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The role of space charge formation in the generation of thermally stimulated current (TSC) spectroscopy data for a model amorphous drug system

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Abstract

Thermally stimulated current (TSC) spectroscopy is attracting increasing attention as a means of materials characterization, particularly in terms of measuring slow relaxation processes in solid samples. However, wider use of the technique within the pharmaceutical field has been inhibited by difficulties associated with the interpretation of TSC data, particularly in terms of deconvoluting dipolar relaxation processes from charge distribution phenomena. Here, we present evidence that space charge and electrode contact effects may play a significant role in the generation of peaks that have thus far proved difficult to interpret. We also introduce the use of a stabilization temperature in order to control the space charge magnitude. We have studied amorphous indometacin as a model drug compound and have varied the measurement parameters (stabilization and polarization temperatures), interpreting the changes in spectral composition in terms of charge redistribution processes. More specifically, we suggested that charge drift and diffusion processes, charge injection from the electrodes and high activation energy charge redistribution processes may all contribute to the appearance of shoulders and 'spurious' peaks. We present recommendations for eliminating or reducing these effects that may allow more confident interpretation of TSC data.

Keywords: Amorphous; Depletion region; Dielectric; Pharmaceutical; Thermally stimulated current; Space charge

1. Introduction

Thermally stimulated current (TSC) spectroscopy has been widely used to study the electrical relaxation properties of materials, particularly within the polymer sciences (Ikezaki, 2002; van Turnhout, 1975a; Vanderschueren and Gasiot, 1979). Recently there has been growing interest in the use of this technique for the characterization of pharmaceutical systems due to the recognized need to understand molecular mobility in relation to physical and chemical stability (Galop and Collins, 2001; Ramos et al., 2002; Ikeda et al., 2005; Shmeis and Krill, 2005). The basic principle of the technique involves the application of an electrical signal to a sample at a specified temperature followed by rapid cooling, leading to the polarization of the sample being 'frozen' into the material in question. On heating the sample, temperature-dependent relaxation and charge redistribution processes govern the depolarization of the sample expressed by

$$P(t) = P_{\mathrm{e}}\left[\exp\left(-\int_0^t \frac{\mathrm{d}t}{\tau}\right)\right] \tag{1}$$

where $P(t)$ is the polarization as a function of time t, P_{e} the equilibrium polarization at infinite time and τ is the relaxation time. Depolarization of the sample leads to a generation of a depolarization current given by

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

where $J(t)$ is the current density as a function of time t. For monotonically varying temperature the relaxation time may be easily calculated via

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

with τ, P and J now expressed as a function of temperature T.

More information on the basic principles of the technique may be found in a number of previous publications (e.g.

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Lacabanne and Chatain, 1973; van Turnhout, 1975b; Ibar et al., 1990).

Such relaxation information may be of considerable use in understanding the behaviours associated with solid and other samples. However, it is well known within the field that the technique may lead to the generation of a range of peaks in addition to those correlated to recognized relaxation processes, such as those associated with T_g. The interpretation of such peaks has remained controversial in many cases, with explanations varying from sub-molecular relaxation to charge redistribution. It may convincingly be argued that in order for the technique to be used outside the specific TSC field it is essential for such effects to be understood and controlled. In relation to this issue, there is a recognized difficulty within the general dielectrics field in distinguishing between dipolar relaxation and charge redistribution processes. In brief, reorientation processes involve highly localised rotational motions of charges in response to an applied field; in general it is these motions that are of particular interest in TSC as they reflect the partial or total molecular mobility of the system under study. However, in addition, charge redistribution and ohmic conduction processes may occur which involve translational motions of ionic groups and/or electrons.

In this study we focus on space charge formation as a possibly highly significant factor in generating charge redistribution currents as well as providing a link to the effects of sample preparation considerations. Space charge formation is a well-recognized phenomenon in the dielectrics literature, particularly in the semiconductor and polymer fields (Wintle, 1971, 1974; Podgorsak and Moran, 1973; Vanderschueren, 1974). The process essentially involves the accumulation and discharge of electrically active species taking place in specific locations within the sample. The associated charge motions comprise three key processes: drift, diffusion and injection (van Turnhout, 1972, 1975a; Calderwood and Scaife, 1970). Charge drift involves the movement of species under the influence of localised electric fields generated by charge inhomogeneities within the sample and is essentially a coulombic as opposed to a concentration-based charge redistribution process. Charge diffusion is similar but involves motion against a charge concentration gradient and is therefore also associated with inhomogeneities within a sample. For the period of motion of the space charge by either mechanism, a discharge current is generated which may be given by the sum of the drift and diffusion contributions:

$$I = en\mu_n F + eD_n \frac{dn}{dx} \tag{4}$$

where e is the electronic charge, n is the free electron density, μ_n is the electron mobility, F is the field and D_n is the electronic diffusion constant (Simmons, 1971a).

The charge injection process is usually associated with the polarization of the sample and results from close contact of dissimilar materials such that charge accumulation on one or other surface takes place. Under conditions of, for example, elevated temperatures these charges may become unentrapped and therefore generate a current as it travels through the sample. The theoretical basis underpinning charge injection via adjacent dissimilar materials is based on the electronic band model, proposed by Simmons and co-workers (Simmons, 1967, 1968, 1971a,b; Simmons et al., 1970; Simmons and Taylor, 1972a,b; Simmons and Nadkarni, 1972) and further developed by Thielen et al. (1996a,b, 1997). In brief, the electrode–sample assembly may be considered to consist of a metal–insulator–metal (MIM) system whereby charges accumulating within the sample at the electrode–sample interface may become unentrapped and escape into the bulk of the sample, the penetration distance depending on the mobility, magnitude and number of charges in relation to the structure and electrical properties of the sample material. The current generated may be described by

$$I = e\mu_n V \left[\int_0^L \frac{dx}{n}\right]^{-1} \tag{5}$$

where V is potential difference and L is the thickness of the sample.

The discharge of space charge is associated with the regions adjacent to the electrodes, which are referred to as cathodic or anodic depletion regions (CDR, ADR). These are considered to be regions of the sample which differ in the concentration of the free electrons. In this case, due to the blocking contact between sample and electrodes, these regions have very low concentration of free electrons and are said to be depleted. The thickness of these regions (λ_0) depends on the size and electrical properties of the sample and electrodes which, in the case of separated regions, can be expressed as

$$\lambda_0 = \left[\frac{2\varepsilon\varepsilon_0(\psi_E - \psi_S)}{e^2 Nt}\right]^{1/2} \tag{6}$$

where ε is the dielectric constant of the sample, ε_0 is the relative permittivity of a vacuum, ψ_E and ψ_S are the work functions of the electrode and the sample, respectively, e is the electronic charge and Nt is the volume density of shallow traps. It should be noted that for the TSC studies outlined here, the upper electrode is the cathode as defined by the polarization process; this is highly significant as the model we propose involves consideration of the effects of electrode contact which will be more of an issue with the upper surface of the sample.

In a previous study, Correia et al. (2001) demonstrated that TSC could be used to identify the glass transition of amorphous indometacin. In addition, several authors (van Turnhout, 1975a; Vanderschueren and Gasiot, 1979; Simmons and Taylor, 1972a; Thielen et al., 1996a) have recognized space charge formation as a possible contributing factor to the response in terms of currents generated at interfaces between amorphous and crystalline regions. Here, we investigate whether space charge formation has a much wider and more general role in TSC data generation. More specifically, we suggest that space charge formation based on poor electrode contact may be a major contributor to the difficulties associated with TSC interpretation. We investigate whether such effects may be influenced by appropriate sample preparation and preconditioning approaches; in particular we introduce an initial stabilization step in order to aid deconvolution of temperature and polarization effects.

2. Materials and methods

Indometacin (1-[4-chlorobenzoyl]-5-methoxy-2-methyl-1-*H*-indole-3-acetic acid) was purchased from Sigma Chemical Company (MO, USA) and converted into the amorphous phase prior to use via melt quenching as follows. Samples of the order of 30 mg were placed in an aluminium pan (used for thermogravimetric analysis experiments) and heated to just above the melting point (433 K) followed by rapid cooling by placing the pan on a cold aluminium block, resulting in glass formation.

Modulated temperature differential scanning calorimetry (MTDSC) was performed using a TA Instruments model 2920 calorimeter. Matched hermetically sealed aluminium pans sourced from TA Instruments were used for all runs. Full calibration was performed before the acquisition of experimental data, using a scanning rate of 2 K min^{-1}. Baseline calibration was performed using matched, empty pans. Temperature calibration runs were performed using *n*-octadecane (99.9%, Riedel-de-Hahn AG, Germany, theoretical melting point 301.39 K), cyclohexane (99.9%, Riedel-de-Hahn AG, Germany, theoretical melting point 279.69 K) and *n*-decane (99.9%, Riedel-de-Hahn AG, Germany, theoretical melting point 246.49 K). Heat capacity constant calibration was performed using aluminium oxide (100 mesh, 99.9% (Aldrich Chemical Co., WI, USA)). The sample and reference pans were loaded into the MTDSC cell at ambient temperature and the chamber sealed. The sample chamber was cooled to 268 K, held at 268 K for 10 min, and then heated at 2 K min^{-1} to 423 K, with a modulation amplitude of ±0.2 K min^{-1} and a modulation frequency of 40 s. The sample size was circa 5 mg.

TSC experiments were performed with a TSC/RMA 9000 (Setaram, France) as follows. The sample of amorphous indometacin was prepared as described above and introduced into the TSC instrument in the aluminim pan, the base of this providing the bottom electrode. The top electrode, a screw electrode of area circa 53 mm^2, was then positioned such that maximum contact was made between the sample and the electrode. Prior to the experimental examination, the chamber was evacuated and flushed with helium several times, to remove air and to improve thermal transfer through the cell.

A thermally stimulated depolarization current (TSDC) method was used. Samples were brought to a 'stabilization temperature' (T_S) with values of T_S between 273 K and 373 K, followed by heating or cooling to the polarization temperature T_P. It should be noted that this stabilization step is not usually included in TSDC studies but is included here for reasons that will be explained in a subsequent section. The samples were then subjected to an electrical field of 100 V mm^{-1} for 120 s at polarization temperatures between 303 K and 323 K. The sample was then cooled at 2 K min^{-1} to 273 K, held for 120 s and then heated at 7 K min^{-1}. After each run the electrode was cleaned with solvent and then heated to 380 K to ensure solvent evaporation. Runs were performed at least in duplicate with the general features outlined here being seen reproducibly, although the magnitudes tended to vary, particularly at low stabilization and polarization temperatures. This is a finding of the study rather than a difficulty and is discussed in more detail below.

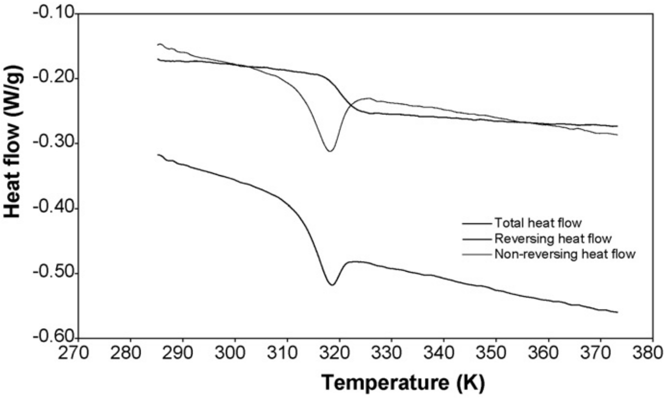

Fig. 1. MTDSC spectrum of amorphous indometacin.

3. Results

Fig. 1 shows the MTDSC spectrum of amorphous indometacin prepared as described above, clearly showing the step change in the reversing heat flow that would be expected for an amorphous material. Concerning the TSDC data, in the first instance the effects of thermal pretreatment on the TSDC spectra were investigated. Fig. 2a and b shows characteristic TSDC spectra obtained for amorphous indometacin at different

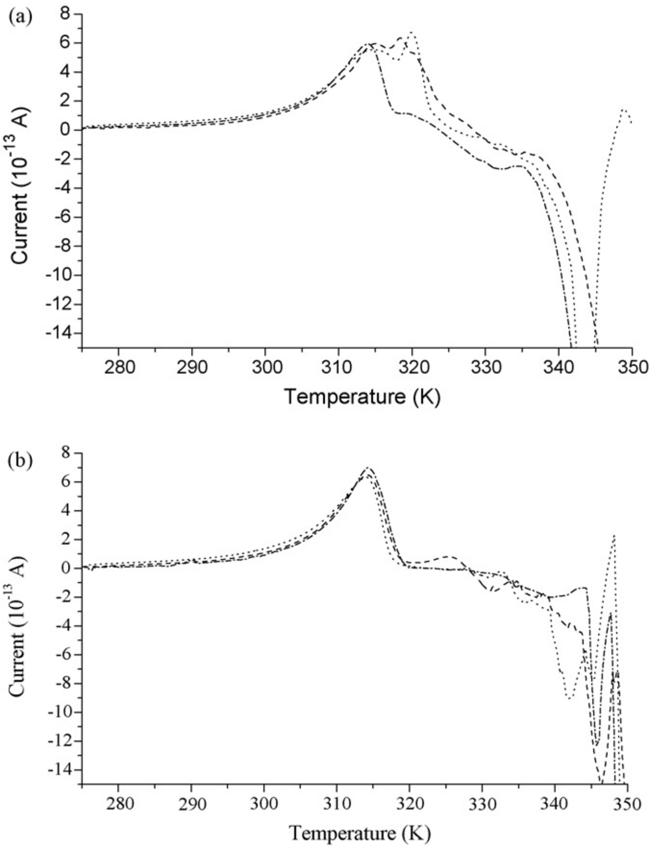

Fig. 2. (a) TSDC spectra of amorphous indometacin obtained with a polarization temperature of 303 K and temperatures of stabilization of 273 K (- - -), 293 K (· · ·) and 313 K (- · -). (b) TSDC spectra of amorphous indometacin obtained with a polarization temperature of 303 K and temperatures of stabilization of 333 K (- - -), 353 K (· · ·) and 373 K (- · -).

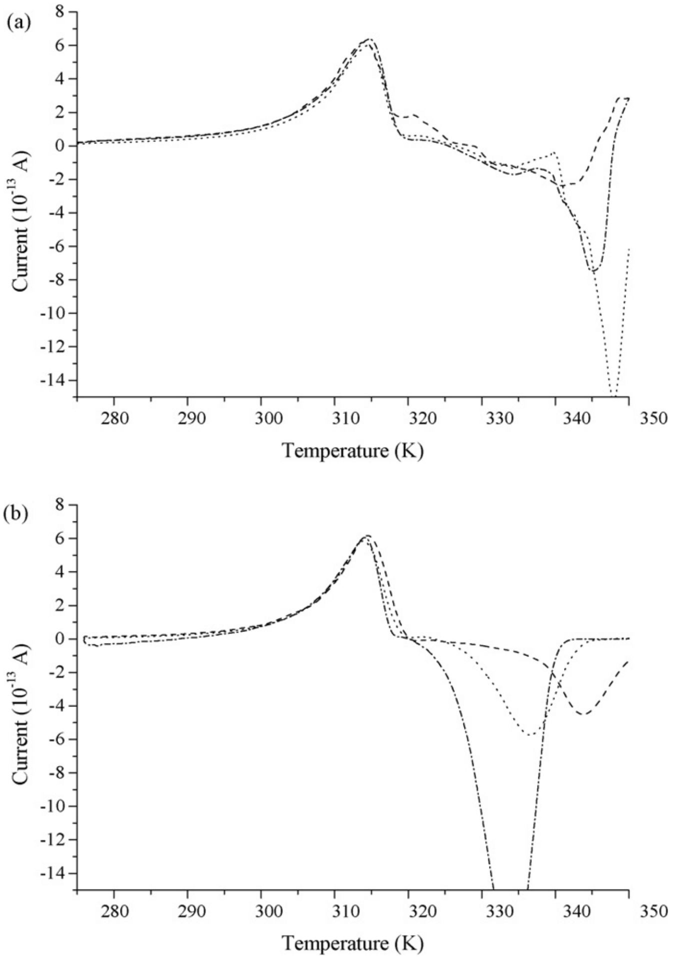

Fig. 3. (a) TSDC spectra of amorphous indometacin obtained with a polarization temperature of 313 K and temperatures of stabilization of 273 K (- - -), 293 K (· · ·) and 313 K (- · · -). (b) TSDC spectra of amorphous indometacin obtained with a polarization temperature of 313 K and temperatures of stabilization of 333 K (- - -), 353 K (· · ·) and 373 K (- · · -).

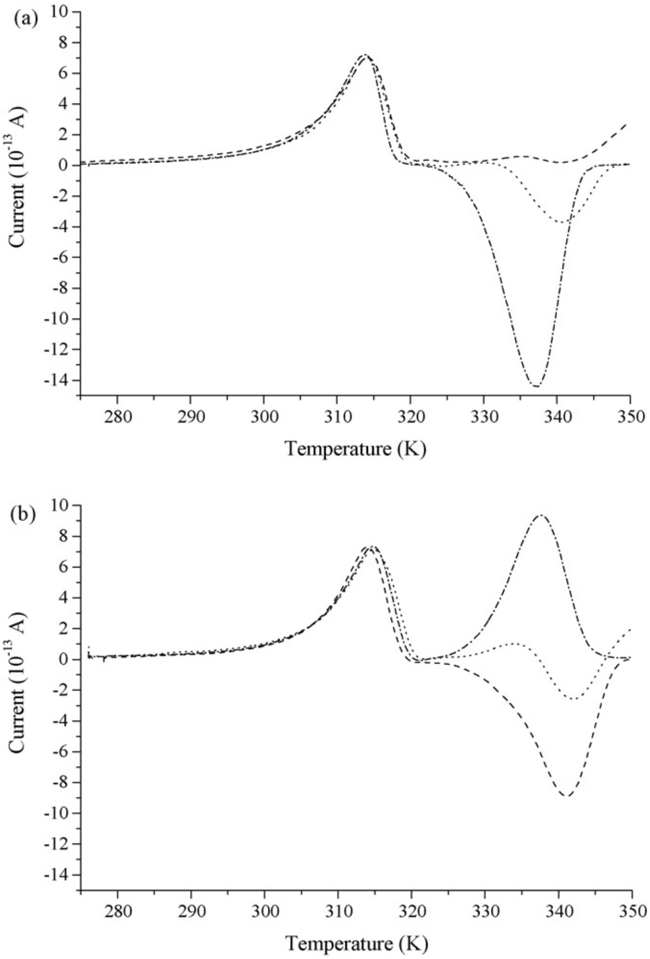

Fig. 4. (a) TSDC spectra of amorphous indometacin obtained with a polarization temperature of 323 K and temperatures of stabilization of 273 K (- - -), 293 K (· · ·) and 313 K (- · · -). (b) TSDC spectra of amorphous indometacin obtained with a polarization temperature of 323 K and temperatures of stabilization of 333 K (- - -), 353 K (· · ·) and 373 K (- · · -).

temperatures of stabilization, T_S, within a range of 273–373 K followed by polarization at 303 K. Three main depolarization processes can be seen. The first relaxation peak (around 314 K) corresponds to the molecular motions of the main segments of the indometacin molecules, this being associated with the glass transition (α-process). Clearly, the clarity with which the peak is observed is significantly influenced by the stabilization treatment, in that the higher temperature pre-treatment leads to a more well defined peak. The second depolarization process occurs only with lower temperatures of stabilization and manifests itself as a high temperature shoulder to the α-peak at around 318 K; this peak is not seen with T_S higher than 313 K (i.e. greater than the glass transition). We suggest that this process is due to the distortion of the CDR, which leads to motion of the space charge driven by the drift and diffusion effect (this is discussed in more detail in the subsequent section). The third depolarization process, which appears as a negative peak in the spectrum between 325 K and 345 K, varies in shape and peak minimum temperature. This may be ascribed to a charge injection peak; again this is discussed in more detail in the following section.

The TSDC spectra of indometacin obtained at the same range of temperatures of stabilization as stated previously, but at a temperature of polarization of 313 K, are shown in Fig. 3a and b. Interestingly, a very different trend with stabilization processing is seen, generally involving a less random and noisy space charge response. At T_S values up to 313 K, the first relaxation peak (α-process) is smooth with no high temperature shoulder peak while the second region (320–350 K) shows variable results with a positive peak at the higher temperatures of the range (Fig. 3a). The intensity of the second peak region varies; at higher temperatures of stabilization, a cleaner response is seen involving a negative current that is greater in magnitude than the main relaxation peak (Fig. 3b). Furthermore, the temperature of the peak current minimum lowers with an increase of the stabilization temperature.

Fig. 4a and b shows the TSDC spectra of indometacin obtained at a temperature of polarization of 323 K with temperatures of stabilization below and above the glass transition temperature, respectively. The first relaxation peak (α-process) is again clean with no high temperature shoulder peak. The intensity and sign of the second peak varies and is strongly dependent on the temperature of stabilization. It increases as a negative peak with increasing temperature of stabilization below the glass transition, decreases with further increase of T_S (above the glass transition), and finally converts into a positive peak when $T_S = 373$ K. It should be noted that at intermediate temperatures the peak appears to be resolved into positive and negative components, the significance of which will be discussed below.

Overall therefore, and treating the data largely empirically at this stage, the study has shown that variation in both the polarization temperature and the stabilization temperature has led to profound changes in the obtained TSDC data. The key effects are the ability to see the T_g relaxation peak unambiguously, which is dependent on the combination of the T_P and T_S, and secondly the processing parameters strongly dictate the post-T_g behaviour, particularly in terms of the sign and magnitude of the high temperature peak. The former is highly important from the viewpoint of reliably identifying T_g responses. It is possible to calculate the relaxation time of the glass via Eq. (3); however we will be outlining and comparing different methods of calculating this parameter in more detail in a subsequent communication.

4. Discussion

From the above results it is evident that amorphous indometacin may undergo several depolarization processes depending on the experimental conditions used. The main depolarization process occurs at 315 K and is acknowledged to be due to the dipolar reorientations associated with the glass transition process (Correia et al., 2001). However, the depolarization peak which appears in some spectra of amorphous indometacin as a shoulder peak in the glass transition region has not been previously explained in the literature. Similarly, the post-T_g responses are not understood in terms of either their interpretation or the parameters associated with their manifestation. It is arguable that such knowledge is essential in order to advance the technique, as without a firm theoretical basis on which to interpret results and plan experiments the TSC approach is unlikely to become widely used within the applied sciences.

The main peak does in fact consist of two processes. Firstly, the dipolar reorientation during depolarization results in the generation of a depolarization current which may be related to the relaxation of the material according to Eqs. (1) and (2). The depolarization results in the movement of charge against the direction of initial polarization as it is a re-equilibration process, hence the current is seen as a positive peak as it represents charge movement towards the cathode. However, inspection of the dielectrics literature (van Turnhout, 1975a) suggests that in addition there will be a component associated with the redistribution of charge due to drift and diffusion (ρ_R), this redistribution process being facilitated by the increased molecular mobility at T_g. In brief, the polarization process will result in an accumulation of charge at the anode which during depolarization will redistribute via the above two mechanisms. Such redistribution may have particular significance here, as it will result in an error when calculating the relaxation time from the peak magnitude which is commonly assumed to be due to reorientation alone; the significance of this error is not yet known.

The low stabilization and polarization temperature systems also showed a shoulder on the glass transition relaxation peak. We suggest that this shoulder is associated with inadequate contact between the sample and electrode (we discuss evidence for this below). The meniscus that is formed during the sample preparation prevents good contact being established between the sample and electrode; this may be easily observed by disassembling the measurement cell after such an experiment using low temperature parameters. Consequently, air gaps are formed within the electrode-sample assembly leading to distortion of depletion regions; the air gap is likely to be much more prevalent at the upper (cathodic) electrode due to gravitational forces resulting in good contact with the lower anode. We base the assertion of contact relevance on two key considerations. Firstly there is a recognized body of literature in the dielectrics field (Gross, 1949; van Turnhout, 1971, 1975a) that clearly supports the presence of air gaps resulting in space charge effects; we outline below how we can adapt these ideas to the system under study here and show that this model leads to projected spectra that are compatible with our observations. Secondly, the effects of experimental conditioning also fully support this hypothesis. Again we demonstrate the interrelationship between the theoretical model and the observed effects below.

It may reasonably be assumed that the sample and anode (in this case, the lower electrode) make a complete blocking contact that leads to the ADR having the same thickness across the sample. In contrast the (upper) sample surface facing the cathode is assumed to have uneven contact with the electrode, leading to distortion of the CDR. On going through the glass transition temperature the sample will physically reorientate within the cell, leading to expansion and levelling off of the meniscus as the sample liquifies. This in turn will lead to additional drift and diffusion processes due to the change in charge density within the CDR as the sample redistributes on a macroscopic scale. The proposed scenarios of good contact and air gap contact are shown in Fig. 5a and b, respectively.

If one accepts the premise that poor electrode contact and CDR distortion are intrinsically related, then CDR space charge effects may be expected to occur at low temperatures of stabilization and polarization, whereby the molecular motions of the sample are slow and the sample shape remains unchanged. In contrast, CDR distortions are expected to be minimised with temperatures of polarization T_P and/or stabilization T_S around and above the glass transition. This is due to improvement of the contact between the sample and the electrode via heating to T_g so as to allow sample flow within the MIM assembly. Indeed, inspection of Figs. 1–3 clearly indicates that the shoulder is seen only at the lowest polarization temperature and for the lowest stabilization temperatures. More specifically, the shoulder is seen for T_P/T_S values of 303 K/273 K and 293 K as well as T_P/T_S values of 313 K/273 K. Clearly, therefore, the effect appears to be eradicated by heating the sample to a temperature whereby molecular mobility is increased and sample flow may occur, leading to improved contact. By using the two temperature cycling parameters in conjunction we are able to distinguish between dipolar and macroscopic effects to reach this conclusion. However, the key finding is that we can reasonably ascribe

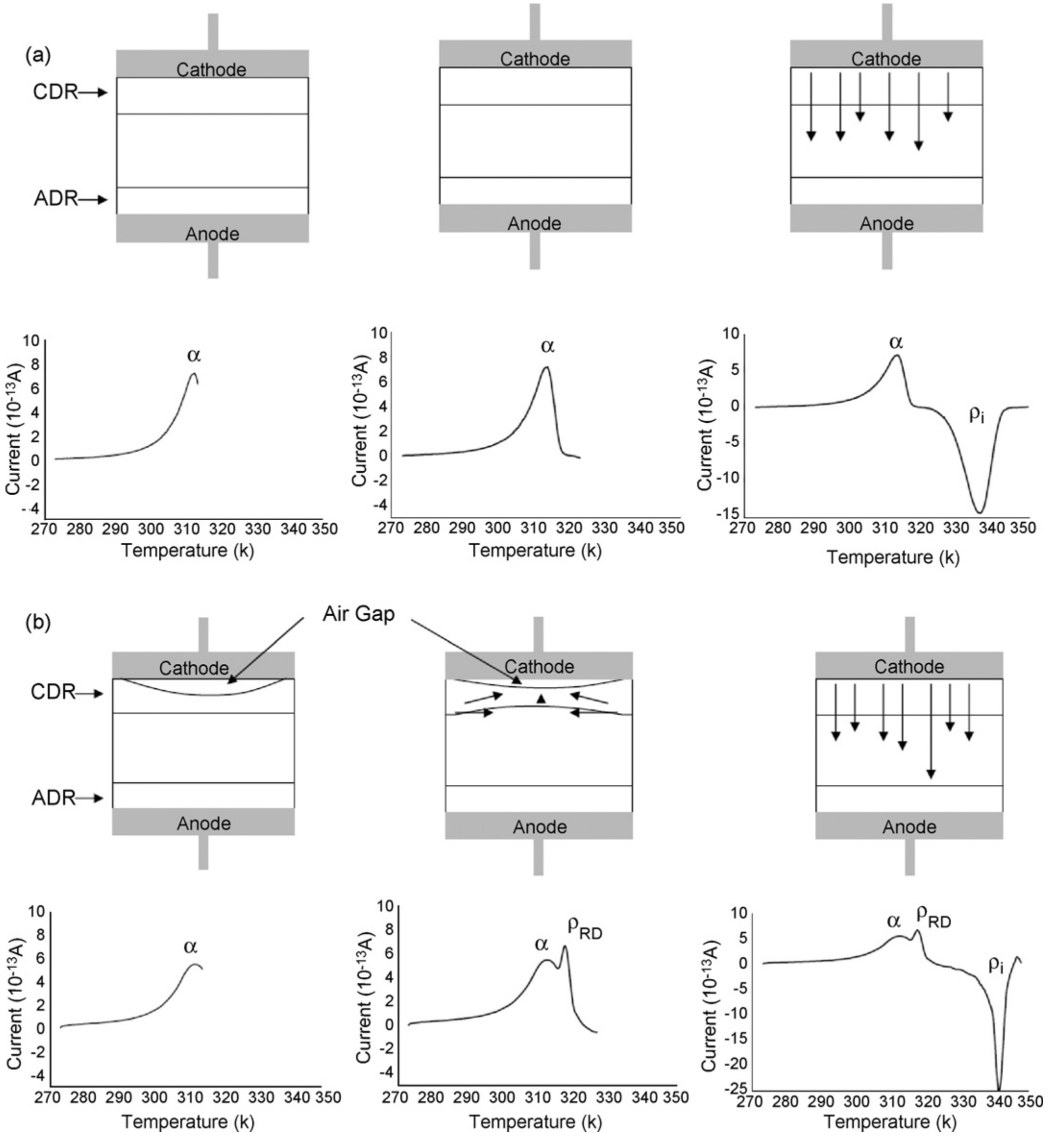

Fig. 5. (a) Progression of a TSDC experiment in a system with perfect contact between the sample and the electrodes. From left to right: the sample undergoes dipolar reorientation resulting in the appearance of the composite relaxation peak (labelled α). The relaxation process comes to completion and the system reequilibrates. A further temperature charge redistribution peak is due to injection of space charge into cathodic depletion region (labelled ρ_i). (b) Progression of a TSDC experiment in a system with an air gap between the sample and the electrode. From left to right: the sample undergoes dipolar reorientation resulting in the appearance of the composite relaxation peak (labelled α). However charge redistribution due to drift and diffusion associated with the air gap is responsible for an additional peak (labelled ρ_{RD}). The ρ_i peak is then observed as before.

this shoulder to physical distortion of the CDR; we will refer to this process as ρ_{RD} where D refers to distortion and R refers to redistribution.

Reference to the dielectrics literature (Vanderschueren and Gasiot, 1979; Thielen et al., 1996b) also allows interpretation of the higher temperature responses. We suggest two mechanisms that may be responsible for these phenomena and present evidence for their involvement from the effects of pretreatment and the comparison with alternative measurement modes. Firstly, charge depletion regions at the electrode–sample interfaces will result in the phenomenon of space charge injection (ρ_I). In brief, the difference in work function between the electrode and the sample will result in the injection of charge from the electrode itself into the CDR in order to promote electrical neutrality. This will represent a movement of charge towards the anode and hence the generation of a (negative) peak. However, it is also the case that the electrodes for the TSC cell are not equivalent, as used in this experimental set-up, hence the two electrodes themselves will have different work functions. Consequently there will be a charge distortion through the sample as a result of these differences; such distortions tend to be long range (in the scale of the sample) and are therefore distinct from the much more localised differences in the CDR and ADR which involve much greater charge concentration gradients. These larger scale distortions may occur only at higher preparation temperatures due to the greater mobility required for such effects to manifest themselves. We suggest that these two processes are of relevance in the present case and indeed have been previously suggested for TSC studies on semiconductor systems (Thielen et al., 1996a,b). The observation that the positive peak is more apparent with higher T_S and T_P values is also wholly consistent with this hypothesis.

5. Conclusion

One of the principal difficulties associated with performing TSC experiments has been the absence of a clear means of differentiating between dipolar and translational charge redistribution effects. This has led to interpretive difficulties which have arguably held back the introduction of the technique to a wider scientific audience. Here we suggest that the redistribution effects may be largely, but by no means entirely, associated with sample contact effects. This is a significant consideration as it is comparatively rare for samples of, for example, a pharmaceutical nature to be entirely flat with concomitant guarantee of reproducible and complete contact. Similarly, even with good contact space charge injection may still result in peaks which may confuse the non-specialist operator. This study indicates that contact may be improved by appropriate thermal preconditioning and that redistribution effects may be differentiated from relaxation ones by varying the experimental protocol. In this way it is hoped that the many significant advantages of TSC (high sensitivity, rapid and simple calculation of relaxation times, etc.) may become available to a wider audience.

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