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POLYMORPHISM OF HYDRATED SORBITOL

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ABSTRACT

The different polymorphic forms of sorbitol have been obtained, and its vitreous state and their monotropic transitions studied in relation to water content. We have isolated a new hydrated form by crystallization in aqueous phase of ultrapure sorbitol. All these forms have been carefully characterized by differential scanning calorimetry, X-ray diffraction and IR spectroscopy.

The relation of sorbitol polymorphism to water content has been examined by different thermal and/or sorption–desorption treatments. The transitions between this new hydrated form and most of the sorbitol polymorphs are also described.

INTRODUCTION

D-Sorbitol is an acyclic polyol obtained by hydrogenation of D-glucose. It is highly soluble in water (2.3 g (g water)$^{-1}$ at room temperature [1]) and also in polar solvents [2].

In the solid state, it exhibits a monotropic complex polymorphism. There are several polymorphs of sorbitol with different melting points. The polymorphism of sorbitol has been studied mainly by melting point determinations [3–16] or calorimetry [7,8,12,13] and X-ray diffraction [3–8,12,14]. A vitreous state is also observed [17–19]. However, the available literature data deal with commercial products with no information about origin and purity.

The aim of this paper is to describe sorbitol polymorphism as fully as possible. First, a short review of the literature on this polymorphism is given. Starting from ultrapure sorbitol, we describe procedures used to obtain well defined polymorphs. A new hydrated polymorphic form was obtained and is described in this paper. Differential scanning calorimetry and X-ray diffraction were used with IR spectroscopy to characterize polymorphs and their phase transitions. Moreover, we attempted to relate this polymorphism to the hydration level of sorbitol.

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TABLE 1

Nomenclature and sorbitol polymorphs data reported in the literature

Melting point (° C)	Jeffrey, Park and coworkers [3,4,5,6]	Gal and coworkers [7,8,13]	Subramanian [12]	Du Ross [14–16]	This paper	Pfanstielh and Black [9]	Rose and Groepp [10]	Schwarz et al. [11]	Emodi [1]
47					SM1 [a]				
50					Hydrate [a]				
55		SM1	SM1			Monohydrate			
67				E	SM2				
75		SM2				Semihydrate		Semihydrate	
85–86	A [a]	A [a] (39.8)		Δ [a] and α [a]					
88			α [a] (37.7)		A [a] (45.0)				
90							Low melting	Anhydrous	γ
92	Γ or C [a]								
92.5									
94.5				β [a]	B [a] (41.4)				
96–97		B [a] (37.8)	β [a] (39.0)				High melting		
98.7					Γ [a] (45.0)				
99			Γ [a] (46.0)						
101				Γ [a]					
110–112						Anhydrous			Anhydrous
127	Racemic DL								

[a] X-ray diffraction data; (), melting enthalpies in cal g^{-1}; SM1 and SM2, solidified melt.

LITERATURE REVIEW ON SORBITOL POLYMORPHS

Table 1 is an attempt to summarize the available calorimetric and X-ray diffraction data reported in the literature. There is no agreement concerning the number of polymorphs, existence of hydrated species, melting points and nomenclature. The results obtained in this study are also indicated in this table.

The melting points of the different crystalline forms range from 55 to 110 °C [1–14]. The most stable polymorphs are called A, B, and C or Γ by Jeffrey, Park and co-workers [3–6]. To clarify the polymorph designation, we have adopted their nomenclature. However, reported polymorphs were generally obtained from commercial powders using methods which were not fully described [1,3–14]. In addition, melting point determination methods were similarly incompletely described leading to difficulties in identifying clearly the polymorphs obtained.

The only structure completely known is that of polymorph A obtained by evaporation of the compound in 95% ethanol solution [4,6]. The A and B polymorphic forms described by Sztatisz and coworkers [7,8] seem to correspond with Jeffrey and Park's A and C forms, respectively [3–6] *.

Also, X-ray diffraction data from Subramanian's *α* form [12] are identical to those given in refs. 4 and 6 for the racemic DL form.

The melting of the different polymorphs gives rise to a liquid which, when cooled, transforms to a vitreous state below a glass transition temperature reported to be from −2 to −9 °C [17–19]. According to Sztatisz and coworkers [7,8] and Subramanian [12], undercooled liquid storage at room temperature leads to the so-called "solidified melt" which exhibits two endothermic peaks at 55 and 75 °C. The solidified melt seems to correspond to the hydrated forms mentioned by Pfanstielh and Black [9] and Schwarz et al. [11].

MATERIALS AND METHODS

Ultrapure sorbitol (purity 99.9%) was obtained by successive chromatographic separations of Neosorb® 70/02 on simulated fluidized bed Duolite C204 type resin (Roquette patent Fr 2 454 830) and then crystallized from the purified aqueous solution (70% by dry weight). It crystallized into thin

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* After correction of their X-ray data using the formula deduced from Bragg's law

$$d = n\lambda/2\sin\left[0.5\arcsin\left(\frac{n\lambda}{2d_S}\right)\right]$$

where d_S is the distance calculated from ref. 7. In fact, the values reported by Sztatisz and coworkers correspond to reticular distances calculated from 2θ angles instead of θ angles.

TABLE 2

Comparison of atomic composition (C, H, O) determined by microanalysis of pure hydrated sorbitol, with calculated hydrate stoichiometries

Sorbitol	Calculated values				Hydrated sorbitol	
	Dry	$+(1/2)H_2O$	$+(2/3)H_2O$	$+1H_2O$	Sample 1	Sample 2
C(%)	39.56	37.70	37.19	36.00	37.86	37.60
H(%)	7.69	7.85	7.90	8.00	8.19	8.13
O(%)	52.75	54.45	54.91	56.13	52.63	53.26

needles (about 1 mm long). The purity of sorbitol was checked by means of HPLC (Waters apparatus using a Biorad Q15S type column and detection by refractive index).

The atomic composition (C, H, O) obtained by microanalysis corresponded to a non-stoichiometric hydrated form (Table 2).

The Γ and A polymorphs were obtained from pure hydrated sorbitol by several treatments (see below). The B polymorph was formed by thermal treatment of industrial sorbitol (purity 98%). Solidified melt was obtained by cooling the undercooled liquid (resulting from the Γ industrial polymorph melting) to room temperature following a few days' storage.

Calorimetric measurements were carried out on a DSC4 Perkin–Elmer differential scanning calorimeter equipped with a Cryoson cooling system. The apparatus was calibrated for temperature and enthalpy measurements with lauric and benzoic acids and cyclohexane at the rates of 4, 8, 20 and 40 °C $\min^{-1}$ [20]. Transition temperatures (T_0) were taken at the onset of the transition. Special thermal treatments including isotherms were achieved either on Perkin–Elmer and Thermanalyse or Arion calorimeters. All water : sorbitol compositions are expressed in % water per 100% dry pure sorbitol (w : w).

IR spectroscopy was performed on a Perkin–Elmer 1710 Fourier transform spectrometer, nujol mull.

Diffraction powder patterns of samples covered with thin mylar film were recorded on a Seifert apparatus equipped with a Berthold goniometer (Cu K_α radiation, Ni filtered, 40 kV, 10 mA, 1 min (degree $\theta)^{-1}$, 3000 counts $\sec^{-1}$, time constant 3 sec).

CHARACTERIZATION OF SORBITOL POLYMORPHS

The calorimetric heating scans of polymorphs of pure and hydrated sorbitol are shown in Fig. 1, and corresponding thermal data are given in Table 3. To simplify, and because of the importance of water in sorbitol crystallization, hydrate is shown as a polymorph.

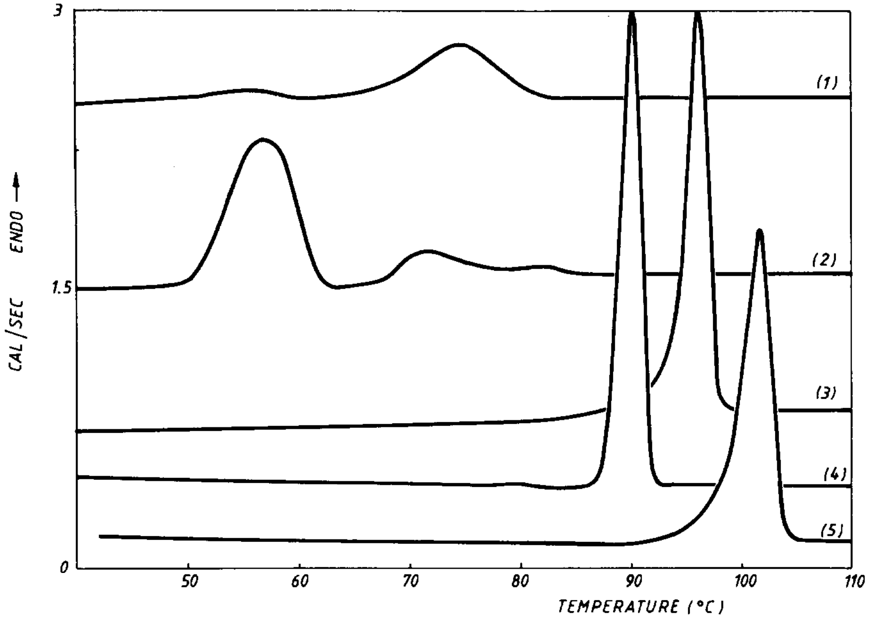

Fig. 1. Calorimetric scans of the different sorbitol polymorphs (scan rate 8°C min^{-1}). 1, Solidified melt; 2, hydrated form; 3, B form; 4, A form; 5, Γ form.

Unlike the A, B, and Γ polymorphs, which are characterized by a sharp melting endotherm, pure hydrated sorbitol and the solidified melt present complex thermal behaviour. The solidified melt exhibits two transitions (denoted SM1 and SM2). Whichever anhydrous polymorph melted, the undercooled liquid displays a glass transition temperature T_g, which is recorded near 0°C when the sample is reheated at 20°C min^{-1} (see below). As the T_g value depends on both the sample memory, that is to say of cooling and heating rates, and of the time–temperature history of the sample [21], and on water content (see below), the lower value reported [17–19] was related to sorbitol purity.

TABLE 3

Thermal properties of the crystalline polymorphic forms of sorbitol. T_0, onset melting temperature; ΔH, melting enthalpy and ΔS, melting entropy

Polymorphic form	T_0 (°C)	ΔH (cal g^{-1})	ΔS (cal mol^{-1} K^{-1})
Solidified melt SM1	47.2	4.4 [a]	2.5
SM2	67.0	13.8 [a]	7.4
Hydrate	50.4	35.1	21.0
B	94.3	41.4	20.5
A	88.1	45.0	22.7
Γ	98.7	45.0	22.0

[a] Partial melting enthalpy.

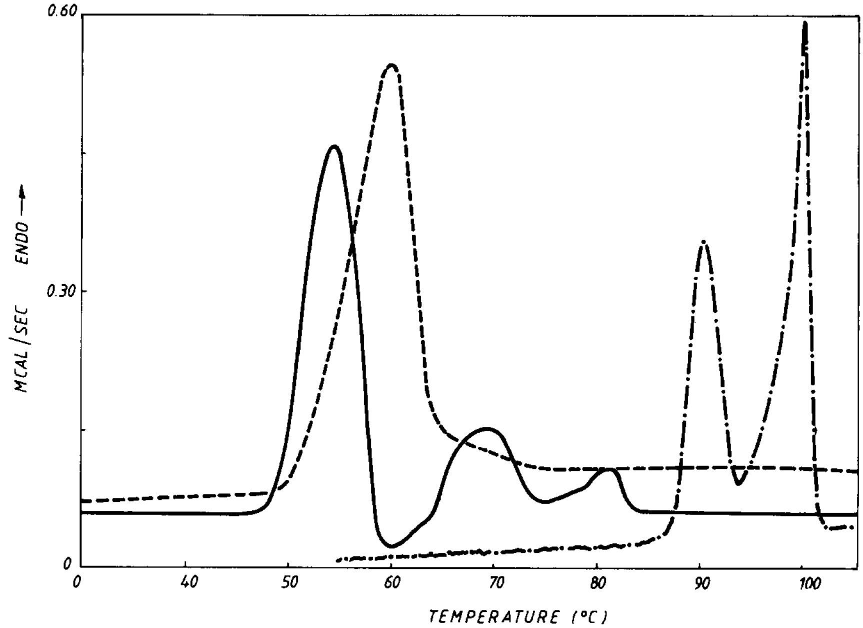

Fig. 2. DSC scans of pure hydrated sorbitol at 4 °C min^{-1} ———, and 40 °C min^{-1} - - - - - - (y scale 5.3), A and Γ forms at 8 °C min^{-1} obtained after thermal treatment (method 2) ·–·–· (y scale 2).

As shown in Fig. 1, the pure hydrated species presents a complex scan with a main endotherm ($\Delta H = 35.1$ cal g^{-1}) at 50.4 °C followed by an exothermic peak and two endotherms, at 58.6, 65.2 and 76.6 °C with −0.5, 7.6 and 1.2 cal g^{-1} enthalpies, respectively. The decrease in these latter three peaks as the heating rate increases indicates that the main endotherm corresponds to melting of the pure hydrated polymorph. The exotherm was attributed to a partial recrystallization via the liquid formed after the hydrate had melted. The following two endotherms are related to the melting of more stable forms (see below). By increasing the heating rate from 4 to 40 °C min^{-1}, only the main transition at 50.4 °C was detected (Fig. 2). This indicated that the hydrated form was a pure polymorph. An investigation of the complete structure of the sorbitol hydrate monocrystals is currently in progress.

Regarding the temperature, enthalpies and entropies of these polymorphs, we observed that, as expected for such monotropic substances, their crystallinities are related to melting points, ΔH and ΔS. The only exception is for the A form which exhibits enthalpy and entropy values comparable to those of the Γ form, but melts 10 °C below the Γ melting point. This behaviour may be attributed to the higher crystallinity exhibited by a particular form obtained by dehydration over P_2O_5 at room temperature from pure hydrated sorbitol crystals, as shown in Fig. 1 where the A melting endotherm peak is much sharper than with the Γ or even B forms.

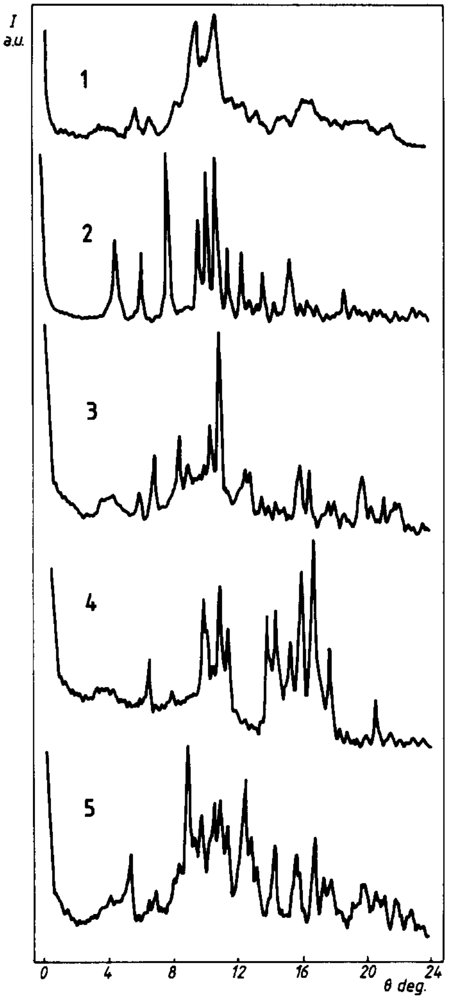

Fig. 3. X-ray powder patterns of the different sorbitol polymorphs. 1, Solidified melt; 2, hydrated form; 3, B form; 4, A form; 5, Γ form.

Starting from anhydrous sorbitol, the A form was generally crystallized from solvent [4,6] and was therefore more crystalline than the B and Γ forms generally given by thermal treatments. Also noteworthy was the thermal behaviour of industrial sorbitol (Neosorb® 20/60 DC). This grade of sorbitol, although containing water, traces of other polyols and being less crystalline, exhibits exclusively the Γ form. Its X-ray diffraction pattern was identical to that of pure Γ polymorph (data not shown).

Powder X-ray diffraction data of the five polymorphs obtained in this study are presented in Fig. 3 and the parameters are shown in Table 4. With thermal data, they confirm the existence of several polymorphic species. The Γ, A and B forms are identical with those described in refs. 3–6.

X-ray pattern powder data of sorbitol polymorphs

Γ form		A form		B form		Hydrated form		Solidified melt	
d (Å)	Intensity (%)	*d* (Å)	Intensity (%)	*d* (Å)	Intensity (%)	*d* (Å)	Intensity (%)	*d* (Å)	Intensity (%)
7.58	38	6.35	41	6.86	15	8.48	48	10.08	23
6.36	12	5.28	14	6.05	34	8.29	41	6.99	36
6.04	19	4.85	5	5.02	44	6.48	42	6.10	29
5.24	26	4.74	6	4.73	29	5.26	100	5.16	40
5.04	33	4.30	81	4.51	23	4.31	60	4.49	94
4.75	100	4.23	100	4.40	91	4.11	89	4.26	70
4.57	47	4.09	19	4.30	29	3.92	98	4.02	100
4.36	62	3.94	94	4.16	48	3.70	41	3.70	43
4.07	68	3.91	82	3.97	100	3.48	38	3.50	38
3.93	68	3.85	18	3.79	17	3.35	11	3.28	34
3.80	55	3.78	69	3.49	29	3.26	9	2.95	30
3.50	79	3.63	6	3.42	28	3.18	25	2.70	40
3.40	46	3.22	11	3.25	15	3.04	10	2.55	30
3.28	30	3.16	12	3.17	12	2.97	5	2.44	28
3.07	39	3.12	6	3.07	13	2.88	38	2.32	26
2.80	36	3.05	27	2.99	10	2.75	11	2.19	21
2.64	47	2.88	32	2.79	32	2.68	13	2.10	23
2.56	28	2.79	17	2.70	32	2.67	9		
2.50	24	2.76	28	2.54	14	2.60	9		
2.42	11	2.65	45	2.49	14	2.38	19		
2.33	15	2.61	5	2.41	9	2.31	10		
2.26	28	2.51	24	2.29	28	2.27	7		
2.18	25	2.35	5	2.22	14	2.23	6		
2.13	23	2.27	5	2.15	20	2.18	9		
2.06	21	2.24	11	2.09	16	2.14	8		
1.98	16	2.19	19	2.06	15	2.11	5		
1.93	8	2.17	9			2.06	7		
1.88	8	2.11	8			1.97	9		
1.83	7	1.98	8			1.93	7		
1.74	8	1.84	5						
1.70	7								

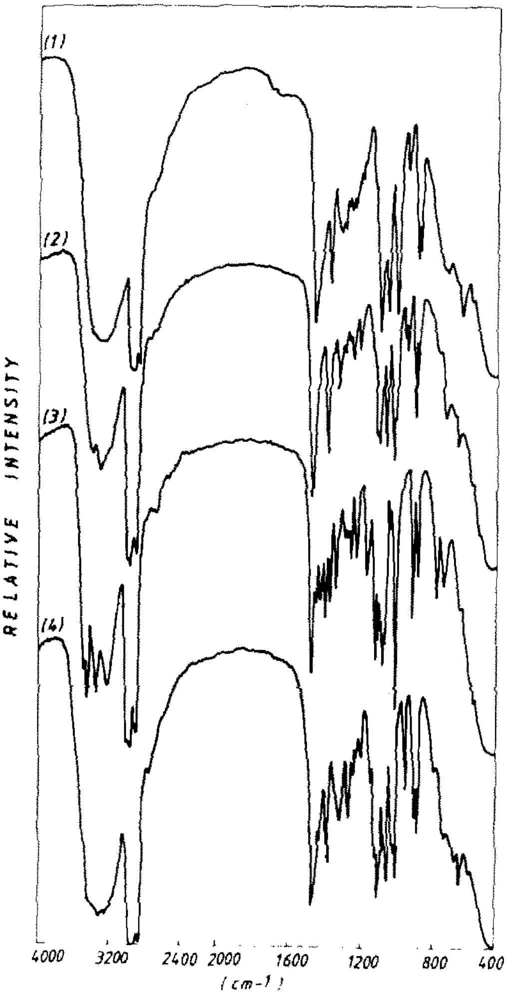

Fig. 4. Infrared spectra of sorbitol polymorphs (% transmittance vs. wave numbers). 1, Hydrated form; 2, B form; 3, A form; 4, Γ form.

The hydrated form displayed a powder pattern which differed from the other polymorphs. As far as we know, the existence of this species has never been reported in the literature.

The solidified melt presented a weak crystalline organization but was not completely amorphous in the solid state as has been suggested by different authors [7,8,12]. A vitreous transition was not observed for this form on cooling.

Characterization of sorbitol polymorphs, by means of their infrared spectra (Fig. 4), is summarized in Table 5: polymorph A is easily identified by the absence of the band at 940 cm^{-1}; the B and Γ forms are rapidly

TABLE 5

Infrared spectra of sorbitol polymorphs: specific bands

Wavenumber (cm^{-1})	Hydrate	A form	B form	Γ form
3200–3450		3445		
νOH		3400	3370	
		3300	3270	3305
	3240			3240
		3175		
1000–1200		995	1000	1000
νC–OH	1010	1020	1010	1015
	1055	1050	1055	1050
		1065		
		1075		
		1090	1090	1095
	1100	1105	1100	
850–950	945 [a]		950	
			940	940
	890	895	895	890
	875	870	875	875

[a] Two unresolved bands.

differentiated by the presence of a band at 950 cm^{-1} for the first polymorph; and the hydrated form gives two bands unresolved at 945 cm^{-1}.

THERMAL AND/OR DESORPTION TREATMENTS OF THE SORBITOL HYDRATE

Most of the known polymorphic forms have been obtained by submitting pure hydrated sorbitol to different thermal and/or desorption treatments. Results are summarized in Table 6.

According to DSC scans, the forms obtained after 65 h at 50 °C in a closed sample holder (method 1) and subsequent cooling to room temperature corresponded either to A or to Γ. The same treatment but in an opened sample holder led to a mixture of the A and Γ forms (method 2 and Fig. 2). Then, the polymorphs resulting from these two treatments transform into the Γ polymorph by dehydration under vacuum at 85 °C for 12 h (method 3). The maximum water loss observed was 6.3% by weight.

In the solid state, polymorph A was also formed by dehydration in the presence of P_2O_5 at room temperature. After 80 days, the resulting water losses reached 6% by weight (method 4).

In conclusion, the Γ form appeared when a dehydration was carried out in addition to a thermal treatment. But to obtain a pure and highly stable Γ form from the hydrate form, it was necessary to completely remove water

TABLE 6

Characteristics of polymorphs obtained by sorbitol hydrate thermal and/or desorption treatments

Method	% water loss	Form	T_0 (°C)	ΔH (cal g^{-1})
1	0	Hydrated A or Γ	88.8	29.5
2	5.9	Anhydrous A + Γ	87.3	12.4
			98.2	24.5
3	6.3	Anhydrous Γ	98.7	45.0
4	6.0	Anhydrous A	88.1	45.0

using vacuum at high temperature. Probably polymorph A crystallized from water solution and Γ from A rearrangement, leading to a less crystalline form via the solid state. Therefore the very similar melting enthalpies of A and Γ polymorphs can be explained by crystallinity difference (Table 6). As shown above by the thermal behaviour of the hydrate seen above (Fig. 1), the rearrangement into other polymorphs seems to be promoted at the hydrate melting temperature, as observed for monotropic transition of lipids such as triglycerides [22]. The presence of nuclei of these more stable forms is often required to initiate the crystallization process. Therefore, we must suppose that these nuclei preexist in trace amounts in the hydrate.

SORPTION TREATMENTS OF THE SORBITOL HYDRATE

At room temperature (25 °C), the equilibrium relative humidity (ERH) of sorbitol hydrate dissolution determined in various relative humidities has been found to be between 75 and 78%. This value is higher than the ERH observed for Γ sorbitol which is 72.5% at 25 °C [23]. Thus, sorbitol hydrate is less hygroscopic than the Γ form. This hydrated sorbitol may therefore be used in the range of application of anhydrous sorbitol with the advantages of reduced hygroscopicity.

The water sorption of sorbitol was studied at both the hydrate fusion endotherm and glass transition temperatures (T_g) of the undercooled liquid.

To study this effect, small hydrate samples (3–4 mg) were kept for intervals ranging from some hours to days at 25 °C at 93% relative humidity, then sealed after different weight gains of water and equilibrated for 48 h before analysis (Figs. 5 and 6). The enthalpy of the main endotherm and the crystallinity diminish as a function of the percentage of sorbed water. At 25 °C as sorbed water content increases, hydrate crystals are then partially

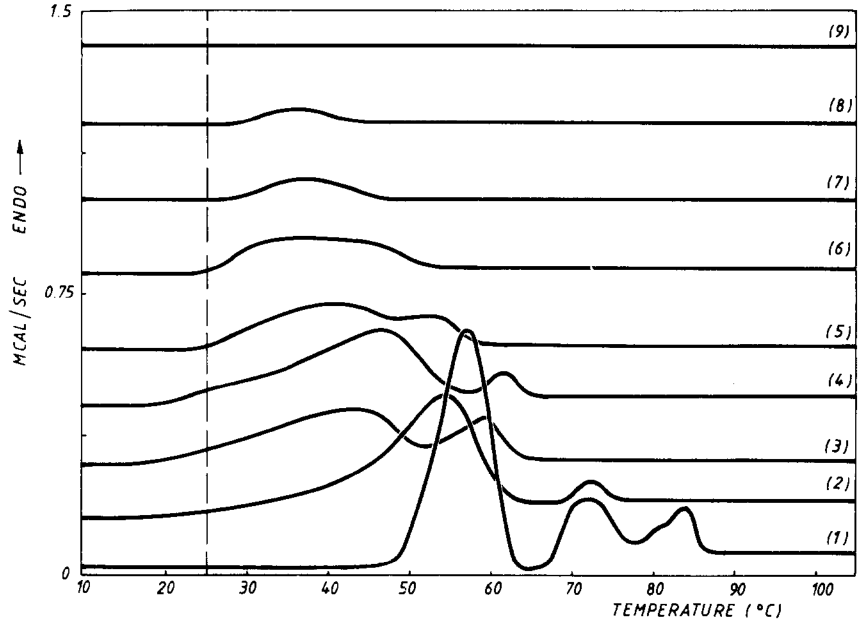

Fig. 5. DSC curves of pure hydrated sorbitol as a function of sorbed water (scan rate 8 °C $\min^{-1}$). The broken line is the storage temperature (25 °C). 1, Pure hydrated sorbitol 6.3%; 2, 10.9%; 3, 14.6%; 4, 17.2%; 5, 20.3%; 6, 22.7%; 7, 30.5%; 8, 34.0%; 9, 37.7%.

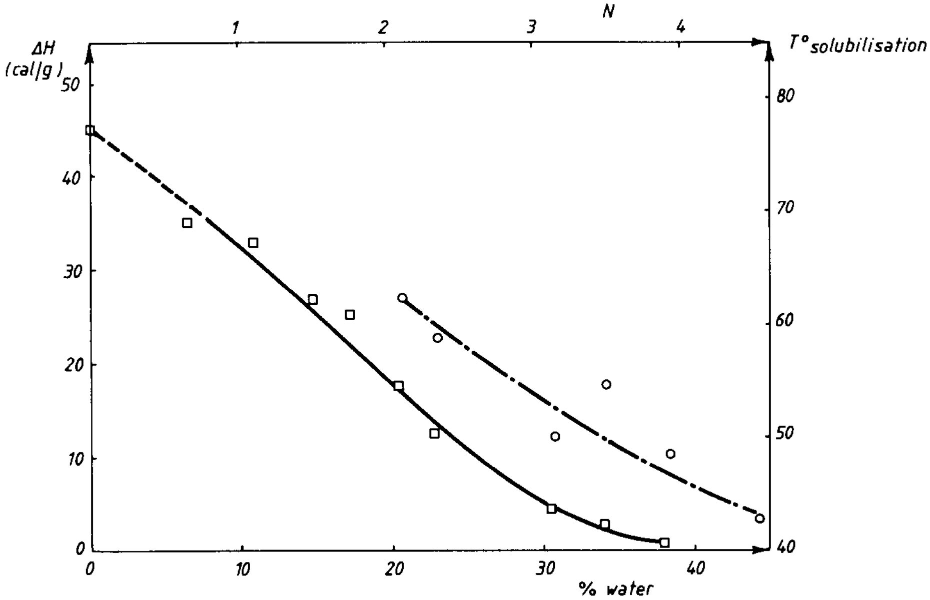

Fig. 6. Influence of water content on melting enthalpies of pure hydrated sorbitol. N represents the average number of water molecules per sorbitol. The broken curve is the solubilization curve.

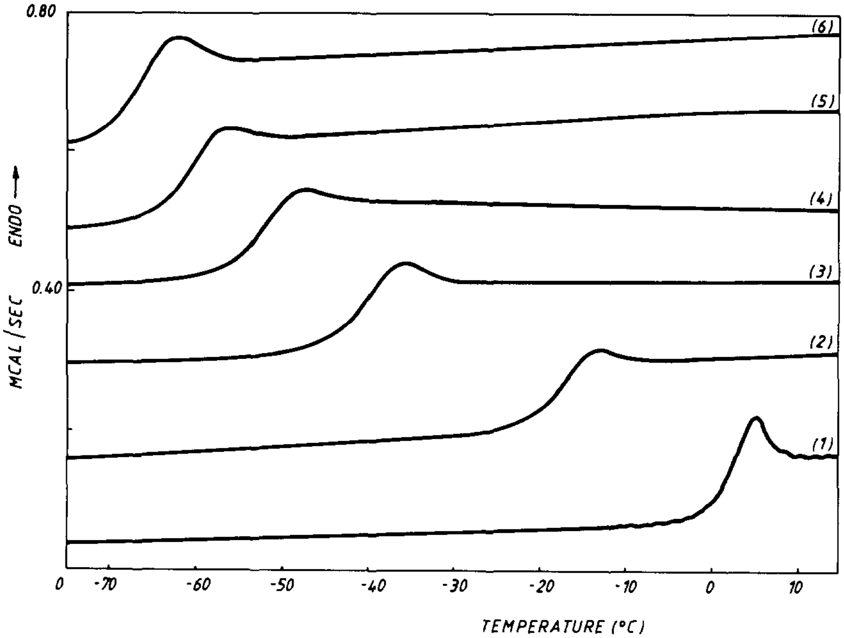

Fig. 7. Dependence of the % water on the glass transition temperature T_g. 1, 0%; 2, 6.3% (pure hydrated sorbitol); 3, 17.2%; 4, 22.7%; 5, 34.0%; 6, 41.0%.

solubilized into sorbitol saturated solution which is in equilibrium with the remaining hydrate crystals. At this temperature, the sample can be considered to be in equilibrium, but not when cooled to a low temperature prior to analysis. Then during this short period of cooling and before the sample reaches 25 °C again, we suppose that no further hydrate crystallization can occur. Therefore, measured enthalpies correspond to solubilization of the remaining hydrate crystals at $T > 25\,^\circ\mathrm{C}$. Assuming there is no delay on melting, the variation of completion temperatures of the solubilization peak as shown in Fig. 6 represents roughly the sorbitol water solubility curve. At room temperature, solubility is achieved for about four water molecules solvating a molecule of sorbitol.

Glass transition temperature (T_g) was then investigated as a function of water on the samples. Values of T_g were recorded on heating at 20 °C min^{-1} after quick cooling in order both to limit relaxation peak amplitude and to avoid possible water crystallization. As shown in Figs. 7 and 8, values of T_g decreased from about 0 to −70 °C as the sorbed water increased from 0 to 55%. However, with the experimental conditions mentioned above, no water crystallization was detected.

Water crystallization occurs for sorbitol solutions containing about 70% water. When cooling at 10 °C min^{-1}, only glass transition is recorded; on heating at 20 °C min^{-1}, glass transition with a relaxation peak was mea-

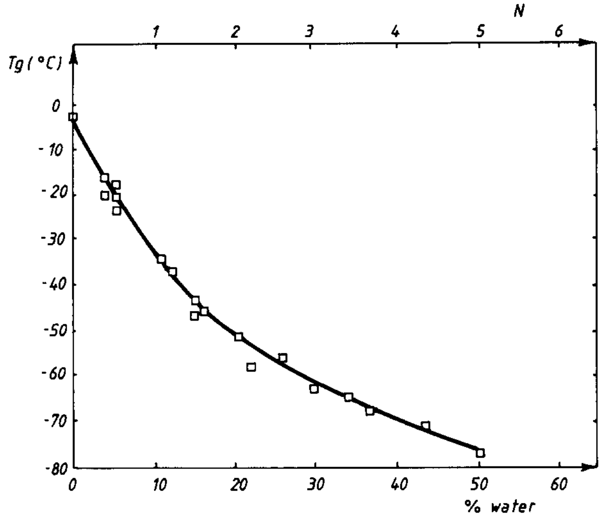

Fig. 8. Effect of water content on the glass transition temperature T_g of pure sorbitol, N as Fig. 6.

sured at about −82 °C. Water crystallization occurred at −42 °C, immediately followed by melting of the ice crystals formed (data not shown).

The glass transition corresponds to the temperature at which sorbitol molecules lose their freedom. It occurs when undercooled liquid viscosity reaches the critical value of 10^{14} N s m^{-2} [21]. This viscosity value is roughly the same for all known glassy states. Therefore, T_g depression as a function of water content is not surprising since water reduces glass viscosity and acts as a plasticizer of the sorbitol [21], and T_g for pure water is probably close to −140 °C [24]. This T_g depression agrees with the behaviour expected for binary mixtures, although no breakpoint was observed [25].

Over the domain in which water crystallization is possible and below the hydrate water concentration there is a zone where water is then rendered incapable of freezing by the high sorbitol concentration: this is often referred to as "unfreezable water" [21,26]. Sorbitol cannot crystallize either because of the high water concentration. Both water and sorbitol act one to the other as "structure breakers" and the supersaturated solution becomes so viscous that any crystallization is inhibited. In this domain, at the glass transition temperature neither water nor sorbitol is able to crystallize. Despite the possible occurrence of a hydrate, relatively few water molecules are "bound" to sorbitol by hydrogen bonds such as in a hydrate conformation, although this possibility cannot be ruled out. Therefore the glass transition must correspond to a blocking of sorbitol and water molecules leading to a glassy metastable structure, this last being probably formed of sorbitol–water crystallites exhibiting limited short range order. Continuous

T_g depression observed as a function of the increase in water content indicates that water as well as sorbitol is contributing to the glassy state (Fig. 8). As neither sorbitol nor water can crystallize alone, the relaxation peaks following glass transitions can be attributed to the melting of the weakly organized crystalline parts of the glass, the so-called above crystallites (Fig. 7). The amplitude of this endotherm is proportional to the crystallinity degree reached by the glass when melting. This crystallinity degree depends on the thermal history of the sample [25].

When the sorbed water content reaches about 60% w/w, the water crystallization observed in the course of rewarming above the vitreous transition occurs through a devitrification process [21,26,27].

On the other hand, crystallization of a more dilute solution leads to a different liquid–solid equilibrium with the separation of ice and the formation of a more concentrated sorbitol solution.

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