Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Research 342 (2007) 961–969
Carbohydrate
RESEARCH

Slow molecular mobility in the crystalline and amorphous solid states of pentitols: a study by thermally stimulated depolarisation currents and by differential scanning calorimetry

Hermínio P. Diogo,[a] Susana S. Pinto[a] and Joaquim J. Moura Ramos[b,*]

[a]*Centro de Química Estrutural, Complexo I, IST, TULisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*
[b]*Centro de Química-Física Molecular, Complexo I, IST, TULisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

Received 18 December 2006; received in revised form 11 January 2007; accepted 28 January 2007
Available online 1 February 2007

Abstract—The molecular mobility of the pentitol isomers (xylitol, adonitol, D-arabitol and L-arabitol) was studied by thermally stimulated depolarisation currents (TSDC) in the crystalline and in the amorphous solid states. Differential scanning calorimetry (DSC) was used to characterise the phase transformations, to detect polymorphism and to analyse the dynamics of the structural relaxation in the glassy state (from the heating rate dependence of the onset temperature of the glass transition signal). The mobility in crystalline xylitol and adonitol displays features that are different compared with crystalline arabitols. No difference of the dynamic behaviour seems to emerge from our results on the primary and secondary relaxations in the amorphous isomeric pentitols. The values of the steepness index or fragility obtained in this work by TSDC and DSC are compared with the values reported in the literature obtained from other experimental techniques, and with values predicted by empirical formulae.

Keywords: TSDC; DSC; Pentitols; Glass transition; α-Relaxation; Fragility; Glass forming liquids; Secondary relaxations; β-Relaxation

1. Introduction

Polyols are low molecular weight carbohydrates that are important in food and pharmaceutical applications. They are used as a substitute for sucrose because they share with sugars the characteristic sweet taste, but they have low energy content when compared with sucrose. Moreover, they reduce the development of dental caries[1] and they do not require insulin or glucose in their metabolism, so that they are suitable for diabetics.[2]

For pharmaceutical applications, the state and phase transitions of drugs and excipients, and of polyols in particular, are very important as they affect the product shelf life and the kinetics of dissolution. It is now recognised that the amorphous solid state offers very interesting possibilities in the control of bioavailability.[3,4] Knowledge of the time scales of molecular motions in amorphous systems, that is, knowledge of the relaxation map that characterises the molecular dynamics in a given material, is needed for profiting from the advantages of the amorphous state, and is an important requirement for safe storage and use of amorphous pharmaceutical solids.[5] The temperature dependence of the molecular mobility in the amorphous state is thus an important problem to be addressed in this context. Another important aspect is the stability of the amorphous state with regard to cold crystallisation (or recrystallisation).[6] The propensity of the amorphous solid and of the supercooled liquid to crystallise is essentially determined by the molecular mobility and by the thermodynamic driving force.

The pentitol isomers, with general name pentane–1,2,3,4,5-pentol, are four: xylitol, adonitol, D-arabitol and L-arabitol. The respective structures are shown in Figure 1. A few studies have been published to date describing the crystalline structure, thermal behaviour and mobility features of the pentitols. The crystal structures were determined[7] and it was found that the

---

* Corresponding author. E-mail addresses: hdiogo@ist.utl.pt; mouraramos@ist.utl.pt

0008-6215/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2007.01.016

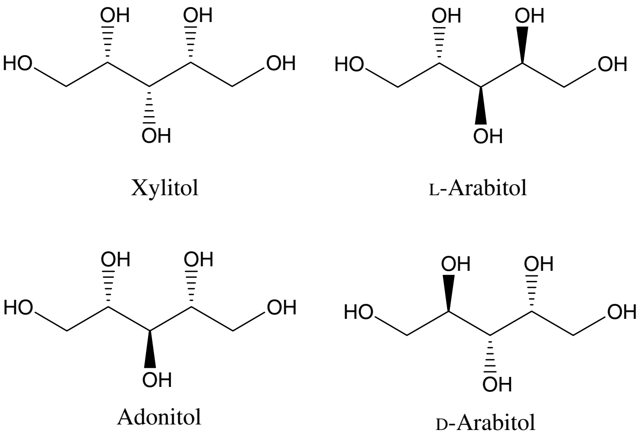
Xylitol
L-Arabitol
Adonitol
D-Arabitol

Figure 1. Chemical structures of pentitols with general formula $HOCH_2–(CHOH)_3–CH_2OH$.

conformation of the chain (planar zigzag or bent non-planar) depends on the configuration at alternate carbon atoms. The melting enthalpy, the glass transition temperature and the heat capacity jump across the glass transition region have been reported for the four pentitols.[8–10] The dielectric,[11–13] mechanical[11] and thermal properties[11] of xylitol have also been addressed, while some features of the molecular mobility in the amorphous solid state of the four pentitols have been determined by temperature modulated differential scanning calorimetry.[9]

In the present study, we wish to characterise in detail the molecular mobility of the pentitol isomers, in the crystalline and in the amorphous solid state, using the experimental technique of thermally stimulated depolarisation currents (TSDC). The study of the mobility in the glass and in the crystal in this family of compounds, as well as the comparison of the stability of the supercooled liquid, is interesting given that we are dealing with molecules that are diastereoisomers: the molecular weight is the same, the connectivity between the different atoms is also the same, but the configuration at the different chiral carbon atoms is different.

2. Materials and methods

2.1. Substances

The four isomeric pentitols have molecular formula $C_5H_{12}O_5$, IUPAC name pentane–1,2,3,4,5-pentol (molecular weight $M = 152.15\ \mathrm{g\,mol^{-1}}$) and the chemical structures are shown in Figure 1 as Masamune formulae.[14] In this representation, the main carbon chain is drawn as a planar staggered zigzag conformation, shown with ligands (other than H) with bonds coming above or going below the plane of the zigzag chain. Xylitol (CAS No. 87-99-0) was purchased from Sigma (mass fraction > 0.99). Adonitol (CAS No. 488-81-3), D-arabitol (CAS No. 488-82-4) and L-arabitol (CAS No. 7643-75-6), all with mass fraction $\geqslant 0.99$, were purchased from Acros. All substances were used as received.

2.2. Techniques

2.2.1. Differential scanning calorimetry (DSC). DSC measurements were performed with a 2920 MDSC system from TA Instruments Inc. Samples of ~5–10 mg were introduced into aluminium pans and hermetically sealed using a sample encapsulating press. The measuring cell was continually purged with high purity helium gas at 30 mL/min. An empty aluminium pan, identical to that used for the sample, was used as reference. Details of the calibration procedures are given elsewhere.[15]

2.2.2. Thermally stimulated depolarisation currents (TSDC). TSDC experiments were carried out with a TSC/RMA spectrometer (TherMold, Stamford, CT, USA) covering the range from −170 to +400 °C. For TSDC measurements, the sample was placed between the electrodes of a parallel plane capacitor with effective area of ~38 mm^2 (thickness of ~0.5 mm). The sample was immersed in an atmosphere of high purity helium (1.1 bar). The fact that the relaxation time of the motional processes is temperature dependent and becomes longer as temperature decreases enables their immobilisation by cooling. This is the basis of the TSDC technique, which is particularly useful for probing slow molecular motions. To analyse specific regions of the TSDC spectrum, different methods of polarising the sample can be used, namely the so-called TSDC global polarisation experiment and the partial polarisation (PP) experiment (often called thermal sampling or windowing or cleaning). The PP method, where the polarising field is applied in a narrow temperature interval, enables to resolve a global peak into its individual relaxation modes.[16] This partial polarisation procedure allows the retention (or freezing) of a polarisation that arises from a narrow variety of dipolar motions. In the limit of a very narrow polarisation window, the retained polarisation (and, of course, the current peak that is the result of a partial polarisation (PP) experiment) would correspond to a single, individual dipolar motion.[17] The physical background of the TSDC technique is presented elsewhere.[18,19] The basic description of the TSDC experiment, and the discussion of the nature of the information it provides, is presented in detail in previous publications.[17,20,21]

3. Results and discussion

3.1. Thermal behaviour and polymorphism

The melting temperature, T_{fus}, and the melting enthalpy, $\Delta_{\mathrm{fus}}H$, of pentitols are shown in Table 1 and compared

Table 1. Melting temperature, T_{fus}, and the melting enthalpy, $\Delta_{\text{fus}}H$, for the pentitols

Pentitol	T_{fus}[a] (°C) (This work)	T_{fus} (°C) (Literature)	$\Delta_{\text{fus}}H$[b] (kJ/mol) (This work)	$\Delta_{\text{fus}}H$ (kJ/mol) (Literature)
Xylitol	95.7	94.9;[c] 92.7[e]	37.3 ± 0.1 (15)	37.7;[c] 37.4;[d] 35[e]
Adonitol	102.8	101.9;[c] 101.6[d]	35.0 ± 1.1 (5)	33.5;[c] 37.6[d]
D-Arabitol	102.9	102.9;[c] 106.3[d]	35.0 ± 0.8 (7)	38.8;[c] 38.9[d]
L-Arabitol	102.0	100.9[c]	34.6 ± 0.3 (8)	43.2[c]

[a] Temperature of the maximum of the DSC peak.

[b] The reported uncertainties correspond to the standard deviation of the mean. The number of determinations is indicated between parentheses.

[c] From Ref. 9.

[d] From Ref. 10.

[e] From Ref. 11.

with values from the literature. The melting temperatures of our samples are in very good agreement with the values of the literature. For the melting enthalpies, the agreement is not so good, particularly in the case of L-arabitol, as shown in Table 1. Our results suggest that the melting energy is nearly the same for the four pentitol diastereoisomers.

The glass transition temperatures, T_g, and the heat capacity jump in the glass transition region, ΔC_P, are shown in Table 2 and compared with values from the literature. The values we obtained for the glass transition temperature confirm that we can group the pentitols in two pairs with respect to the value of T_g, as suggested before.[9] However, the values of the heat capacity jump, ΔC_P, presented in Table 2 do not corroborate the same grouping.

A common behaviour shared by the four pentitols is that none of them crystallise on cooling from the melt, even if the cooling rate was low (<2 °C min^{-1}). However, some differences were observed in their thermal behaviour. Our samples of xylitol were, among the four pentitols, those that showed a stronger resistance to crystallisation (most stable metastable supercooled liquid): after melting the crystalline as received samples, no crystallisation was observed neither on cooling from the melt nor on heating from the glassy solid. Furthermore, we did not observe any polymorphism in xylitol, despite the fact that a metastable crystalline form melting at 61 °C was reported in the early literature.[22] In the case of D-arabitol, cold crystallisation was always observed if the sample was heated from the glassy state (below T_g) with heating rates between 1 and 19 °C min^{-1}, giving rise to a crystal whose melting temperature is 102 °C. Sometimes, particularly when the heating rates lie between 10 and 12 °C min^{-1}, a polymorph of D-arabitol melting at ~83 °C was detected. The DSC thermogram indicates that this polymorph easily converts in the most stable one. L-Arabitol and adonitol, on the other hand, displayed cold crystallisation on heating from the glassy state with heating rates lower than 6 °C min^{-1}. However, cold crystallisation was a relatively infrequent occurrence for heating rates higher than 6 °C min^{-1}. In L-arabitol and adonitol, cold crystallisation on heating from the glassy state always led to the most stable polymorph melting at 102 °C, but there is evidence for polymorphism in these two pentitols. In the case of L-arabitol, if the isotropic liquid is cooled down to room temperature (well above T_g) and heated up, a polymorph melting at ~83 °C is formed by cold crystallisation. If the rate of heating from room temperature is low (1–2 °C min^{-1}), the pure polymorph melting at ~83 °C is formed. However, for higher heating rates (in the range 3–6 °C min^{-1}) a mixture of the two polymorphs (melting at 83 and 102 °C) is obtained, and there is no indication of interconversion between them. In contrast, for adonitol, a polymorph melting at ~83 °C was observed, but it was never formed by cold crystallisation. Instead, it was formed by cooling from the melt down to room temperature and annealing for several hours (at least 12–15 h) at that temperature. In

Table 2. Glass transition temperatures, T_g, and heat capacity jump at the glass transition region, ΔC_P, for the pentitols

Pentitol	T_g (°C) (This work)	T_g (°C) (Literature)[c]	ΔC_P (J °C^{-1} mol^{-1}) (This work)[d]	ΔC_P (J °C^{-1} mol^{-1}) (Literature)
Xylitol	−25.5;[a] −20.5[b]	−29;[e] −23.2;[f] −24.1[h]	145 ± 2 (101)	174;[f] 202;[g] 148[h]
Adonitol	−24.9;[a] −18.7[b]	−21.2[f]	168 ± 2 (91)	176[f]
D-Arabitol	−15.0;[a] −10.6[b]	−12.2[f]	160 ± 2 (53)	205;[f] 202[g]
L-Arabitol	−15.8;[a] −10.1[b]	−12.2[f]	173 ± 2 (35)	205[f]

[a] Temperature of maximum intensity of the partial polarisation peak with higher intensity in the glass transition region, T_M (see later).

[b] Onset of the DSC signal at 10 °C min^{-1}.

[c] The values from Ref. 9 correspond to the midpoint of the C_P jump.

[d] The reported uncertainties correspond to the standard deviation of the mean. The number of determinations is indicated between parentheses.

[e] From Ref. 8.

[f] From Ref. 9.

[g] From Ref. 10.

[h] From Ref. 11.

conclusion, a crystalline form melting at ~83 °C was observed for all pentitols except xylitol, but the thermal conditions for its formation seem to be rather different. The fact that, for D-arabitol, the DSC thermogram indicates that this crystalline form easily converts in the most stable one probably indicates that we are in the presence of a true polymorphic form.

3.2. Mobility in the crystalline state

The TSDC study of the four pentitols showed relaxations in the crystalline state. However, some differences are to be underlined with respect to the features of this mobility. Figure 2 shows the partial polarisation peaks of the relaxations observed in the crystalline (most stable structure, as received) form of the four studied pentitols.

It is true that the dynamic features observed by dielectric methods, and particularly by TSDC, in the crystalline state can originate from material discontinuities. These anomalous effects are usually called Maxwell–Wagner effects, and may arise from some residual non-crystalline material eventually present (semi-crystallinity) and also from the grain boundaries. Based on our DSC and TSDC results, we have reasons to believe that our crystalline samples are fully crystalline. On the other hand, the relaxation peaks showed a very high reproducibility along the hundreds of thermal cycles to which the crystalline samples were subjected, reinforcing our belief that the relaxation peaks observed in the crystalline samples of pentitols correspond to dipolar reorientational motions. In all the four cases shown in Figure 2, we observe two kinds of mobility in the crystal: one with higher dielectric strength at higher temperatures, and another one at lower temperatures with lower intensity (shown in the insets of Fig. 2). In the cases of D- and L-arabitols (Fig. 2c and 2d, respectively) the two relaxations are well separated in the temperature axis. For xylitol and adonitol (Fig. 2a and 2b, respectively) however, the two processes merge in the temperature axis, so that the low intensity mobility appears in the lower temperature side of the dominant relaxation (see the insets of Fig. 2a and b).

Some relaxations in molecular crystals studied by TSDC show a dielectric strength that continuously increases as the temperature increases up to the vicinity of the melting temperature. They appear as a premonition of melting, announcing the proximity of the transition as its temperature is approached on heating. Oppositely, the relaxation observed in the crystalline phase of the pentitols (Fig. 2) shows a well defined

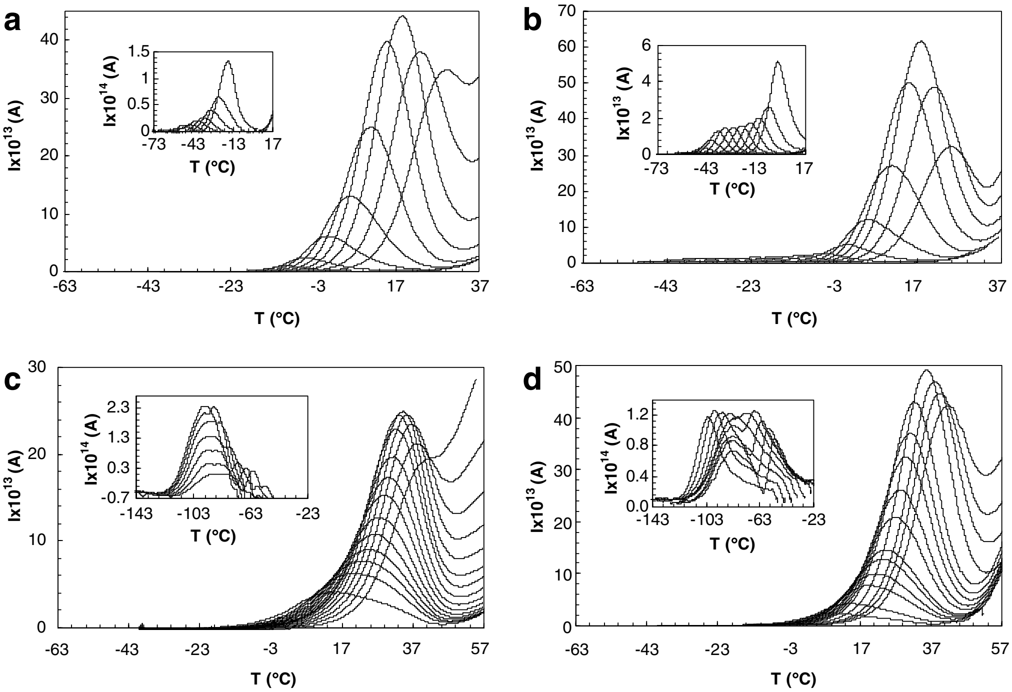

Figure 2. Partial polarisation components of the slow mobility of the crystalline pentitols obtained at a heating rate of 4 °C min^{-1}, with a polarising electric field of $E = 450$ V/mm, and with a polarisation window of $\Delta T = 2$ °C. The property in the ordinate axis is the current intensity expressed in ampere, $I(A)$. (a) Xylitol with polarisation temperatures, T_p, ranging from −15 up to +25 °C. The inset displays the lower temperature and lower intensity peaks with polarisation temperatures, T_p, from −75 up to −25 °C. (b) Adonitol with polarisation temperatures, T_p, ranging from −15 up to +25 °C. The inset displays the lower temperature and lower intensity peaks with polarisation temperatures, T_p, from −60 up to −5 °C. (c) D-Arabitol with polarisation temperatures, T_p, ranging from 10 up to 38 °C. The inset displays the lower temperature and lower intensity peaks with polarisation temperatures, T_p, from −100 up to −70 °C. (d) L-Arabitol with polarisation temperatures, T_p, ranging from 0 up to 38 °C. The inset displays the lower temperature and lower intensity peaks with polarisation temperatures, T_p, from −105 up to −70 °C.

higher temperature limit (or boundary), relatively far from the melting temperature. We would thus say that this mobility cannot be ascribed to the 'softening' of the crystalline sample, but rather corresponds to a specific motional mode present in the crystal. A similar mobility was observed by TSDC in different crystals, as, for example, salicylsalicylic acid.[23]

The analysis of these PP peaks using the usual Bucci integration procedure[24] allowed the determination of the corresponding temperature dependent relaxation time, $\tau(T)$. The fitting of the $\tau(T)$ lines using an appropriate equation (Arrhenius, Eyring, Vogel, etc.) provides the kinetic parameters which characterise the studied mobility. Figure 3 shows the activation enthalpy, $\Delta H^{\neq}$, of the partial polarisation components of all the relaxations observed in the four pentitols, plotted as a function of the peak's location, T_m. Figure 3a concerns xylitol and adonitol, while Figure 3b concerns D- and L-arabitols. The relaxations in the amorphous solid state will be discussed later, so that we will focus now on the mobility in the crystalline state that corresponds to the points in the right-hand side of Figure 3a and b with $T_m > -5$ °C.

It can be concluded from the observation of Figure 3 that these molecular motions in the crystalline phase of pentitols are narrowly distributed in energy. Furthermore, from the comparison of the results obtained on the four pentitols it comes out that the degree of cooperativity of those motions in the crystal, quantified by the deviation of the activation enthalpy from the zero entropy behaviour, is higher in xylitol and adonitol when compared with the arabitols. Let us briefly elucidate that the zero entropy behaviour corresponds to the motional processes with no activation entropy, that is, to the noncooperative modes of motion. Such processes have activation enthalpies that obey to the zero entropy line shown in Figure 3. The observation reported previously is an interesting finding as the crystal-structure determination of pentitols showed that the conformation of the carbon chain is bent, nonplanar, for xylitol and adonitol, while it is extended, staggered and planar, for the two arabitols.[7] We thus conclude that the different mobility features in the crystal arise from the different rotameric conformations of the different pentitol molecules in the crystalline state.

3.3. Mobility in the amorphous state

The pentitols in the solid amorphous phase were prepared by rapid cooling (~30 °C min^{-1}) of the isotropic liquid from 10° above the melting temperature down to ~50° below T_g.

3.3.1. Secondary relaxations. The four pentitols show secondary relaxations that are observable in the TSDC spectra between −165 °C (lower temperature limit of our TSDC equipment) and the glass transition temperature region. They appear as broad relaxations that merge with the α-relaxation in the higher temperature side, and correspond to zero entropy motions. To prevent excessive lengthening of this manuscript, we do not show partial polarisation components of the secondary relaxations. However, Figure 3 displays the activation enthalpy, $\Delta H^{\neq}$, plotted as a function of the peak's location, T_m, for many partial polarisation components of all the relaxations in the four pentitols. The points in Figure 3a that lie in the temperature region such that $T_m < -45$ °C correspond to the secondary relaxations of xylitol (triangles) and adonitol (circles); the points with $T_m < -35$ °C in Figure 3b correspond to the secondary relaxations of D-arabitol (triangles) and L-arabitol (circles). In all the cases, we can see that

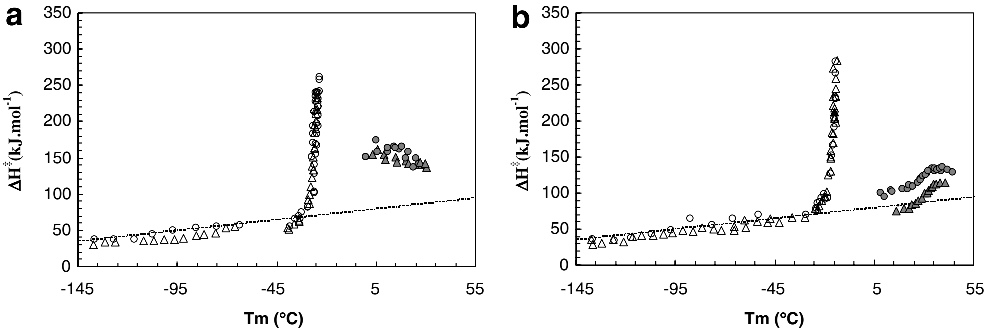

Figure 3. Activation enthalpy, $\Delta H^{\neq}$, of the partial polarisation components of the relaxations in pentitols as a function of the peak's location, T_m. The uncertainty in the enthalpy values is less than 2%. The line describes the zero entropy behaviour. (a) Xylitol (triangles) and adonitol (circles). The higher temperature points ($T_m > -15$ °C, filled symbols) correspond to the relaxation in the crystalline phase, while the other points (open symbols) refer to the mobility in the amorphous solid state. The points on the left-hand side of the figure correspond to the secondary relaxations, while the points in the region $-45 < T_m < -15$ °C correspond to the glass transformation range. (b) D-Arabitol (triangles) and L-arabitol (circles). As in (a) the higher temperature points ($T_m > -5$ °C, filled symbols) correspond to the relaxation in the crystalline phase, the points on the left-hand side correspond to the secondary relaxations, and the points strongly deviating the zero entropy line ($-35 < T_m < -15$ °C) correspond to the glass transformation range.

the zero entropy behaviour is obeyed. The kinetic features of this mobility are similar for the four pentitols. On the other hand, the intensity of the partial polarisation peaks of the secondary relaxation is of the same order of magnitude for the different pentitols.

3.3.2. The glass transition relaxation and the fragility.

The mobility in the glass transformation range was studied by TSDC using the partial polarisation (PP) procedure. Figure 4 shows some selected PP peaks of the α-relaxation of the four pentitols.

Again, the temperature dependent relaxation time, $\tau(T)$, was obtained using the Bucci integration procedure,[24] and the kinetic parameters which characterise the studied mobility were obtained by fitting the $\tau(T)$ lines with an appropriate equation. The points in the region $-45 < T_m < -15$ °C of Figure 3a correspond to the partial polarisation components of the α-relaxation of xylitol (triangles) and adonitol (circles), while those in the region $-35 < T_m < -5$ °C of Figure 3b correspond to the partial polarisation components of the α-relaxation of D-arabitol (triangles) and L-arabitol (circles). It is clear that the mobility in the glass transformation range of the four pentitols shows a clear deviation from the so-called zero entropy line (also called compensation behaviour). The strong deviation from the zero entropy line observed in the glass transformation region consists in fact of a concomitant increase with temperature of the activation enthalpy and entropy of the motional processes in the transformation range. This effect is often called compensation.

The peak with higher intensity in the glass transition region is the manifestation of a mobility component that is characteristic of the glass transition. The temperature of maximum intensity of this peak, labelled T_M (see Table 2), is the glass transition temperature provided by the TSDC technique (at the heating rate of the experiment, 4 °C min^{-1} in the present case). The analysis of this singular peak for each one of the pentitols in Figure 4 allows the determination of the relaxation time at the glass transition temperature, $\tau(T_g)$, of the activation energy for the structural relaxation, $E_a(T_g)$, and also of the steepness index or fragility of the glass forming system, m. Table 3 displays the values of the activation enthalpy, $E_a(T_g)$, and of the relaxation time, $\tau(T_g)$, for the four pentitols obtained from the analysis of the peak with higher intensity in the glass transition region.

It can be concluded from the data in Table 3 that the relaxation time at T_g is identical for the four pentitols. On the other hand, the activation energy of the structural relaxation appears as slightly higher in the arabitols compared with xylitol and adonitol.

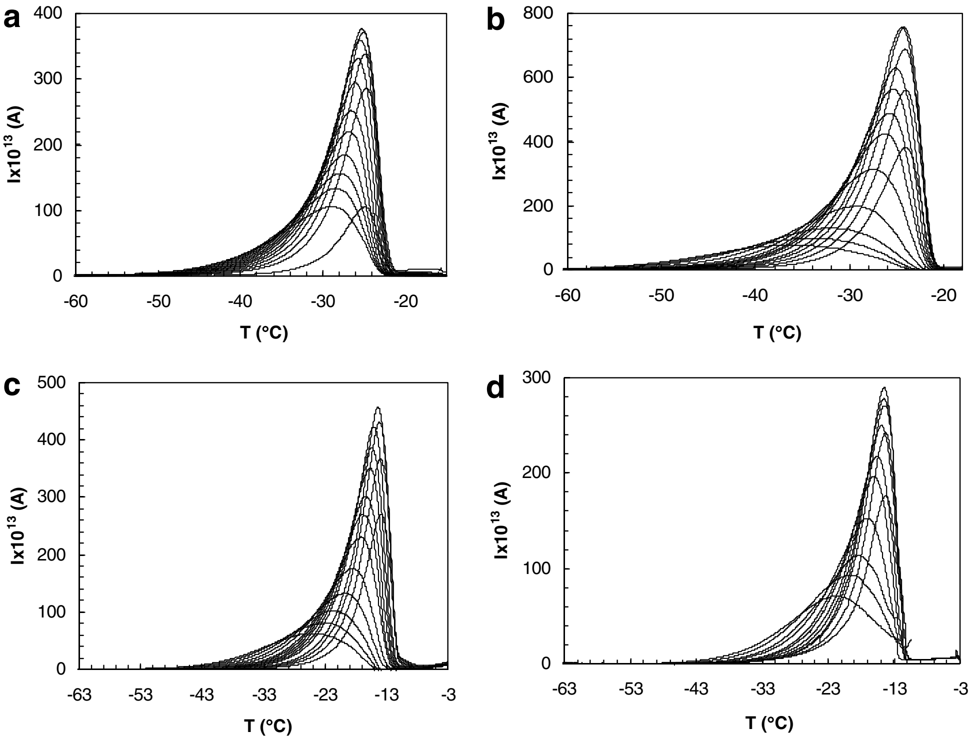

Figure 4. Partial polarisation (PP) components of the glass transition relaxation of the four pentitols. The experimental conditions were strength of the polarising electric field, $E = 450$ V mm^{-1}; polarisation time, $t_P = 5$ min; width of the polarisation window, $\Delta T = 2$ °C; heating rate, $r = 4$ °C min^{-1}. The polarisation temperatures, T_P, were (a) xylitol, from −40 up to −26 °C, with intervals of 1 °C; (b) adonitol, −47, −45, −43, −40, −37 and −35 up to −26 °C, with intervals of 1 °C; (c) D-arabitol, −36, −34, −32, −30, −28 and −26 up to −16 °C, with intervals of 1 °C; (d) L-arabitol, −32, −30, −28, −26 and −24 up to −17 °C, with intervals of 1 °C.

Table 3. Relaxation time at the glass transition temperature, $\tau(T_g)$, and activation energy for the structural relaxation, $E_a(T_g)$, for the pentitols obtained from TSDC data

Pentitol	$\tau(T_g)$ (s)	$E_a(T_g)$ (kJ mol^{-1})
Xylitol	26	275
Adonitol	26	278
D-Arabitol	27	295
L-Arabitol	26	289

From the value of the activation energy of the structural relaxation, the fragility (temperature dependence of the relaxation time normalised at T_g) was calculated as

$$m = \left[\frac{\mathrm{d}\log_{10}\tau(T)}{\mathrm{d}(T_g/T)}\right]_{T=T_g} = \frac{E_a(T_g)}{2.303RT_g}. \quad (1)$$

Several experimental techniques enable the determination of the activation energy of the structural relaxation: dielectric relaxation spectroscopy, conventional DSC, temperature modulated DSC and TSDC. The fragility indexes of the pentitols obtained in this work by TSDC (temperature dependent relaxation time, $\tau(T)$, of peak with higher intensity in the glass transition region) are presented in Table 4. Because the arabitols have simultaneously higher activation energy and higher glass transition temperature, the consequence is that the fragility values obtained in the present work by TSDC are very similar for the four isomeric pentitols.

On the other hand, it was shown[25] that the dependence of the glass transition temperature, T_g, on the heating or cooling rate, $|r|$, of a conventional DSC experiment is given by

$$\frac{\mathrm{d}\ln|r|}{\mathrm{d}1/T_g} = -\frac{E_a}{R}, \quad (2)$$

where E_a is the activation energy for the relaxation times controlling the structural enthalpy relaxation, and R is the perfect gas constant. The fragility values we obtained based on this method are also shown in Table 4, together with values determined by other techniques. We note that the onset temperature was obtained at a given heating rate q after cooling from the metastable undercooled liquid at the same rate $-q$. From those values we can draw the following observations:

1. The fragility values obtained in the present work by TSDC are very similar for the four isomeric pentitols.
2. The fragility indexes obtained in the present work on the basis of conventional DSC data have values in reasonable agreement with those obtained by TSDC.
3. The fragility indexes obtained by DSC and by TSDC are significantly lower compared with those reported in the literature based on modulated temperature DSC data.[9]
4. The results obtained in the present work do not support the suggestion that pentitols can be grouped into two pairs according to their dynamic behaviour in the glassy state, as suggested previously.[9] In fact, according to our results we can group the pentitols in two pairs (xylitol/adonitol and D/L-arabitols) with respect to the value of T_g and with respect to the values of E_a. However, the values of the heat capacity jump, ΔC_P, presented in Table 2, and of the fragility, m, presented in Table 4, do not corroborate the same grouping. We have also underlined before that no difference of the dynamic behaviour seems to emerge from our results on the secondary relaxations of the isomeric pentitols.

An excellent empirical correlation was found by Wang and Angell[26] for glass-forming liquids, between some kinetic properties (fragility index, m, and glass transition temperature, T_g) and some thermodynamic properties (molar heat capacity jump at T_g, ΔC_P, and molar enthalpy of melting, $\Delta_{fus}H$). The empirical formula looks like

$$m = 56\frac{T_g\Delta C_P}{\Delta_{fus}H}. \quad (3)$$

On the other hand, a formally similar relationship was proposed,[27] based on a random first-order transition theory

$$m = 34.7\frac{T_m\Delta C_P}{\Delta_{fus}H}. \quad (4)$$

Table 4. Fragility index, m, of pentitols calculated from data obtained by different experimental techniques, and from the equations proposed by Angell (Eq. 3) and by Wolynes (Eq. 4)

	Xylitol	Adonitol	D-Arabitol	L-Arabitol
Dielectric relaxation spectroscopy	66;[a] 87[b]	—	—	—
DSC (temperature modulated)	76[c]	78[c]	92[c]	90[c]
TSDC (temperature dependent relaxation time)	60	60	61	60
DSC (heating rate dependence of the onset temperature)	75	55	60	75
From Eq. 3	54	67	69	71
From Eq. 4	50	62	63	64

[a] From Ref. 11.
[b] From Ref. 26.
[c] From Ref. 9.

Table 4 also shows the values of the fragility index, *m*, estimated on the basis of Eqs. 3 and 4 using data obtained in the present work and displayed on Tables 1 and 2. It can be concluded that the results on Table 4 do not support the suggestion that pentitols can be grouped into two pairs. Furthermore, the fragility values on Table 4 are in reasonable agreement with those obtained by TSDC and by conventional DSC, but are much lower compared with those obtained by temperature modulated DSC.

Let us finally call attention to some discrepancies that are observed in the value of the fragility obtained by different, and well established, experimental techniques. In fact, the fragility values displayed in Table 4, obtained from several experimental techniques, show a considerable dispersion. We believe that the origin of this dispersion is not the presence of residual water in the pentitol samples. Dehydration during melting was assumed because temperatures above 100 °C are needed for preparation of the pentitol melts. The scatter of the fragility values has been reported before,[28,29] and is not a new finding. It is well known that various experiments such as viscosity, thermal, mechanical and dielectric relaxations, and optical and nuclear magnetic resonance techniques lead to somewhat different values of fragility, an effect which becomes more pronounced for high fragility liquids.[26] On the other hand, it is well known that the thermodynamic and kinetic data of polyols and sugars are quite divergent.[26] Nevertheless, we need to draw attention for the reasonable agreement observed between the fragility values obtained by TSDC and by conventional DSC.

4. Conclusions

Crystal polymorphism was detected by differential scanning calorimetry in the cases of adonitol and D- and L-arabitols, but not in xylitol. Some information was obtained about the general conditions allowing the formation of the less stable polymorph and of transformation between the different polymorphs of the same substance.

The different pentitol isomers displayed different mobility features in the crystal that arise from the different rotameric conformations of the pentitols in the crystalline state. In particular, the degree of cooperativity of the molecular motions appeared to be higher in xylitol and adonitol when compared with the arabitols.

On the other hand, the results obtained in the present work do not support the suggestion that pentitols can be grouped into two pairs according to their dynamic behaviour in the glassy state, as previously suggested in the literature. In contrast, no difference of the dynamic behaviour of the isomeric pentitols in the glassy state seems to emerge from our results on the primary and secondary relaxations.

Furthermore and finally, some scatter of the fragility values of the pentitols obtained from different experimental techniques was observed.

Acknowledgement

A Grant (SFRH/BD/12330/2003) from Fundação para a Ciência e a Tecnologia (FCT, Portugal) is gratefully acknowledged by S.S.P.

References

1. deMan, J. M. *Principles of Food Chemistry*; Aspen: Gaithersburg, MD, 1999.
2. Whistler, R. L.; BeMiller, J. N. *Carbohydrate Chemistry for Food Scientists*; Eagan Press: St. Paul, MN, USA, 1997.
3. Hancock, B. C.; Zografi, G. *J. Pharm. Sci.* **1997**, *86*, 1–12.
4. Craig, D. Q. M.; Royal, P. G.; Kett, V. L.; Hopton, M. L. *Int. J. Pharm.* **1999**, *179*, 179–207.
5. Shambling, S. L.; Tang, X.; Chang, L.; Hancock, B. C.; Pikal, M. J. *J. Phys. Chem. B* **1999**, *103*, 4113–4121.
6. Hartel, R. W. *Crystallization in Foods*; Aspen: Gaithersburg, MD, 2001.
7. Jeffrey, G. A.; Kim, H. S. *Carbohydr. Res.* **1970**, *14*, 207–216.
8. Roos, Y. *Carbohydr. Res.* **1993**, *238*, 39–48.
9. Carpentier, L.; Desprez, S.; Descamps, M. *J. Thermal Anal. Calorim.* **2003**, *73*, 577–586.
10. Barone, G.; Gatta, G. D.; Ferro, D.; Piancente, V. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 75–79.
11. Talja, R. A.; Roos, Y. H. *Thermochim. Acta* **2001**, *380*, 109–121.
12. Doβ, A.; Paluch, M.; Sillescu, H.; Hinze, G. *Phys. Rev. Lett.* **2002**, *88*, 095701–1/4.
13. Psurek, T.; Maslanka, S.; Paluch, M.; Nozaki, R.; Ngai, K. L. *Phys. Rev. E* **2004**, *70*, 011503–1/6.
14. Robinson, M. J. T. Organic Stereochemistry. *Oxford Chemistry Primers No. 88*; Oxford University Press: Oxford, 2000.
15. Moura Ramos, J. J.; Taveira-Marques, R.; Diogo, H. P. *J. Pharm. Sci.* **2004**, *93*, 1503–1507.
16. Teyssèdre, G.; Lacabanne, C. *J. Phys. D: Appl. Phys.* **1995**, *28*, 1478–1487.
17. Correia, N. T.; Moura Ramos, J. J.; Descamps, M.; Collins, G. *Pharm. Res.* **2001**, *18*, 1767–1774.
18. van Turnhout, J. *Thermally Stimulated Discharge of Polymer Electrets*; Elsevier Science: Amsterdam, 1975.
19. Chen, R.; Kirsch, Y. *Analysis of Thermally Stimulated Processes*; Pergamon Press: Oxford, 1981.
20. Correia, N. T.; Alvarez, C.; Moura Ramos, J. J.; Descamps, M. *J. Phys. Chem., B* **2001**, *105*, 5663–5669.
21. Sauer, B. B. Thermally Stimulated Currents: Recent Developments. In *Handbook of Thermal Analysis and Calorimetry*; Cheng, S. Z. D., Ed.; Applications to Polymers and Plastics; Elsevier: Amsterdam, 2002; Vol. 3, Chapter 15.
22. Dunitz, J. D.; Bernstein, J. *Acc. Chem. Res.* **1995**, *28*, 193–200.
23. Moura Ramos, J. J.; Diogo, H. P.; Godinho, M. H.; Cruz, C.; Merkel, K. *J. Phys. Chem. B* **2004**, *108*, 7955–7962.

24. Bucci, C.; Fieschi, R.; Guidi, G. *Phys. Rev.* **1966**, *148*, 816–823.
25. Moynihan, C. T.; Esteal, A. J.; Wilder, J.; Tucker, J. *J. Phys. Chem.* **1974**, *76*, 2673–2677.
26. Wang, L.-M.; Angell, C. A.; Richert, R. *J. Chem. Phys.* **2006**, *125*, 074505–1/8.
27. Stevenson, J. D.; Wolynes, P. G. *J. Phys. Chem., B* **2005**, *199*, 15093–15097.
28. Moura Ramos, J. J.; Correia, N. T.; Diogo, H. P. *J. Non-Cryst. Solids* **2006**, *352*, 4753–4757.
29. Diogo, H. P.; Moura Ramos, J. J. *J. Mol. Liquids* **2006**, *129*, 138–146.