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Organic Chemistry

THERMAL BEHAVIOUR OF SOME SUGAR ALCOHOLS

H. K. Cammenga[1], *L. O. Figura*[2] *and B. Zielasko*[1]

[1]Technical University of Braunschweig
[2]German Institute for Food Technology at Quakenbrueck, Germany

Abstract

The glass transition of isomalt and its components, the enthalpy of solution (crystalline state, glassy state) and the enthalpy of melting are reported. From the measured data (solution enthalpy, enthalpy of fusion and heat capacities) a cycle like the BORN-HABER cycle can be constructed. It is possible to calculate the amounts of amorphous isomalt from measured solution enthalpies; however, the values obtained do not agree with those provided by X-ray powder diffraction studies.

Keywords: sugar alcohols

Introduction

Sugar alcohols are extensively used as sweetening agents. They sometimes possess advantages over the parent sugars in sweetness, caloric reduction and noncarciogenicity.

The physical state of carbohydrates in food and confectionary affects both the properties of the product during production and the quality of the final product. Certain food product contain sugars in various forms (crystalline or glassy states). Sucrose is crystalline in sugar candy but amorphous in boiled sweets. All the amorphous carbohydrates are extremely destructible. If the storage temperature is higher than the glass transition temperature, the amorphous forms change into supercooled liquid.

Material

The examined materials are isomalt and its constituents α-*D*-Glucopyranosyl-1-6-sorbitol (GPS) and α-D-Glucopyronosyl-1-6-mannitol (GPM). Both are

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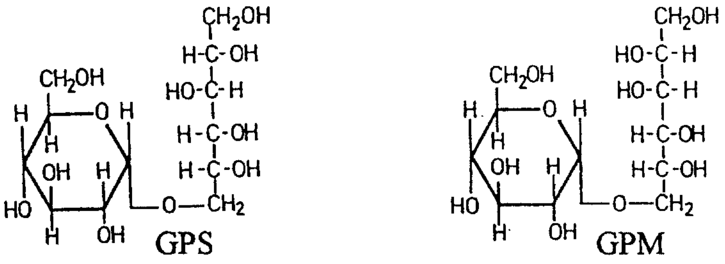

Fig. 1 Structural formulae of GPS and GPM

disaccharide alcohols as they consist of a monosaccharide and a sugar alcohol (Fig. 1). Isomalt is an approximately equimolar mixture of GPS and GPM, which is manufactured and marketed under the trade Palatinit^{TM} by Palatinit Süßungsmittel GmbH, a wholly owned subsidiary of Südzucker AG Mannheim/Ochsenfurt.

The amorphous preparation may be obtained in two ways:

1. Fusion of the crystalline solid and rapid cooling (these sugar alcohols do not decompose upon melting).
2. Sugar alcohol solutions (5% by weight) are frozen by dripping into liquid nitrogen and then freeze-dried.

The anhydrous crystalline phases are prepared by drying one hour at 378 K [1].

Solution enthalpy

The enthalpy of solution of a substance is the enthalpy change accompanying dissolution in a specified amount of solvent. The enthalpy of solution can have positive or negative values according to hydration and polymorphism. When sugar alcohols are dissolved is the mouth from the crystalline state, a mouth-cooling effect is often perceptible. The effect is desirable e.g. for peppermint or menthol flavoured products but considered inappropriate for many other products, such as baked goods and chocolates.

Measurements of enthalpies of solution were carried out in an LKB 8700-1 Precision Calorimetry System at 298.15 K using a 25 ml reaction vessel and leading to aqueous solutions of sugar alcohols with a final concentration between $1\cdot10^{-2}$ and $5\cdot10^{-2}$ mol kg^{-1}.

Differential scanning calorimeter

A Mettler FP 80/FP 84 differential scanning calorimeter was used to observe the thermal properties of various isomalt modifications in the temperature range from 293 to 453 K. The measurements were carried out at atmospheric pressure in an air atmosphere. For the calibration of heat capacity measurements Al_2O_3 (sapphire) was used.

T_g is manifested as a detectable, discontinuous change in heat capacity (signifying a second-order transition), which is observed as an endothermic step change (i.e. baseline shift) in a DSC heat flow curve. Glass transition temperatures T_g are determined in two ways [2]. In Table 1 are shown the average values of T_g calculated in both ways, for single values see Cammenga, Zielasko [1]. The fusion temperature T_{fus} given is the extrapolated peak onset temperature.

Table 1 Glass transition temperatures T_g, melting temperature T_{fus} and enthalpies of fusion ΔH_{fus}

	T_g/K average value	T_{fus}/K (onset)	T_g/T_{fus}	ΔH_{fus}/ kJ mol^{-1}
GPS	326	439.0±0.5	0.74	56.36±0.77
GPM	339	440.8±2.3	0.77	55.0±2.7
Isomalt	331	414.0±1.6	0.80	46.5±3.1

X-ray powder diffraction

A Philips PW 1730 X-ray generator with a Philips PW 2253/11 X-ray tube was used to determine the X-ray diffractograms of various isomalt modifications at room temperature. When X-ray are scattered by an amorphous phase, the intensity $I(\theta)$ of scattered radiation is a function only of the scattering angle θ.

Results and conclusions

Isomalt and its components in their crystalline forms have positive heats of solution, whereas amorphous forms have negative heats of solution (Tables 2 and 3). The hydrated crystalline substances have higher positive heats of solution than the corresponding anhydrous substances. The lattice contribution $\Delta H_{lattice}$ is endothermic, whereas the solvation $\Delta H_{solvation}$ is exothermic. In solid solvates or hydrates of compounds, bonds (often hydrogen bonds) are already formed within the solid lattice so that the lattice energy is already partly compensated. In the case of amorphous solids the cohesion energy is considerably reduced and solvation dominates the dissolution process and makes it strongly exothermic.

For GPS T_{fus}=439.0 K and the enthalpy of fusion is 56.36 kJ mol^{-1}. Raemy and Schweizer [3] examined the process of melting and decomposition of many carbohydrates. They found 180 J g^{-1} (equal to 62.0 kJ mol^{-1}) for the melting of GPS at 175°C (448 K), the temperature being given for the peak maximum.

From the data measured, the energy difference between the amorphous and crystalline states can be deduced. This energy difference is 21.4 kJ mol^{-1} in the case of the amorphous and crystalline forms of GPS calculated on the basis of

Table 2 Heat of solution of various GPS- and GPM phases

	Phase	Water content/ %	End concentration of the solution/ mol substance/kg H_2O	Integral enthalpy of solution/ kJ mol^{-1}
GPS	crystalline	0.03	0.05	10.39±0.01
	amorph., glass	0.00	0.04	–10.99±0.04
	amorphous	1.13	0.01	–10.78±0.34
GPM·$2H_2O$	crystalline	9.43	0.03	30.02±0.20
GPM	crystalline	0.00	0.04	6.30±0.12
	amorph., glass	0.00	0.04	–12.90±0.02
	amorphous	1.11	0.01	–17.10±0.29
mixture of 50.9% GPS + 49.1% GPM	crystalline	0.00	0.04	8.45±0.07

Table 3 Heat of solution of various isomalt-phases and the calculation of the crystallinity via solution enthalpies (further information is given in the text)

	Phase	Water content/ %	End concentration of the solution/ mol substance/kg H_2O	Integral enthalpy of solution/ kJ mol^{-1}	Crystallinity/%
Isomalt	crystalline	4.53	0.04	15.77±0.02	87.8
	crystalline	2.94	0.04	11.45±0.04	84.9
	crystalline	2.80	0.04	10.58±0.03	82.9
	crystalline	2.16	0.04	9.61±0.03	84.2
	crystalline	2.04	0.04	10.31±0.03	87.9
	crystalline	1.62	0.04	7.84±0.05	81.6
	crystalline	0.00	0.04	5.29±0.23	85.3
	amorph., glass	0.00	0.03	−12.48±0.07	
	amorphous	0.86	0.01	−12.42±0.25	

the solution calorimetric measurements at 298 K. If the enthalpy change for a phase transition is known at one temperature, it can be calculated at another temperature if the heat capacities of both phases are known over the intervening temperature range. Consequently, it is possible, similarly to the cycle of Born and Haber, to determine the enthalpy change for the above-mentioned phase transition:

$$\text{GPS (crystalline)} \xrightarrow{25^{\circ}\text{C}} \text{GPS (amorphous)}$$

from the enthalpy of ΔH_{fus} and the corresponding heat capacities C_p of the crystalline and amorphous phases (Fig. 2). It must be noticed that in calculations from DSC data small differences between large numbers are involved and thus the result received for the phase transition has a large statistical error. Measurements with solution calorimetry have a higher precision than those with DSC.

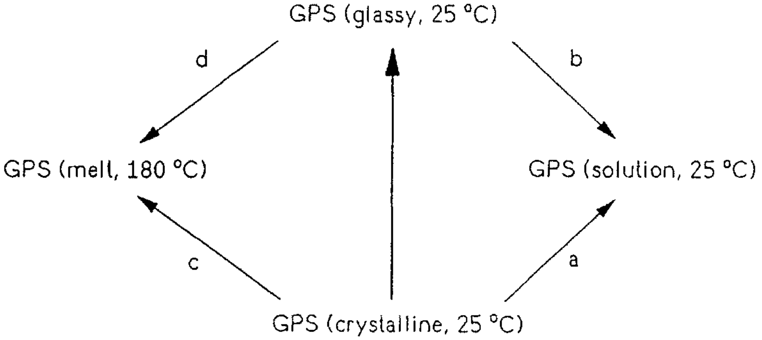

Fig. 2 Determination of the change for the phase transition from crystalline to amorphous – a comparison between solution-calorimetry and DSC

a $\Delta_{\mathrm{is}}H^{\ominus}_{298} = 10.4\ \mathrm{kJ\ mol^{-1}}$,

b $\Delta_{\mathrm{is}}H^{\ominus}_{298} = -11.0\ \mathrm{kJ\ mol^{-1}}$

c $$\int_{T_1}^{T_{\mathrm{fus}}} \overline{C_p}(\mathrm{cr})\mathrm{d}T + \Delta H_{\mathrm{fus}} + \int_{T_{\mathrm{fus}}}^{T_2} \overline{C_p}(lq)\mathrm{d}T =$$
$$= \int_{298}^{439} 668\ \mathrm{J\ K^{-1}mol^{-1}d}T + 56360\ \mathrm{J\ mol^{-1}} + \int_{439}^{453} 1178\ \mathrm{J\ K^{-1}d}T =$$
$$= 167.0\ \mathrm{kJ\ mol^{-1}},$$

d $$\int_{T_1}^{T_g} \overline{C_p}(\mathrm{glass})\mathrm{d}T + \int_{T_g}^{T_2} \overline{C_p}(lq)dT =$$
$$= \int_{298}^{326} 612\ \mathrm{J\ K^{-1}\ mol^{-1}d}T + \int_{326}^{453} 1073\ \mathrm{J\ K^{-1}mol^{-1}d}T = 153.4\ \mathrm{kJ\ mol^{-1}}$$

Solution calorimetry: a–b $= 21.4\ \mathrm{kJ\ mol^{-1}}$,
differential scanning calorimetry: c–d $= 13.7\ \mathrm{kJ\ mol^{-1}}$

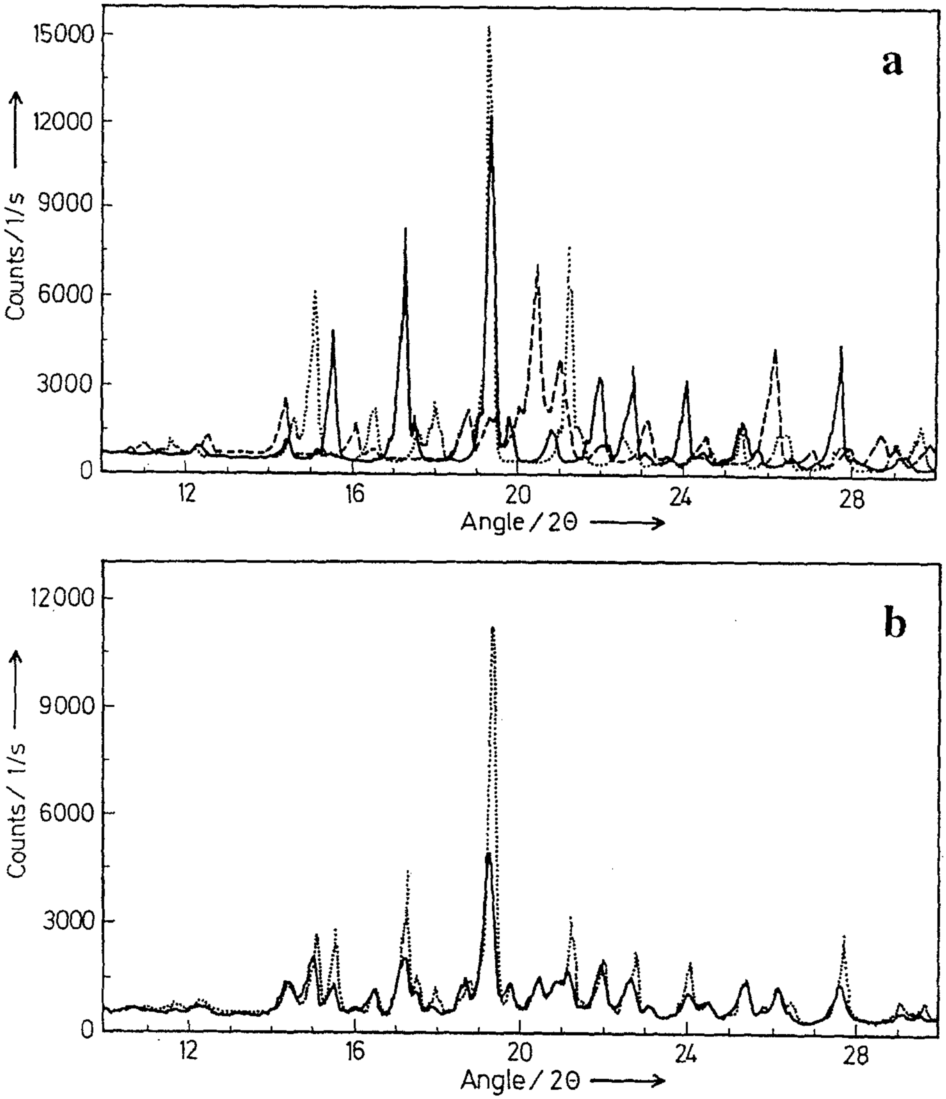

Fig. 3 Calculation of the crystallinity by X-ray powder diffraction

The reproducibility of solution calorimetry is high, thus it is possible to study the enthalpy changes of isothermal phase transitions by solution calorimetry with a high accuracy.

A further application of solution calorimetry is calculation of the amorphous fraction if the solution enthalpies of the amorphous and crystalline phases are known. The degree of crystallinity in different industrial isomalt-charges is quantified by means of the following equation [4]:

$$\text{Crystallinity} = 100\,\frac{\Delta H_s - \Delta H_a}{\Delta H_c - \Delta H_a} \qquad (2)$$

where ΔH_s, ΔH_a and ΔH_c are the heats of solution of the samples, of the amorphous form *a* and of the crystalline form *c*. The results of calculations of crystallinity of industrial isomalt samples are shown in Table 3. One example of the calculation of the crystallinity by X-ray powder diffraction is given in Figs 3. As pure crystalline isomalt is not available, it is necessary to calculate the X-ray powder-diagram from the single phases of isomalt: GPM, GPM-dihydrate and GPS. Unfortunately, the agreement between the results of the two methods is not satisfactory.

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