Can the Thermodynamic Melting Temperature of Sucrose, Glucose, and Fructose Be Measured Using Rapid-Scanning Differential Scanning Calorimetry (DSC)?

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S *Supporting Information*

ABSTRACT: The loss of crystalline structure in sucrose, glucose, and fructose has been shown to be due to the kinetic process of thermal decomposition (termed apparent melting), rather than thermodynamic melting. The purpose of this research was to investigate whether or not it is possible to scan quickly enough to suppress the kinetic process of thermal decomposition and reach the thermodynamic melting temperature of these sugars using a new rapid-scanning DSC. Indium, a thermodynamic melting material, and sucrose, glucose, and fructose were analyzed at three heating rates from 1 to 25 °C/min using standard DSC and at seven heating rates from 50 to 2000 °C/min using rapid-scanning DSC. Thermodynamic melting was achieved when the onset temperature ($T_{m\ onset}$) of the endothermic peak leveled off to a constant value independent of heating rate. The $T_{m\ onset}$ for indium was constant (156.74 ± 0.42 °C) at all heating rates. In the case of fructose, the $T_{m\ onset}$ increased considerably until a heating rate of approximately 698 °C/min, after which the average $T_{m\ onset}$ for the remaining three heating rates was constant at 135.83 ± 1.14 °C. Thus, 135.83 °C is proposed to be the thermodynamic melting temperature of fructose. It is important to note that the heating rate at which this thermodynamic melting temperature is achieved is most likely influenced by the type and amount of trace components (e.g., water and salts) contained in the fructose, which are known to vary widely in sugars. In the case of sucrose and glucose, thermodynamic melting temperatures were not able to be obtained, because the upper limit heating rate used was not fast enough to suppress thermal decomposition and achieve thermodynamic melting, perhaps due to the higher apparent $T_{m\ onset}$ for sucrose and glucose compared to that for fructose.

KEYWORDS: thermodynamic melting temperature, rapid-scanning DSC, thermal decomposition, kinetics, sucrose, glucose, fructose

INTRODUCTION

Differential scanning calorimetry (DSC) has been extensively used for material characterization in a wide variety of research areas, including food science, pharmaceutics, material science, (bio)chemistry, and physics, due to a number of significant advantages, such as ease of sample preparation, applicability to solid and liquid samples, fast analysis time, and a broad temperature range.[1] Because of its many advantages, DSC is the most frequently used thermal analysis technique, accounting for probably 70% of all thermal analysis measurements.[2] DSC provides both quantitative and qualitative thermal and physical material property information (e.g., phase transition, glass transition, cold crystallization, polymorphism, and purity) as a function of time and temperature. Because every change in structure (transition) either absorbs or releases heat, DSC is the universal detector for measuring structural changes.

Because of a number of material characterization challenges, a new DSC technique, which performs at much faster heating and cooling rates than attainable with a conventional DSC, has recently received a great deal of attention.[3] This new faster heating and cooling DSC technique is currently referred to by a variety of names in the literature, including high-speed DSC,[4−7] high-performance DSC,[8] high-sensitivity, high-speed DSC,[9] rapid-scanning DSC,[3] and fast scan DSC.[10]

As demonstrated in the literature, this new rapid-scanning DSC technique has a number of exciting applications. Faster scanning rates greatly increase heat flow sensitivity (signal

height) for small transitions, because the same amount of energy (the DSC output, mJ/s) is released (or adsorbed) over a much shorter time, although this benefit is somewhat tempered by the requirement of using small sample sizes to attain the fast scanning rates. For example, a number of publications have shown the possibility of detecting and quantifying low levels of amorphous content in lactose,[6,9] maltitol,[11] and sucrose[7] using rapid-scanning DSC.

An application of importance to the present research is the use of rapid-scanning DSC for studies that require suppression of time-dependent (kinetics) transitions (e.g., polymeric conversion,[3,8,12,13] recrystallization,[5,8,14−17] or thermal decomposition[18]) for accurate material characterization. For example, Wurm and others[18] reported reaching the melting temperature of fibrous silk protein without interference from thermal decomposition using rapid-scanning DSC (300 K/min scanning rate), whereas using conventional DSC (10 K/min) resulted in thermal decomposition before melting.

Lee et al.[19,20] have shown that the loss of crystalline structure in sucrose, glucose, and fructose is due to the kinetic process of thermal decomposition, termed apparent melting, rather than thermodynamic melting. Apparent melting is a new term proposed by Lee et al.[19,20] to distinguish the loss of crystalline structure caused by kinetic processes (e.g., thermal decomposition, dehydration, and chemical interactions/reactions) from that caused by thermodynamic melting. Unlike thermodynamic melting, apparent melting parameters show a strong heating rate dependency. Thus, the purpose of this research was to investigate whether or not it is possible to scan quickly enough to suppress the kinetic process of thermal decomposition and reach the thermodynamic melting temperature of these sugars using rapid-scanning DSC.

■ MATERIALS AND METHODS

Materials. Crystalline sucrose ($\geq$99.5%), D-(+)-glucose (99.5%), and D-(−)-fructose ($\geq$99.5%) were purchased from Sigma-Aldrich Co. (St. Louis, MO). These analytical reagent grade samples were used without further purification and stored under room conditions in their original containers, wrapped tightly with parafilm after opening. The water contents (wet basis, wb) of the three sugars were measured using coulometric Karl Fischer titration with Hydranal Coulomat AG as a solvent and were 0.004% wb for sucrose, 0.048% wb for glucose, and 0.033% wb for fructose. Material information, including trace anions and cations, for sucrose, glucose, and fructose, obtained from the Sigma-Aldrich Co. and analyzed by the authors of this study, is available as Supporting Information. Because of the very small sample sizes used in the rapid-scanning DSC, these samples were prepared using a microscope.

Standard DSC (SDSC) Measurements. Sample measurements with relatively slow heating rates (1−25 °C/min) were performed using a DSC Q2000 (TA Instruments, New Castle, DE), equipped with a refrigerated cooling system (RCS 90). Prior to sample measurements, the calibration for enthalpy (cell constant) and temperature was completed using indium ($T_{m\ onset}$ = 156.60 °C and ΔH = 28.71 J/g). Hermetic aluminum Tzero pans and lids (TA Instruments) were used for calibration and all sample measurements. An empty pan was used as the reference, and dry nitrogen, at a flow rate of 50 mL/min, was used as the purge gas. Sucrose, glucose, and fructose (approximately 2.75 mg) sealed in hermetic pans were equilibrated at 25 °C and then heated at scan rates of 2, 5, and 10 °C/min to temperatures after completion of the endothermic peak (220 °C for sucrose, 195 °C for glucose, and 180 °C for fructose). Measurements for each heating rate were done in

duplicate. Indium also was heated at scan rates of 1, 5, and 25 °C/min to compare with the $T_{m\ onset}$ for the sugars as a function of heating rate.

Rapid-Scanning DSC Measurements. The rapid-scanning DSC used in this study was developed by TA Instruments, known as project RHC (Rapid Heating and Cooling). The rapid-scanning DSC has a liquid nitrogen cooling system (LNCS), which ranges in temperature from −180 to 700 °C. The unique features of the rapid-scanning DSC (i.e., use of a small transducer, which is surrounded by an infrared furnace system instead of a resistance furnace system, and a very small pan and sample size, typically 20−100 μg) make it possible to achieve extremely fast scan rates (up to 2000 °C/min).

Prior to sample measurements, initial temperature calibration was carried out using indium (approximate sample weight 240 μg) at a heating rate of 500 °C/min. To ensure the reliability of the rapid-scanning DSC temperature data, indium was heated at the same scan rates to be used in subsequent sample measurements. The heating rates employed were 50, 100, 250, 500, 1000, 1500, and 2000 °C/min. Over all the heating rates, the standard deviation in $T_{m\ onset}$ for indium was ±0.42 °C. For temperature calibration and all sample measurements, rapid-scanning DSC aluminum pans with crimped lids were used, and an empty pan was used as the reference. Sample measurements were begun at room temperature and heated at the scan rates specified below to just after the peak temperature was reached. Dry nitrogen, at a flow rate of 25 mL/min, was used as the purge gas. In addition to the measurement of indium alone, indium was added to the fructose sample as an internal temperature standard to ensure the reliability of the rapid-scanning DSC temperature data. A 1:2 weight ratio (w/w) of crystalline fructose to indium (total sample weight approximately 300 μg) was analyzed at the same heating rates as indium alone. For fructose (approximately 100 μg) samples, the rapid-scanning DSC measurements were done in duplicate over the heating rate range of 50−2000 °C/min, except for the heating rates of 50, 100, and 2000 °C/min, which were done only once, due to limited use of the new rapid-scanning DSC. For sucrose and glucose (approximately 100 μg) samples, the rapid-scanning DSC measurements were performed in duplicate at heating rates of 250, 500, 1000, and 1500 °C/min. Experiments at the highest heating rate (2000 °C/min) were attempted for sucrose and glucose; however, the rapid-scanning DSC was not able to maintain the 2000 °C/min at the higher temperatures required for loss of crystalline structure in sucrose and glucose compared to fructose, due to the fact that at higher temperatures there is more heat loss to the environment around the furnace. Since these measurements were obtained, TA Instruments has improved the robustness of maintaining the high heating rates in the high-temperature range.

Determination of Thermodynamic Melting Temperatures. Universal Analysis (UA) software (TA Instruments) was used to analyze the $T_{m\ onset}$ values for all sample measurements obtained using standard DSC and rapid-scanning DSC. The $T_{m\ onset}$ values were plotted as a function of heating rate. The thermodynamic melting temperature ($T_{m\ onset}$) was determined as the temperature at which $T_{m\ onset}$ leveled off to a constant value irrespective of the heating rate. The heating rate at $T_{m\ onset}$ was considered as the minimum heating rate required for reaching thermodynamic melting.

Statistical analyses were carried out using SAS software (SAS Institute Inc., Cary, NC). For the three sugars and the mixture of fructose and indium, the general linear model (GLM) procedure was utilized for the analysis of variance. Tukey's studentized range test was used to determine any significant difference between means at p = 0.05. For indium, a single-sample t test at p = 0.05 was used to compare the $T_{m\ onset}$ for indium to the population mean (156.60 °C).

■ RESULTS AND DISCUSSION

Example rapid-scanning DSC thermograms for fructose and sucrose are shown in Figure 1, and the resultant $T_{m\ onset}$ values for sucrose, glucose, fructose, the mixture of fructose and indium,
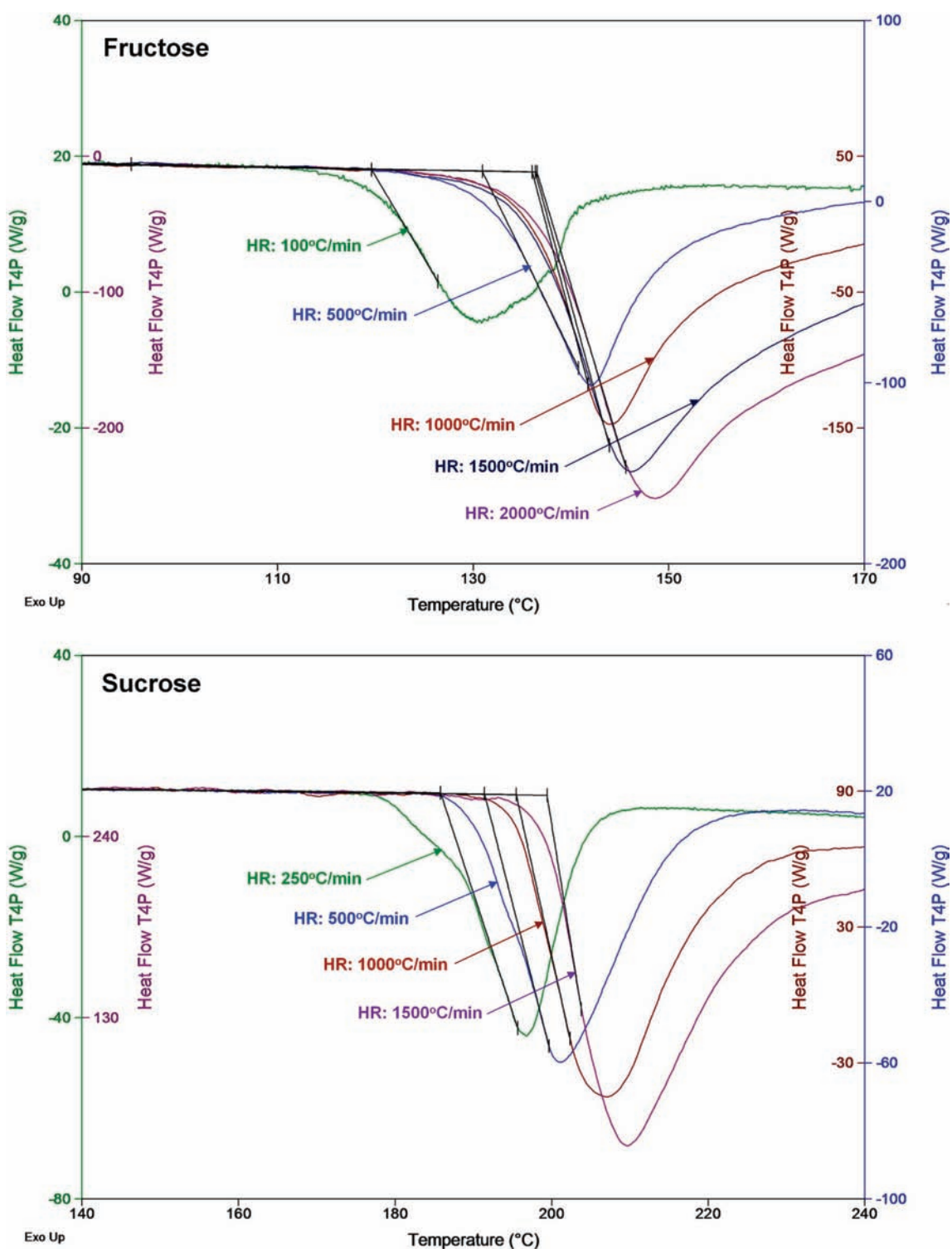
Figure 1. Example rapid-scanning DSC thermograms for fructose and sucrose compared as a function of heating rate. Only fructose and sucrose are shown, because glucose exhibited behavior similar to that of sucrose. An extrapolated $T_{m\ onset}$ value for each replicate at each heating rate was obtained using Universal Analysis (UA) software (TA Instruments, New Castle, DE). Replicate values were then averaged and are given in Table 1.
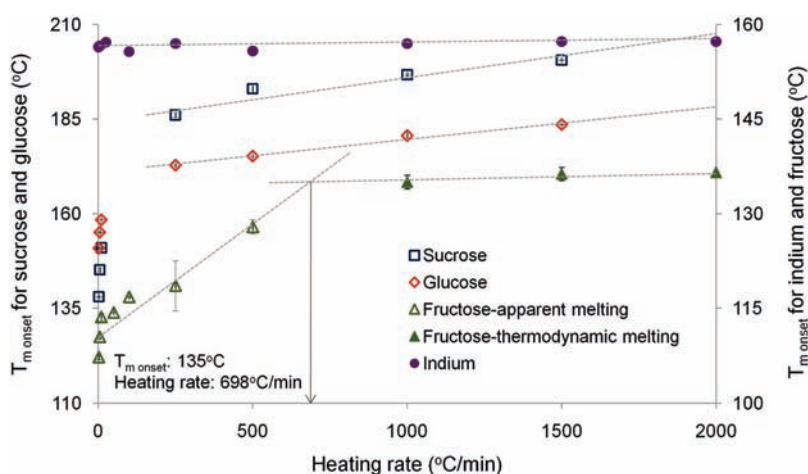
and indium as a function of heating rate are given in Table 1 and plotted in Figure 2 (except for the mixture because these data would directly overlap with the individual indium and fructose data). As expected, because indium is a thermodynamic melting material, the $T_{m\ onset}$ values for indium remained relatively

constant (156.74 ± 0.42 °C) over the entire heating rate range employed and were not significantly different from the population mean (156.60 °C) at $p = 0.05$. In contrast, the sugars exhibited an increase in $T_{m\ onset}$ as a function of heating rate. For sucrose and glucose, this heating rate dependency continued

Table 1. $T_{m\ onset}$ Values and Standard Deviations for Sucrose, Glucose, Fructose, a Mixture of Fructose and Indium, and Indium as a Function of Heating Rate Using Rapid-Scanning DSC

heating rate (°C/min)	$T_{m\ onset}{}^a$ (°C)				
	sucrose	glucose	fructose	fructose in the mixture of fructose and indium	indium[b]
1					156.45
2	$138.01 \pm 0.12g$	$150.89 \pm 0.08g$	$107.25 \pm 1.05f$		
5	$145.15 \pm 0.49f$	$155.11 \pm 0.10f$	$110.45 \pm 0.30e$		156.60
10	$150.97 \pm 0.51e$	$158.40 \pm 0.14e$	$113.59 \pm 1.51d$		
25					157.20
50			$114.30 \pm 0.13cd^c$		
100			$116.77 \pm 0.08cd^c$	$117.44 \pm 0.10d$	155.70
250	$186.09 \pm 0.56d$	$172.84 \pm 0.27d$	$118.56 \pm 0.04c^c$	$118.38 \pm 0.15c$	156.82
500	$193.01 \pm 1.29c$	$175.23 \pm 0.12c$	$127.91 \pm 3.97b$	$128.04 \pm 0.05b$	156.68
1000	$196.70 \pm 0.20b$	$180.66 \pm 1.06b$	$135.02 \pm 1.10a$	$135.86 \pm 0.05a$	157.01
1500	$200.62 \pm 0.09a$	$183.57 \pm 0.07a$	$136.30 \pm 1.04a$	$135.92 \pm 0.09a$	157.23
2000			$136.54 \pm 0.07a^c$	$136.37 \pm 0.12a$	157.30

[a] Means with the same letter within a column (difference among different heating rates) are not significantly different ($p = 0.05$). [b] Using a single-sample t test, the $T_{m\ onset}$ values for indium were not significantly different from the population mean (156.60 °C) at $p = 0.05$. [c] Individual measurements were taken due to limited availability of the new rapid-scanning DSC instrument. For each measurement, data analysis was done in triplicate.

Figure 2. $T_{m\ onset}$ values and standard deviation error bars for sucrose, glucose, fructose, and indium as a function of heating rate. Open symbols indicate apparent melting, and solid symbols indicate thermodynamic melting.

over the entire heating rate range, whereas for fructose the $T_{m\ onset}$ significantly increased with heating rate until 1000 °C/min, after which $T_{m\ onset}$ values remained relatively constant at 135.83 $\pm$ 1.14 °C for the remaining three heating rates. Thus, we propose 135.83 °C to be the thermodynamic melting temperature ($T_{m\ onset}$) of fructose. By extrapolation, the minimum heating rate required to reach the thermodynamic melting (heating rate independent $T_{m\ onset}$) of fructose was 698 °C/min. The mixture of fructose and indium exhibited $T_{m\ onset}$ values very similar to those for fructose alone (Table 1). It is important to mention that the minimum heating rate at which the transition from apparent to thermodynamic melting occurs is likely affected by the type and amount of trace components (e.g., water and salts) contained in the fructose. These same trace components are also likely responsible for the variation in the apparent melting temperature ($T_{m\ onset}$ of thermal decomposition) at the same heating rate for different sugar sources (e.g., analytical grade sucrose versus commercial available sucrose) and even

within a sugar source. For example, according to Eggleston and others,[21,22] trace components [e.g., water, salts, reducing sugars (i.e., glucose and fructose), and organic acids], which have been reported to accelerate sucrose decomposition, vary widely among different sucrose samples and even between lots of the same sucrose sample. Therefore, the minimum heating rate required to reach the thermodynamic melting temperature, as well as the apparent melting temperature, could be different for every sugar sample studied. Further research is needed to investigate the influence of trace components on both apparent and thermodynamic melting of sugars.

Unlike fructose, the thermodynamic melting temperatures for both sucrose and glucose were not attained (Figure 2). Possibly, the 1500 °C/min upper limit heating rate was not fast enough to suppress the kinetic process, that is, thermal decomposition, and achieve thermodynamic melting, because of the higher apparent $T_{m\ onset}$ of sucrose and glucose compared to fructose.

In conclusion, this study demonstrates the ability of rapid-scanning DSC to determine the thermodynamic melting temperature of fructose by eliminating the kinetics-based interference of thermal decomposition. However, the minimum heating rate required to reach the thermodynamic melting temperature could be different for every sugar sample, because the rate of thermal decomposition is influenced by the various types and amounts of trace components in the sample. Further research is needed to determine the influence of trace components on both apparent and thermodynamic melting of sugars. Accurate determination and interpretation of material properties are critical to process and product development as well as quality improvement. Therefore, the new rapid-scanning DSC will be of great benefit to the food, pharmaceutical, and material industries for investigating materials that exhibit complicated thermal behaviors, such as the sugars studied herein.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Material information for sucrose, glucose, and fructose obtained from the Sigma-Aldrich Co. and analyzed by the authors of this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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