



# Heat capacity and transition behavior of sucrose by standard, fast scanning and temperature-modulated calorimetry<sup>☆</sup>



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## ARTICLE INFO

### Article history:

Received 6 February 2014

Received in revised form 23 May 2014

Accepted 26 May 2014

Available online 29 May 2014

### Keywords:

Sucrose

Heat capacity

Melting

Glass transition

Standard

Fast and temperature modulated differential scanning calorimetry

## ABSTRACT

The heat capacity ( $C_p$ ) of crystalline and amorphous sucrose was determined using standard and quasi-isothermal temperature modulated differential scanning calorimetry. The results were combined with the published data determined by adiabatic calorimetry, and the  $C_p$  values are now reported for the wide 5–600 K range. The experimental  $C_p$  of solid sucrose at 5–300 K was used to calculate the vibrational, solid  $C_p$  based on the vibrational molecular motions. The calculated solid and liquid  $C_p$  together with the transition parameters for equilibrium conditions were used as references for detailed quantitative thermal analysis of crystalline and amorphous sucrose. Melting temperature ( $T_m$ ) of the crystalline sucrose was identified in a broad 442–465 K range with a heat of fusion of 40–46 J/mol determined at heating rates 0.5–20 K/min, respectively. The equilibrium  $T_m$  and heat of fusion of crystalline sucrose were estimated at zero heating rate as  $T_m^0 = 424.4$  K and  $\Delta H_f^0 = 32$  kJ/mol, respectively. The glass transition temperature ( $T_g$ ) of amorphous sucrose was at 331 K with a change in  $C_p$  of 267 J/(mol K) as it was estimated from reversing heat capacity by quasi-isothermal TMDSC on cooling. At heating rates less than 30 K/min, thermal decomposition occurred during melting, while at extreme rate of 1000 K/s, degradation was not observed. Data obtained by fast scanning calorimetry (FSC) at 1000 K/s, showed that  $T_m$  was 483 K and  $T_g$  was 364 K. Superheating effects were observed during the melting with the maximum value around 46 K at 1000 K/s.

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## 1. Introduction

Sucrose is the most common disaccharide used in households, the food and pharmaceutical industries [1]. In solid state, it can exist in crystalline and amorphous form. The molar mass of sucrose is 342.3 g/mol and the chemical structure is presented in Fig. 1.

Crystalline sucrose melts in the temperature range 440–470 K [2–7] with the heat of fusion 55–146 J/g [2,3,5–7]. The melting parameters depend on crystal polymorphism, impurities present in the sample, heating rate, and method of determination [2–4,6]. The decomposition that occurs during melting has been considered by authors of papers [3,8] as the main cause of so called “kinetic losses of the crystalline structure of sucrose”. According to Hurtt [2], the degradation can be avoided with heating rates of 20 K/min and

higher. However, it has been shown that thermal decomposition may still occur at heating rates higher than 20 K/min, up to 40 K/min using standard DSC [9], and even up to 1500 K/min using rapid scanning DSC [3,8]. At the low heating rates, the onset melting temperature ( $T_m$ ) is shifted toward the lower temperature, while at the high heating rates, the  $T_m$  is shifted to higher temperatures. At low heating rates, the sucrose decomposition starts with breaking of the glycosidic bond and release of glucose and fructose [8,9]. The presence of the reducing sugars, as well as salt residues, organic acids, and water can further catalyze degradation of crystalline sucrose and lower the onset of  $T_m$  [2,8,10,11]. On contrary, at high heating rates, the superheating effect results in an increase of  $T_m$  due to the melting process happening at the slower rate than the rate of heating [12]. Ross et al. [13], also pointed out that melting and decomposition in sucrose are separate phenomena occurring simultaneously in the same temperature region.

The effect of manufacturing methods of sugar on its thermal behavior has been well described [2,6,10,14–20]. Recrystallization of sucrose from solutions in the presence of mineral salts or other

<sup>☆</sup> This work was presented in part at 37th NATAS Conference in Lubbock, TX, September 20–23, 2009.

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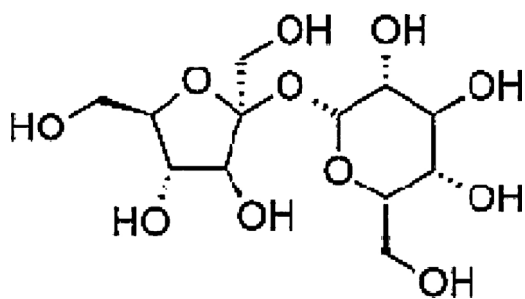


Fig. 1. Chemical structure of sucrose.

impurities leads to polymorphism commonly observed as additional peaks in DSC scans [6,11,14,21–23]. On cooling from the melt, sucrose becomes a fully amorphous material with a glass transition temperature ( $T_g$ ) 325–348 K [9,24–26] and with a change in heat capacity ( $C_p$ ) of 0.54 J/(g × K) [26–28] or 0.74–0.77 J/(g × K) [27,29]. The broad range of the literature values is due to variation in heating rate applied to measurements, thermal degradation at the melting temperature, and possible presence of water residues [13]. For example, the increase of the upper temperature during first heating step, prolonged annealing, or higher heating rate result in decrease of  $T_g$  [9]. These conditions apparently cause degradation of sucrose to glucose and fructose, what consequently lowers  $T_g$ . On the other hand, increase of  $T_g$  after cooling from the melt has been observed when conditions of heating of crystalline sucrose were extreme (very slow heating rate, much longer duration of annealing, or very high temperature) and led to the condensation of small molecules (glucose and fructose) on to high molecular (disaccharide) mass structures [9,22,30]. Amorphous sucrose is more susceptible to degradation than crystalline [22] and annealing at temperature in the melting region leads to the increase of this process dependent on applied temperature and time of annealing [9].

The knowledge of the heat capacity ( $C_p$ ) and transitions parameters of crystalline and amorphous sucrose allows calculating the thermodynamic functions, such as enthalpy ( $H$ ), free enthalpy ( $G$ ), entropy ( $S$ ). The goal of this research was to describe heat capacity, and thermodynamic functions of sucrose in a wide temperature range of 5–600 K. The low temperature heat capacity was explained by the vibrational molecular motion. Specifically, the objectives were (1) to determine the vibrational heat capacity of the sucrose molecule to be used together with liquid  $C_p$  as the baselines for quantitative thermal analysis; (2) to determine the effect of heating rate on thermodynamic parameters of sucrose, including  $T_m$ ,  $\Delta H_f$ ,  $\Delta C_p$ , and  $T_g$ ; and (3) to estimate possible decomposition of sucrose during the measurements.

Full thermodynamic characterization was performed based on data  $C_p$  from literature [31–33], our measurement by standard DSC, TMDSC, TGA as well as FSC and quantitative thermal analysis using ATHAS scheme [34–41]. Standard DSC and TGA are techniques which are used very often for characterization of sucrose [2–29], also now more often TMDSC [3–5,8,42]. With early development of fast scan calorimetry [43] it is now possible to study melting behavior. Using FSC with heating rates up to 60,000 K/s for thermal analysis of materials such as sucrose we can have numbers advantages, one of them is to avoid decomposition. More specific description can be seen in Ref. [44].

## 2. Materials and methods

### 2.1. Materials

Crystalline sucrose samples (minimum 99.5%) were supplied by Sigma and analyzed as obtained. Completely amorphous samples

were achieved by heating crystalline sucrose in a calorimeter with a constant rate of 10 K/min to 478 K (205 °C) followed by cooling to a temperature below  $T_g$ . The samples were prepared in standard aluminum pans and sealed by the Sample Press of TA Instruments. For standard DSC measurements the samples mass was 8–15 mg, and for quasi-isothermal TMDSC measurements 4–8 mg.

Calibration of temperature and heat of fusion calibration were performed by indium using extrapolated melting onset temperature of  $T_m = 429.75$  K (156.6 °C) and heat of fusion of 28.45 J/g. Heat capacity at each temperature was calibrated by sapphire ( $Al_2O_3$ ).

### 2.2. Methods

#### 2.2.1. Calculations of the $C_p$ of the solid state (vibrational heat capacity, $C_p(\text{vibration})$ )

The  $C_p$  of the solid state of sucrose was computed in respect to the procedures of calculations described in literature as the ATHAS scheme [34–41,45]. The values for low temperature  $C_p$  of sucrose in the range of 5–342 K have been determined by adiabatic calorimetry [2,31] and the published data were used in the work presented here to calculate solid, vibrational  $C_p$ . Assuming that the heat capacity at low temperature originates solely from vibrational motions, the  $C_p$  is characterized by an approximate vibrational spectrum of each group and skeletal vibrations [45,46]. In order to mathematically relate the  $C_p$  with molecular motions at low temperature, the first step was to convert the experimental  $C_p$  at constant pressure ( $C_p(\text{exp})$ ) to  $C_v$  at constant volume ( $C_v(\text{exp})$ ) using the thermodynamic relationship [43]:

$$C_p(\text{exp}) - C_v(\text{exp}) = \frac{TV\alpha^2}{\beta} \quad (1)$$

where  $\beta$  is compressibility in 1/Pa (for all temperature of interest),  $\alpha$  is temperature function of expansivity in 1/K (also the thermal expansion coefficient),  $V$  is molar volume in  $m^3/\text{mol}$  and  $T$  is temperature in K.

In the case when values from Eq. (1) are unavailable, the conversion of  $C_p(\text{exp})$  to  $C_v(\text{exp})$  has to be conducted by Nernst–Lindemann’s approximation [47,48]:

$$C_p(\text{exp}) - C_v(\text{exp}) = 3RA_0 \frac{C_p^2(\text{exp})}{C_v(\text{exp})} \times \frac{T}{T_m^0} \quad (2)$$

where  $A_0$  is approximately universal constant ( $\sim 0.0039$  K mol/J),  $T_m^0$  is equilibrium melting temperature in K,  $T$  is temperature and  $R$  is the gas constant.

The total number of vibrational degrees of freedom in the vibrational spectrum of solid state is  $3N$ , where  $N$  describes the total number of atoms in the repeating unit (for polymers) or in the whole molecule (for small molecules). This number is separated into group vibrations ( $N_{gr}$ ) and skeletal vibrations ( $N_{sk}$ ) and is expressed by  $3N = N_{gr} + N_{sk}$ .

Assuming that at low temperature contributions to the  $C_v(\text{exp})$  are only from vibrational heat capacity, it can be separated into heat capacity from group vibrations ( $C_v(\text{group})$ ) and the skeletal vibrations ( $C_v(\text{skeletal})$ ), as following:

$$C_v(\text{exp}) = C_v(\text{group}) + C_v(\text{skeletal}) \quad (3)$$

The  $C_v(\text{group})$  is obtained from IR and Raman spectroscopy and are represented by a sum of separate normal, Einstein, modes ( $C_v$  (Einstein)) and box distributions over narrow frequency-ranges ( $C_v$  (box)) [46,49,50].  $C_v(\text{box})$  is the heat capacity at constant volume, which is originated from the group vibration and described by the areas represented by a box-like spectrum. The boxes are depicted

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