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Thermal behaviour of isomalt¹

H.K. Cammenga*, B. Zielasko

*Institute of Physical and Theoretical Chemistry, Technical University of Braunschweig,
D-38106 Braunschweig, Germany*

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Abstract

The technological properties of isomalt and its enthalpy of solution and glass transition are described. The transformation temperature (glassy state → subcooled liquid) T_g is usually readily obtainable by differential scanning calorimetry (DSC), which detects a characteristic change in the specific heat capacity at T_g .

Keywords: Isomalt; Enthalpy of solution; Glass transition

1. Introduction

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

The physical status of carbohydrates in food and confectionery affects both the properties of the product during production and the quality of the final product. Certain food products contain sugars in several polymorphic forms (crystalline or glassy state). Sucrose is crystalline in sugar candy but amorphous in boiled sweets. All the amorphous carbohydrates are extremely destructible. The amorphous phases recrystallise into the stable crystalline forms in the presence of atmospheric moisture. If the storage temperature is higher than the glass transformation temperature, the amorphous forms change into subcooled liquid.

The sugar alcohol isomalt (Palatinit®) is manufactured and marketed by Palatinit Süßungsmittel GmbH, a wholly owned subsidiary of Südzucker AG Mannheim/Ochsenfurt.

* Corresponding author.

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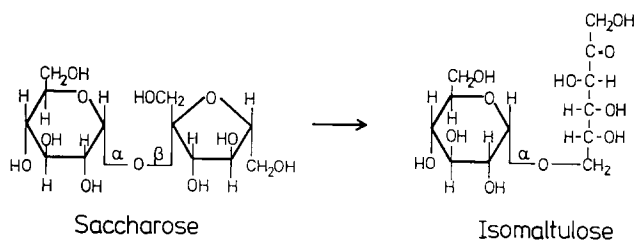


Fig. 1. The enzymatic conversion of sucrose into isomaltulose.

Isomalt is an approximately equimolar mixture of α -D-glucopyranosyl-1–6-sorbitol (GPS) and α -D-glucopyranosyl-1–6-mannitol (GPM). Both belong to the group of disaccharide alcohols as they consist of a monosaccharide and a sugar alcohol.

Isomalt is produced from sucrose in a two-step process. First the sucrose is enzymatically converted to isomaltulose by changing the disaccharide bond from 1–2 to 1–6 (see Fig. 1). The hydrogenation of isomaltulose in aqueous solution by hydrogen with Raney Nickel as catalyst yields an equimolar mixture of the diastereomers α -D-glucopyranosyl-1–6-sorbitol (GPS) and α -D-glucopyranosyl-1–6-mannitol (GPM) (see Fig. 2). GPS crystallises as anhydrous crystals, GPM crystallises as a dihydrate [1].

2. Methods and materials

2.1. Calorimetry

Measurements of enthalpies of solution took place in a LKB 8700-1 Precision Calorimetry System at 298.15 K using a 25 ml reaction vessel and leading to aqueous solutions of sugar alcohol with a final concentration of about (1×10^{-2}) – (5×10^{-2}) mol kg⁻¹. The Mettler FP 800/FP 84 differential scanning calorimeter was used to observe the thermal properties of the various isomalt modifications in the temperature range from 293 to 453 K. The measurements were carried out at atmospheric pressure in air atmosphere. 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

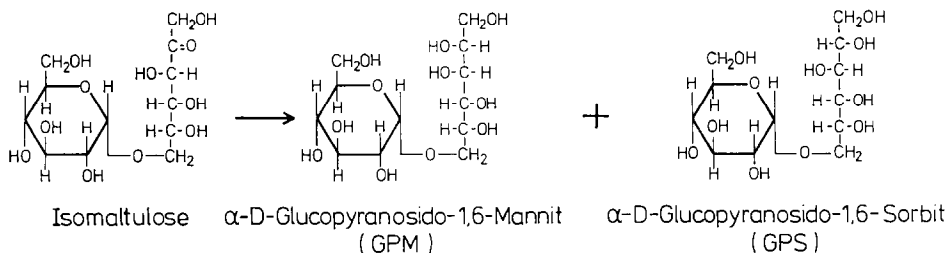


Fig. 2. The hydrogenation of isomaltulose to GPS and GPM.

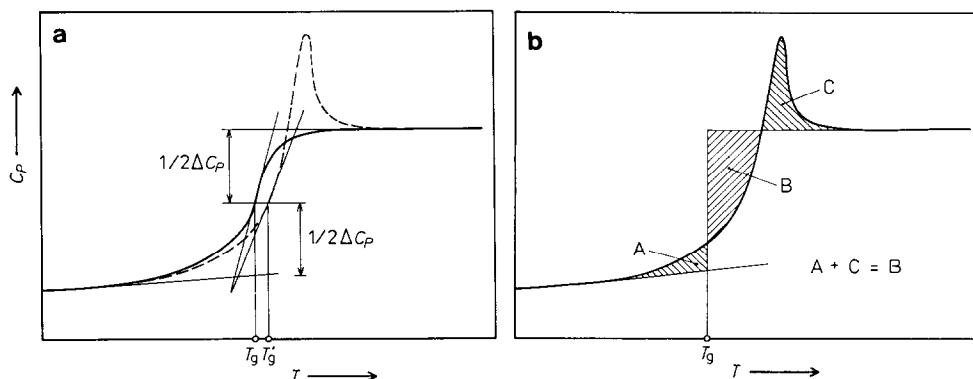


Fig. 3. Two procedures to determine the glass transition temperature: (a) half-height method; (b) equivalence of areas method.

shift) in a DSC heat flow curve. This is schematically illustrated in the two thermograms shown in Fig. 3.

The glass transition temperatures can be determined in two ways (see Fig. 3) [2]: the half-height method (Fig. 3a) and equivalence of areas method (Fig. 3b).

2.2. Preparation of amorphous state

The following method of preparing the amorphous state is used for the determination of T_g . Fusion of the crystalline solid and rapid cooling. Melting is impossible with most sugars without causing decomposition, e.g. sucrose; but the sugar alcohol isomalt does not decompose upon melting. Five milligrams of water-free crystalline samples (drying for 1 h at about 378 K) were hermetically sealed in an aluminium sample pan and scanned (against an empty reference pan) at a heating rate of 5 K min^{-1} , from 293 K to 453 K (melting). GPM-dihydrate melts after water vaporisation had occurred through a pinhole. After controlled storage (3 weeks at 255 K, 2 days at 293 K and 1 h at 255 K) the sample is heated again at a rate of 10 K min^{-1} to determine the glass transition temperature.

Sugar alcohol solutions (5% by weight) were produced, frozen as single drops by dripping into liquid nitrogen and then freeze-dried. This resulted in porous "balls". The specific surface area obtained by the Brunauer-Emmett-Teller (BET) method was $2.5 \text{ m}^2 \text{ g}^{-1}$. Because of their high hygroscopicity and large surface, amorphous samples were handled under dry air (the relative humidity was below 1%) until used for the solution calorimetric measurement. These forms are only called amorphous in Table 2. The forms which were produced by melting and cooling (quenching subcooled liquid) are additionally called glass.

3. Results and discussion

The results of solution calorimetry measurements are listed in Table 1. When isomalt or its components GPS, GPM or $\text{GPM} \cdot 2\text{H}_2\text{O}$ dissolve in the mouth from the crystalline

Table 1

Heat of solution of various isomalt phases

	Phase	Water content in %	End concentration of the solution, mol substance (kg H ₂ O) ⁻¹	Integral enthalpy of solution in kJ mol ⁻¹
GPS	Crystalline	0.03	0.05	10.39 ± 0.01
	Amorphous, glass	0.00	0.04	-10.99 ± 0.04
	Amorphous	1.13	0.01	-10.78 ± 0.34
GPM·2H ₂ O	Crystalline	9.34	0.03	30.02 ± 0.20
GPM	Crystalline	0.00	0.04	6.30 ± 0.12
	Amorphous, glass	0.00	0.04	-12.90 ± 0.02
	Amorphous	1.11	0.01	-17.10 ± 0.29
Isomalt	Crystalline	4.53	0.04	15.77 ± 0.02
	Crystalline	2.94	0.04	11.45 ± 0.04
	Crystalline	2.80	0.04	10.58 ± 0.03
	Crystalline	2.16	0.04	9.61 ± 0.03
	Crystalline	2.04	0.04	10.31 ± 0.03
	Crystalline	1.62	0.04	7.84 ± 0.05
	Crystalline	0.00	0.04	5.29 ± 0.23
	Amorphous, glass	0.00	0.03	-12.48 ± 0.07
	Amorphous	0.86	0.01	-12.42 ± 0.25

state, a mouth-cooling effect is perceptible. The effect is desirable, e.g. for peppermint or menthol flavoured products but considered undesirable for many other products, such as baked goods and chocolates. Isomalt and its components as crystalline forms have a positive heat of solution, but the amorphous forms have a negative heat of solution (see Table 1). The hydrated crystalline substances have a higher positive heat of solution than the corresponding water-free substances.

The enthalpy change connected with the dissolution of a solid substance upon forming a solution of a certain concentration c may be subdivided into three contributions:

$$\Delta_{\text{is}}H_c = \Delta_{\text{lattice}}H + \Delta_{\text{solv}}H_0 + \Delta_{\text{dil}}H \quad (1)$$

$\Delta_{\text{lattice}}H$ is the lattice enthalpy, $\Delta_{\text{solv}}H_0$ the enthalpy of solvation (in the case of water hydration) of the species dissolved at infinite dilution and $\Delta_{\text{dil}}H$ the integral enthalpy of dilution from $c \rightarrow 0$ to the final concentration c . Of these the lattice contribution is endothermic, whereas the 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. From the data measured, the energy difference between the amorphous and crystalline states can be deduced. This energy difference is 47.1 kJ mol⁻¹ in the case of the amorphous and hydrated forms of GPM and 21.3 kJ mol⁻¹ in the case of the amorphous and crystalline forms of GPS.

Table 2

Glass transition temperatures T_g and melting temperatures T_{fus}

	T_g /K Half height	T_g /K Equivalence of areas	Tendency towards enthalpy relaxation	T_{fus} /K	T_g/T_{fus}
GPS	328.1 ± 0.6	323.6 ± 2.6	Violent	439.0	0.74
GPM	338.9 ± 1.6	338.6 ± 1.7	Little	441.0	0.77
Isomalt	332.5 ± 0.7	329.4 ± 0.2	Moderate	415.0	0.80

The results of the measurements by DSC are shown in Table 2. T_g/T_{fus} is 0.5–0.7 for many glasses and polymers as a rule of thumb [3]. The T_g/T_{fus} values for isomalt and its components are slightly higher than those of polymers.

If there is any enthalpy relaxation, then T_g as determined by the half-height method is higher than T_g as determined by the equivalence of areas method. The phenomenon of enthalpy relaxation is dependent on:

- the substance
- the speed of cooling of the melt
- time and temperature of storage.

The higher the temperature and the longer the storage of GPS, the higher the relaxation enthalpy; the highest results only some degrees below T_g . Isomalt is an equimolar mixture of GPS and GPM and as well its T_g as its phenomenon of enthalpy relaxation fall between those of GPM and GPS.

Acknowledgements

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