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Intrinsic compensation phenomenon in thermally stimulated depolarisation studies

João F. Mano[a,b,*]

[a] *Department of Polymer Engineering, University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal*
[b] *3B's Research Group – Biomaterials, Biodegradables and Biomimetics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal*

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Abstract

The compensation behaviour as observed in thermally stimulated depolarisation currents (TSDC) corresponds to the linear relationship found between the Arrhenius (or Eyring) apparent thermokinetic parameters obtained in a series of thermal sampling (TS) experiments performed in the region of cooperative relaxation processes, particularly around the glass transition of glass forming materials. The compensation effect exhibits the same features of the intrinsic compensation found for any given TS curve, where the values of E_a and τ_0, in the region where the sum of square residues is low, are highly correlated, being this correlation similar to the conventional compensation. This intrinsic compensation is a result, and exhibits the same features, of the compensation found in the description of a given set of points obtained with the Arrhenius equation with the own Arrhenius equation. This compensation is transmitted directly to the equation that describes the temperature dependence of the depolarisation currents, $J(T)$, as a nearly direct relationship exists between $J(T)$ and $\tau(T)$. In fact, it was shown that $J(T)$ for an elementary process could be approximated by $P_0 \exp[-c/\tau(T)]/\tau(T)$, c being a constant.

Keywords: TSC; Glass transition dynamics; Compensation; Isokinetic effect; Activation energy

1. Introduction

Many experimental techniques have been used to depict and analyse relaxation processes and their underlying molecular motions [1], due to the fact that they allow to establish correlations between their macroscopic properties and the corresponding molecular structure. In this context, the thermally stimulated depolarisation currents technique (TSDC) has been used to study a variety of low and high molecular weight materials, crystalline as well as amorphous insulators and semiconductors [2,3]. Due to its low equivalent frequency [4] it is particularly useful to be used in systems exhibiting multiple relaxations, as sensitivity is enhanced with decreasing frequency.

Another advantage that has been claimed of using thermally stimulated techniques is the possibility to experimentally decompose a complex process, characterised by a distribution of characteristic times, into its quasi-elementary components, enabling the analysis of the fine structure of the global spectra [5]. This is achieved by using a specific experimental protocol (thermal sampling, TS), where only a fraction of the relaxing species are polarised, by applying the electric field in a narrow temperature region (see procedure in Fig. 1). During one of such experiments the molecular groups that are activated (i.e. the one that will give rise to the depolarisation peak during heating), are those having relaxation times at T_p around a certain characteristic time τ_p which depends, for instance, on the period of time in which the electric field is applied.

If we assume that the characteristic times associated with the processes that are polarised (and hence depolarised upon

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[*] Tel.: +351 253510330; fax: +351 253510339.
E-mail address: jmano@dep.uminho.pt.

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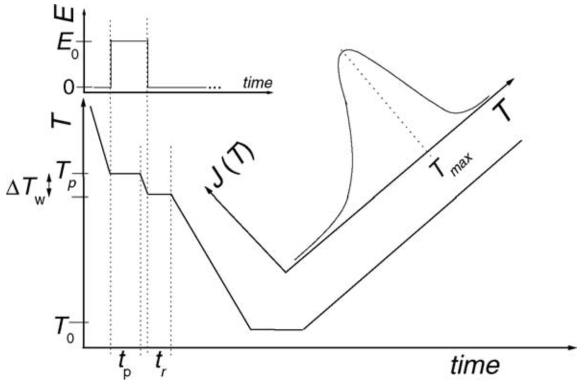

Fig. 1. General scheme of a TS experiment where the electric field (E_0) is applied only in a narrow temperature range within the temperature region where the global process appears: (i) a static electric field E_0 is applied at T_p during a time period t_p (polarisation period); (ii) the sample is quenched to $T_\mathrm{p} - \Delta T_\mathrm{w}$ with the electric field on; (iii) the field is removed and the polarisation is allowed to recover during a period of time t_r (recovery period); (iv) the sample is quenched to T_0, well below the temperature region of the global process; and (v) the electric current released is monitored during a controllable heating, from T_0 up to a final temperature well above T_p; a peak in the density current J is found in the temperature axis, with a maximum at T_max (inset graphics).

heating) in a TS experiment follow an Arrhenius dependence with temperature, each TS experiment will be characterised by a set of parameters: activation energy, E_a, and a pre-exponential factor, τ_0. Within an Eyring formalism of the rate theory those would be the activation enthalpy and entropy, ΔH and ΔS. Historically, it has been found that if we collect the (E_a, log τ_0) pair of values obtained in TS experiments at different polarisation temperatures (T_p), in the region of the glass transition, a quasi-perfect linear relationship is observed. The same is observed between ΔH and ΔS. This observation has been named "compensation" or "isokinetic" effect, and has been reported in numerous TSDC studies (see, for example, Refs. [6,7] and references quoted therein). Some aspects of this observation may be also included among a broader discussion, as the compensation effect has been detected in other areas such as the study of the kinetics and equilibrium processes in chemistry or biology [8].

For the specific case of thermally stimulated experiments, the origin of the compensation phenomenon has not been yet fully clarified, existing still controversial explanations. Some authors attribute this effect to meaningful physical aspects of the system under study, based on molecular interpretations assigned, for example, to the cooperative nature of the relaxational process (e.g. Ref. [9] and references cited therein). However, the compensation effect was also assigned to pure experimental propagation errors or to intrinsic mathematical consequences of the physical description of the process (e.g. Ref. [7,10] and references cited therein). In particular it was found that, for each TS result, an intrinsic compensation behaviour exists between the (E_a, log τ_0) pair of values that better describes the depolarisation curve, and that this intrinsic compensation observed in different TS experiments around T_g is very similar to the overall compensation phenomenon observed between the values of E_a and log τ_0 of the different TS experiments [10]. This finding was reported after analysing thermally stimulated recovery results (TSR), i.e. the mechanical equivalent of the TSDC technique, where a mechanical load is applied instead of an electric field, being the strain recorded during heating. In this work, the debate explored in Ref. [10] is extended to the TSDC technique. Most of the underlying arguments will be transformed for the dielectric formalism. Previously published data will be used in this discussion that were obtained in a side-chain liquid crystalline polymer (SCLCP) [11]. Moreover, a discussion will be included in this work on the origin of this intrinsic compensation phenomenon.

2. Description of TSDC data

Fig. 2 reproduces some previously published TSDC data on an SCLCP [11] in the glass transition region (full points). A common way to describe a TS curve is to assume a simple Debye model [2]. Note that this formalism assumes an exponential time-response for the polarisation, which corresponds to a rough simplification when the studies are conducted in the glass transition range. Nevertheless, this model will be used in this work, as one pretends to analyse the compensation phenomenon as it is currently described in the literature, where the results are treated under the simple Debye model.

For a depolarisation process during heating at a constant rate, $\beta = \mathrm{d}T/\mathrm{d}t$, the temperature dependence of the polarisation may be easily obtained, under the assumption of a Debye behaviour [2]:

$$P(T) = P_0 \exp\left[\frac{-1}{\beta}\int_{T_0}^{T}\frac{\mathrm{d}T'}{\tau(T')}\right] \tag{1}$$

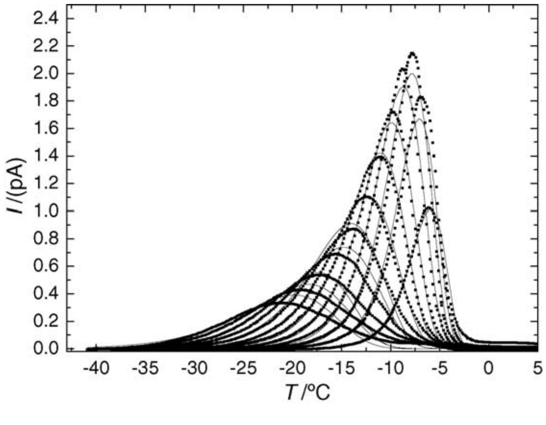

Fig. 2. Full points: thermally cleaned results obtained in the glass transition behaviour of a side-chain polysiloxane liquid crystal [11], in the region of the glass transition (the experimental conditions were: electric field $E_0 = 600\ \mathrm{V\,mm^{-1}}$, heating rate $\beta = 4\,^\circ\mathrm{C\,min^{-1}}$ and window width $\Delta T_\mathrm{w} = 2\,^\circ\mathrm{C}$). Solid lines: best results obtained by directly fitting the experimental data with the Debye model.

where P_0 is the initial polarisation (at $T = T_0$) of the ramp process. Moreover, the current density during this heating process (with no electrical current on) is

$$J(t) = -\frac{\mathrm{d}P(t)}{\mathrm{d}t} = \frac{P(t)}{\tau(T)} \tag{2}$$

and thus,

$$J(T) = P_0\tau^{-1}(T)\exp\left[\frac{-1}{\beta}\int_{T_0}^{T}\frac{\mathrm{d}T'}{\tau(T')}\right] \tag{3}$$

Experimental results are usually expressed as current intensity (I), instead of current density, where $J = I/A$, being A the electrode area. Moreover, P_0 is the total area under the $J(t)$ peak, and thus the total electrical charge, Q_0 is the total area under the $I(t)$ peak. As $\mathrm{d}P(t)/\mathrm{d}t = \beta\,\mathrm{d}P(T)/\mathrm{d}T = J(T)$, we have, for the remaining polarisation at a given temperature, $P(T) = \beta^{-1}\int_T^\infty J(T')\,\mathrm{d}T'$, and, from Eq. (2), we may write:

$$\tau(T) = \beta^{-1}\frac{\int_T^\infty J(T')\,\mathrm{d}T'}{J(T)} \tag{4}$$

This equation is on the base of the Bucci method, which enables to extract the temperature dependence of the characteristic times of an elementary process [12]. Arrhenius lines of the data in Fig. 2 were obtained (not shown), that were fitted with the Arrhenius equation, $\tau(T) = \tau_0\exp(E_a/RT)$. This permitted to extract both activation energy and the pre-exponential factor for the 12 curves of Fig. 2, by simple linear regression of the $\log\tau(T)$ versus $1/T$ data of each TS curve. Both Arrhenius parameters are shown in Fig. 3 as a function of the polarisation temperature. It should be noted that the dynamics associated with the glass transition should not be described by the Arrhenius model, and others have been frequently used (e.g. VFT or WLF equations). However, the Arrhenius equation has been widely used in the context of TSDC experiments, as the relaxation map appears generally quite linear due to the short range of retardation times covered. Therefore, it was opted to maintain the Arrhenius formalism, although the thermokinetic parameters obtained must be considered as apparent ones.

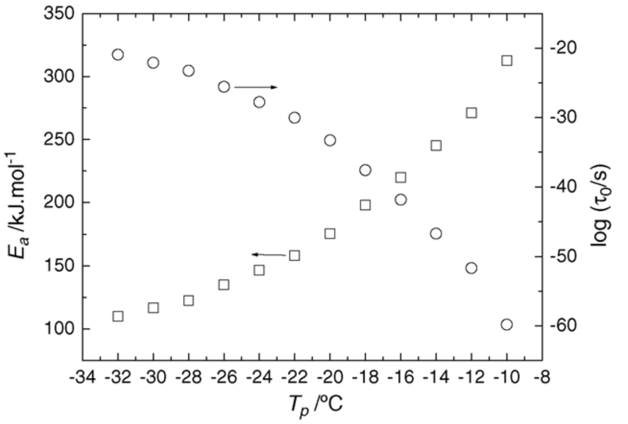

Fig. 3. Arrhenius parameters of the curves presented in Fig. 2 obtained by fitting, with the Arrhenius equation, the $\tau(T)$ data obtained using the Bucci method.

3. Conventional compensation phenomenon

The ensemble of Arrhenius lines for a series of TS results (obtained at different T_p) in the glass transition region shows typically a convergence trend towards a ($1/T_c$, $\log\tau_c$) pair of values, where T_c and τ_c are the compensation temperature and compensation times, respectively. If $\tau_{0,i}$ and $E_{a,i}$ are the pre-exponential factor and the activation energy of the TS line i, then the convergence of the Arrhenius lines implies that at T_c all lines i have the same characteristic time (τ_c), and one has

$$\log\tau_{0,i} = \log\tau_c - \frac{E_{a,i}}{\ln(10)RT_c} \tag{5}$$

As T_c and τ_c are constant for the set of the TS curves, we should observe a linear relationship between the different (E_a, $\log\tau_0$) pair of values. This is, in fact, observed in Fig. 4 for the TS data that have been analysed (open symbols). From the linear regression one can obtain the compensation parameters: $\tau_c = 2.1 \pm 0.3$ s and $T_c = 272 \pm 5$ K.

As commented by other authors, the linear correlation found between ΔH and ΔS (or between E_a, and $\log\tau_0$) could be a statistical consequence of the propagation of experimental errors, due to the fact that the errors between such parameters are highly correlated [8,13,14]. A statistical analysis was performed with the results of the studied material and it was found that the observed compensation phenomenon

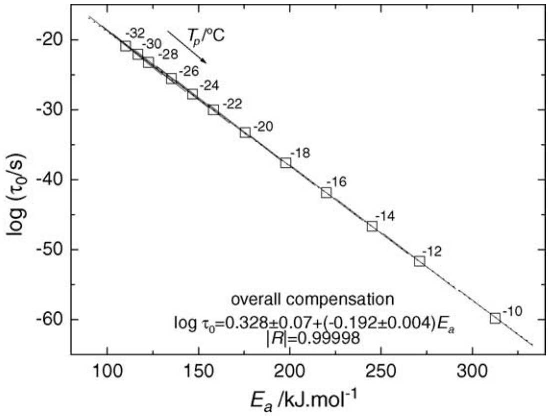

Fig. 4. Open symbols: compensation plot ($\log\tau_0$ vs. E_a) of the thermal sampling results of Fig. 2 (obtained at the different T_p, indicated next to each point). The compensation line (dotted line) was obtained by linear regression of such points (the obtained expression of this regression is shown in the graphics). Over each point a solid line depicts the intrinsic compensation line of the corresponding TS experiment, obtained from the direct fitting of the data using Eqs. (3) and (6).

could not be a pure consequence of such statistical effect [11].

4. Intrinsic compensation

We may also obtain the apparent Arrhenius parameters of a given TS curve by fitting directly the experimental data to Eq. (3). Any TS curve may be described by a series of pair of $(T_i, I_{\mathrm{exp}}(T_i))$. A common procedure is to find the best ($\log \tau_0$, E_a) pair of values that minimises the sum of square residues, S^2:

$$S^2 = \sum_i^n [I_{\mathrm{exp}}(T_i) - I_{\mathrm{theor}}(T_i, E_\mathrm{a}, \log \tau_0)]^2 \qquad (6)$$

where I_{exp} are the experimental values (n points) and I_{theor} is the expected current intensity at temperature T_i that may be obtained from Eq. (3). Eq. (6) was used for the TS results obtained at $T_\mathrm{p} = -20\,^\circ\mathrm{C}$, where E_a and $\log \tau_0$ were scanned independently. For each pair of ($\log \tau_0, E_\mathrm{a}$) values, Eq. (6) was used to obtain the value of S^2. Only the experimental points below T_{max} were used and Q_0 was obtained from the integration of the experimental data. The values of S^2 obtained in this analysis are shown in Fig. 5a, as a function of $\log \tau_0$ and E_a. The S^2 surface is very steep and the lower values of S^2 form a valley that is extended throughout an elongated region in the ($\log \tau_0$, E_a) plain. This behaviour was previously reported for TSR results [10] and seems to be a general trend in thermally stimulated results. The results in Fig. 5a suggest that the minimisation of S^2 is a quite ill-posed problem: if a ($\log \tau_0$, E_a) pair of values describes well a given experimental curve, there will be always a new value of $\log \tau_0$ for another value of E_a that will also provide again a reasonable description of the data.

A deeper inspection of the S^2 surface in Fig. 5a allows to conclude that the bottom region of the valley forms a perfect straight line in the ($\log \tau_0$, E_a) plain (see projection of this region in Fig. 5b). This behaviour was observed before in TSR results [10], being named intrinsic compensation, and may be found in any given TS experimental curve obtained by TSDC. This intrinsic compensation, that appears in a single TS experiments, does not possess any particular physical origin; it is rather a consequence of the mathematical description of the results, leading to this kind of convergence plot. In the next section the possible origin for this intrinsic compensation phenomenon will be proposed.

The linear regression of the overall "conventional" compensation plot (Fig. 4) is numerically similar to the intrinsic compensation regression in Fig. 5b. Further analysis also permitted to conclude that the linear regressions of the intrinsic compensation plots for the other TS curves were also similar to each other. Therefore one should be tempted to join in the same plot the overall compensation and the intrinsic compensation lines of all TS experiments. This was done in Fig. 4 that allows to conclude that the overall compensation is, in fact, very similar to the intrinsic compensation lines of all TS experiments. It is even difficult to distinguish between both kinds of compensations.

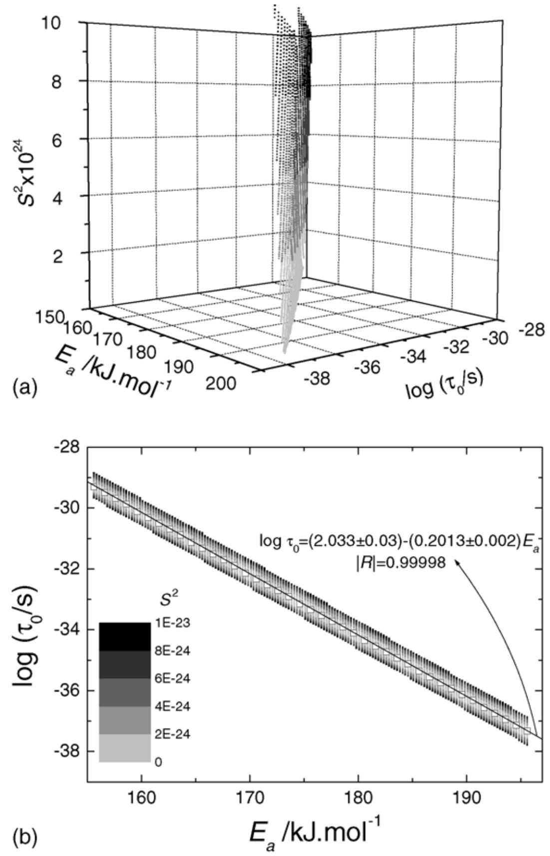

Fig. 5. (a) Convergence surface plot for the TS experiment obtained with $T_\mathrm{p} = -20\,^\circ\mathrm{C}$, using Eq. (6), where the theoretical points were obtained from Eq. (3), in the range of E_a and $\log \tau_0$ shown in the graphics. (b) Projection of $S^2(E_\mathrm{a}, \log \tau_0)$ in the valley region, indicating that the lower values of S^2 (corresponding to the bottom region of the valley) show a nearly perfect correlation between E_a and $\log \tau_0$ (intrinsic compensation); the open symbols correspond to some values of E_a, $\log \tau_0$ that minimises S^2 throughout the E_a scale, used to obtain the intrinsic compensation line (linear regression fitting shown in the graphics).

The above findings strongly suggest that the conventional compensation phenomenon seen in the glass transition region by TSDC, using the TS technique, is very similar to a merely mathematical consequence of the Debye model, combined with the Arrhenius equation that is used to describe each individual TS curve. The Arrhenius parameters that are included in this physical model are intrinsically combined in such a way that they naturally compensate, giving rise to this compensation effect.

5. Origin of the intrinsic compensation

In order to have a clear picture on the nature of the intrinsic compensation behaviour, a deeper analysis of the model used to describe the TS data will be made. First, the integral in

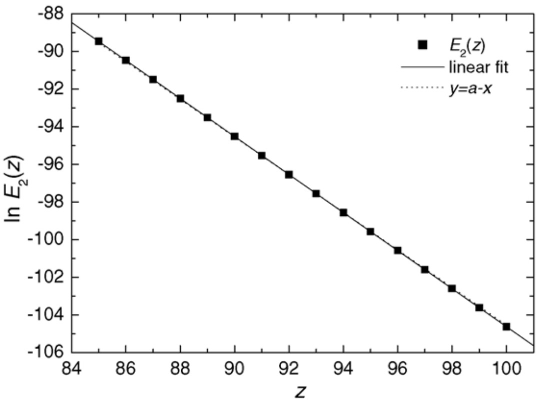

Fig. 6. Points: values of $\ln E_2(z)$ obtained in the z range 85–100. The linear regression fitting ($y = a + bx$) is shown as the solid line, where $a = -3.567 \pm 0.006$ and $b = -1.0106 \pm 0.00006$ ($|R| = 1$); the dotted line shows the fitting by fixing $b = -1$, where it was obtained $a = -4.547 \pm 0.01$ ($|R| = 0.9999$).

Eq. (3) cannot be resolved in a simple expression. Often, the transcendental equation $E_2(x)$ is used [15]:

$$E_2(x) = \int_1^\infty \frac{e^{-xt}}{t^2}\,dt = x\int_x^\infty \frac{e^{-y}}{y^2}\,dy \tag{7}$$

Therefore, assuming an Arrhenius behaviour, Eq. (3) can be written as

$$J(T) = P_0\tau^{-1}(T)\exp\left[-\frac{E_a}{R\tau_0\beta}\left(\frac{E_2(z)}{z} - \frac{E_2(z_0)}{z_0}\right)\right] \tag{8}$$

where $z = E_a/RT$ and $z_0 = E_a/RT_0$. As $E_2(z)/z$ decreases strongly with T, $E_2(z_0)/z_0$ may be neglected, provided that T_0 is sufficiently low:

$$J(T) = P_0\tau^{-1}(T)\exp\left[-\frac{T}{\tau_0\beta}E_2(z)\right] \tag{9}$$

A linear relationship was found before between $\ln E_2(z)$ and z in a large range of z [10]. Fig. 6 shows such plot in the range of z between 85 and 100. This interval was chosen to be consistent with the values of z that are found within the temperature of interest of the TS curve obtained at $T_p = -20\,^\circ$C. A perfect regression is found in the points of Fig. 6, with a slope, b, close to -1 (see Fig. 6). A new linear fitting was carried out by fixing $b = 1.0$. In this case the intercept was $a = -4.547 \pm 0.01$ and an excellent fitting was maintained. Therefore, one could introduce the simplification $E_2(z) = \exp(a - z)$ into Eq. (9), giving,

$$\begin{aligned} J(T) &\approx P_0\tau^{-1}(T)\exp\left[-\frac{T}{\tau_0\beta}e^{-z}e^{a}\right] \\ &= P_0\tau^{-1}(T)\exp\left[-\frac{T}{\beta\tau(T)}e^{a}\right] \end{aligned} \tag{10}$$

as $\tau(T)$ varies much more than T, Eq. (10) may be simplified:

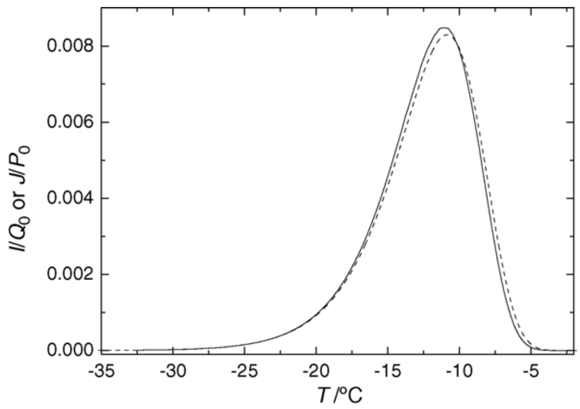

Fig. 7. Solid line: simulation of a TS curve (normalised current) of a system that better describes the experiment at $T_p = -20\,^\circ$C, using Eq. (3) (this curve appears also in Fig. 2, compared with the experimental data). Dashed line: the same simulation using the approximation given by Eq. (11), with $a = -4.547$.

$$\begin{aligned} J(T) &\approx P_0\tau^{-1}(T)\exp\left[-\frac{T_{\max}\,e^{a}}{\beta\tau(T)}\right] \\ &= P_0\tau^{-1}(T)\exp\left[-\frac{c}{\tau(T)}\right] \end{aligned} \tag{11}$$

c being a constant for a given TS curve. A simple test was performed to confirm that Eq. (11) deviates slightly from the exact form of Eq. (3). A simulation of the TS experiment obtained at $T_p = -20\,^\circ$C, using the best thermokinetic parameters obtained from the direct fitting method (Fig. 5a), was done using the exact values of $I(T)$ with Eq. (3), where E_2 was calculated with a numerical form of Eq. (7) [17]. The normalised current intensity is shown in Fig. 7 (solid line), together with the curve computed using Eq. (11) with $a = -4.547$ (dashed line). A good concordance is found between both curves, indicating, in a broad general case, that Eq. (11) is a simple alternative to represent TSDC results from elementary processes.

Eq. (11) shows that the dependence of the temperature on the current density is basically located in the $\tau(T)$ term. Thus, the intrinsic compensation effect seen in TSDC should be assigned to an intrinsic compensation effect between the Arrhenius parameters in the $\tau(T)$ function. This can be easily checked by using Eq. (6) to construct an $S^2(\log\tau_0, E_a)$ map for a set of points generated with the Arrhenius equation and analysed with the own Arrhenius model. The “experimental” points were obtained using the thermokinetic parameters used to simulate the curves in Fig. 7. The obtained S^2 surface exhibits, as in Fig. 5a, a deep valley shape (results not shown). Thus, the $\log\tau_0$ and E_a parameters are quite correlated in the Arrhenius equation. The points with the lowest values of S^2 where projected in the $(\log\tau_0, E_a)$ plane and, as found for the TS curves in Fig. 5b, a clear linear relationship was detected between their thermokinetic values. Moreover, the linear regression is very similar to the one obtained for the TS curves (Fig. 5b). This clear demonstrates that the intrinsic compensation found in TS curves is directly assigned to the statistical correlation that exists between the thermokinetic parameters in the Arrhenius equation.

6. Final remarks

The results of this work provided evidences that allow to conclude that the compensation as detected in thermally stimulated depolarisation current experiments (using the thermal sampling procedure), near the glass transition, should be merely a consequence of the mathematical description that models the physical process. It was clearly seen that an intrinsic statistical compensation effect exists between the Arrhenius parameters when one analyses the sum of square residues of experimental data with a simple Debye model. This intrinsic compensation matches almost perfectly with the conventional compensation effect. Moreover, it was shown that the origin of the intrinsic compensation should be assigned to the high correlation existing between the thermokinetic parameters in the own Arrhenius equation.

There have been other evidences from previous works that give further arguments for the assignment of the compensation phenomenon to a pure mathematical consequence or to error propagation (pure statistical effects) associated with the technique that is probing molecular mobility. Most of those were presented before [10] and are now summarised.

- There is always an error associated with the determination of $\tau(T)$ from a TS curve, and therefore experimental and statistical errors are always present in the calculation of E_a and $\log \tau_0$. It was shown in a previous work that if the same TS experiment is repeated, the variation of the corresponding E_a values could be of the order of 10% [16]. It is also frequently observed $E_a(T_p)$ plots that the points do not follow a perfect trend and some natural fluctuations exists (this was not the case of the data analysed in this work – see Fig. 3). However, despite the errors and fluctuations observed, there is always a nearly perfect linear relationship between E_a and $\log \tau_0$, or between ΔH and ΔS. Therefore, it is highly probable that the propagation of experimental errors play an important role in the appearing of the compensation phenomenon.
- It has been shown that the activation Gibbs energy ($\Delta G = \Delta H - T\Delta S$) appears to have a “universal” linear relationship with temperature in TS results [7]. This behaviour is a general consequence of the thermally stimulated technique. Therefore, in relaxations with strong variation of ΔH in a relatively narrow temperature range, such as the glass transition (as comparing with some secondary relaxations that appear in a large temperature range), a natural linear relationship between ΔH and ΔS should appear, and may be enhanced by the propagation of experimental errors.
- The thermokinetic parameters depend on the thermal history in the glass below T_g, due to the occurrence of structural relaxation (e.g. Ref. [17]). The set of thermokinetic parameters obtained in different TS experiment, just by changing the annealing conditions before the TS procedure, also present a compensation effect [17]. Moreover, the features of such compensation effect are the same of the conventional compensation effect obtained for TS experiments at different temperatures [17]. Such coincidence disclaims again a genuine physical significance of the compensation phenomenon and of the corresponding compensation parameters.
- From complementary thermally stimulated recovery and DMA experiments on poly(ethylene terephthalate) it was shown that a broad distribution of retardation times exists at the compensation temperature, T_c [18]. This is in contradiction with an authentic compensation phenomenon, where all the Arrhenius lines of the TS results converge to the same retardation time at T_c, thus suggesting that all individual processes that describe the complex behaviour relax with the same rate at T_c.
- A perfect compensation phenomenon is typically observed using the thermokinetic results obtained from TS results that are treated under quite crude approximations, namely the Arrhenius (or Eyring) equation for the temperature dependence of the retardation time and the Debye model for the evolution of the response. Therefore, a direct link between the compensation parameters and any physical meaningful characteristic of the system studied is highly questionable.
- Finally, up to now no conclusive correlation has been found between the compensation parameters and the chemical (chemical structure, branching, composition in a blend, cross-linking, molecular weight, etc.) or morphologic (molecular or crystallinity anisotropy, degree of crystallinity, etc.) features of the system studied. For example, no relationship could be found between the compensation temperature and the chemical architecture of a series of side-chain liquid crystalline polymers [7].

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