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Melting behaviour of D-sucrose, D-glucose and D-fructose

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Abstract—The melting behaviour of D-sucrose, D-glucose and D-fructose was studied. The melting peaks were determined with DSC and the start of decomposition was studied with TG at different rates of heating. In addition, melting points were determined with a melting point apparatus. The samples were identified as D-sucrose, α-D-glucopyranose and β-D-fructopyranose by powder diffraction measurements. There were differences in melting between the different samples of the same sugar and the rate of heating had a remarkable effect on the melting behaviour. For example, T_o, ΔH_f and T_i (initial temperature of decomposition) at a $1\,^{\circ}C\,min^{-1}$ rate of heating were 184.5 °C, $126.6\,J\,g^{-1}$ and 171.3 °C for D-sucrose, 146.5 °C, $185.4\,J\,g^{-1}$ and 152.0 °C for D-glucose and 112.7 °C, $154.1\,J\,g^{-1}$ and 113.9 °C for D-fructose. The same parameters at $10\,^{\circ}C\,min^{-1}$ rate of heating were 188.9 °C, $134.4\,J\,g^{-1}$ and 189.2 °C for D-sucrose, 155.2 °C, $194.3\,J\,g^{-1}$ and 170.3 °C for D-glucose and 125.7 °C, $176.7\,J\,g^{-1}$ and 136.8 °C D-fructose. At slow rates of heating, there were substantial differences between the different samples of the same sugar. The melting point determination is a sensitive method for the characterization of crystal quality but it cannot be used alone for the identification of sugar samples in all cases. Therefore, the melting point method should be validated for different sugars.

Keywords: Melting point; D-Sucrose; D-Glucose; D-Fructose

1. Introduction

The melting point is widely used in the characterization of materials. As a thermal value, the melting point is used in development, research and quality control, for example, for the identification of different samples or the determination of purity. Determination of the melting point provides qualitative information about the sample measured. In melting, the solid and liquid are in thermodynamic equilibrium at constant temperature and pressure.[1] The melting is usually determined by raising the temperature at a certain rate of heating over the range of the melting point. This causes a temperature gradient in the sample and an apparent rise of the observed melting temperature. For that reason, the melting proceeds over an apparent temperature range, which result from the lag in heat transfer and the range is larger the faster the rate of heating. The melting can be said to be anomalous if the form recrystallized from the melt is different from the original form or if a change of the conformation of molecules occurs during melting. Also a decomposition taking place at the melting temperature range changes the melting to anomalous. The anomalous melting temperature is strongly dependent on the rate of heating.

Melting temperatures may be determined by differential scanning calorimetry (DSC). The shape of the DSC peak depends strongly on the test conditions and parameters. For example, the position of the peak maximum changes with the rate of heating, the thermal conductance and the sample mass. Only the extrapolated onset temperature is relatively independent of experimental parameters. A properly calibrated DSC gives the melting temperature as the onset temperature of the melting endotherm. If the crystals vary in their melting properties, there may be a melting temperature range, as in the case of sugars.[2] In DSC, the thermodynamic melting point is determined by extrapolating an onset temperature to a rate of heating approaching zero. However, if there are other events that relate to melting, especially at slow rates of heating, a thermodynamically

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well-defined melting point cannot be determined in DSC. The melting point can also be determined by the standardized pharmacopeian melting method where the sample is melted in a capillary and the melting temperature is registered when the sample is completely melted.[3]

Crystalline sugars melt, when they are heated to or above their melting temperature. Sugars do not have sharp melting temperatures and their melting proceeds over a temperature range. For this reason, melting endotherms are fairly broad. The melting temperatures of sugars are sensitive to water, impurities and crystallinity. Some sugars may caramelize and become brown concomitantly with the melting process and they may also decompose before melting.[4] If the enthalpy related to decomposition is smaller than the enthalpy of melting, the total enthalpy is lower if the decomposition begins before melting occurs and the total enthalpy is larger if decomposition happens after the melting peak.

In this study, the melting of sugars has been studied more comprehensively. The samples selected were D-sucrose, D-glucose and D-fructose. Anhydrous D-sucrose exists in only one form and its crystal structure has been determined.[5–7] Crystalline D-glucose exists as both α- and β-D-glucopyranose, of which α-D-glucopyranose is more common and its crystal structure has been determined.[8–10] The only known crystalline isomer of D-fructose is β-D-fructopyranose and its crystal structure has determined.[8,11,12]

When melting temperatures of sugars are reviewed in the literature, it is discovered that values for the same sugar may slightly differ from each other. The articles are mainly general and the melting temperatures of various sugars are summarized into one table. The melting behaviour of individual sugars is usually not studied. However, the melting point is one of the parameters commonly used to identify and characterize the material. The literature values of the melting temperature of D-sucrose, D-glucose and D-fructose are collected in Table 1. The melting temperatures of the same sugar differ substantially between different references. D-Sucrose melts at the highest temperature of these sugars and the reported melting range is 160–192 °C. However, it should be noted that the reported values are generally 185–190 °C and only a few values deviate from that range. The melting peak of D-glucose is 146–165 °C and the deviations are larger than those of D-sucrose. In only two studies[8,24] has the form (α- or β-) studied been reported. For D-fructose, the literature values of the melting temperature vary between 102 and 132 °C and the values are uniformly divided over that range.

The melting temperatures may differ between sugar anomers.[4] α- and β-Anomers of the same sugar are in equilibrium in water, but in the crystalline state one anomer dominates.[25] The conformation of the sugar may change in the melting process. Broido et al.[13] studied the mutarotation of α- and β-D-glucose near the melting point and the process of mutarotation was found to become very fast as soon as the bulk material melted. Farhoudi and Mauch[26] studied mutarotation of D-fructose, and reported that during melting β-D-fructopyranose was converted into α- and β-D-fructofuranose, but D-fructofuranose in the melted state was reconverted into D-fructopyranose.[27]

Table 1. Literature values of melting temperatures of D-sucrose, D-glucose and D-fructose[a]

Reference	Melting temperature (°C)		
	D-Sucrose	D-Glucose	D-Fructose
Shallenberger and Birch[8]	160–186	146 (α) 148–150 (β)	102–104
Broido et al.[13]		146	
Roos[14]	(173) 190	(143) 158	(108) 127
Raemy and Schweizer[15]	(160) 185	(135) 150	(80) 115
Slade and Levine[16]	192	158	124
Ramos-Sanchez et al.[17]	180	156	121
Wungtanagorn and Schmidt[18]		(158) 164	(114) 132
Fan and Angell[19]			105
Saleki-Gerhardt and Zografi[20]	188		
Órsi[21]		165	120
Gloria and Sievert[22]	188		
Vanhal and Blond[23]	190		
Lide[24]	185–186	146 (α) 150 (β)	103–105

[a] The values in parentheses are onset temperatures.

The differences between the literature values for the same sugar indicate that the melting of sugars is not an unambiguous event. In this study, we investigated how the melting temperature changed and how the differences could be explained. The melting temperatures were determined with DSC and the decomposition of the same sugars using thermogravimetric analysis (TGA). Different rates of heating were used in both measurements. In addition, some measurements were made with a TG/DTA that gave both TG and DTA results in one measurement. Melting points were also determined using a melting point apparatus.

2. Experimental

Two different samples of each sugar were used. Crystalline D-sucrose (2820 Sucrose Pharma 51115) *[sucrose A]* and D-fructose (A125 Fructofin C 10098) *[fructose A]* were obtained from Danisco Sweeteners. In addition, D(+)-sucrose *[sucrose B]*, D(−)-fructose *[fructose B]* and D(+)-glucose anhydrous (Fluka BioChemica, >99.5%) *[glucose B]* and D(+)-glucose (BDH, AnalR) *[glucose A]* were used. Sucrose A and fructose A were bulk materials, whereas the others were fine chemicals made for laboratory use. Before measurements all samples were dried at 50 °C for two days and then stored in a desiccator over P_2O_5.

The DSC measurements were carried out on a Perkin–Elmer Pyris DSC Diamond using 50 μL aluminium sample cups with capillary holes and a dynamic nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The rates of heating used were 0.5, 1, 2, 10, 20, 50 and 100 °C min^{-1}. The measurements were started at 25 °C and stopped when a melting peak was observed. Three parallel measurements were taken at each rate of heating, using 4–6 mg samples. The temperature calibration was done by indium and zinc standards and the heat flow was calibrated by the melting enthalpy of indium standard. The calibration was done with a 10 °C min^{-1} rate of heating and the results at different rates of heating were corrected by a thermal lag of 0.034 min.[28] For the slowest measurements (0.5 and 1 °C min^{-1}), the calibration was done at the same rate of heating used in the measurement and the thermal lag correction was not used. The onset and peak temperatures were calculated automatically by software and the average values of three parallel measurements were calculated.

The TG measurements were carried out on a Perkin–Elmer TGA 7 Thermogravimetric Analyzer using an open Pt-pan and a dynamic nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The measurements were started at 25 °C and stopped when decomposition had clearly started (250–300 °C). The rates of heating used (0.5, 1, 2, 10, 20, 50 and 100 °C min^{-1}) were the same as in DSC. The sample weights were 4–6 mg. The temperature calibration was done at a 2 °C min^{-1} rate of heating by using the Curie-point temperatures of alumel, nickel, nicoseal, perkalloy and iron. From TG measurements, the initial temperature of decomposition was taken as the temperature where the reduction of weight was greater than the noise in the TG curve.

Some measurements were made also with a Perkin–Elmer Pyris Diamond TG/DTA that gave both TG and DTA results simultaneously. The purpose of these measurements was to compare the results obtained by two different instruments and verify that the results of TG and DSC were comparable. The measurements were made using an open Pt pan and a dynamic nitrogen atmosphere with a flow rate of 110 mL min^{-1}. The sample chosen was glucose B. The sample weights were 8–10 mg. The rates of heating were 1, 10, 50 and 100 °C min^{-1} and the temperature range was 25–300 °C.

Melting points were also determined with a Mettler Toledo FP 62 melting point apparatus. Samples were dried over silica gel for 24 h and lightly ground in a porcelain mortar just before the measurements. At least three parallel measurements were made with each sugar.

The X-ray powder diffraction patterns were recorded using a Huber Imaging Plate Guinier camera G670. Germanium crystal monochromatized Cu$K_{\alpha 1}$-radiation was used ($\lambda = 1.54056$ Å) and the X-ray tube was operated at 45 kV and 25 mA. The samples were prepared on Mylar film using Vaseline. The exposure time was 30 min and the imaging plate was scanned six times. ZDS software was used to process the measurement data. The measured powder patterns were identified with the PDF-2 database of known powder diffraction patterns.

3. Results and discussion

From the powder diffraction measurements, both sucrose samples were identified as D-sucrose, both D-glucose samples as α-D-glucopyranose and both D-fructose samples as β-D-fructopyranose. All identifications were unambiguous.

The results of thermal analysis measurements (TG and DSC) are presented in Table 2. Increasing the rates of heating moved both the onset and the peak temperatures to higher temperatures in all samples studied. The enthalpy of melting increased as the rate of heating increased. Also, the initial temperature of TG measurements moved to higher temperatures as the rates of heating increased.

In the case of sucrose A, the peak and onset temperatures clearly increased as the rate of heating was increased to 10 °C min^{-1} but the onsets were nearly constant at higher rates of heating. The peaks became slightly broader as the rate of heating was increased. When TG and DSC results were compared, at slower rates of heating the decomposition started before the melting occurred. On the other hand, at higher rates of heating the melting occurred before the decomposition started. Almost the same conclusions could be drawn for sucrose B, but the increase in the onset and peak temperatures was not so marked and the peaks were narrower.

There were differences among the D-sucrose samples. At slow heating rates, melting occurred at a lower temperature for sucrose A than sucrose B. Also the enthalpy of the melting differed, especially at low rates of heating: the enthalpy of melting of sucrose A was nearly half of that of sucrose B. The low enthalpy can be explained by the enthalpy of decomposition being lower than the enthalpy of melting. There were also differences in the shape of the DSC curves (Fig. 1). At slow rates of heating, the peak of sucrose A was not sharp but wide and had a saw-tooth appearance and the start of decomposition was also seen. The peak of sucrose B was almost a normal melting peak. At the faster rates of heating, caramellization could be seen before the melting peak of sucrose A but not in the melting peak of sucrose B. The melting of sucrose was anomalous, especially at slow rates of heating, due to partial thermal decomposition.

In the D-glucose samples, both the onset and peak temperatures moved higher as the rate of heating increased. This movement was larger at slow rates of heating than at faster rates. In glucose A, the peaks were narrow even at the fastest rates of heating and they were

Table 2. The results of DSC and TG measurements[a]

Rate of heating (°C min^{-1})	Onset (°C)	Peak (°C)	ΔH_f (J g^{-1})	T_i (°C)
Sucrose A				
0.5	167.9±1.3	169.9±0.6	54.8±7.8	159.6
1	173.7±1.6	176.6±0.1	72.1±5.6	161.1
2	178.2±1.6	181.4±1.1	111.4±8.8	169.6
10	185.9±1.0	190.5±0.2	126.4±0.4	179.7
20	187.5±0.2	191.9±0.3	130.8±0.4	192.2
50	188.3±0.5	193.7±0.3	136.9±0.3	207.5
100	189.0±0.4	196.1±0.5	143.2±0.6	235.3
Sucrose B				
0.5	181.4±0.3	182.7±0.5	119.8±2.6	167.0
1	184.5±0.8	186.6±1.0	126.6±2.3	171.3
2	187.1±0.1	189.3±0.1	128.0±1.0	178.8
10	188.9±0.0	191.5±0.1	134.4±1.2	189.2
20	189.6±0.5	192.9±0.8	135.4±2.0	200.7
50	191.1±1.5	196.1±2.4	138.8±1.1	214.9
100	190.8±0.5	196.5±0.6	145.4±0.5	228.4
Glucose A				
0.5	147.5±0.2	149.1±0.2	182.7±2.0	146.4
1	149.8±0.1	151.7±0.2	189.1±1.2	149.8
2	152.8±0.4	154.8±0.4	189.0±1.5	151.4
10	160.4±0.7	163.1±0.0	195.9±1.2	166.4
20	164.8±0.0	167.4±0.1	200.1±2.0	176.5
50	169.4±0.0	172.6±0.1	208.0±0.5	191.6
100	171.8±0.5	176.1±0.6	220.7±3.6	194.4
Glucose B				
0.5	145.1±0.7	147.5±0.6	180.1±2.1	147.0
1	146.5±0.6	149.3±0.7	185.4±1.8	152.0
2	148.9±1.3	151.9±1.1	187.1±2.4	159.1
10	155.2±0.6	159.4±0.5	194.3±1.4	170.3
20	158.3±0.8	163.8±1.0	199.1±0.5	183.5
50	163.3±0.7	168.9±0.3	206.9±1.0	201.1
100	166.7±0.8	173.8±1.3	218.9±1.9	204.3
Fructose A				
0.5	108.2±2.6	114.3±0.6	147.6±0.3	110.7
1	113.6±2.6	118.4±0.2	156.0±1.8	116.3
2	112.0±1.6	123.2±0.4	161.5±1.3	122.8
10	125.8±0.2	134.1±0.0	174.8±4.4	138.7
20	131.3±0.3	137.8±0.2	185.9±3.3	145.0
50	135.7±0.2	140.6±0.4	197.8±2.2	161.6
100	137.0±0.1	142.6±0.1	212.8±1.5	166.1
Fructose B				
0.5	110.0±1.0	113.0±1.0	151.6±0.7	110.4
1	112.7±0.7	116.7±0.0	154.1±4.0	113.9
2	116.2±0.6	121.0±0.2	163.9±1.6	119.0
10	125.7±0.8	131.7±0.3	176.7±2.8	136.8
20	130.0±0.2	136.0±0.2	185.5±1.3	147.1
50	134.9±0.1	139.8±0.4	199.2±3.9	157.0
100	136.8±0.4	142.0±0.5	203.7±3.2	165.4

[a] Onset and peak temperatures of melting and the heat of fusion (ΔH_f) are from DSC. T_i is the initial temperature of decomposition (from TG).

narrower than in glucose B. In both D-glucose samples studied, the shape of peaks was normal but at faster rates of heating the peak broadened towards higher temperature (Fig. 2). The enthalpy of melting of both D-glucose samples equated very well in all measurements. Comparison of the TG and DSC results showed that the decomposition that started before melting was stopped at slow rates of heating. In contrast to D-sucrose, the increase of the onset temperature continued also at high rates of heating in D-glucose. This could be explained if, in addition to the melting, thermal decomposition and mutarotation also occurred at slow rates of heating. At high rates of heating, the change was mostly due to mutarotation.

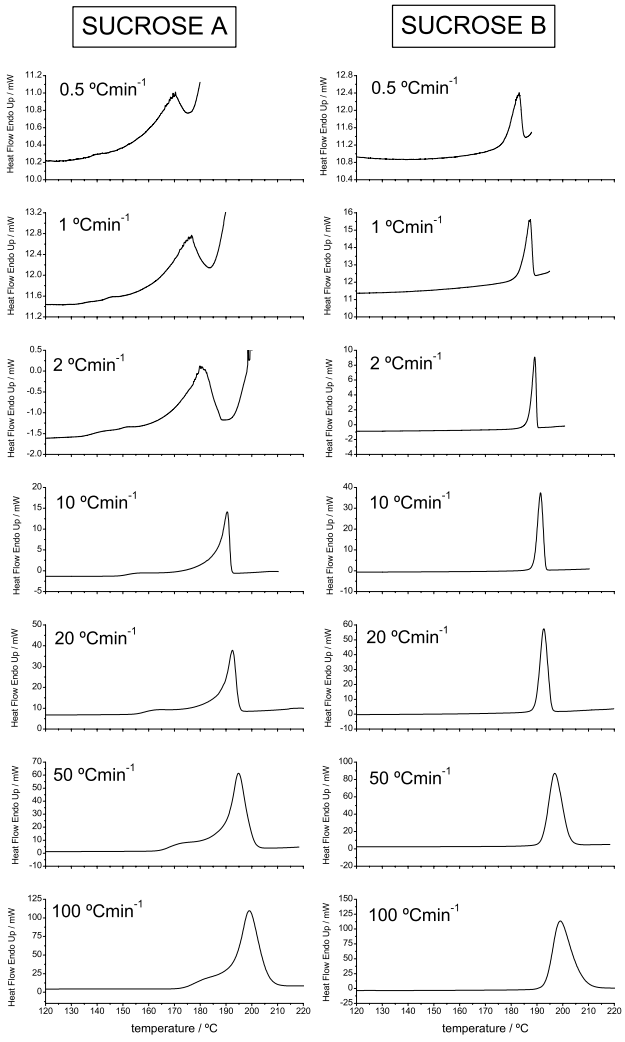

Figure 1. DSC curves of D-sucrose samples.

There were differences between the D-glucose samples. Glucose A melted at higher temperatures than glucose B. The onset temperatures of glucose A corresponded with the peak temperatures of glucose B and the onset temperatures of glucose A were clearly lower. However, on the grounds of TG measurements, the decomposition of glucose A started at a slightly lower temperature than that of glucose B.

The melting peaks of the D-fructose samples moved to substantially higher temperatures with increasing rate of

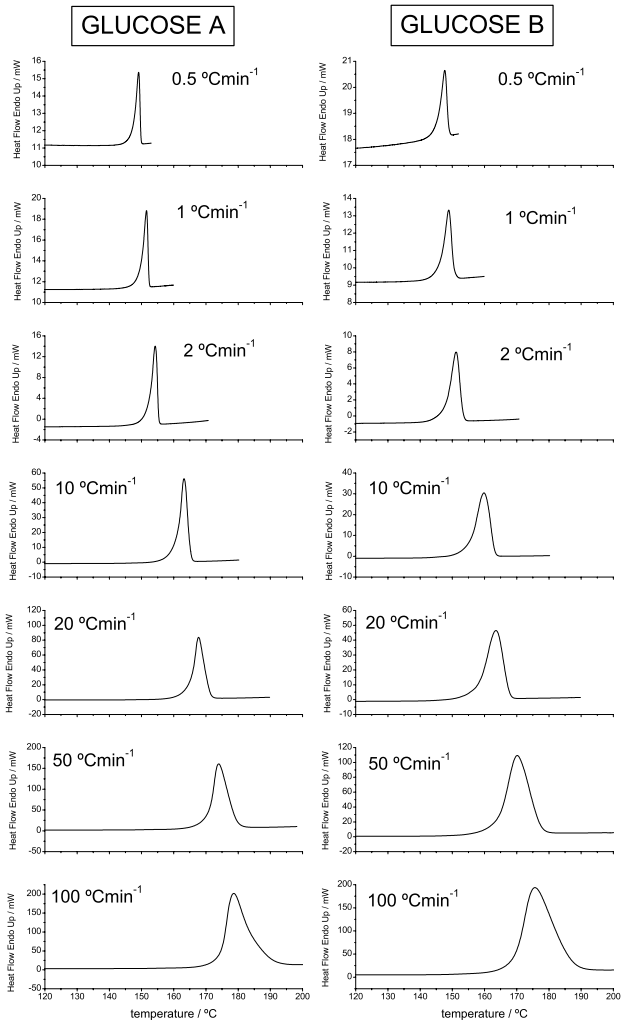

Figure 2. DSC curves of D-glucose samples.

heating. The peaks were broad already at low rates of heating in both D-fructose samples, but overall a little broader in fructose A. Decomposition started before melting at a 10 °C min^{-1} rate of heating and at faster rates of heating the decomposition started only after the melting. In D-fructose, the onset temperature increased at all rates of heating in the same way as in the case of D-glucose. However, the change was larger at slow rates of heating than at fast rates. At low rates of heating, the melting temperature was lowered by both thermal decomposition and mutarotation. On the grounds of values given by TG, the mutarotation was the predominant factor in the change of the melting point, especially at high rates of heating.

In comparing the D-fructose samples, the melting temperatures were nearly equal and the enthalpy of melting was also almost the same for both D-fructose samples (except at the 100 °C min^{-1} rate of heating, in which the energy of fructose A was clearly larger). Despite that fact, there was a difference in the shape of the DSC peaks (Fig. 3). At slow rates of heating, the peaks of fructose A were broad and they had no sharp heads. As the rate of heating increased, the peak became sharper but the lowest part was still broad. The peaks of fructose B were sharper and not so broad, but the end parts of peaks were broad at fast rates of heating.

All measurements in this study were performed by raising the temperature from room temperature to the melting point at different rates of heating. In official melting point determination methods, the temperature of the bath should be raised to about 10 °C below the presumed melting point and the sample should then be inserted into the apparatus only 5–10 °C before the presumed melting point, so that thermally sensitive samples do not decompose during the measurement. For that reason, for thermally sensitive samples, for example, for different sugars, the melting point results should always be validated.[3,29]

For interpretation of the results, more discussion regarding rates of heating is necessary. Besides the mutarotation and decomposition, the kinetics of melting

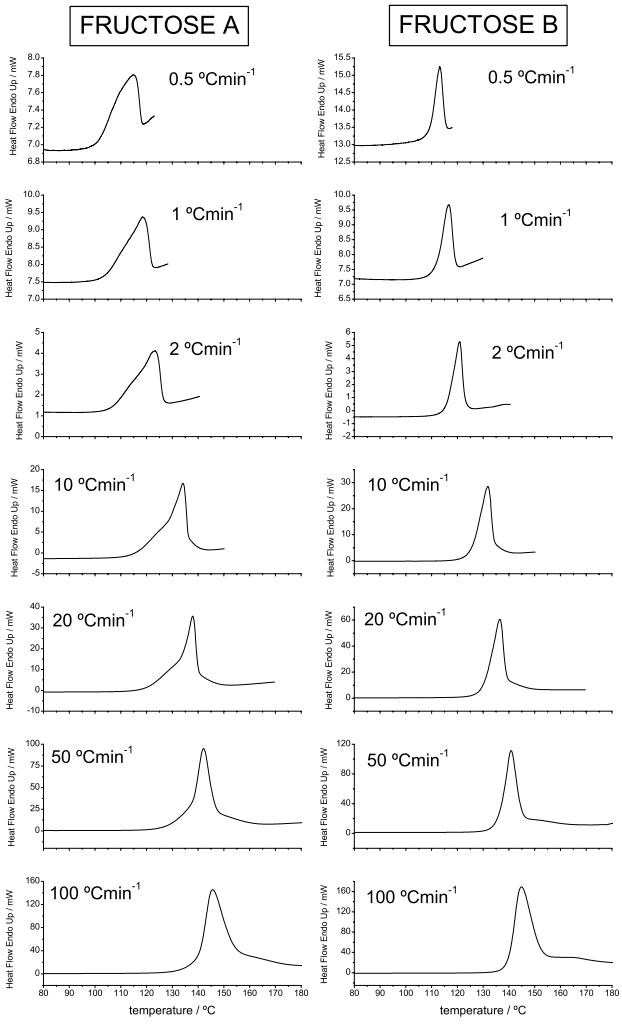

Figure 3. DSC curves of D-fructose samples.

may also have an impact on the results of DSC. The instrument settings were used in defining various rates of heating in the melting experiments. Although the thermal lag had been taken into account in DSC measurements, it was unlikely that the thermal lag of the sample is identical with the one measured with indium, particularly at high rates of heating. There were also problems in comparing the high and low rates of heating because of the problem of resolution from high rates of heating due to power input versus sensitivity from low rates of heating. Endothermal/exothermal changes associated with caramellization/decomposition may also have affected the onset temperature and ΔH_f values, particularly at very low rates of heating.

The results of melting point apparatus measurements are provided in Table 3. The melting points of the two different D-sucrose samples clearly differed from each other, sucrose A melting at a lower temperature than sucrose B. The melting points of both D-fructose samples were almost the same and the difference between the melting points of D-glucose samples were very small. The standard deviations are low, ensuring the reliability of parallel measurements. The standard deviation of the results of glucose B was much higher than that of the other samples studied although 10 parallel measurements were made. This phenomenon may be due to mutarotation. However, the mean value of parallel measurements was almost the same as that of glucose A.

As the results of melting point apparatus were compared with melting temperatures using DSC (Tables 2 and 3), the general conclusions were that the melting point apparatus gave lower melting points than DSC. The values obtained by the melting point apparatus were low and comparable only to the slowest rates of heating (0.5–1 °C min^{-1}) using DSC. The melting points of the D-sucrose samples correspond to the peak temperatures of DSC measured at a 1 °C min^{-1} rate of heating. For the D-glucose samples, the melting point apparatus gave melting points almost the same as the peak temperatures of DSC measured at a 0.5 °C min^{-1} rate of heating. For the D-fructose samples, the melting point apparatus gave lower melting points than the onset or peak temperatures of the slowest rate of heating used in DSC, the difference of the melting point and the peak temperature of 0.5 °C min^{-1} rate of heating being almost 10 °C for both D-fructose samples. Because of this, the melting of D-fructose was also measured with DSC using 2 atmosphere aluminium cups but the onset and peak temperatures were similar to those obtained with pinhole cups.

Table 3. The results obtained with the melting point apparatus[a]

Sample	Melting point apparatus	DSC	
	Melting point (°C)	Onset temperature (°C)	Peak temperature (°C)
Sucrose A	179.7 ± 0.2	173.7 ± 1.6	176.6 ± 0.1
Sucrose B	186.8 ± 0.5	184.5 ± 0.8	186.6 ± 1.0
Glucose A	148.6 ± 0.3	149.8 ± 0.1	151.7 ± 0.2
Glucose B	146.4 ± 3.4	146.5 ± 0.6	149.3 ± 0.7
Fructose A	103.8 ± 0.4	113.6 ± 2.6	118.4 ± 0.2
Fructose B	103.2 ± 0.2	112.7 ± 0.7	116.7 ± 0.0

[a] Three parallel measurements were done for each sample (except for ten parallel measurements for glucose B), and the average values were calculated. The onset and peak temperatures at rate of heating of 1 °C min^{-1} measured by DSC are listed for comparison.

Table 4. Comparison of the results for glucose B[a]

Heating rate (°C min^{-1})	Onset (°C)		Peak (°C)		T_i (°C)	
	DTA	DSC	DTA	DSC	TG	TGA7
1	147.4	146.5	148.7	149.3	155.4	152.0
10	155.8	155.2	158.2	159.4	179.4	170.3
50	163.4	163.8	168.4	170.2	208.0	201.1
100	165.0	166.7	175.3	173.8	211.7	204.3

[a] TG and DTA results were measured with Perkin–Elmer Pyris Diamond TG/DTA. TGA 7 results were measured with Perkin Elmer TGA 7 Thermogravimeter Analyzer. DSC results were measured with Perkin–Elmer Pyris DSC Diamond.

The onset and peak temperatures and the initial temperatures of decomposition of glucose B measured with two different instruments have been compared in Table 4. The onset and peak temperatures (DSC and DTA measurements) are almost the same. A little difference exists in the results of TG measurements. This can be explained by small different calibrations. On the basis of these results, the DSC and TG measurements are comparable although they were made using two different instruments.

One primary objective of this paper was the formulation of recommendations regarding appropriate rates of heating for the melting determinations. Based on the results, the absolute melting can be seen in DSC best at a high rate of heating because the other events are slower. The only standardized melting method is the pharmacopeian method. If this is taken into account, the DSC rate of heating should be 1 °C min^{-1} and measurements should be performed in an inert atmosphere. However, the melting point determined in this way is anomalous and the differences between samples are clearly seen at this rate of heating.

4. Conclusions

The D-sucrose samples behaved in different ways at slow rates of heating, and decomposition started before melting. Distinct changes were seen in the shape of the melting peak and the enthalpy of melting was also very low. The low enthalpy can be explained by the enthalpy of decomposition being lower than the enthalpy of melting.

At a 10 °C min^{-1} rate of heating and faster the melting was normal. Onset temperatures were nearly constant and the peak temperatures changed only slightly. At slow rates of heating, the onset temperature changed because of decomposition.

In the D-glucose samples studied, the melting peaks moved to a higher temperature as the rate of heating was increased. Decomposition started before melting at slow rates of heating. The shift of onset temperature can be explained by partial decomposition and mutarotation.

The melting peaks of the D-fructose samples studied were shifted most of all. Decomposition started before melting at the slow rates of heating but the effect of mutarotation on the melting temperature was significant at all rates of heating used. With D-fructose, the melting point apparatus gave about 10 °C lower melting points than DSC at the same rate of heating.

This work shows that the melting of sugars is a multiphased phenomenon and the results are affected by both the determination method and the origin and quality of samples. The results show that there can be differences between different samples of the same sugar. The differences in the literature values can be explained by different origins of materials and the different methods of determination. The melting point alone cannot be used for identification of sugar samples in all cases.

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