}{\tau_0} - \frac{E_a}{RT_m} - S(T_m) \tag{B.7}$$

Combining Eqs. (A.6) and (B.4), the function S can be written as follows:

$$S(z_m) = -z_m^2\exp(z_m)\int_{z_0}^{z_m} z^{-2}\exp(-z)dz \tag{B.8}$$

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 depolarization current is negligibly small (where the polarization is P_0). The graphical representation of $S(z_m)$ as a function of z_m (which can easily performed using a software like Mathematica) clearly shows that it is very slightly dependent on z_m (i.e., on T_m) if $z_m = E_a/RT_m \geq 60$, situation in which it takes values very near the unity (0.97–0.98). For the TS peaks in the glass transition region, the quantity E_a/RT_m has in general values much higher than 60 (~140 in our case) and, consequently, $S(T_m)$ behaves as a constant. It is thus expected from Eq. (B.7) that $\ln J(T_m)$ shows a linear dependence on l/T_m, with a slope equal to $-E_a/R$, as indicated in Eq. (13). The same behavior is expected for the maximum current intensity, $I(T_m)$ because the current intensity, $I(T)$, and the current density, $J(T)$, are related by $J(T) = I(T)/A$, where A is the effective area of the electrodes [Eq. (7)].

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