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Study of the respective binary phase diagrams of sorbitol with mannitol, maltitol and water

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Abstract

Differential scanning calorimetry (DSC) was used to investigate the thermal behaviour of sorbitol, mannitol, maltitol and to establish the following phase diagrams: sorbitol/mannitol, sorbitol/maltitol, sorbitol/water and maltitol/water. Pure sorbitol and maltitol (4-Oα-glucopyranosyl-*D*-glucitol) vitrified uniquely upon cooling, once obtained under a melt form. Mannitol crystallized systematically in our conditions. These differences in behavior were discussed in terms of different molecular conformations in the liquid and crystalline states for sorbitol (hence, the difficulty to crystallize), whereas mannitol would present the same conformations in the two states. For sorbitol/mannitol and sorbitol/maltitol mixtures, the equilibrium phases could not be obtained (despite annealing experiments being carried out) and only the out of equilibrium phase diagrams were established. The tentative equilibrium sorbitol/water and mannitol/water phase diagrams were constructed but no hydrates were observed in our conditions (synthetic preparation of samples). The maltitol/water phase diagram presented simpler behavior than sorbitol/water despite the fact that maltitol is a larger and more complicated molecule (it is a derived sorbitol molecule).

Keywords: DSC; Sorbitol; Polyol; Water; Conformations; Glass/crystal

1. Introduction

Hexitols are polyols corresponding to the general formula CH_2OH–$(CHOH)_4$–CH_2OH. Among them sorbitol is used frequently in the industrial manufacture of food ingredients [1–3]. It is of particular interest because it is easily compressible (tabletting), non-carciogenic and presents a large variety of polymorphic forms [4–11] (Γ being the preferred for commercial applications). On the negative side, it is hygroscopic and requires controlled environment conditions during the production. The present work would be of interest to the candy industry. Indeed, sorbitol for example can be used both in the manufacture of polyol-based boiled sweets and chewing gums. In the case of boiled sweets, sorbitol cannot be used alone (its T_g is too low) and must be used with other polyols whose function is to increase T_g and viscosity. Maltitol, for example, seems to be a very good candidate along with some hydrogenated oligosaccharides.

A previous study [12,13] concerning the thermal behavior of hexitols: sorbitol, iditol, mannitol and dulcitol Fig. 1 enabled us to classify them by pairs: sorbitol and iditol on the one hand and mannitol and dulcitol on the other hand. Indeed, mannitol and dulcitol crystallize easily from their melt, whereas

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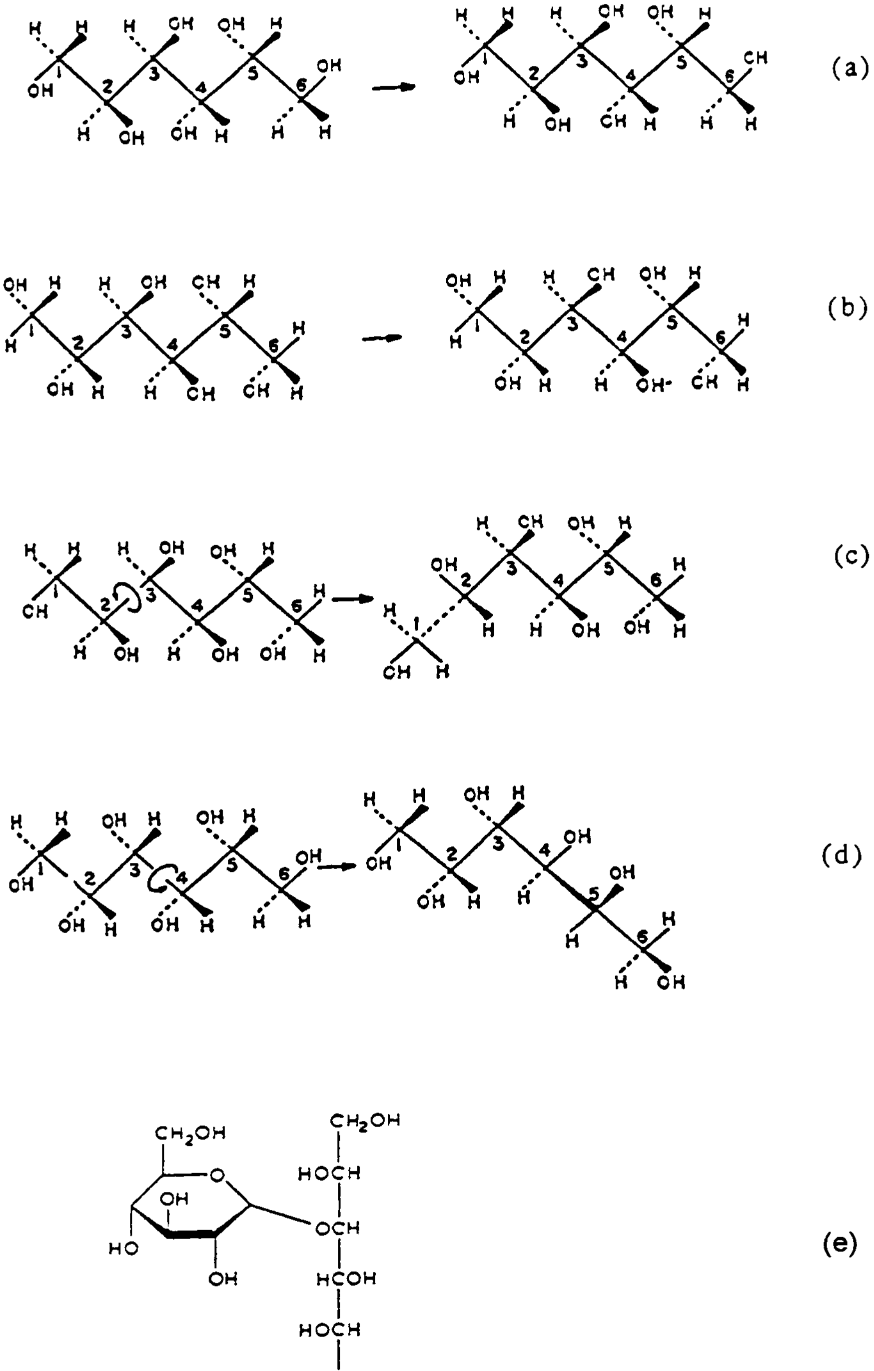

Fig. 1. Molecular conformations of (a–d) hexitols in the 'free state' (left) and in the crystal (right): (a) dulcitol, (b) D-mannitol, (c) sorbitol, (d) L-ditiol (e) maltitol (4-O-α-glucopyranosyl-*D*-glucitol).

sorbitol and iditol vitrify systematically. For that matter, mannitol and dulcitol present higher melting temperatures and larger melting enthalpies. These differences were attributed to different molecular conformations in the solid state.

In this paper, the influence of the presence of various quantities of mannitol in sorbitol samples on the crystallization and vitrification of the latter will be studied (will the presence of mannitol lead to the crystallization of sorbitol?). The same study will be carried out with maltitol/sorbitol mixtures. Indeed, maltitol [14,15] (Fig. 1) is a frequently used polyol which can be considered as a substituted or derived sorbitol molecule (4-O-α-glucopyranosyl-*D*-gulcitol). Maltitol vitrifies systematically once obtained under the melt form.

This paper will also concern the investigation of the possible existence of sorbitol and maltitol hydrates in the sorbitol/water and maltitol/water equilibrium phase diagrams. In the case of sorbitol, several authors concluded to the existence of hydrates [8–11]: a hydrate containing three molecules of sorbitol for two molecules of water [10] and obtained by recrystallization from purified aqueous solutions (70% in weight); a hemihydrate containing one molecule of water for two of sorbitol and monohydrate [11].

2. Experimental

A DSC Mettler TA 8000 calorimeter was used. It was calibrated for temperature and heat flow using the temperatures and enthalpies of melting of high purity metals and compounds. The calorimeter was flushed with pure dry argon.

Crystalline maltitol with a purity >99% was supplied by Roquette Fréres. Crystalline sorbitol and mannitol with a purity >99% were purchased from Aldrich. Samples were prepared by mixing the corresponding compounds (synthetic method), in the solid state (sorbitol/mannitol, sorbitol/maltitol and high polyol content solutions) or liquid state (high water content solutions). They were then sealed in aluminum crucibles. Masses were in the range from 20 mg to 40 mg.

All DSC scans were performed at a heating rate of 3.5 K min^{-1}. Programmed cooling rates of 10 Kmin^{-1} were used. Annealing experiments were performed at the peak temperature of the crystallization events to obtain the equilibrium phases.

The glass transition temperature T_g was taken as the inflection point of the change in the calorimetric signal associated with the glass transition. The crystallization temperature T_c was taken as the intersection of the slope of the exothermal crystallization event and the base line. The melting temperature T_m of the pure compounds was determined using the DSC purity method. Finally, the liquidus temperature T_l was taken as the peak of the endothermal dissolution event.

3. Results

3.1. Thermal behaviour of pure mannitol, sorbitol and maltitol

The thermal characteristics of the three polyols upon heating (first scan) and upon reheating following a programmed cooling at 10 Kmin^{-1} (second scan) are summarized in Table 1. In our conditions, sorbitol and maltitol vitrified systematically once obtained under the melt form. On the contrary, mannitol crystallized during programmed cooling and no glass transition was observed on the second DSC scan. However, quenched mannitol samples (liquid nitrogen) presented glass transition (14.6°C) upon reheating followed by cold crystallization and then melting of the sample.

3.2. x Sorbitol – (1−x) mannitol phase diagram

The first and second scans of a sample with composition $x = 0.53$ are shown (Fig. 2). The first scan Fig. 2(a) showed the separate melting of the two polyols. The second scan (Fig. 2(b)) exhibited glass

Table 1
Thermal characteristics of the studied polyols

	T_m (°C)[a]	ΔH_m/(Jg^{-1})[a]	T_g (°C)[b]
Sorbitol	100.7	196	−1.3
Mannitol	169.0	326	–
Maltitol	149.0	173	50

[a] First DSC scan.
[b] Second DSC scan following programmed cooling at 10°C min^{-1}. T_g, glass transition temperature; T_m, melting temperature, ΔH_m, melting enthalpy.

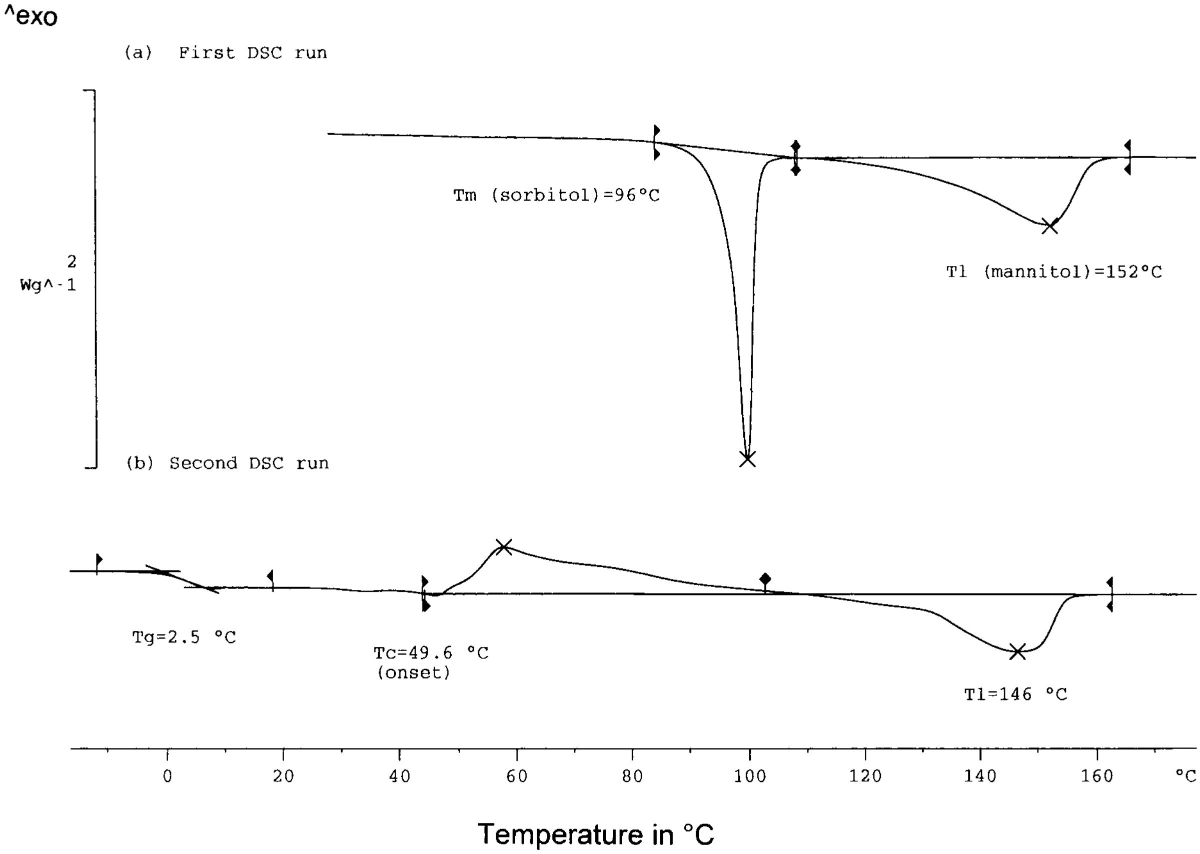

Fig. 2. DSC runs of a sample with composition $x = 0.53$ in the x sorbitol $(1-x)$ mannitol phase diagram. (a) First DSC run showing the separate melting of the two polyols; (b) second DSC run (after programmed cooling at 10°min^{-1}) showing glass transition crystallisation and dissolution.

transition, crystallization of mannitol followed by the dissolution of mannitol. Fig. 3 represents the out of equilibrium phase diagram (constructed using the second DSC scans) illustrating T_g, T_c and T_l. Three types of behavior were observed depending on composition:

- For $0.86 < x \leq 1$ mixtures, only glass transition was detected.
- For $0.4 \leq x < 0.86$ mixtures, glass transition, crystallization of mannitol and dissolution were observed. Note that crystallization of mannitol and dissolution were observed. Note that crystallization of mannitol occurs down to $x \approx 0.86$, i.e., a mixture that is relatively poor in mannitol.
- $0 < x < 0.4$ mixtures demonstrated glass transition and dissolution of mannitol, the latter crystallizing on cooling. Note that for $x < 0.3$ mixtures, the amplitude of glass transition was too weak to permit a correct determination of T_g.

Finally, no sign of sorbitol crystallization was detected even when annealing experiments were performed. Thus, it was not possible to obtain the equilibrium phases in our conditions.

The results are presented in Table 2.

3.3. x Sorbitol – (1−x) maltitol

A first DSC scan showed the separate melting of the two polyols for all compositions. Upon reheating, the second DSC runs presented glass transition only and

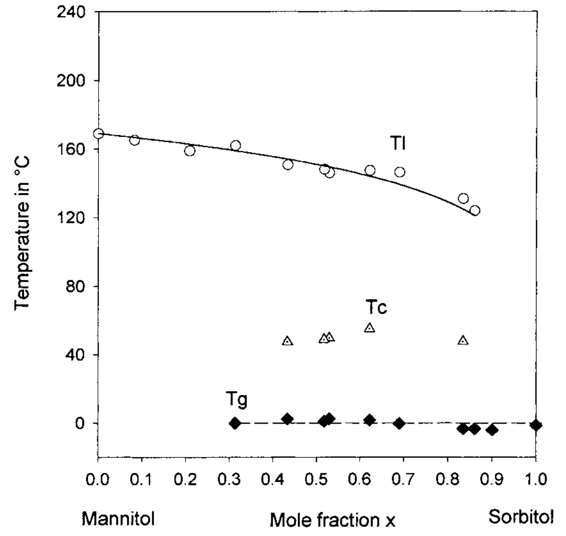

Fig. 3. Out of equilibrium x sorbitol – $(1-x)$ mannitol phase diagram T_g, glass transition temperature; T_c; crystallisation temperature; T_l, liquidus temperature.

no sign of crystallization whatsoever. In other words, it was not possible to obtain equilibrium phases for this system.

Consequently, the out of equilibrium phase diagram presented in Fig. 4 consists of a glass transition curve in the whole composition range.

The results are reported in Table 3.

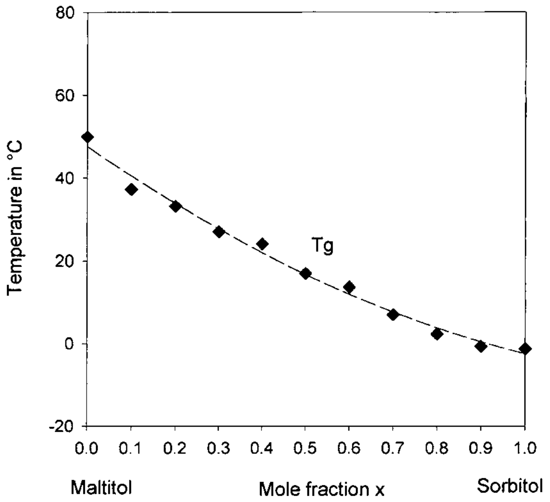

Fig. 4. Out of equilibrium x sorbitol – $(1-x)$ maltitol phase diagram T_g, glass transition temperature.

3.4. x Sorbitol – (1−x) water phase diagrams

Fig. 5 represents the tentative equilibrium phase diagram. Fig. 6 shows the out of equilibrium phase diagram. The corresponding results are summarized in Tables 4 and 5, respectively.

3.4.1. Tentative equilibrium phase diagram

The tentative equilibrium phase diagram (Fig. 5) was extrapolated from the experimental results. It was

Table 2
x Sorbitol – $(1-x)$ mannitol out of equilibrium phase diagram

x/(Mole fraction of sorbitol)	T_g (°C)	T_c (°C)	T_l (°C)	ΔH_{diss}/(Jg^{-1})
0.00	–	–	169.00	326.00
0.08	–	–	165.20	286.00
0.21	–	–	158.90	221.00
0.31	0.00	–	162.00	192.00
0.43	2.40	47.40	150.70	102.00
0.52	1.00	48.70	148.00	97.00
0.53	2.50	49.60	146.00	73.00
0.62	1.80	55.10	147.30	52.00
0.69	−0.30	–	146.20	57.00
0.83	−3.30	47.60	131.00	15.00
0.86	−3.30	–	124.00	3.00
0.96	−4.00	–	–	–
1.00	−1.30	–	–	–

T_g, glass transition temperature; T_c, crystallisation temperature, T_l, liquids temperature, ΔH_{diss}, dissolution enthalpy.

Table 3
x Sorbitol – $(1-x)$ maltitol out of equilibrium phase diagram

x/(Mole fraction of sorbitol)	T_g (°C)
0.00	50.00
0.10	37.30
0.20	33.20
0.30	27.00
0.40	24.05
0.50	17.00
0.60	13.70
0.70	7.00
0.80	2.30
0.90	−0.70
1.00	−1.30

T_g, glass transition temperature.

constructed using the first DSC scans. However, for samples showing a crystalliztion event, it was constructed upon reheating, after annealing experiments were performed at the peak temperature of the crystallization events. The experimental results showed three different thermal behaviors depending on the mole fraction x of sorbitol:

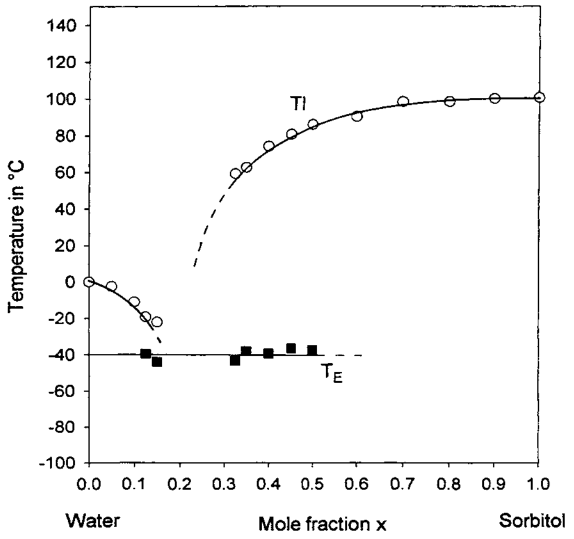

Fig. 5. Tentative equilibrium x sorbitol – $(1-x)$ water phase diagram. No hydrates were observed in our conditions (synthetic preparation of samples). Note the existence of a ‘glass well’ for $0.175 < x < 0.30$ T_l, liquidus temperature; T_E, eutectic temperature.

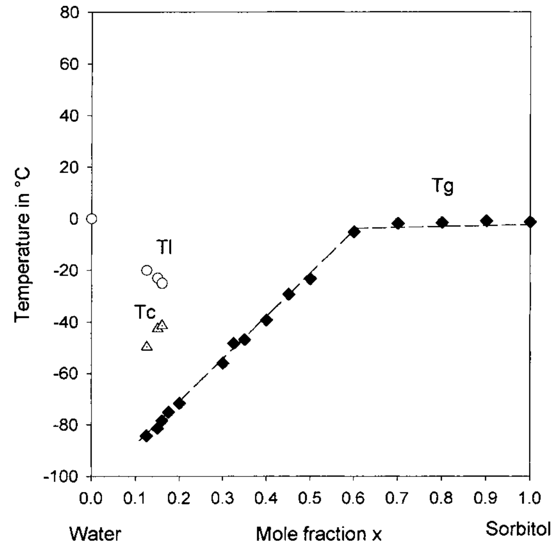

Fig. 6. Out of equilibrium x sorbitol – $(1-x)$ water phase diagram (constructed upon melting and reheating samples used to establish the equilibrium phase diagram (Fig. 5)). T_g, glass transition temperature; T_c; crystallisation temperature; T_l, liquidus temperature.

- High water content solution ($0.05 < x < 0.10$) and high sorbitol content solutions ($0.60 < x < 0.90$) demonstrated a dissolution event only (the amplitude of T_g was too weak to be interpreted).
- For $0.125 < x < 0.16$ and $0.325 < x < 0.50$ mixtures, an eutectic phase was observed in addition to dissolution (equilibrium phases). However, the determination of the enthalpy associated with the eutectic peak was difficult to determine for $x > 0.325$ mixtures because the eutectic peak was relatively spread out. As for $x < 0.16$ mixtures, no resolution between the eutectic and the dissolution peak was possible. Consequently, it was not possible to apply the Tamman method in order to determine the eutectic composition with accuracy. However, the representation of the dissolution enthalpies versus composition permitted to situate roughly the eutectic in the composition range of $0.16 < x < 0.20$. The mean eutectic temperature was determined as −40°C.
- $0.175 < x < 0.30$ mixtures featured glass transition only.

3.4.2. Out of equilibrium phase diagram

The out of equilibrium phase diagram was constructed after a programmed cooling of the samples

Table 4
x Sorbitol – $(1-x)$ water tentative equilibrium phase diagram

x/(Mole fraction of sorbitol)	T_1 (°C)	T_E (°C)	$\Delta H_{diss}/(Jg^{-1})$	$\Delta H_E/(Jg^{-1})$
0.00	0.00	–	334.00	–
0.05	−2.40	–	127.50	–
0.10	−11.00	–	62.00	–
0.13	−19.20	−39.50	56.00	–
0.15	−22.00	−44.00	45.00	–
0.33	59.20	−43.50	75.00	22.00
0.35	62.70	−38.00	80.00	24.00
0.40	74.20	−39.40	97.00	15.00
0.45	80.70	−36.60	105.00	10.00
0.50	86.00	−37.60	119.00	8.00
0.60	90.30	–	139.00	–
0.70	98.40	–	183.00	–
0.80	98.50	–	185.00	–
0.90	100.20	–	193.00	–
1.00	100.70	–	195.60	–

T_1, liquids temperature, ΔH_{diss}, dissolution enthalpy, T_E eutectic temperature, ΔH_E, eutectic enthalpy.

Table 5
x Sorbitol – $(1-x)$ water out of equilibrium phase diagram

x/(Mole fraction of sorbitol)	T_g (°C)	T_c (°C)	T_1 (°C)	$\Delta H_{diss}/(Jg^{-1})$
0.00	–	–	0.00	334.00
0.05	–	–	–	–
0.10	–	–	–	–
0.13	−84.20	−49.70	−20.00	40.00
0.15	−81.30	−42.60	−23.00	25.00
0.16	−78.30	−41.40	−25.00	3.60
0.18	−75.00	–	–	–
0.20	−71.60	–	–	–
0.30	−56.00	–	–	–
0.33	−48.30	–	–	–
0.35	−46.80	–	–	–
0.40	−39.20	–	–	–
0.45	−29.20	–	–	–
0.50	−23.30	–	–	–
0.60	−5.10	–	–	–
0.70	−1.90	–	–	–
0.80	−1.60	–	–	–
0.90	−0.90	–	–	–
1.00	−1.30	–	–	–

T_g – glass transition temperature; T_c – crystallisation temperature; T_1 – liquidus temperature; ΔH_{diss} – dissolution enthalpy.

used to establish the tentative equilibrium diagram, once they were completely melted.

The phase diagram is presented in Fig. 6. Three thermal behaviour were observed:

- $x > 0.160$ mixtures showed glass transition only.
- For $0.125 < x < 0.160$ mixtures, glass transition was followed by crystallization of water and then dissolution was observed.

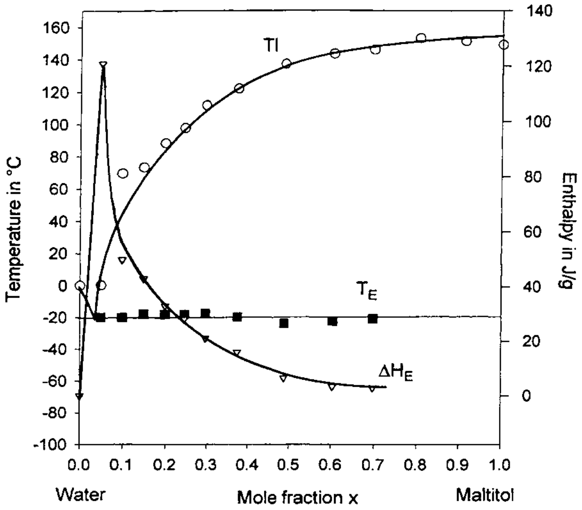

Fig. 7. Tentative equilibrium x maltitol – $(1-x)$ water phase diagram T_l, liquidus temperature; T_E eutectic temperature; ΔH_E, eutectic enthalpy.

- $x < 0.125$ mixtures exhibited a negligible residual glass transition followed by dissolution. Consequently, crystallization of water took place on cooling.

Finally, note that T_g increases linearly between $x = 0.125$ and $x = 0.60$, whereas it is practically constant for higher sorbitol content solutions.

3.5. x Maltitol – (1–x) water phase diagrams

3.5.1. Tentative equilibrium phase diagram

The tentative equilibrium phase diagram is shown in Fig. 7. Experimental results presented two thermal behaviors depending on composition:

- $0.10 < x < 1$ mixtures demonstrated equilibrium phases, i.e., an eutectic phase at a temperature of -19°C and dissolution. The eutectic composition lies between $x = 0.03$ and 0.05.
- For $x < 0.10$ mixtures, congealing of water occurred on cooling and only a dissolution peak was observed upon reheating.

Contrary to the sorbitol–water results (Section 3.4.1), we did not observe a composition domain presenting glass transition only (a glass well). Indeed, it was possible to determine a liquidus temperature in the whole composition range.

The results are summarized in Table 6

3.5.2. Out of equilibrium phase diagram

The diagram featured two thermal behaviors a illustrated in Fig. 8:

- $0.1 < x \leq 1$ mixtures showed a monotonous glass transition curve.
- For $x < 0.10$ mixtures, a minor residual glass transition followed by dissolution were observed. Consequently, crystallization of water occurred

Table 6
x Maltitol – $(1-x)$ water tentative equilibrium phase diagram

x/(Mole fraction of maltitol)	T_l (°C)	T_E (°C)	ΔH_{diss}/(Jg^{-1})	ΔH_E/(Jg^{-1})
0.00	0.00		330.00	0.00
0.05	0.20	−20.00		121.00
0.10	69.70	−20.00	44.00	50.00
0.15	73.40	−18.00	64.00	43.00
0.20	88.40	−18.30	72.00	33.00
0.24	97.80	−18.30	88.00	28.00
0.30	111.80	−17.60	95.00	21.00
0.37	122.10	−19.70	125.00	16.00
0.49	137.10	−23.90	135.00	6.50
0.60	143.40	−22.40	141.00	3.30
0.70	145.90	−20.90	149.10	2.90
0.80	153.10	–	167.00	–
0.91	151.20	–	173.00	–
1.00	149.00	–		–

T_l, liquidus temperature, ΔH_{diss}, dissolution enthalpy, T_E eutectic temperature, ΔH_E, eutectic enthalpy.

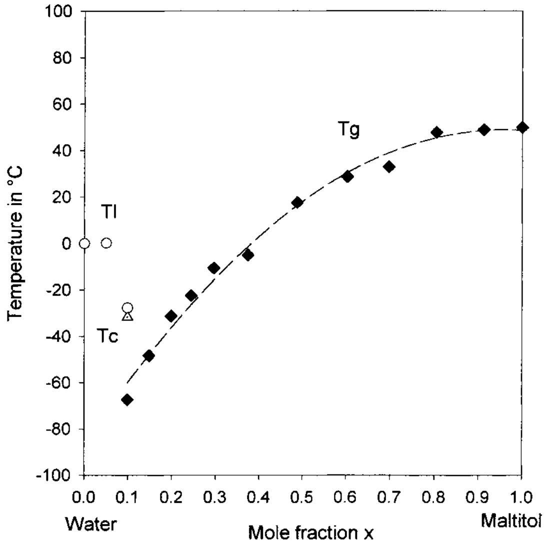

Fig. 8. Out of equilibrium x maltitol – $(1-x)$ water phase diagram (constructed upon melting and reheating samples used to establish the equilibrium phase diagram (Fig. 7)) T_g, glass transition temperature; T_c crystallisation temperature; T_l liquidus temperature.

on cooling the solutions (note, however, a minor crystallization exotherm obtained for $x = 0.10$).

The results are summarized in Table 7.

4. Discussion and conclusion

In this work, it was not possible to obtain the crystallization of sorbitol in the case of sorbitol/mannitol mixtures, whereas the solubility curve of mannitol was observed in a large domain of composition (Fig. 3). This is certainly due to the different molecular conformations of sorbitol and mannitol in the solid state as was discussed in [12,13]. Fig. 1 shows a schematic representation of the conformations of hexitols in the 'free' and crystalline states, as was established by Jeffery and Kim [16]. The mannitol and dulcitol molecules do not undergo deformations in the crystalline state contrary to sorbitol and iditol. Indeed, hexitols present a staggered conformation in the free state and the six atoms are located in the same plane. For sorbitol and iditol, the hydroxyls of alternated carbons point in the same direction which results in repulsive interactions and a de-stabilization of the molecules. Consequently, the sorbitol molecules must adopt a rotation around the C_2–C_3 bond to minimize this type of interactions in the crystalline state. This would be the reason why crystallization of sorbitol and iditol is very difficult once obtained under the melt form.

In our conditions, the presence of mannitol did not favor in any way the crystallization of sorbitol. As a consequence, the conformation of sorbitol in the liquid state seems to be the same as in pure liquid sorbitol

Table 7
x Maltitol – $(1-x)$ water out of equilibrium phase diagram

x/(Mole fraction of maltitol)	T_g/°C	T_c/°C	T_l/°C	ΔH_{diss}/(Jg^{-1})
0.00	–	–	0.00	334.00
0.05	–	–	0.20	119.00
0.10	−67.40	−31.60	−27.60	18.00
0.15	−48.30	–	–	–
0.20	−31.10	–	–	–
0.24	−22.30	–	–	–
0.30	−10.60	–	–	–
0.37	−5.00	–	–	–
0.49	17.60	–	–	–
0.60	28.70	–	–	–
0.70	33.00	–	–	–
0.80	47.90	–	–	–
0.91	49.00	–	–	–
1.00	50.00	–	–	–

T_g – glass transition temperature; T_c – crystallisation temperature; T_l – liquidus temperature, ΔH_{diss} – dissolution enthalpy.

and does not seem to be influenced by that of mannitol. It is difficult, however, to conclude as to the conformation of sorbitol in the liquid state (free state conformation or deformed conformation (Fig. 1)). Indeed, one may think to two reasons why sorbitol cannot be re-crystallized from its melt:

1. The molecules adopt the free state conformation in the liquid, hence the great difficulty to crystallize since it involves compulsory rotations of the molecules which may correspond to a large energy barrier jump.
2. The molecules adopt a deformed conformation in the liquid state (as in the crystal) but two types of conformations arise from the C_2–C_3 rotations on the one hand and the C_3–C_4 rotations on the other hand. As a consequence, the existence of the two conformations might hinder the formation of crystal nuclei or crystal growth. Note that the C_3–C_4 rotation has not been observed in the crystalline form.

In a previous paper [17], we discussed the influence of the existence of several molecular conformations on the crystallization and vitrification of smaller polyol molecules. For example, the presence of two enantiomers in the case of commercial 1,2-propanediol hinders nucleation and crystal growth of the latter compound. In the same way, it is very likely that the presence of conformations, other than the $\alpha\alpha$ conformation in which it crystallizes, makes the crystallization of glycerol difficult [18]. This is why seeding or undercooling for long periods of time are necessary.

In the case of the sorbitol/maltitol phase diagram (Fig. 4), no sign whatsoever of crystallization was detected. This can be readily explained by the fact that maltitol is a derived sorbitol molecule and would eventually present different conformations in the liquid and solid states as sorbitol. The crystallization of maltitol may also be sterically impeded by the presence of the pyranosil group (Fig. 1)

Finally, the tentative equilibrium sorbitol/water and maltitol/water phase diagrams did not reveal any presence of hydrates in our conditions (one should note, however, the sharp break in the T_g curve around $x \approx 0.6$ in the out of equilibrium diagram (Fig. 6), which might eventually point to the underlying existence of the hydrate observed by Quinquenet et al. [10]). However, the different hydrates mentioned in literature [8–11] were obtained by re-crystallization from aqueous solutions which was not our case. Given the size of the sorbitol and maltitol molecules, it might seem surprising that sorbitol/water mixtures (Section 3.4.1) feature of slightly more complicated behavior (presence of a 'glass well' for $0.175 < x < 0.30$ (Fig. 5)). This may be due to the existence of more molecular conformations in the case of sorbitol than in the case of maltitol (for which some conformations may be precluded by the presence of the pyranosil group) or to the existence of various polymorphic forms in the case of the former compound whereas no polymorphism was signalized for maltitol.

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