THERMODYNAMIC STUDY OF THE GLASS RELAXATION PHENOMENA
DSC study of annealing of maltitol glass

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Abstract

A thermodynamic study of the influence of the thermal treatments (annealing), below the glass transition temperature, on the thermal behavior and enthalpy of maltitol glass was carried out by differential scanning calorimetry (DSC). An enthalpic effect (exothermal) produced by the isothermal treatment of the quenched glass was found and measured.

The origin of the thermal effect was assigned to a physicochemical transformation of molecular associations in the solid (glass).

To achieve a correct description of the thermodynamic functions of glasses, another parameter, in addition to T and P, is introduced, namely the degree of advance of the above mentioned transformation.

Introduction

Glass transition is one of the highlights of some very advanced scientific research being carried out at present. The objective is, of course, to establish a theoretical approach along with development of the models for the phenomena that accompany the glass transition of vitreous materials.

Bibliographical study shows that the classical concepts of the glass transition unfortunately remain little known. Satisfactory answers have not yet been found for several important fundamental questions, of which the main ones are as follows:

- what is the origin of the glass transition?
- what is the nature of glass?
- is there an enthalpic effect in the glass transition?

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Glasses are known to change with time in their properties when annealed below their glass transition temperature T_g [1–8]. This is the relaxation process. Particularly, the enthalpy of glass decreases with annealing time and temperature. The corresponding phenomenon is called the enthalpic relaxation of glass. The relaxation enthalpy corresponds to the enthalpy difference between the annealed and the quenched (non-annealed) glasses.

$$\text{quenched glass} \xrightarrow{\Delta_r H_T^0} \text{annealed glass}$$

$C_{pq}(T)$ and $C_{pa}(T)$ are respectively the apparent (measured) heat capacity, at constant pressure, of the quenched and annealed glass *vs.* temperature. The relaxation enthalpy can be obtained by subtracting the curves $C_p = f(T)$ from the initial state (T_i) to the final state (T_f), using:

$$\Delta_r H_T^0 = \int_{T_i}^{T_f} [C_{pa}(T) - C_{pq}(T)]\,dT \tag{1}$$

The schematic enthalpic diagram $H = f(T,t)$ for glasses, as found in literature [9–11] does not give a correct description of the enthalpic state of glass in the glass transition range. Indeed, the corresponding entropic diagram led to a paradox, which was raised by Kauzman [12]. The nature and the origin of these structural changes and of the equilibrium state reached when glass relaxes are subject of many questions.

The main problem is that the thermodynamic variables required to describe the properties of glass are not known at present. Several authors [9, 10] suggested that glass is not in thermodynamic equilibrium and cannot be described by a set of two variables (T, p).

In this way, the concept of fictive temperature was introduced to allow the configuration of glass to be taken into account [11, 13]. Theoretical models of the relaxation phenomenon based on the concept of the fictive temperature state when a glass is kept, below T_g, at constant temperature for an infinite annealing time, it will return to the equilibrium state: the liquid. In fact, this has never been observed.

According to Prigogine and Defay [14], the glassy state stands out from the liquid state by its internal equilibrium, which is not realized. A physicochemical transformation (molecules in vibration ↔ molecules in rotation) may occur in the glass system. Then a supplementary variable, is addition to T and p, is needed to describe the glassy state. This variable is the degree of advance ξ of the mentioned transformation. It characterizes the configuration or the structure of the system.

In this paper, an investigation of the influence of the thermal treatments (annealing), below the glass transition temperature, on the thermal behavior and enthalpy of maltitol glass using differential scanning calorimetry is carried out. The aim is to provide key information on the supplementary variable to be added to p and T, for the comprehension and interpretation, of the phenomena encountered in the glass transition range.

Materials and methods

Apparatus

A Mettler TA 2000B heat flow DSC apparatus was used. It was controlled by an H.P.85 microcomputer, which measured the calorimetric signal via a digital voltmeter. The apparatus was calibrated for temperature and heat flow using the temperatures and enthalpies of melting of high purity metals and compounds [15].

The calorimeter was flushed with pure and dry argon. Argon was used owing to its chemical inertia, density and low thermal conductivity.

All DSC scans were performed with a heating rate of 3.5 K min^{-1} in the temperature range –50 to 100°C. Programmed cooling rate of 10 K min^{-1} were used.

Materials

Crystalline maltitol (4-O-a-*D*-glucopyranosyl-*D*-glucitol: $C_{12}H_{22}O_{11}$) was supplied by Roquette Frères Company. Its purity as measured by DSC [16, 17], was found to be 100%.

The glass transition temperature is 323 K and the change in specific heat capacity at T_g is 0.72 J g^{-1} K^{-1}. DSC study of the thermal behavior of vitreous maltitol showed that its glass transition is situated in a temperature range that can be explored easily by means of experiments.

In addition, it is a compound with a simple thermal behavior (no polymorphism was observed). No trace of recrystallization was detected in the glass transition range. Recrystallization would make the thermodynamic study of the glass relaxation complex and unclear. Maltitol is thus an adequate material for the study to be carried out.

Preparation of the samples

Glass transition is highly sensitive to impurity. Glass must be obtained in a reliable and reproducible manner under similar experimental conditions. For this reason, a particular technique was used to prepare maltitol glass. All the operations were done in a glove box under a dry argon atmosphere.

Crystalline maltitol is introduced in a glassy carbon crucible and heated, using an electrical furnace, to 180°C (melting temperature of maltitol is 145°C) and kept at that temperature for 15 min. The liquid is poured between two contrarotating metallic cylinders cooled at 0°C. This allows for a uniform and regular quenching.

The final product (glass) is a small plate with a constant thickness (1 mm). It is stored at –30°C. Experiments have shown that no measurable change occurs, even on long duration (1 month), at this temperature.

The samples were sealed in aluminum crucibles (40 µl), weighed and transferred to a thermoregulated bath previously maintained at the annealing temperature $T_a < T_g$. The annealing temperatures were: 293, 298, 303 and 308 K. For each temperature, the annealing time t_a varied from 1 to 96 h.

Reference glass

The present study is based on the comparison of the thermal behavior of the annealed glass (T_a, t_a) to a quenched one taken as a reference. In a first step, the quenched glass prepared as described before was taken as reference.

However, the inconvenience of using this reference is that a possible shift when superposing the DSC curves may arise from a mass difference between the quenched and annealed glass crucibles. To avoid this problem, the same sample must be used to obtain the annealed and the quenched (reference) glasses. For this reason the following procedure was used to run the experiments:
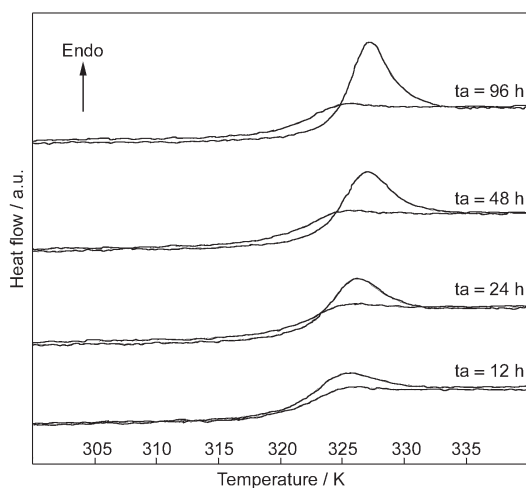
- the annealed sample is introduced in the calorimeter previously cooled at –50°C,
- measurement of the DSC curve of the annealed sample from –50 to 100°C with a heating rate of 3.5 K min^{-1} is done,
- the liquid is cooled from 100 to –50°C with a cooling rate of 30 K min^{-1},
- the DSC curve of this quenched glass is measured from –50 to 100°C with a heating rate of 3.5 K min^{-1}.

Thereafter, the quenched glass prepared inside the calorimeter will be taken as a reference to calculate the relaxation enthalpy.

Results

Influence of annealing on the thermal behavior of maltitol glass

In Fig. 1 are plotted the DSC curves recorded, from –50 to 100°C, after annealing at 298 K for different annealing times. For comparison, the corresponding curve with no thermal treatment (reference) is also shown.
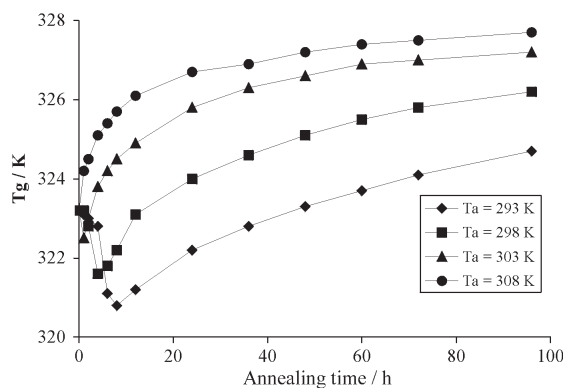

Fig. 1 DSC curves of maltitol glass after annealing at T_a=298 K, for comparison, DSC curve of non-annealed glass (reference glass) is also plotted

DSC curves of annealed maltitol glass show an endothermal effect (overshoot) in the glass transition range. Both the location and the amplitude of this effect are sensitive to the annealing parameters. Its amplitude increases with increasing annealing time. This increase is more rapid when the annealing temperature is higher and close to the glass transition temperature.

Influence of the annealing on the glass transition temperature of maltitol glass

For reliability and reproducibility reasons, the glass transition temperature T_g was taken as the inflexion point of the DSC curve associated to the glass transition. This determination does not depend on the choice of the base lines to calculate the heat capacity change.

In Fig. 2, glass transition temperature as a function of annealing time is plotted for different annealing temperatures.

Fig. 2 Variation of the glass transition temperature T_g of maltitol glass with annealing parameters (T_a, t_a). T_a, annealing temperature; t_a, annealing time

For low annealing temperatures, the behavior depends on whether the annealing time is shorter or longer than 10 h. The glass transition appears at temperatures below T_g of the reference glass (T_g=323 K) for short annealing time (1 to 10 h). When annealing time increases, the glass transition moves towards higher temperatures.

However, for the higher annealing temperatures (308 K), the glass transition temperature increases and shifts from 323 to 328 K as the annealing time increases from 1 to 96 h.

It should be noticed that this behavior does not agree with the schemiatic enthalpic diagram $H=f(T, t)$ found in literature [6–8]. According to this diagram, the glass transition should appear at lower temperatures as the annealing time increases, independently of the annealing temperature.

Influence of the annealing time and temperature on the fictive temperature of maltitol glass

Fictive temperature is defined as the temperature where the liquid has the same configuration as the corresponding glass [11, 13, 18]. In an enthalpic diagram, at the fictive temperature T_{fictive}, the enthalpy of the glass is equal to that of the liquid [19].

Fictive temperatures of maltitol glass are calculated using the procedure reported by Moynihan *et al.* [13] and Flynn [18]. Figure 3 shows an example of the determination of fictive temperature from the DSC curve of maltitol glass.

The following operations are applied:

- determination of the base line for the integration of the curve $C_p=f(T)$,
- integration of the curve $C_p=f(T)$,
- calculation of the enthalpic curve of the liquid,
- extrapolation of the enthalpic curve of the liquid and that of the glass.

The values of the fictive temperature obtained using the above described method are summarized in Table 1.

Whatever the annealing temperature, fictive temperature of annealed glass decreases as the annealing time increases. This result agrees with those reported in literature [20].
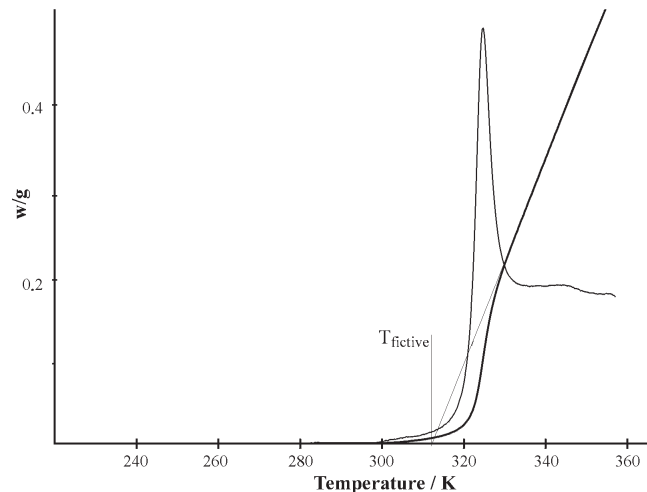
The empiric relation:

$$T_{\text{fictive}}=(a+bT_a)\ln t_a+c \qquad (2)$$

allows to express the variation of the fictive temperature with annealing parameters (T_a, t_a). The best adjustment was obtained, using the least squares method, with the following constants:

$$a=5.38087, b=-0.01926, c=319.93$$

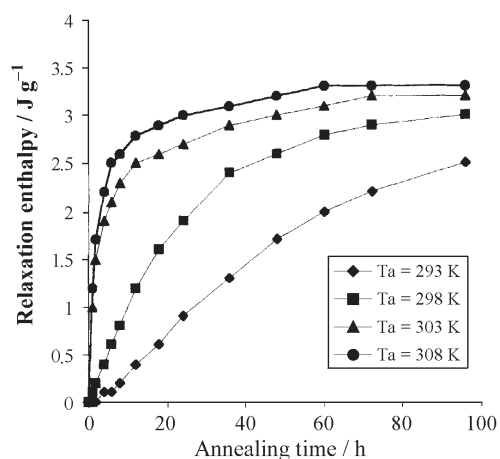Note that, in equation (2), the annealing time t_a is expressed in seconds.

Fig. 3 Determination of the fictive temperature of maltitol glass

Table 1 Fictive temperature of maltitol glass after annealing, T_a – annealing temperature: t_a – annealing time

t_a/h	Fictive temperature			
	T_a=293 K	T_a=298 K	T_a=303 K	T_a=308 K
0	319.3	319.3	319.3	319.3
1	320.2	318.7	314.9	317.5
2	320.5	318.5	314.3	317.5
4	319.2	318.4	314.0	312.8
6	318.1	318.7	314.0	313.7
8	317.4	316.9	314.6	313.9
12	317.0	316.9	313.0	313.9
18	315.7	316.3	313.5	312.7
24	313.9	315.6	314.0	312.1
36	315.4	316.7	312.8	312.4
48	315.1	316.4	312.2	313.3
60	315.4	316.0	312.7	311.8
72	315.1	315.1	312.0	311.5
96	315.4	313.9	311.9	311.0

Influence of the annealing time and temperature on the enthalpy of maltitol glass

In Fig. 4 the evolution of the relaxation enthalpy as a function of annealing time for different annealing temperatures is shown. The values of $\Delta_r H_T^0$ obtained using equation (1) are given in Table 2.
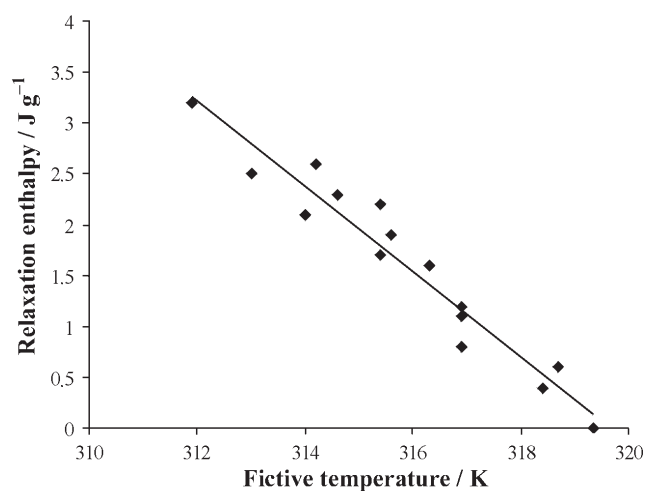

Fig. 4 Variation of the relaxation enthalpy ($-\Delta_r H_T^0$) of maltitol glass with annealing parameters (T_a, t_a). T_a, annealing temperature; t_a, annealing time

Table 2 Relaxation enthalpy $\Delta_r H_T^0$ of maltitol glass after annealing, T_a – annealing temperature; t_a – annealing time

t_a/h	$\Delta_r H_T^0$/J g^{-1}			
	T_a=293 K	T_a=298 K	T_a=303 K	T_a=308 K
0	0	0	0	0
1	0	–0.1	–1.0	–1.2
2	0	–0.2	–1.5	–1.7
4	–0.1	–0.4	–1.9	–2.2
6	–0.1	–0.6	–2.1	–2.5
8	–0.2	–0.8	–2.3	–2.6
12	–0.4	–1.2	–2.5	–2.8
18	–0.6	–1.6	–2.6	–2.9
24	–0.9	–1.9	–2.7	–3.0
36	–1.3	–2.4	–2.9	–3.1
48	–1.7	–2.6	–3.0	–3.2
60	–2.0	–2.8	–3.1	–3.3
72	–2.2	–2.9	–3.2	–3.3
96	–2.5	–3.0	–3.2	–3.3

The relaxation enthalpy reaches, likely, a limit value (–3.3 J g^{-1}) which does not depend on the annealing temperature. This value is rapidly reached for the higher annealing temperatures 303 and 308 K.

Fig. 5 Relaxation enthalpy ($-\Delta_r H_T^0$) of maltitol glass *vs.* its fictive temperature

Relationship between relaxation enthalpy and fictive temperature

In Fig. 5 the variation of the relaxation enthalpy of annealed glass $\Delta_r H_T^0$ *vs.* fictive temperature T_{fic} for all the annealing parameters (T_a, t_a) is shown. A straight line is obtained.

$$-\Delta_r H_T^0 = aT_{fic} + b \tag{3}$$

with $a = -0.4034$ and $b = 129.1169$

$$\Delta_r H_T^0 = 0.4034(T_{fic} - 320.05) \tag{4}$$

where, $\Delta_r H_T^0$ and T_{fic} are expressed in (J g^{-1}) and K respectively.

For $\Delta_r H_T^0 = 0$, $(t_a = 0)$, non-annealed glass, $T_{fic} = 320.05$ K. In addition, the application of the first law of thermodynamic to the enthalpic diagram of annealed glass lead to the relation:

$$\Delta_r H_T^0 = \Delta C_p(T_{fic} - T_0) \tag{5}$$

where $\Delta C_p = C_{pl} - C_{pg} =$ heat capacity jump at the glass transition, $T_{fic} =$ fictive temperature of the annealed glass, $T_0 =$ fictive temperature of the non-annealed glass (quenched glass).

Comparison of equations (4) and (5) leads to: $-C_p = 0.4034$ J g^{-1} K^{-1}. The measured value of maltitol glass is 0.72 J g^{-1} K^{-1}. This difference may arise from the method used to determine the fictive temperature of glass. Indeed, in this method, the heat capacity of the glass and liquid are considered independent of temperature. $T_0 = 320.05$ K, this value is close to that measured for the non-annealed maltitol glass $(T_{fic} = 319.30$ K).

Note that a similar relation was given by Bauwens–Crowed and Bauwens in [1] where, instead of the 'usual' fictive temperature, structural temperature θ is used. The latter temperature is calculated using a differential equation which stems from the volume and activation concepts. It should be noticed that the fictive temperature can be a very practical way of calculating $\Delta_r H_T^0$ provided ΔC_p is known with high precision. This is difficult in practice, since ΔC_p appreciably depends on the choice of baselines used to calculate its value.

Discussions

At constant temperature and pressure, enthalpy of glass decreases $(\Delta_r H_T^0 < 0)$. It is thus impossible to describe and represent correctly the thermodynamic functions of glass using temperatures T and pressure p, only.

As shown by Prigogine and Defay [14], *A* supplementary variable must be introduced, allowing the variation of the enthalpy of glass, at constant temperature and pressure, to be taken into account.

In addition to this, the relaxation enthalpy of glass depends on annealing time t_a and temperature T_a. For a fixed annealing time t_a, the relaxation enthalpy increases, in

absolute value, as the annealing temperature increases. This result indicates that the variable to be added to p and T, is time and temperature dependent.

Let us take the annealing process as a transformation proceeding from the initial state (reference) to a final state, which is the annealed glass. If ξ is the degree of advance of this transformation, we can then express the enthalpy change of the glass, when the transformation occurs, as follow:

$$dH = \left(\frac{\partial H}{\partial T}\right)_{p\xi} dT + \left(\frac{\partial H}{\partial p}\right)_{T\xi} dp + \left(\frac{\partial H}{\partial \xi}\right)_{Tp} d\xi \tag{6}$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{p\xi} dT + \left(\frac{\partial H}{\partial \xi}\right)_{Tp} d\xi \quad \text{at constant pressure} \tag{7}$$

Then,

$$C_p = \left(\frac{dH}{dT}\right)_p = \left(\frac{\partial H}{\partial T}\right)_{p\xi} + \left(\frac{\partial H}{\partial \xi}\right)_{Tp}\left(\frac{d\xi}{dT}\right) = C_{p\xi} + \Delta_r H\left(\frac{d\xi}{dT}\right) \tag{8}$$

where

$$C_{p\xi} = \left(\frac{\partial H}{\partial T}\right)_{p\xi} \quad \text{and} \quad \Delta_r H = \left(\frac{\partial H}{\partial \xi}\right)_{Tp}$$

$C_{p\xi}$ is the thermal capacity at constant pressure and composition sometime called the true heat capacity of the system. $\Delta_r H$ is the enthalpy of the transformation at fixed T and p. $\Delta_r H(d\xi/dT)$ is due to a variation of the degree of advance of the transformation vs. temperature. According to Prigogine and Defay [14], ξ may characterize the structure or the configuration of the system.

In a particular case (annealing) in which temperature and pressure are constant, the above equation is written as:

$$dH = \left(\frac{\partial H}{\partial \xi}\right)_{Tp} d\xi \tag{9}$$

This equation states that, at constant temperature and pressure, the variation of the enthalpy of glass corresponds to the variation of the degree of advance of the transformation and, therefore, to a change of the composition of the system. If several transformations occur;

$$dH = \sum_{1}^{n} \left(\frac{\partial H}{\partial \xi_i}\right)_{Tp} d\xi_i \tag{10}$$

We can conclude that the system of variables (T, p, ξ) allows a better characterization of the enthalpic state of the glass.

$\Delta_r H$ also corresponds to an enthalpic effect taking place at the glass transition. Its relative sign would be positive on heating and negative on cooling or annealing.
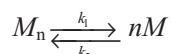
Because the variation of the extent of a transformation with temperature ($d\xi/dT$) can be written as:

$$\left(\frac{d\xi}{dT}\right)=\left(\frac{d\xi}{dt}\right)\left(\frac{dt}{dT}\right)$$

The dependence on time (kinetics) is thus introduced. The simplest way of expressing ($d\xi/dt$) in chemical kinetics is:

$$\left(\frac{d\xi}{dt}\right)=f(\xi)k(T)$$

On the other side, enthalpy and entropy of glass decrease during annealing. The enthalpic effect produced can be attributed to the formation of molecular associations or aggregates, the size of which depends on the temperature and annealing time. The annealing process can then be assimilated to a physicochemical transformation of molecular associations:

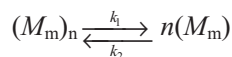$$M_n \underset{k_2}{\overset{k_1}{\rightleftarrows}} nM$$

where M and n are respectively the maltitol molecule and the number of the associated maltitol molecules. These associations involve only hydrogen or van der Waals bonding.
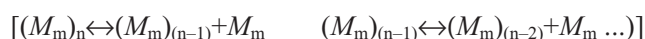
This transformation is only a simple representation of all the transformations that could occur when annealing glass. Other transformations should be considered:

$$(M_n \leftrightarrow M_{(n-1)}+M \qquad M_{(n-1)} \leftrightarrow M_{(n-2)}+M \ ...)$$

It is likely that maltitol molecules are already associated in the liquid state:

$$(M_m)_n \underset{k_2}{\overset{k_1}{\rightleftarrows}} n(M_m)$$

with $m<n$.

$$[(M_m)_n \leftrightarrow (M_m)_{(n-1)}+M_m \qquad (M_m)_{(n-1)} \leftrightarrow (M_m)_{(n-2)}+M_m \ ...)]$$

The enthalpic effect (endothermic) observed, on heating, at the glass transition corresponds to the destruction of molecular associations formed when glass is annealed. The formation of the molecular associations is more rapid as the annealing temperature is higher and close to the glass transition temperature. Thereafter, the resultant endothermal enthalpic effect will be more important. The glass transition of the annealed glass should, therefore, take place at high temperatures against the reference glass.

A previous study in the laboratory [20] on the glass transition of glycerol by step heating DSC has shown that the observed apparent heat capacity in the glass transition range is, indeed, the sum of two terms:

- change in true heat capacity from that of the liquid to that of glass (below the glass transition range)
- a temperature and time dependent enthalpy effect (configurational heat capacity), very likely due to molecular associations.

A simulation of the calorimetric signal in good agreement with experimental results, was made assuming the following equilibrium transformation of molecular associations in the glass transition range:

$$A_n \leftrightarrow nA$$

with A_n associations or clusters of the A species (A representing, as for example, molecular of glycerol). It is the formation (cooling) and destruction (heating) of the associated species that involves an enthalpic effect.

In this view, the concentration (or size) of associated species (clusters) in the glass transition range on cooling would be such that congealing of the structure of the liquid occurs, leading to the formation of a solid (glass) at lower temperatures (this would explain the change of true heat capacity, from liquid to that of a solid since degrees of freedom have been frozen in). On heating, the progressive destruction of these molecular associations takes place in the glass transition range. Note that the idea of molecular organizations in the vitreous state was already introduced by Tammann in 1933 [21] and more recently by Hoare [22]. The latter author advanced the idea that the glass transition on heating could correspond to the 'melting' of clusters present in the vitreous state. A recent study by Jabrane *et al.* [23] on the application of Van Laar type equations to the composition dependence of T_g reinforced this view.

According to Fig. 4 it is likely that the relaxation enthalpy reaches a limit value (-3.3 J g^{-1}) for a sufficiently long time. This limit does not depend on the annealing temperature and corresponds likely to a metastable equilibrium state. The curves show that the higher the annealing temperature is, the faster the equilibrium is reached.

Figure 2 shows that the glass transition shifts towards low temperatures for short annealing times when annealing is carried out at low temperatures. This displacement let us think that at least two dual phenomena occur when glass is annealed. A first process, which is rapid takes place after short annealing times and a second one which is very slow.

These phenomena seem to be simultaneous, otherwise the glass transition temperature of the annealed glass at 308 K (Fig. 2) should decrease for the short annealing times as is the case for other annealing temperatures. This behavior is in agreement with the results obtained by Boesh *et al.* and Tauke *et al.* [5, 6]. These results are to be correlated to the frequency dependent α and β relaxation processes.

Therefore, in addition to pressure and temperature, supplementary macroscopic thermodynamic variables are necessary for a correct description of the studied glass. We believe that these variables are the degrees of advance of the above mentioned transformations. These transformations are temperature and time dependent, and are most probably due to molecular associations. These results joint those obtained by Claudy *et al.* [24] when they studied the isothermal relaxation of glycerol glass.

From equation (5), it can be deduced that the fictive temperature is expressed in terms of temperature of the relaxation enthalpy. Consequently, the fictive temperature is a mean parameter representing, in terms of temperature, the supplementary thermodynamic variables, to be added to p and T, that are necessary for a correct ther-

modynamic description of glass. These supplementary variables are the degrees of advance of the transformations of molecular associations, taking place in the glass transition range during the thermal treatment of annealing. On a microscopic level, the complexity of the molecular processes may be such that, very likely, there exists a distribution of molecular mechanisms.

Conclusions

The influence of the thermal treatments, below the glass transition temperature, on the thermal behavior and enthalpy of maltitol glass was studied using differential scanning calorimetry.

The origin and the nature of the thermal effect produced by the annealing were assigned to a physicochemical transformation of molecular associations, in the glass, the size of which (or concentration) depends on annealing parameters.

To describe correctly the properties of glasses, it is necessary, in addition to p and T, to introduce another parameter, namely the degree of advance of the above mentioned transformation, allowing the enthalpic effect in the glass transition to be taken into account.

The annealed glass, for a sufficiently long time, is a metastable equilibrium state.

The proposed model enables a correct interpretation of the glass relaxation processes and gives key information on the comprehension of the glass transition phenomenon.

A linear relation was also found between fictive temperature and relaxation enthalpy after annealing experiments were performed. This well-known result was established from the experimental results of this study. The fictive temperature is, consequently, the expression in terms of temperature of relaxation enthalpy. As a result, the fictive temperature is a mean parameter, which expresses in terms of temperature, the variable supplementary to pressure and temperature that is necessary for a correct description of the vitreous state, i.e. $T_{fic}=f(\xi)$.

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