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Carbohydrate Research 341 (2006) 2591–2599
Carbohydrate RESEARCH

DSC study of sucrose melting

Stephen T. Beckett,[b] M. Grazia Francesconi,[a] Peter M. Geary,[a] Grahame Mackenzie[a,*] and Aurélia P. E. Maulny[a]

[a]*Department of Chemistry, University of Hull, Cottingham Road, Hull HU6 7RX, UK*
[b]*Nestlé PTC, Haxby Road, York YO91 1XY, UK*

Received 8 June 2004; accepted 19 June 2006
Available online 17 August 2006

Abstract—An early endothermic peak at ~150 °C was observed for crystalline sucrose by differential scanning calorimetry. The enthalpy at this temperature was found to vary with recrystallised sucrose from different sources. The addition of mineral salts to recrystallisation solutions decreased the enthalpy of the peak at around 150 °C, whereas the absence of salts increased it. The presence of organic solvents and polysaccharides in solution had a minor effect compared to the inorganic impurities. The peak was also depleted by increasing the amount of stirring and temperature at which recrystallisation was performed.

Keywords: Sucrose; Recrystallisation; Melting enthalpy; Impurities

1. Introduction

Sucrose is one of the most abundant pure chemicals produced worldwide. The refinement level of granulated sucrose is high, affording a material with purity above 99.8%.[1] Nevertheless, a wide range of melting points for crystalline sucrose have been reported, for example, Roos[2] gives melting points for sucrose varying from 186 to 192 °C, whereas Okuno et al.[3] quote references in which melting points of sucrose range from 160 to 191 °C. Even though the lowering of the melting points of substances is usually explained by the presence of impurities, Kamoda[4] showed that this cannot be applied to the lowering of sucrose melting, since the melting points of sucrose crystals containing K^+ were higher than that of ‘pure sucrose crystals’.

In recent years, the melting of sucrose has been examined by differential scanning calorimetry (DSC). In a study of the co-crystallisation of sucrose with either glucose or fructose, Bhandari and Hartel[5] observed a small peak just before the main melting endotherm of sucrose. They suggested that this could be due to the devitrification of amorphous matter or the solubilisation of the surface of the crystals by residual moisture. Okuno et al.[3] observed the occurrence of three endothermic peaks around 153, 160 and 172 °C by DSC for sucrose recrystallised from pure water. The two first peaks were decreased by the presence of KCl. The appearance of fine cracks during the heating was thought to be responsible for the first two endothermic peaks. Other melting characteristics have been observed for sucrose. Mathlouthi et al.[6] showed differences in crystalline, freeze-dried and quenched-melt forms of sucrose. The crystalline and freeze-dried samples showed the expected peak at 180 °C but the freeze-dried samples showed an exothermic peak at 110 °C, which was absent in the crystalline form. The freeze-dried form, whilst mostly amorphous, contained sufficient crystal nuclei to promote recrystallisation at 110 °C. The quenched form showed a glass–solid transition at 60 °C and an endothermic peak at 135 °C that was assigned to a decrease in viscosity rather than a phase transition. Mathlouthi concluded that his sample contained sucrose in its amorphous state.

In the present work, sucrose from different commercial sources was recrystallised, and the parameters influencing the appearance of a peak around 150 °C before

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* Corresponding author. Tel.: +44 1482 465479; fax: +44 1482 466410; e-mail: g.mackenzie@hull.ac.uk

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doi:10.1016/j.carres.2006.07.004

the main endothermic peak of sucrose melting (~190 °C) were investigated. These included the amount of either inorganic or organic impurities, amount of stirring and temperature to which the recrystallisation solution is raised.

2. Experimental

2.1. Materials

Granulated analytical grade sucrose from Fisher Chemicals (FC: heavy metal $\leqslant$ ppm Pb; sulfated ash $\leqslant 0.01\%$; insoluble matter $\leqslant 0.005\%$; titratable acid $\leqslant 0.0008$ mequiv/g; invert sugar $\leqslant 0.05\%$; SO_4, SO_3, as $SO_4 \leqslant 0.005\%$; Cl $\leqslant$ 50 ppm; Fe $\leqslant$ 5 ppm obtained from Fisher Scientific Catalogue 2003–2004) and high-ash granulated sugars from Silver Spoon (SP), Tate & Lyle (T&L) and Lancaster (L) were used in the recrystallisation experiments. Analytical grades of KCl, NaCl and K_2SO_4 and the Amberlite monobed were used. Spray-dried glucose syrups and maltodextrins were obtained from Cerestar. The polar aprotic solvents, dimethyl sulfoxide (Me_2SO) and *N*,*N*-dimethylformamide (DMF) were acquired from Aldrich and Avocado Research Chemicals Ltd, respectively.

2.2. Methods of recrystallisation

A mixture of sucrose (100 g) and purified water (25 mL) was heated on a hot plate rapidly to 128 °C in an open beaker, allowing free evaporation of water during the process. The choice of this temperature was based on the work of Bhandari and Hartel,[5] who found it to be optimum for their crystallisation studies but avoiding degradation of the sugar. Once the temperature was reached, the solution was removed immediately from the heating source. At this point, the solution was stirred for 30 s with a spatula to initiate the crystallisation. The temperature of the solution was allowed to drop to room temperature, and the crystals were dried over P_2O_5 overnight. No by-products were observed by HPLC using this recrystallisation technique in any of the studies which we performed. For the experiments in the presence of impurities, the same method as above was repeated, but with potassium chloride, sodium chloride and potassium sulfate, respectively, present in the initial solution of sucrose from Fisher Chemicals. These salts were added at different concentrations, namely 0.1%, 0.5% and 1% by weight of dry matter. Recrystallisation in the presence of an aprotic solvent or polysaccharide was carried out by adding DMF, Me_2SO, maltodextrin or spray-dried glucose syrup, accordingly, before applying any amount of stirring to nucleate the solution. The solvents were added in the concentrations 2%, 5% and 10% (by weight), respectively, whereas the polysaccharides were added in the concentrations 5%, 10%, 15% and 20% (by weight of dry matter), respectively.

For the experiments involving the removal of mineral salts, a solution of 61.5% by weight of sucrose from Silver Spoon was prepared using purified water. This solution (100 mL) was passed through a column (diameter: 2.5 cm) packed with an Amberlite monobed ion-exchange resin (50 g). The exchangeable ions were H^+ and OH^-. The treated solution was recrystallised following the same method as before.

Successive recrystallisations were performed on sucrose where the crystals were obtained by centrifugal filtration. For this type of filtration, the materials were placed on top of glass cylinders fitted with a sinter (porosity 2) in their middle section. These cylinders were then introduced in conventional centrifugal tubes. The centrifuge used was a Centaur 2 run at 3600 rpm (1130*g*). The recovered crystals were dried. The procedure was repeated three times.

The different recrystallisations were prepared in triplicates.

2.3. Differential scanning calorimetric analysis

The endotherm scans of the different materials were obtained by differential scanning calorimetry, using a scanning rate of 10 °C/min from 25 to 200 °C. A Pyris DSC 7 (Perkin–Elmer) system connected to a low-temperature refrigerator system (Intracooler II) was used. Dry nitrogen was used to purge the sample head and glove box. The instrument was calibrated using indium at the same scanning rate as the samples. The product was ground using a pestle and mortar; it weighed ~5 mg and was sealed in aluminium pans. All DSC runs were repeated in triplicate.

2.4. HPLC analysis of the sugars

The sucrose samples were analysed by HPLC using a Gilson 203 pump and an Apex Carbohydrate column from Jones Chromatography. The different sugars were detected by a Sedex 55 light detector and the traces recorded using a Chessell BP 2404 recorder. The mobile phase passing through the column was 4:1 acetonitrile–water at a flow rate of 1 mL/min. Each time 20 μL of a solution containing 0.15 g of product per 50 mL of water was injected.

2.5. Conductivity measurements

Conductivity measurements were carried out on solutions of sugars at a concentration of 28% by weight prepared with purified water and using a Jenway 4510 Conductivity Meter.

2.6. Scanning electron microscopy

The samples were sprinkled on a double-sided sticky tape placed on aluminium SEM stubs, which were dried in a desiccator for 1 h and sputter-coated 2 × 4 min with gold/palladium. The coated samples were immediately examined using a Hitachi S-1200 at 10 kV.

3. Results and discussion

3.1. Purity analyses

The sugars from different commercial sources, FC, T&L and SP, were each examined for their melting behaviour by differential scanning calorimetry (DSC) and HPLC. The sugars were also investigated by DSC following their being recrystallised from an aqueous solution (see Fig. 1).

The DSC results for the parent sugars and the recrystallised sugars are shown in Table 1. It may be observed that both sugars from Silver Spoon (SP) and Lancaster (L) showed a single peak at 192 ± 1 °C. In contrast, the sugars from Tate & Lyle (T&L) and Fisher Chemicals (FC) exhibited two peaks: one (*T*1) at 154 °C and a higher melting (*T*2) at 190 °C. In each case, the lower melting peak showed a lower enthalpy. Of the recrystallised sugars, the SP sugar showed no melting at ~150 °C but had a melting at 192.4 ± 0.2 °C, which was the highest of the recrystallised sugars examined. The higher melting temperature (*T*2) diminished in the order SP > L > T&L > FC. The enthalpy of the lower-melting peak (*T*1) increased in the same order.

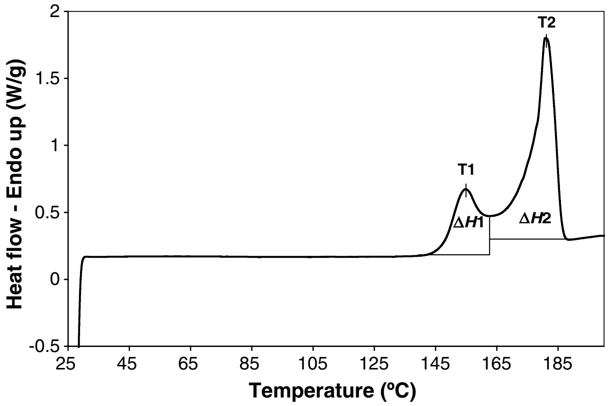

Figure 1. Typical DSC thermogram for recrystallised sucrose showing *T*1, Δ*H*1 and *T*2, Δ*H*2.

The lower melting of the *T*1 peaks observed by DSC of sucrose from FC and T&L were found to be consistent with that which might be expected for the presence of impurities. However, it was found by HPLC that no invert sugar was present when a light-scattering detector was used; however, a more sensitive pulsed amperometric detector may have detected very minor traces. To better examine the possibility of there being any influence of small amounts of invert sugar, the foregoing experiments were repeated with the introduction of invert sugar at 1% w/w, but no significant change in respect of the *T*1 endotherm was observed. This result reflects that which we have already reported[7] in respect of the presence of a *T*1 endotherm observed when FC was crystallised in the presence of honey up to 20% w/w. Thus it would appear that the endotherm at ~150 °C is due to another factor.

Comparing with Mathlouthi's[6] work, we neither found any evidence of an exothermic peak at 110 °C, a glass–solid transition at 60 °C, nor an endothermic peak at 135 °C in our work, which might suggest that our samples were lacking sucrose in their amorphous state and therefore were predominantly crystalline. The study by Richards et al.,[8] in which he described the decomposition of sucrose occurring near to its melting point, involved heating at 194 °C for long periods to obtain a mixture of products via an initial intramolecularly formed anhydride. The possibility of the peak at ~150 °C corresponding to a product of sucrose degradation seems improbable, since the comparatively much shorter period at 128 °C, used in our recrystallisation protocol is unlikely to promote the same type of degradation products. Furthermore, if the peak did correspond to degradation products, it would be expected that all of the recrystallised sucrose samples would exhibit a peak at ~150 °C, not only those with trace amounts of cations. Eggleston et al.[9–11] showed the catalytic effect of mineral salts on the thermal degradation of concentrated sucrose solutions. However, such studies, even though at a lower temperature (100 °C), involved significantly longer heating of the salt solutions

Table 1. Melting property of commercial and recrystallised sugars

Sucrose		*T*1 (°C)	*T*2 (°C)	Δ*H*1 (J/g)	Δ*H*2 (J/g)
Commercial	FC	154.3 ± 0.2	190.5 ± 0.3	1.1 ± 0.1	116.0 ± 1.3
	T&L	154.4 ± 0.1	190.9 ± 0.1	0.9 ± 0.1	122.0 ± 0.8
	SP	—	192.4 ± 0.2	—	131.4 ± 1.6
	L	—	191.7 ± 0.1		132.8 ± 1.4
Recrystallised	FC	154.8 ± 0.5	180.8 ± 0.1	33.3 ± 0.8	85.4 ± 0.7
	T&L	152.2 ± 0.4	185.2 ± 0.2	17.1 ± 0.6	101.0 ± 1.2
	SP	—	190.0 ± 0.1	—	119.3 ± 0.5
	L	154.3 ± 0.2	186.8 ± 0.3	3.9 ± 0.2	108.5 ± 0.3

(0.05 M) than in our case, and all of our products which recrystallised from salt solutions failed to reveal any trace of sugar degradation products by HPLC. In addition, we have shown in an earlier study that the presence of honey, which contains monosaccharides and acidic components, failed to make significant differences to the observation of a peak at 150 °C. Therefore, our attention was directed towards comparing small amounts of mineral salt present. It is known that sodium, potassium and low concentrations of sulfates are not completely removable by clarification of the sugar juices.[12] Mineral salt levels in sucrose are usually determined by analysis of the ash content by conductivity measurements (Table 2).[13] The results indicate that the FC sucrose contains the least amount of mineral salts of the four sugars studied, with SP possessing the highest. Such a result is perhaps not surprising since sucrose from T&L is obtained from sugarcane (*Saccharum officinarum*), whereas sucrose from SP is obtained from sugar beet (*Beta vulgaris*). Sugar beets are known to be maritime plants[14] and by their nature absorb more minerals than sugar derived from sugarcane. However, it should also be noted that the level of salts present can also be influenced by the processing units used when refining the sugar, as these can vary from factory to factory; hence the salt content may also vary accordingly.

An indication of mineral content was also determined by measurement of the conductivity of sucrose solutions. As might be expected, the sucrose solution from FC gave the lowest conductivity value and sucrose from SP the highest. Thus, it would appear that the presence of such salts inhibits the formation of the first melting peak ($T1$) at 150 °C during crystallisation. The peak at $T1$ appears not to be related to the degradation in this study. If it were, higher salt levels would be expected to increase the extent of degradation, which would, in turn, be reflected by elevated values of ΔH for the peak at ~150 °C. Flame photometry was used to quantify the amount of cations present in two sucrose samples. Both sodium and potassium assays for SP sucrose showed it to be some 17-fold higher than in FC.

The observation that a lower melting is observed for the purer sugars appears to be contradictory to that expected, but there appears to be a strong link between the concentration of mineral salts and the enthalpy of the lower melting peak ($T1$) at 150 °C.

Table 2. Mineral salt analysis of commercial sugar solutions: absorption at 420 nm, conductivity measured at 22 °C, sodium and potassium concentrations

	C (μS cm^{-1})	Na (ppm)	K (ppm)
Purified water	1.97 ± 0.05	—	—
FC	3.32 ± 0.15	0.2	1.5
L	16.27 ± 0.19	—	—
T&L	15.90 ± 0.18	—	—
SP	17.98 ± 0.23	4.0	26.0

3.2. DSC study of recrystallised sucrose from which mineral salts have been removed

3.2.1. Removal of mineral salts by successive recrystallisations. To further endorse this observation, a high-ash sugar (T&L) was recrystallised three times from aqueous solutions (85%) which were boiled at 128 °C. The purified crystals were obtained by centrifugal filtration. The conductivities of solutions made up from the recrystallised fractions were found to be significantly lower than that of the parent sugar, indicating a depletion of mineral salts (Table 3). It appears that repeated recrystallisation steps (second R and third R in Table 3) do not reduce the conductivity of the sucrose samples significantly, indicating that most of the inorganic solute has been removed on the first recrystallisation. However, with each recrystallisation the enthalpy ($\Delta H1$) of the peak at ~150 °C increased (compared to the enthalpy of the peak at ~150 °C with no recrystallisation step) by 14.49% for the first recrystallisation step, 18.91% for the second and 19.81% for the third. The difference in enthalpy ($\Delta H1$) of the peak at ~150 °C between the first and the second recrystallisation products is more significant than that between the second and the third recrystallisation products, indicating only a marginal improvement in purity through repeated recrystallisations. Thus, each recrystallisation was found to reduce the salt content of the sugar, which is accompanied by an increase in the enthalpy value for the peak at ~150 °C. If the peak were to be a function of sucrose degradation, removal of salts would be expected to decrease the enthalpy of the peak, but this was not observed. It should be noted that successive recrystallisations can lead to the formation of invert sugar, but this was not observed in this study by HPLC using a light scattering detector.

3.2.2. Removal of mineral salts by purification on an ion-exchange column. A solution of high-ash sucrose (SP) was passed through an ion-exchange resin (50 g of monobed resin in a column of 2.5 cm of diameter). The conductivity of the solutions was measured before and after passing through the resin. The purified solution from the high-ash sugar (SP) yielded crystals whose DSC melting characteristics are presented in Table 4.

Table 4 shows that the conductivity of the solution decreased after passage through the ion-exchange resin, indicating that a large proportion of the mineral salts was removed. Thus, either purification by successive recrystallisations or treatment with an ion-exchange resin was found to produce a peak at ~150 °C which is consistent with lower conductivity measurements and hence lower amounts of mineral salts impurities.

Table 3. Melting property and purity property (conductivity measured at 20 °C) of the sugars after successive recrystallisations

	Melting property				Purity property
	*T*1 (°C)	*T*2 (°C)	Δ*H*1 (J/g)	Δ*H*2 (J/g)	*C* (μS cm^{-1})
NR	154.4 ± 0.1	190.9 ± 0.1	0.9 ± 0.1	122.0 ± 0.8	23.90 ± 0.53
First R	152.3 ± 0.4	185.1 ± 0.2	17.5 ± 0.6	101.4 ± 1.2	13.76 ± 0.23
Second R	151.5 ± 0.3	182.7 ± 1.0	22.0 ± 0.5	94.5 ± 2.3	14.09 ± 0.17
Third R	151.0 ± 0.5	182.1 ± 0.4	22.3 ± 0.4	91.8 ± 1.1	13.81 ± 0.12

NR = No recrystallisation.
R = recrystallisation.

Table 4. Melting and purity properties (conductivity measured at 24 °C) of recrystallised high-ash sucrose (SP) before and after purification on an ion-exchange column

	Melting property				Purity property
	*T*1 (°C)	*T*2 (°C)	Δ*H*1 (J/g)	Δ*H*2 (J/g)	*C* (μS cm^{-1})
Before ion-exchange treatment	—	190.0 ± 0.1	—	119.3 ± 0.5	24.50 ± 0.55
After ion-exchange treatment	151.9 ± 0.2	174.3 ± 0.6	13.9 ± 1.2	81.0 ± 2.3	9.32 ± 1.46

3.3. DSC study of recrystallised sucrose to which mineral salts have been added

To explore this phenomenon more thoroughly, it was envisaged that the addition of a mineral salt such as potassium chloride, which is one of the impurities contained in commercial sucrose, to a sugar showing the peak at ~150 °C should cause its disappearance. The peak at 150 °C is well pronounced in the low-ash sucrose obtained from Fisher Chemicals. Therefore, this sugar was contaminated by recrystallising it in the presence of different amounts of potassium chloride. It was found that the peak at 150 °C completely disappeared with sucrose recrystallised from as little as 0.1% solutions of potassium chloride (Fig. 2). This result correlates with the data obtained previously; the peak at ~150 °C appears not to be related to the degradation of sucrose. The melting peak of sucrose (*T*2) appeared at a lower temperature and concomitantly the peak became broader and the enthalpy lower.

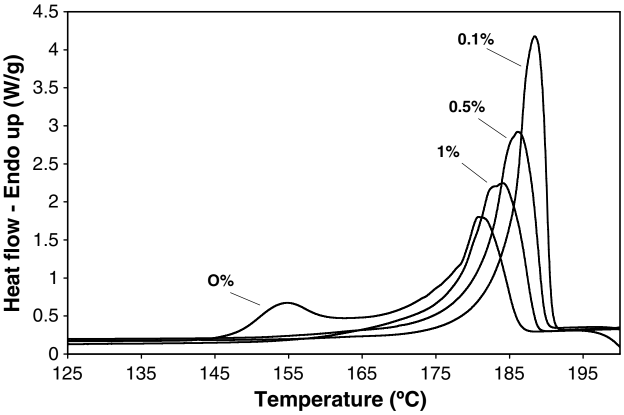

Figure 2. DSC thermograms of the low-ash sucrose (FC) recrystallised in the presence of potassium chloride at concentrations of 0%, 0.1%, 0.5% and 1% by weight of dry matter, respectively.

Parallel experiments in which either NaCl or K_2SO_4 replaced KCl showed a similar disappearance of the peak (*T*1) at ~150 °C (Table 5). Recrystallisations using increased concentrations of sodium chloride similarly resulted in a decrease in the enthalpy and melting point of sucrose.

The presence of as little as 0.1% of mineral salts (KCl and NaCl) showed a complete inhibition of the formation of the phase melting at ~150 °C (*T*1), leaving only a single melting peak (*T*2) for sucrose. Above this concentration, the extra salts act in the manner expected for the presence of impurities by decreasing the melting point (*T*2) of sucrose. In contrast, recrystallisation with increasing potassium sulfate concentrations above 0.1% did not decrease either the melting point (*T*2) or the enthalpy Δ*H*2 of sucrose melting in the range of concentrations studied.

Table 6 gives the melting property of the low-ash sucrose (FC) re-crystallised using tap water; and the conductivity of tap and purified water. As expected, recrystallisation of sucrose from tap water resulted in the disappearance of the peak at 150 °C.

It was observed that the addition or removal of mineral salts from sucrose alters its thermal profile such that the presence of mineral salts induces a sole melting peak (*T*2) in the range 180–190 °C. In contrast, in the absence of mineral salts an additional peak (*T*1) emerges in the range 151–154 °C. The recrystallised low-ash (FC) and high-ash sugars were analysed by HPLC (T&L and SP); the recrystallised high-ash sucrose samples showed no trace of invert sugars, whereas the low-ash sucrose possessed a small amount (0.22%).

3.4. DSC study of recrystallised sucrose in the presence of organic impurities

As already mentioned, several explanations have been offered in the literature for the appearance of melting

Table 5. Melting properties of the low-ash sucrose (FC) recrystallised in the presence of potassium chloride, sodium chloride and potassium sulfate

	% Salt	$T1$ (°C)	$T2$ (°C)	$\Delta H1$ (J/g)	$\Delta H2$ (J/g)
KCl	0	154.8 ± 0.5	180.8 ± 0.1	33.3 ± 0.8	85.4 ± 0.7
	0.1	—	188.4 ± 0.5	—	119.7 ± 1.4
	0.5	—	186.1 ± 0.3	—	110.0 ± 1.1
	1	—	184.1 ± 0.6	—	112.6 ± 0.8
NaCl	0	154.8 ± 0.5	180.8 ± 0.1	33.3 ± 0.8	85.4 ± 0.7
	0.1	—	189.1 ± 0.8	—	122.7 ± 3.1
	0.5	—	183.8 ± 0.1	—	111.0 ± 1.5
	1	—	184.3 ± 0.3	—	112.5 ± 1.2
K_2SO_4	0	154.8 ± 0.5	180.8 ± 0.1	33.3 ± 0.8	85.4 ± 0.7
	0.1	—	189.0 ± 0.9	—	117.7 ± 1.2
	0.5	—	190.1 ± 0.6	—	125.2 ± 2.4
	1	—	190.8 ± 0.5	—	124.5 ± 1.8

Table 6. Melting properties of the low-ash sucrose (FC) recrystallised from tap water and conductivity measurements (at 18 °C) of tap and purified water

	Melting property of the recrystallised sucrose				Purity property of the water used
	$T1$ (°C)	$T2$ (°C)	$\Delta H1$ (J/g)	$\Delta H2$ (J/g)	C (μS cm^{-1})
Purified water	154.8 ± 0.5	180.8 ± 0.1	33.3 ± 0.8	85.4 ± 0.7	2.2 ± 0.05
Tap water	—	189.4 ± 0.3	—	122.3 ± 1.3	644.0 ± 8.2

peaks for sucrose lower than that around 190 °C. The possibility of the formation of a hydrate of sucrose[15] and the inclusion of mother liquor in the crystal lattice or the presence of amorphous matter at the surface of the crystals has been mentioned.[5] In our work, the influence of mineral salts on the thermal properties of crystalline sucrose has been found to be significant. In contrast, it has been seen[7] that the addition of the monosaccharide sugars from honey in the concentration range 0–20% had little influence on changes in temperature and enthalpy of the extra peak at ~150 °C. If the phase were to be due to the inclusion of water, the enthalpy of the peak at ~150 °C would be influenced by the type of impurity added and its interaction with water. Thus, other organic substances were utilised in an attempt to better understand the reasons for the appearance of this phase. Two aprotic solvents, DMF and Me_2SO, along with two carbohydrates, spray-dried glucose syrup GL01934® and maltodextrin MD01915®, respectively, were added to a low-ash sucrose solution and recrystallised using the methodology used throughout this work (Table 7).

DMF showed the strongest influence on the peak at ~150 °C by completely removing any trace of the peak at ~150 °C at the proportion of 10% w/w. The presence of Me_2SO gave an irregular base line on the DSC traces. The low-ash sucrose and GL01934® mixtures showed a peak at ~150 °C with higher enthalpy values as compared to the other organic substances investigated. This observation appears to be related to the affinity of the

Table 7. DSC results of the low-ash sucrose (FC) recrystallised in the presence of GL01934®, MD01915® DMF and Me_2SO

	%	$T1$ (°C)	$T2$ (°C)	$\Delta H1$ (J/g)	$\Delta H2$ (J/g)	ΔHT (J/g)
GL01934®	5	152.7 ± 0.1	178.2 ± 0.5	47.7 ± 3.6	56.8 ± 2.3	104.6 ± 6.1
	10	153.4 ± 0.3	180.2 ± 0.3	25.7 ± 2.1	56.0 ± 1.5	81.7 ± 3.8
	15	151.6 ± 0.1	176.4 ± 0.2	37.9 ± 1.3	45.9 ± 3.6	83.7 ± 5.4
	20	151.0 ± 0.2	176.2 ± 0.4	40.8 ± 2.4	40.9 ± 1.2	81.7 ± 3.9
GL01915®	5	151.2 ± 0.3	180.3 ± 0.5	36.8 ± 1.4	65.7 ± 1.4	102.4 ± 3.0
	10	153.3 ± 0.2	180.6 ± 0.4	37.6 ± 1.7	62.2 ± 1.2	99.8 ± 3.2
	15	153.1 ± 0.3	181.6 ± 0.5	29.1 ± 2.5	61.6 ± 2.5	90.5 ± 5.4
	20	152.7 ± 0.3	183.5 ± 0.2	18.6 ± 1.6	62.6 ± 0.9	91.2 ± 2.7
DMF	2	158.9 ± 0.3	188.6 ± 0.3	3.2 ± 0.4	111.2 ± 0.8	114.4 ± 1.2
	5	166.0 ± 1.0	189.1 ± 0.7	1.5 ± 0.1	110.8 ± 0.4	112.3 ± 0.8
	10		190.9 ± 0.5		122.5 ± 3.5	122.5 ± 3.5
Me_2SO	2	156.1 ± 0.4	183.8 ± 0.3	22.6 ± 0.2	88.0 ± 2.4	110.6 ± 2.8
	5	159.4 ± 0.2	184.3 ± 0.8	18.3 ± 0.5	83.6 ± 1.9	101.9 ± 2.5
	10	160.8 ± 0.3	181.9 ± 0.8	16.7 ± 0.5	68.4 ± 2.7	85.1 ± 4.0

other organics used for water; the stronger the affinity the less available water there is for hydrating sucrose. Thus the addition of the polar aprotic solvent, DMF, resulted in the complete removal of the peak at ∼150 °C; the higher polarity of DMF compared to polysaccharides resulted in a more significant effect on the amount of water available for hydration. Similarly, the addition of Me_2SO, resulted in a decrease in enthalpy of the peak at ∼150 °C, but to a lesser extent. In contrast to the behaviour of *T*1, increasing amounts of maltodextrins showed little effect. The addition of DMF also increased the peak temperature (*T*2) for the peak at 180–190 °C, whilst the addition of GL01934® decreased it. The presence of only 2% w/w of either DMF or Me_2SO decreased the enthalpy of the peak at ∼150 °C compared sharply to the enthalpy of the peak at ∼150 °C with no added aprotic solvent. This reflects the dependency on water for the formation of the peak at ∼150 °C. Above this level the decrease in enthalpy was less significant, perhaps due to available water already being taken up by the aprotic solvent. The presence of the maltodextrin MD01915® also decreased the enthalpy of the peak at ∼150 °C but the influence of the glucose syrup GL01934® was less distinct. DMF and Me_2SO had contrasting effects on the enthalpy of the second melting peak (*T*2). Interestingly, increased amounts of DMF increased $\Delta H2$, whereas increasing the amount of Me_2SO decreased $\Delta H2$. In keeping with the observations, the maltodextrins did not show a dramatic effect on the enthalpy of the second peak (*T*2) (see Fig. 3).

As observed for honey,[7] the addition of polysaccharides did not show a significant effect on the peak at ∼150 °C. On the contrary, the addition of the polar aprotic solvents, DMF and Me_2SO, showed a large decrease in enthalpy of this peak with DMF having the stronger effect. This difference of behaviour between Me_2SO and DMF was unexpected since both of them have similar dipolar moments; Me_2SO having the higher.[16] The effect of the different impurities on the value of ΔH for the peak at ∼150 °C appears to relate to the strength of their interactions with water. An impurity interacting mainly via hydrogen bonds appears to compete poorly with sucrose, whereas the mineral salts and, to a lesser extent, polar aprotic solvents which have stronger interactions with water compete more strongly with sucrose. Water forms clusters around the minerals salts with a hydration shell that increases in density with increasing concentration.[17] The hydration number for sodium is 5 or 6 water molecules,[18,19] whereas for potassium, this value ranges from 5 to 10.[18] Such clusters are more extremely hydrated by the formation of layers of spatially oriented water molecules.[17] It is of note that clusters of the types $1Me_2SO–2H_2O$ and $1Me_2SO–3H_2O$ have been predicted by molecular dynamic simulations[20] and $DMF–2H_2O$ complexes have been proposed on the basis of viscosity and dielectric constant measurements.[21,22] The association of sucrose with water appears to be the major reason of the lower melting phase at *T*1, such that in the absence of components which can compete with sucrose for water, a stronger phase is observed, whilst when impurities are present which have demands on available water for their solvation, the phase is much weaker or absent altogether.

3.5. DSC study of the influence on temperature to which the recrystallisation solution is raised

A low-ash sucrose (FC) and high-ash sucrose (T&L) were each recrystallised from solution at different temperatures. Crystals were obtained for the study by centrifugal filtration after 1 and 2 h. Figure 4 shows the variation of enthalpy ($\Delta H1$) of the peak appearing at ∼150 °C with the temperature of the solution used to recrystallise sucrose. One can see that the enthalpy of the peak at ∼150 °C decreased as the temperature of the sucrose solution increased. When crystals were obtained by filtration after 2 h, the enthalpy of the peak

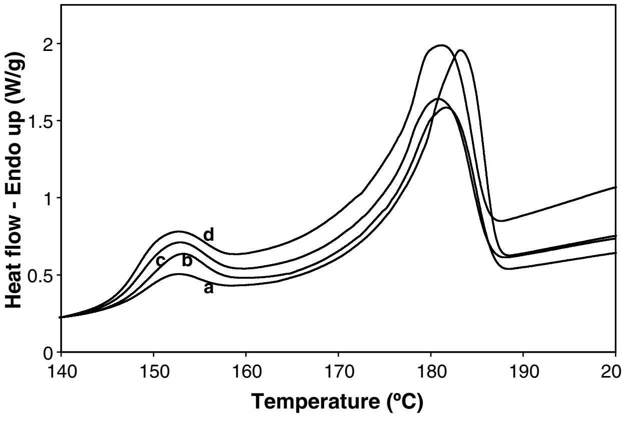

Figure 3. DSC thermograms of the low-ash sucrose (FC) recrystallised in the presence of maltodextrins (*a* = 20%, *b* = 15%, *c* = 10%, *d* = 5%).

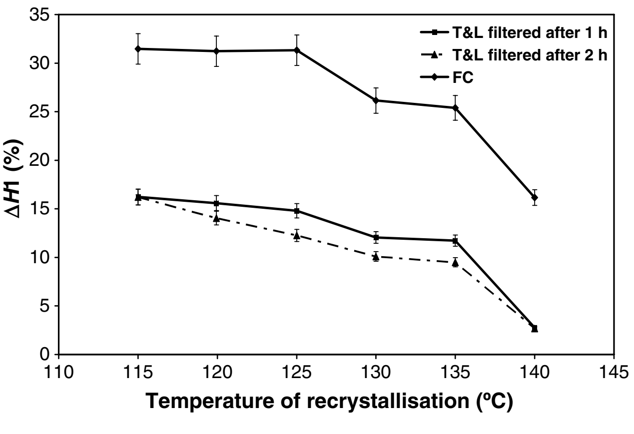

Figure 4. Evolution of the ratio $\Delta H1/(\Delta H1 + \Delta H2)$ with increasing temperature of sucrose solutions.

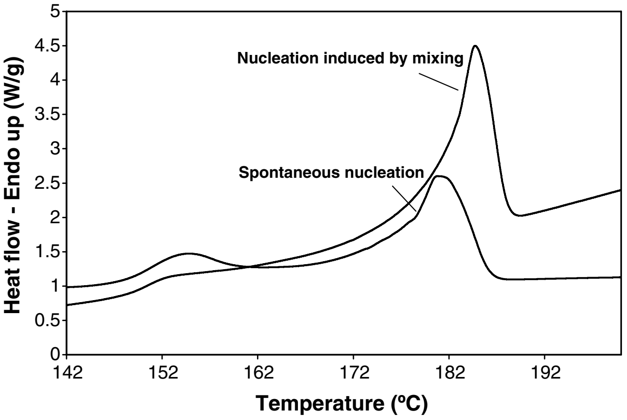

Figure 5. DSC thermograms of the low-ash sucrose (FC) recrystallised without or with stirring (2000 rpm).

at ~150 °C decreased slightly. Furthermore, whatever the temperature used, the proportion of the peak (Δ*H*1) appearing at ~150 °C was consistently higher when using the low-ash sucrose.

The temperature of the solution used to recrystallise sucrose had a marked influence on the enthalpy of the peak appearing at ~150 °C. By increasing the solution temperature, further traces of water could have been removed by evaporation, an indication that the appearance of the endotherm at 150 °C might depend on the presence of available water during crystallisation.

3.6. Influence of the amount of stirring

The enthalpy of the peak at ~150 °C was decreased when a mixer (2000 rpm) was used in the recrystallisation process (Fig. 5). Stirring usually has the effect of speeding up the rate of nucleation[23] as well as the rate of crystal growth.[24,25] If the peak forming at ~150 °C is due to the inclusion of water in a crystal lattice, our results indicate that a slow rate of nucleation and growth is required to obtain the inclusion of water. Nevertheless, it has been found that an increase in the growth rate increased the inclusion concentration.[26,27]

3.7. Influence of crystal size

Scanning electron microscopy showed little differences in crystal size in accordance with the presence of inorganic or organic products added. In this study, the samples showed crystal sizes ranging from ~3 to 20 μm.

4. Conclusions

The melting behaviour of sucrose has been studied by DSC. The appearance of an endotherm at ~150 °C has been found, as well as the main melting peak of sucrose at ~190 °C. The presence of the peak at ~150 °C was found to be highly dependent on the purity of the sucrose used, especially in terms of the mineral salt content. The addition of mineral salts to the sucrose solutions resulted in a complete removal of the peak at ~150 °C. However, the peak neither appeared to be related to the presence of amorphous material within sucrose, nor the result of any salt-catalysed degradation of sucrose. Recrystallisations of sucrose solutions with polysaccharides had little effect on the value of Δ*H* for the peak at ~150 °C whereas recrystallisations with aprotic solvents resulted in a significant reduction in the value of Δ*H* for the peak at ~150 °C. Thus, the affinity of added impurities for available water appears to have a direct effect on the emergence of the peak at 150 °C. Available water and rate of nucleation appear to affect the intensity of the phase. Crystal size seemed relatively unaffected by the mineral salts or organic components used in this study.

Acknowledgements

This work was gratefully funded by grants from the Biotechnology and Biological Science Research Council (BBSRC) and the Nestlé Product and Technology Centre, York.

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