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Polymorphic status of sorbitol: solution calorimetry versus DSC[1]

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Abstract

The knowledge of the polymorphic status of sorbitol ($C_6H_{14}O_6$: D-glucitol, a sugar substitute) is very important for its use in industrial processes. To investigate this problem we have used differential scanning calorimetry (DSC). The derived enthalpies of fusion of three different sorbitol modifications show noticeable deviations from literature data. Therefore we have carried out measurements of the enthalpies of solution, which lead to a contrary result with respect to polymorphic status.

INTRODUCTION

Sorbitol ($C_6H_{14}O_6$, D-glucitol) is a sugar-alcohol, which is well known to occur in high concentrations in fruit such as cherries, plums, apples and pears, being stored as an intermediate of the biochemical synthesis of starch and cellulose [1]. As it does not raise blood sugar levels it can be added to diabetic food as a substitute for sugar. Tablets may contain sorbitol as a binding agent [2,3]. Its chemical formula is shown in Fig. 1.

Sorbitol is a hygroscopic substance, its molar mass is 182.17 $\mathrm{g\,mol^{-1}}$. It is commercially produced by hydrogenation of aqueous solutions of D-glucose at temperatures above 120°C with hydrogen at pressures of about 100 bar using a nickel catalyst [4]. Evaporation of most of the water yields a 70% sorbitol solution, from which solid sorbitol is recovered by crystallization. Thereby various modifications of sorbitol can be formed which differ in their physicochemical properties. For commercial manufacture and use only the Γ-modification is the preferred product. Therefore it is important to know the correct polymorphic status. In addition we wanted to find out whether DSC might serve as a quick, economic and reliable method to determine the polymorphic status of sorbitol samples.

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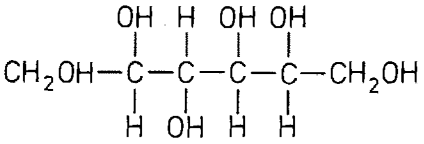

$$CH_2OH-\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-CH_2OH$$

Fig. 1. Chemical formula of sorbitol.

METHODS AND MATERIALS

Calorimetric and X-ray-diffraction measurements

DSC measurements were carried out with a Heraeus TA 500 heat flux calorimeter in a temperature range 273.15–403.15 K with heating rates of 2–5 K min^{-1} in aluminium capsules, containing samples in the range 3–4 mg.

Measurements of enthalpies of solution took place in a LKB 8700-1 Precision Calorimetry System [5] at 298.15 K in a 100 ml reaction vessel leading to aqueous solutions of sorbitol with a final concentration of about 3×10^{-2} mol kg^{-1}.

X-Ray diffraction (XRD) measurements were carried out on a Philips PW-System in aluminium sample holders.

Preparation of Γ-sorbitol

As starting material for all following experiments we used D-sorbitol from Fluka (MicroSelect, HPLC). Because of the hygroscopic properties of sorbitol it had to be dried under vacuum (1 mbar) for 2 h at 75–80°C to remove adhering water. With DSC and XRD measurements we controlled this modification to be pure and free from water.

Preparation of SM-sorbitol

SM-Sorbitol (solidified melt) was prepared from Γ-sorbitol which had been molten at 120°C and then quenched by pouring it into liquid nitrogen. The obtained soft adhesive mass solidified during storage for some days over silica gel. The substance kept changing for three weeks with obviously increasing enthalpies of fusion.

Preparation of sorbitol hydrate

A saturated aqueous solution of Γ-sorbitol was prepared and kept in a Dewar vessel in a refrigerator for slow cooling. This procedure yielded long thin needles of sorbitol hydrate, which were pressed between filter paper until no more liquid was adsorbed. Thermogravimetric (TG) measurements found a water content of 7.1% for the hydrate as had been expected for a 2/3-hydrate.

We were not able to produce the A and B polymorphs of sorbitol, which may exist according to the literature [6, 7].

RESULTS AND DISCUSSION

All results are shown in Table 1.

Obviously, the measured enthalpies of fusion deviate from the literature data [6]. In the case of SM-sorbitol this is probably caused by differing ages of the samples: in the literature no exact age was reported. Anyway, it would not be very satisfactory to derive enthalpies of phase transition from these enthalpy of fusion data.

It is much preferable, however, to use enthalpy of solution data to evaluate enthalpies of phase transition. There are three reasons for this conclusion: (i) In solution calorimetry all measurements are carried out at the same constant temperature (298.15 K) while temperatures differ in DSC measurements. (ii) All measurements of enthalpies of solution lead to the same final state (an aqueous solution of sorbitol with a concentration of about 3×10^{-2} mol kg^{-1}) whereas DSC measurements lead to different states. Γ-Sorbitol and SM-sorbitol form waterfree melts; sorbitol hydrate melts in its own crystal bound water leading to a water-containing melt. (iii) The accuracy of solution calorimetry is considerably higher than that of DSC.

The discrepancy between the calculated data for the enthalpies of

TABLE 1

Results of the calorimetric investigations

	DSC				Solution calorimetry
	Enthalpy of fusion, $\Delta_{fus}H$/kJ mol^{-1}		Onset temperature, ϑ_e/°C		Integral enthalpy of solution, $\Delta_{is}H^{\ominus}_{298}$/kJ mol^{-1}
	Measured	Literature	Measured	Literature	Measured
Γ-Sorbitol	31.36(78)	34.31	95.26(50)		17.36(11)
Sorbitol hydrate	30.79(77)	28.5	48.63(50)	50.4	26.27(11)
SM-Sorbitol					
0 [a]	4.09(10)		71.01(50)		
"some" [a]		13.9		67.0	
13 [a]	18.95(47)		71.77(50)		
21 [a]	21.15(53)		69.10(50)		
31 [a]	21.16(53)		70.84(50)		
46 [a]	21.13(53)		70.67(50)		15.00(01)

[a] Age in days.

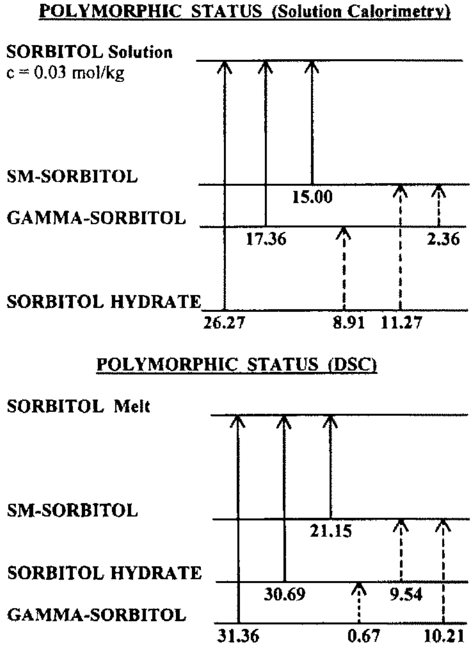

Fig. 2. Polymorphic status of sorbitol. All data are in kJ mol^{-1}.

transition is evident, as shown in Fig. 2. As may be seen, the polymorphic status derived from these data is completely different. We trust the solution calorimetry data, which give sorbitol hydrate as the most stable form followed by Γ-sorbitol and SM-sorbitol. In addition, it can be stated that DSC is most probably not suited to serve as a quick, efficient and reliable method to elucidate the phase status of sorbitol.

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