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Calorimetric study of the glass transition occurring in fructose solutions

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ABSTRACT

The glass transition temperatures for dilute and concentrated fructose–water solutions have been determined by differential scanning calorimetry. The supplemented phase diagram is presented, and from this, the glass transition temperature (T_g') and concentration (C_g') of the maximally freeze-concentrated glass have been determined and found to differ, significantly for the latter and slightly for the former, from recently published values. Reasons for this discrepancy are discussed. Annealing vitrified fructose–water glasses above their T_g allows the fructose concentration in the amorphous phase to approach C_g' as a result of ice formation.

INTRODUCTION

D-Fructose, together with D-glucose and sucrose, is one of the most widely occurring sugars in Nature. Within the living organism, it has a diverse range of functions, while the chemical and food industries are finding it an increasingly important component of food products[1].

The tendency for freezing of sugar solutions to be non-equilibrium in character has become the subject of increasing interest[2–19]. It has been shown[8] that when a dilute aqueous solution of a sugar is rapidly frozen, a considerable amount of unfrozen water coexists with the ice crystals. This water exists in an amorphous metastable glass, since eutectic formation rarely occurs, and it is generally accepted that the physical state of the system is dominated by kinetics. This approach has been extensively discussed by Levine and Slade[9–14], who have proposed that a kinetic, rather than a thermodynamic, approach is more applicable to describe the system. They used differential scanning calorimetry (DSC) in order to develop a kinetic description of the events that occur on warming frozen saccharide solutions.

T_g' and C_g' are two parameters which reflect the physical state of the non-crystallising solute[14]. T_g' represents the glass transition temperature of the maximally freeze-concentrated solution, corresponding to the intersection of the extension of the equilibrium liquidus curve with the glass curve[5] in a supplemented phase diagram. C_g' is equal to the composition of the glass having a transition temperature T_g' and is expressed as % solute (w/w). Levine and Slade[9-13] have used DSC exclusively as the method to determine these parameters.

The interpretation of the DSC thermograms, in order to provide information on T_g' and C_g', has become a very controversial subject, and different interpretations have been suggested by Levine and Slade[14], Simatos et al.[15], Izzard et al.[16], Ablett et al.[17,18], and Roos and Karel[19]. A compendium summarising the various interpretations of the published DSC data has recently been published[20].

For fructose, T_g' and C_g' have been reported by Levine and Slade[9-14] as being equal to −42°C and 51% w/w, respectively, as measured for a 20% solution of fructose (w/w).

This study is a continuation and a further extension of previous investigations made on sucrose solutions[16-18]. The supplemented phase diagram of fructose is provided, together with information on the effect of annealing time on ice–solution mixtures. The C_g' value determined in this study is significantly different from the previously published value[9-14], except for the 78.6% reported by Roos and Karel[19]; a reason for this discrepancy is proposed. The T_g' value is shown to occur at a slightly lower temperature than the previously published value[9-14].

The intention of this paper is to assist in developing a rigorous description of the events that take place on warming frozen aqueous systems. With the original hypotheses of Franks[5] and Levine and Slade[9-14], and other recent advances in the interpretation of DSC data[2,15-19], it is possible to provide a description of the thermal events occurring when frozen saccharide glass–ice mixtures are warmed.

EXPERIMENTAL

Materials and methods.—D-(−)-Fructose, Analytical Reagent Grade, was obtained from Fisons Laboratories and used as supplied. Fructose solutions for calorimetric studies were prepared by gently heating weighed dispersions of fructose and water in a water bath with continuous, vigorous stirring, until a clear, colourless solution was produced. Supersaturated solutions were analysed immediately after cooling down to room temperature. Solutions below 70% w/w fructose could be kept at room temperature for several days, before fructose crystallisation occurred. Above 70% w/w, fructose crystallisation took place more rapidly, and solutions had to be used almost immediately. Dilute fructose solutions containing ice were easily returned to homogeneous solutions by warming up to room temperature.

The concentration of fructose solutions was confirmed either by reweighing the solutions or by refractive index measurements. Following refractive index measurements, the concentration was determined according to eq *1*, which had been derived from previously published values[21].

$$\%\ \text{Fructose w/w} = 3479.41\ \text{RI} - 1051.25\ \text{RI}^2 - 2769.93 \qquad (1)$$

A fructose glass was prepared by freeze-drying a frozen 50% fructose solution at −60°C in an Edwards Modulyo freeze-drier at a pressure of 0.8×10^{-1} mbar for four days. The freeze-dried fructose samples were used immediately after their preparation, allowing no time for any possible collapse to occur.

Differential scanning calorimetry.—This was performed with Perkin–Elmer DSC-7 and DSC-2 calorimeters equipped with liquid nitrogen cooling accessories. The purge gases used were dry helium and dry nitrogen. Temperature calibration was carried out at scan rates of 5°C/min and 10°C/min using GPR grades of dodecane, octane, and cyclohexane. Calibration of the heat flow was carried out by references to the known melting enthalpy of indium metal (99.99%, from Goodfellows Metals). Fructose solutions were accurately weighed into aluminium pans, using a Sartorius six-place electronic balance, and sealed hermetically. Sample weights of 1–10 mg were used for T_m measurements on solutions that formed ice on cooling. Larger sample weights of 10–35 mg were used for fructose glasses and glass–ice mixtures when carrying out T_g or T_g' measurements, in order to improve the signal-to-noise ratio for the latter.

Glass transition temperatures (T_g) (midpoint of transition) were calculated by peak analysis of the derivatized thermograms[9–14,16]. Changes in specific heat capacity (ΔC_p) were calculated according to previously described procedures[16]. The "equilibrium" liquidus curve T_m was confirmed[21,22] for dilute solutions by measuring the temperature of the peak maximum for the ice-melting endotherm in fructose solutions of 20–50% w/w, scanned at a rate of 0.1°C/min. The estimation of ΔH_m, used in calculating C_g', was made according to previous publications[16,17,18].

Optical microscopy.—The fructose solutions were placed between two 16-mm circular microscope coverslips and placed in a Linkam THM600 programmable stage powered by a Linkam TMS90 temperature controller. Fast cooling at 99°C/min was achieved by coupling the stage to a Linkam CS196 liquid nitrogen cooling unit. Temperature calibration was carried out using octane, dodecane, and water.

Good agreement between the literature melting points[2,21–24] and the displayed temperature was found at heating rates up to 10°C/min. Photomicrographs were taken using transmitted light on a Reichert Polyvar microscope.

RESULTS AND DISCUSSION

Fructose glasses.—These were formed when fructose solutions having a concentration greater than 60% w/w were rapidly cooled in the DSC (Fig. 1). The T_g obtained was found to vary from −85°C to +10°C for fructose concentration of 60.2 to 100% (Table I). The T_g obtained for the pure fructose glass was found to be in good agreement with recently published[2,19,23,24] values.

Glasses showing devitrification.—During the timescale of a typical storage experiment (including both the times in the DSC and in the deep freeze), which was at

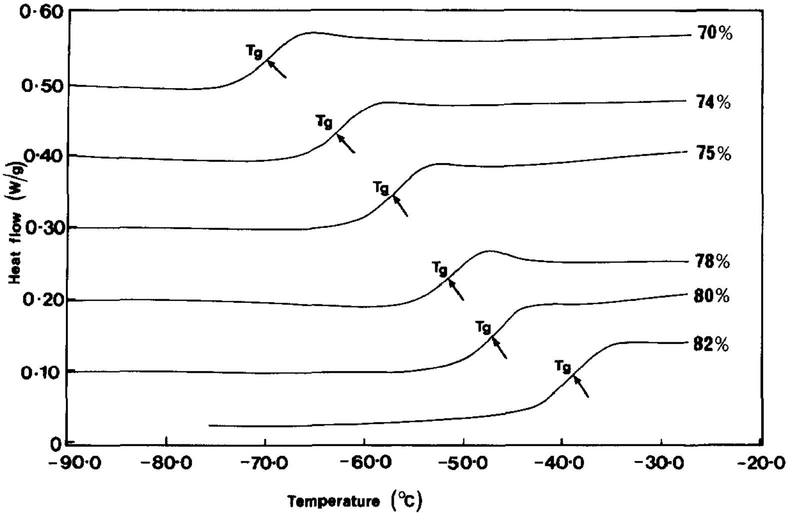

Fig. 1. DSC thermograms showing the thermal event at the glass transition for vitrified fructose solutions of the indicated concentration.

least 15 days, no ice was formed during cooling or heating in the DSC for fructose solutions above 70%. When the concentration fell below 70%, ice was frequently formed as a result of devitrification during heating. The amount of ice formed was dependent on the heating rate used (Fig. 2). The large exotherm present in the thermograms of the vitrified glasses (Fig. 2) was confirmed by optical microscopy (Fig. 3) to be due to ice formation.

Devitrification could also be induced in these vitrified solutions below 70% concentration by annealing at a temperature above T_g. Table II demonstrates how the measured T_g of the liquid (i.e., non-ice) phase of a vitrified 60% fructose solution increased with annealing time at -50°C, due to increasing devitrification .

TABLE I

Effect of concentration on the T_g of fructose-water glasses [a]

Fructose (% w/w)	T_g (°C)
60.2	−85
65	−78
70	−69
74	−63
76	−57
78.5	−50
80.1	−46
82	−38
90	−17
95	4
100	10

[a] Duplicate measurements of the midpoint of the transition.

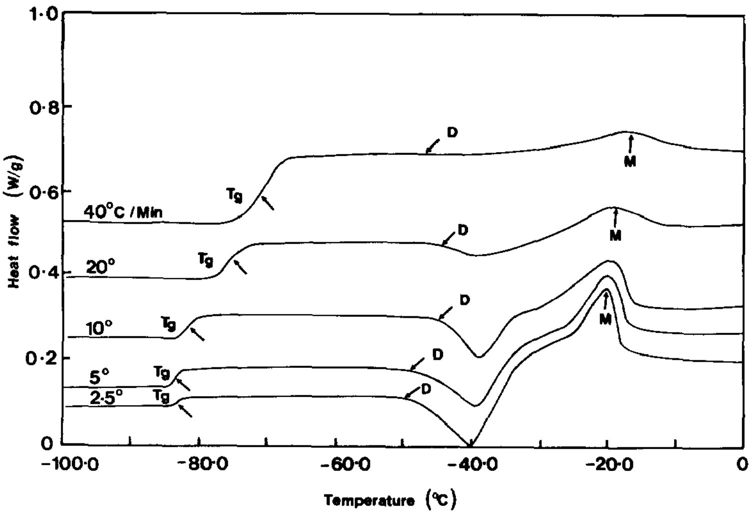

Fig. 2. DSC thermograms for 60% fructose solutions recorded at different heating rates. T_g, glass transition; D, ice devitrification; M, ice dissolution.

Also included in this table is the corresponding concentration of fructose derived from the data shown in Table I or the supplemented phase diagram. The DSC thermograms as a function of annealing time for the 60% fructose solution are given in Fig. 4. Table II shows that, after annealing a 60% fructose solution for 0.75 h at −50°C, the T_g had increased from −84 to −80°C, whereas, on annealing for a further 0.25 h (i.e., for 1 h in total), the T_g increased substantially to −53°C. This effect is reproducible but the reason for this behaviour is obscure.

Dilute solutions.—When dilute fructose solutions (20 and 40% w/w) were rapidly cooled in the DSC, two thermal events were easily discernible (Fig. 5) immediately prior to the large endotherm due to ice dissolution. The change in heat capacity (ΔC_p) for each of these thermal events is shown in Fig. 6.

Table III lists the calculated concentration of the freeze-concentrated glass (so-called "C_g' concentration"), determined from the area of the ice-melting endotherm[25].

Supplemented phase diagram.—The results of this study, together with literature values for the liquidus curve[21,22], the T_g of amorphous fructose[2,23,24], and the T_g of glassy water[26], were used to construct the supplemented phase diagram (Fig. 7). The intersection of an extrapolation of the equilibrium liquidus curve and the glass transition curve is at a temperature, T_g', of ~ −48°C and a concentration, C_g', of ~79% w/w; these T_g' and C_g' values could also have been obtained from maximally freeze-concentrated solutions as a result of an optimal annealing procedure[17]. These values are different from previously reported values of T_g' of −42°C and C_g' of 51%[9–14], which were measured for an initial fructose solution concentration of 20% w/w, but are closer to the respective values of −53°C and 78.6% w/w reported by Roos and Karel[19].

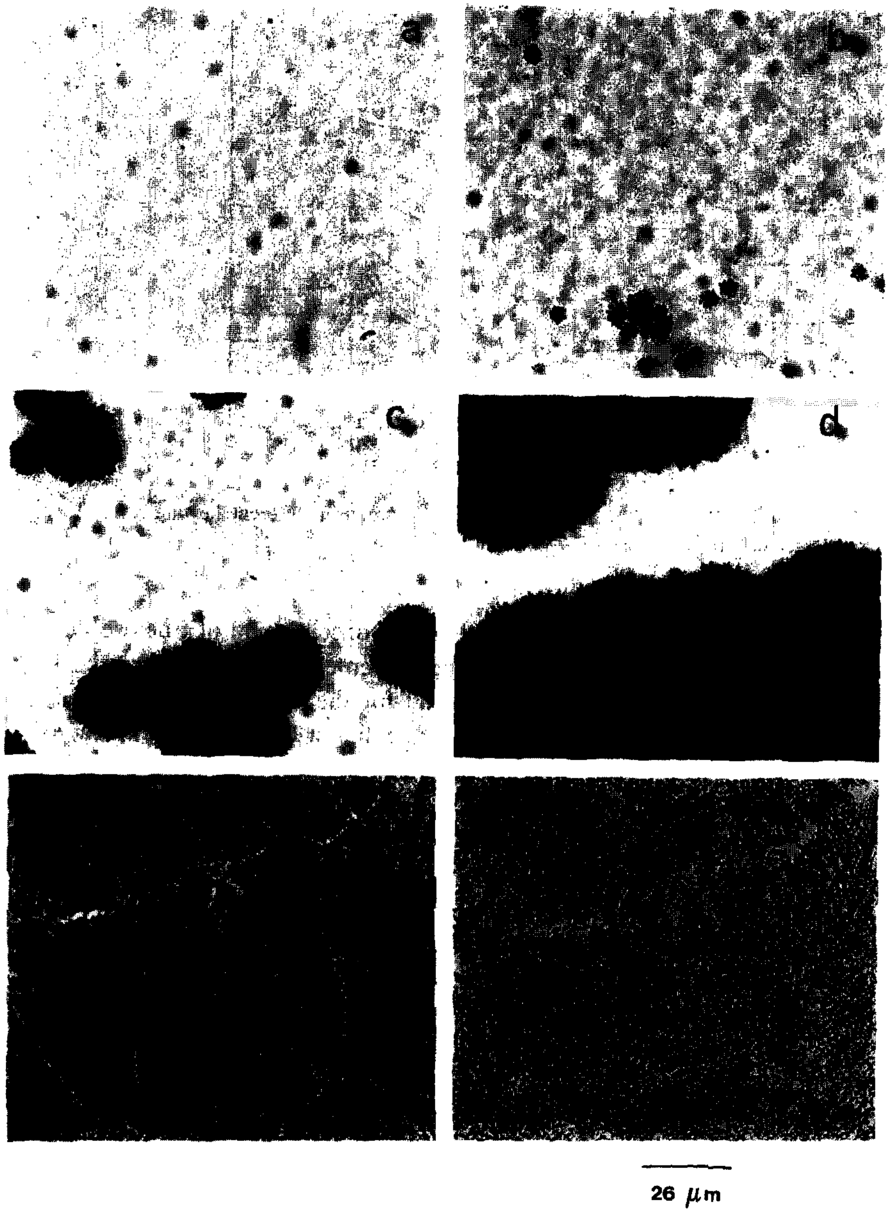

Fig. 3. Optical micrographs obtained with a heating rate of 5°C/min (to the temperatures indicated) on a vitrified 60% fructose solution after rapid cooling to (a) −100°C, (b) −70°C, (c) −53°C, (d) −46°C, (e) −32°C, (f) −25°C.

C_g'.—We have concluded from this study that C_g' for fructose has a value of ~ 79% w/w. It should be noted, however, that ice formation did not occur in fructose solutions between 70–79% w/w during the timescales of the experiments since the behaviour of the solutions was controlled by kinetics.

TABLE II

Effect of annealing time at −50°C on the T_g of a vitrified 60% fructose solution

Time at −50°C (min)	T_g	Fructose concentration (% w/w) [a]
0	−84	60.5
4	−83	61.5
15	−82	62.5
45	−80	64
60	−53	77

[a] Determined from data shown in Table I.

Ice formation has been observed in fructose solutions up to concentrations of 70% w/w (Table II), both in this study and as previously reported by Schenz et al.[27] and by Roos and Karel[19]; this suggests that C_g' has a value which is at least 70% w/w. However, if C_g' is calculated simply from the area under the ice-melting endotherm, then the value obtained was found to vary considerably with initial solution concentration (Table III), and for dilute solutions was significantly below 70%. This result clearly calls into question the validity of the calculation approach used in Table III[9-14].

Amongst others[19], we have recently reported similar C_g' results for sucrose solutions[16,17]. We have proposed[18], from a theoretical modelling study of the profile of the DSC thermograms, that the origin of the discrepancy in reported C_g' values is primarily due to the use of an incorrect baseline for the evaluation of the area of the ice-melting endotherm and to the temperature dependence of the enthalpy of ice melting not being taken into account. This results in a systematic

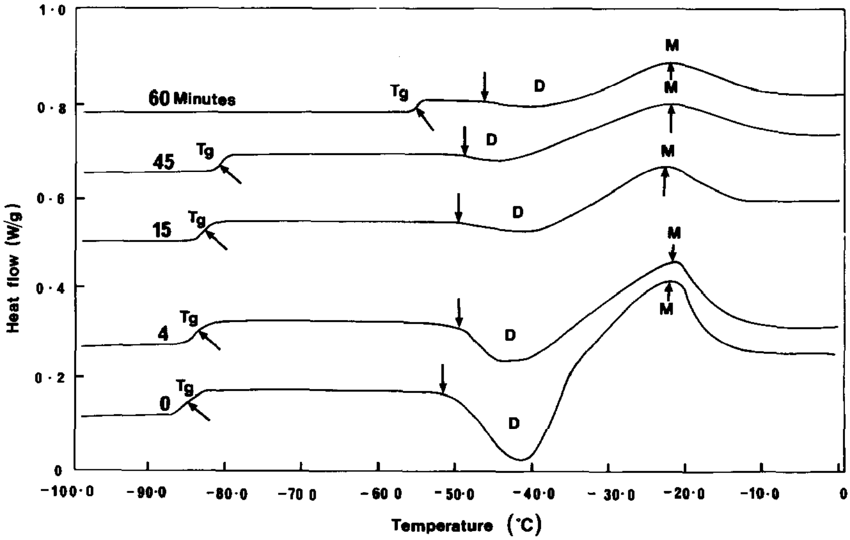

Fig. 4. DSC thermograms for a series of 60% fructose solutions annealed at −50°C for different times. For key, see Fig. 2.

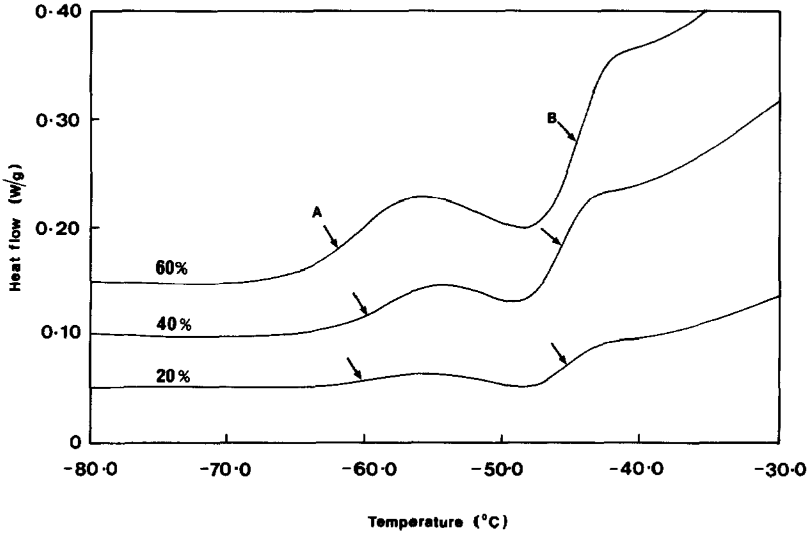

Fig. 5. DSC thermograms for frozen fructose solutions (of indicated concentration), showing the two transitions (labelled A and B) which occur before the dissolution of ice.

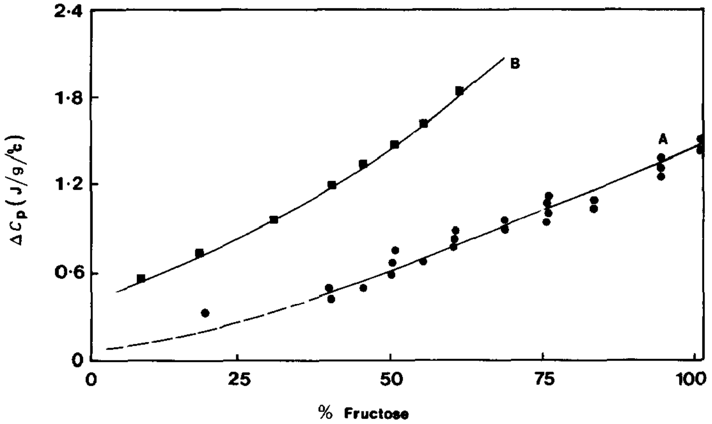

Fig. 6. The change in heat capacity associated with each of the two transitions A and B (see Fig. 5), as a function of concentration for annealed fructose solutions.

TABLE III

Calculated freeze-concentrated concentration (C_g') [a] as a function of the initial concentration

Fructose (% w/w)	C_g'
20.4	50
40.4	66.8
60.2	73.5

[a] C_g' values calculated from the area of the DSC ice endotherm, using the method proposed by Levine and Slade[25].

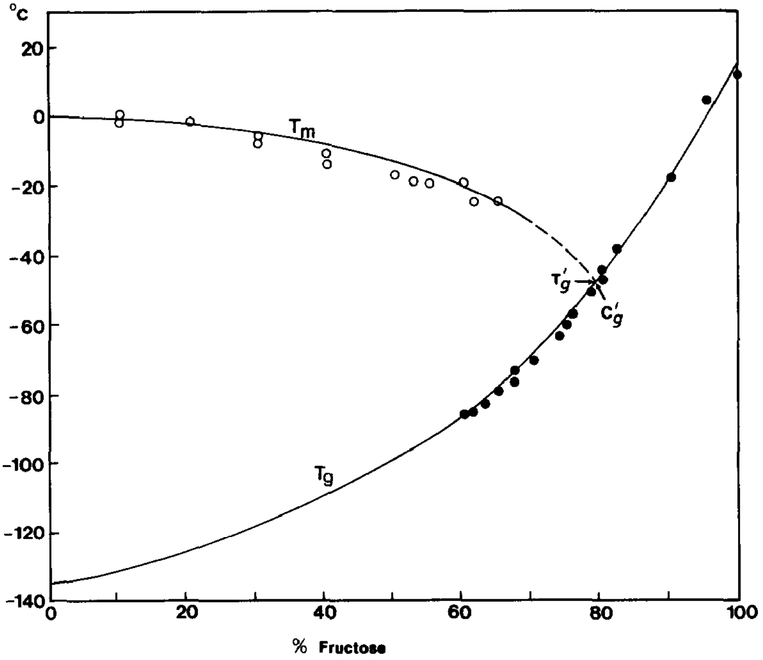

Fig. 7. Supplemented phase diagram for fructose. T_m, liquidus curve; T_g, glass-transition curve; T_g' is −48°C; C_g' is 79% w/w.

underestimate of the concentration (C_g') of the liquid phase present. Whilst the supplemented phase diagram approach to estimate C_g' is extremely useful, it should be borne in mind that it involves a considerable amount of DSC effort.

T_g'.—In fructose–water systems which do not form ice during the timescale of the DSC experiment or during annealing of the glass, the T_g can be easily observed as a step-change in the heat-flow thermogram (Fig. 1). For the thermograms in Fig. 1, the change in heat capacity occurring at T_g is significantly higher than published values[2,19,24] for fructose alone. The reason for this is unclear.

For fructose solutions where ice formation occurs as a result of devitrification, the T_g can be seen to increase in temperature as a result of freeze-concentration (Fig. 4), as previously described[16,17,19]. In solutions which did form ice on cooling (Fig. 5), the glass transition T_g (A) precedes a second transition (B), the midpoint of which has been referred to as the T_g' glass transition[9–14,26].

These results are similar to those previously reported by us for sucrose solutions[16,17]. We have modelled[18] the sucrose data, and this modelling has demonstrated that a second transition will occur in the DSC thermogram at the temperature of the onset of ice dissolution. We propose that the same mechanism applies to these fructose results, with the second transition being due to the onset of ice dissolution, and that the true T_g' temperature is somewhere *between* the T_g transition and this second transition, i.e., at ~ −48°C, as shown in Fig. 7.

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