

## Modeling of the water–sucrose state diagram below 0 °C

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### Abstract

The state diagram of sucrose–water solutions was constructed by the use of model calculations; the activity coefficient from the UNIQUAC model allowed determination of the solution–ice equilibrium curve and the glass transition temperature as a function of the composition was evaluated from the Gordon–Taylor equation. The accuracy of the glass transition temperature ( $T'_g$ ) of the maximally freeze-concentrated fraction, determined from the intersection of both curves, was analyzed and discussed. While the UNIQUAC model predicted reliable ice melting temperatures in the high sucrose concentration range, a significant variation of the fitted glass transition curve was obtained due to the selected temperature values for the glass transition temperature. The calculated glass temperatures ( $T'_g$ ) were compared with direct DSC experiments. © 1997 Elsevier Science Ltd. All rights reserved.

*Keywords:* Computer simulation; Solid–liquid equilibrium; Glass transition; Water; Sucrose

### 1. Introduction

When a diluted sucrose solution is cooled, the formation of ice progresses as a function of temperature according to the liquid or solid–liquid equilibrium curve ( $T_m$ ). The ice crystals grow until the viscosity of the unfrozen liquid phase becomes a limiting factor. At low temperatures, the rate of nucleation and growth of ice crystals being faster than that for sucrose, the solution can be concentrated

beyond the theoretical eutectic concentration [1]. The crystallization of sucrose is dramatically hindered by the viscosity increase associated with the low temperature and the increasing concentration of the amorphous sucrose solution surrounding ice crystals. The freezing of water and consequently the concentration increase of the solution are stopped when the solution viscosity [2] is close to  $10^{12}$  Pa. At this viscosity level the state of freeze-concentrated solution is expected to change from a liquid to a glassy solid, a process known as the liquid–glass transition. A glass transition curve can be drawn, which represents the temperature of the glass transition ( $T_g$ ) versus water

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content. MacKenzie [3] proposed that this  $T_g$  curve be added on the phase diagram, which was said to be supplemented.

For a frozen mixture at equilibrium, it is generally accepted that the concentration of the unfrozen solution is independent of the initial concentration and depends only on temperature. This applies when the cooling rate is not too fast, i.e. when the freezing process follows the freezing point ( $T_m$ ) curve down to the critical point where the residual solution turns into a glass. The coordinates  $C'_g$  and  $T'_g$  [4] for the maximally freeze-concentrated system correspond to the point where the freezing-point ( $T_m$ ) curve intersects the glass transition ( $T_g$ ) curve.

At temperatures below  $T'_g$ , the freeze-concentrated phase is a glass, and the stability of the fully solid product is expected to be good. Levine and Slade [4] have argued that the temperature  $T'_g$  would be the predictive key temperature for understanding the stability of frozen foods. However, questions still remain concerning the determination of the actual temperature of the glass transition and the concentration of the maximally freeze-concentrated phase. There is a general agreement with the concepts, but it is surprising to observe important discrepancies concerning the values reported for the glass transition temperature of the freeze-concentrated phase [5–9]. This is mainly due to the complicated features shown by the differential scanning calorimetry (DSC) thermograms obtained with frozen sugar solutions.

Due to the difficulty in unambiguously assigning the feature corresponding to the glass transition of the freeze-concentrated phase in DSC thermograms obtained with frozen sugar solutions, it was suggested that more reliable values of  $T'_g$  and  $C'_g$  would be obtained from the intersection of the  $T_m$  and  $T_g$  curves. Besides, there have been important developments in process simulation due to the fast improvement in computing power and the necessity to cut the cost of experimental work. From the theory of solutions, activity coefficient models coupled with mass balances permit calculation of all the equilibrium phases (solid–liquid, liquid–liquid or liquid–gas phases) and thermodynamic properties. One of them, the UNIQUAC (Universal Quasi Chemical) method [10] derives activity coefficients from the excess Gibbs function considered to be a sum of two terms: a combinatorial term (entropic contribution) accounting for the difference in size and shape between molecules, and a residual term (enthalpic contribution) accounting for the attractive-repulsive forces between the molecules in the mixture. This method is

reliable and fast for predicting liquid phase activity coefficients in non-electrolyte, non-polymeric mixtures at low to moderate pressures and temperatures.

The aim of this study was to better characterize the glass transition temperature of the amorphous sucrose–water phase in the presence of ice. This required more accurate defining of the diagram in the region surrounding the intersection of the  $T_m$  curve with the  $T_g$  curve. This was achieved by use of: (i) new experimental data obtained by DSC measurements; (ii) the Gordon–Taylor equation [11] fitted to the experimental DSC data; (iii) an improved extrapolation of the solid–liquid curve from published excess properties and solid–liquid equilibria using a UNIQUAC model.

## 2. Materials and methods

*Materials.*—Sucrose was used as obtained from E. Merck. The solutions were prepared by gently heating sugar + water mixtures at known concentrations expressed in mass percent (g sucrose/100 g soln) in a water bath until clear solutions were obtained. Solute concentration was controlled by refractive index measurements.

The high concentrations were produced by dehydration of a 60% solution in the DSC pans, over phosphorous pentoxide, at ambient temperature; the final concentrations were determined by weighing.

*Differential scanning calorimetry measurements.*—DSC measurements were carried out using a Perkin–Elmer DSC-7 equipped with a liquid nitrogen cooling accessory. Cooling and heating rates of 10 °C/min were used throughout these studies. The temperature calibration was made using water and cyclohexane, and the energy calibration using pure indium supplied by Perkin–Elmer.

Dry amorphous sucrose was obtained from the crystalline product, heated in DSC pans up to 200 °C, then cooled down to 30 °C; the glass transition could be observed on the second heating curve (Fig. 1). The insert shows the determination of the two main characteristic  $T_g$  values, measured with a heating rate of 10 °C min<sup>-1</sup> after cooling with the same scanning rate. These are the extrapolated onset of the heat capacity jump ( $T_{g\text{onset}}$ ) and the temperature corresponding to half of the heat capacity increment ( $T_{g\text{mid}}$  = standard  $T_g$  for ASTM) [12].

Sucrose solutions were cooled down to –80 °C and characteristic temperatures were determined on the heating scans (Fig. 2). They were:  $T_{g\text{onset}}$ , corre-

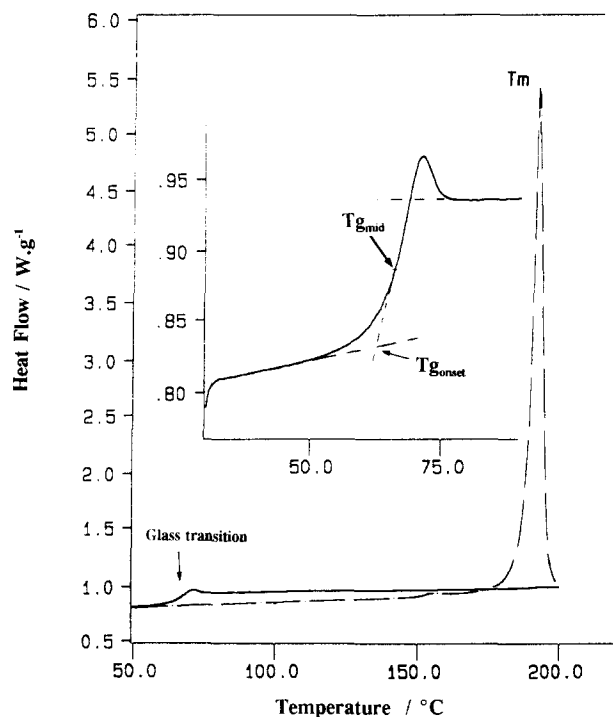


Fig. 1. DSC thermograms of dry sucrose: the first heating scan (dotted line) shows the crystal melting, the second heating scan (full line) the glass transition. Inset:  $T_{g\text{ onset}}$  and  $T_{g\text{ mid-point}}$  determination.

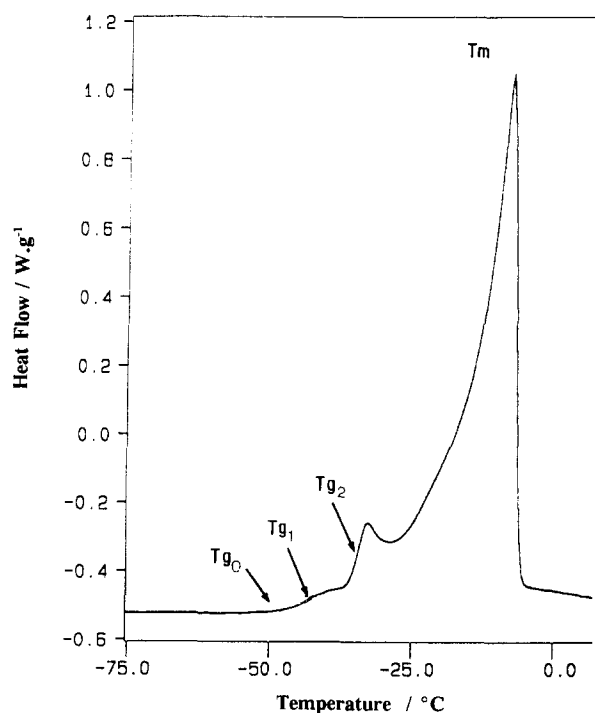


Fig. 2. DSC thermograms of 55% frozen sucrose solution.  $T_{g0}$ ,  $T_{g1}$  and  $T_{g2}$  are defined as the temperatures allowing to characterize the different steps of the glass transition.

responding to the extrapolated onset of the glass transition,  $T_{g1}$  and  $T_{g2}$  to the middle of the  $G_1$  and  $G_2$  events such as defined previously [13,14] and  $T_m$  the temperature of the maximum of the melting peak.

With concentrated solutions, a cooling rate of  $10\text{ °C min}^{-1}$  being too fast for all freezable water to crystallize, the stabilization of the sample in a maximally freeze-concentrated state was obtained from a thermal treatment. The first cooling was followed by a first heating up to above the glass transition temperature range, then the sample was cooled to low temperature again. The second heating scans were used to determine  $T_m$  and the characteristic temperatures of the glass transition. The limited first heating allowed a further cryoconcentration of the unfrozen fraction.

*Models for the state diagram curves.*—The model for the solid–liquid curve was the UNIQUAC model modified by Larsen [15] together with the interaction parameters given by Catté et al. [16] to describe thermodynamic properties of aq solns of sugars.

The Gordon–Taylor equation (1) was used to model the glass transition curve for aqueous sucrose glasses

$$T_g = \frac{xT_{g1} + k(1-x)T_{g2}}{x + k(1-x)} \quad (1)$$

where  $x$  is the mass fraction of component 1,  $T_g$  is the glass transition temperature of the mixture,  $T_{g1}$  and  $T_{g2}$  of the pure components 1 and 2, and  $k$  is an adjustable parameter. The composition dependence of the glass transition temperature for binary mixtures which obey the laws of regular solutions, allows us to identify  $k$  as  $\Delta C_{p2}/\Delta C_{p1}$  [17],  $\Delta C_p$  being the change in heat capacity of the material at the glass transition. The SAS non-linear procedure [18] was used to fit the experimental values with eq (1).

### 3. Results and discussion

In this work, only the curve corresponding to the ice-solution equilibrium was considered.

*Experimental curve.*—The temperature  $T_m$  corresponding to the maximum of the ice melting endotherm (Fig. 2) can be considered as the temperature at which the last ice crystal melts and therefore as the temperature for the appearance of the first ice crystal upon cooling, i.e. the freezing (cryoscopic) point. The freezing point ( $T_m$ ) curve can be confidently drawn from the experimental DSC results for the concentrations of sucrose solutions between 0 and ca. 60%

Table 1  
Calculated and experimental melting points of sucrose solutions as a function of the sucrose concentration

Sucrose concentration (g/100 g sol.)	UNIQUAC $T_m$ (K)	DSC $T_m$ (K)	$T_m$ [19] (K)
20	271.5	270.5	271.5
25	271	271	271
30	270	270.5	270
35	269.3	269.5	269
40	268	267	268
45	266.8	266.5	267
50		265	
50.7	265		265
55		263	
57.8	262.3		262
60		259	
63	259		
67.2	255.5		
70.5	252		
75.5	244.8		
79	237.7		

(Table 1). For higher concentrations (65–72%), the thermal treatment procedure was not efficient to obtain maximally freeze-concentrated systems, and for the highest concentrations (72–80%) no ice crystallization occurred during the experimental time, only the glass transition of the solution could be observed. Thus, the extrapolation of the equilibrium curve is expected to be inaccurate, because of the large variation of  $T_m$  in this concentration range due to the sharp increase of non-ideality at high solute concentrations.

*Model for the melting curve.*—UNIQUAC  $T_m$  values for sucrose solutions are reported in Table 1, with some experimental data [19]. The predicted  $T_m$  curve is shown in Fig. 3. Compared to the curve previously published by Simatos and Blond [8], the small changes in the predicted  $T_m$  values (1 K lower at 70%, 2 K lower at 80% sucrose) must be attributed to the fact

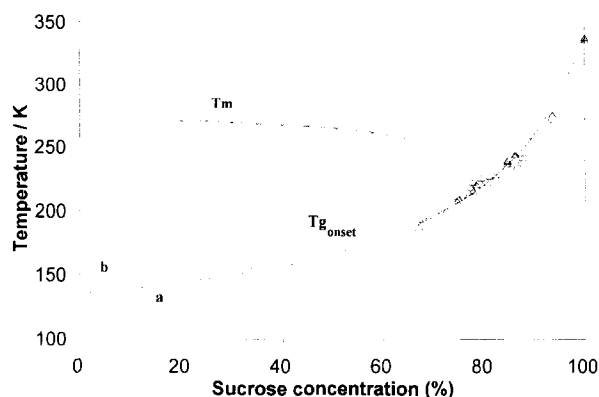


Fig. 3. Experimental data [19] ( $\times$ ) and calculated  $T_m$  curve, experimental data ( $\Delta$ ) and calculated  $T_{g\text{onset}}$  curves of water–sucrose glasses for two sets of  $T_{g\text{water}}$  and  $k$  values (curve a:  $T_{g\text{water}} = 135$  K,  $k = 5.46$ ; curve b:  $T_{g\text{water}} = 139$  K,  $k = 5.7$ ).

that the interaction parameters of Catté et al. [16] were calculated from more experimental data including the excess Gibbs energy and excess enthalpy data of Barone et al. [20,21].  $T_m$  decreases more rapidly above 60% sucrose than those estimated from experimental data published before [6,7].

The glass transition of amorphous dry sucrose and sucrose solutions has been described with two temperatures:  $T_{g\text{onset}}$ ,  $T_{g\text{mid}}$ , because the glass transition spread over a large temperature range where a progressive change of the physical properties of the glass (heat capacity, viscosity, ...) was observed.

*Experimental  $T_g$  values.*—Although relaxation features were obvious (Fig. 1) in DSC thermograms obtained for dry amorphous sucrose, they were not taken into account when determining  $T_{g\text{mid}}$ . The use of the derivative curve, which has been recommended by Levine and Slade [4], must be done with caution, as the maximum of the derivative corresponds to the middle point of the glass transition only in the case of a unique feature without relaxation. The temperature

Table 2  
Literature data for thermodynamic parameters characterizing transitions of sucrose and frozen sucrose solutions

Authors	Dry sucrose		Frozen solutions	
	$T_{g\text{mid}}$ (K)	$\Delta C_p$ ( $\text{J g}^{-1} \text{K}^{-1}$ )	$T'_g$ (K)	$C'_g$ ( $\text{g}_{\text{sucrose}}/\text{g}_{\text{solution}}$ )
Levine et al. [4]	325		241	0.641
Hatley et al. [5]	331		241	0.830
Ablett et al. [6]			233	0.812
Roos et al. [7]	340	0.60	227	0.795
Simatos et al. [8]			236	0.800
Shalaev et al. [9]			224	0.790
Orford et al. [26]	343	0.77		

differences between the onset and the middle points were always around 3 to 5 °C.

With sucrose solutions, experimental  $T_g$  values could be obtained only for sugar concentration higher than 65%, because highly concentrated sucrose solutions can easily be cooled without any crystallization. In contrast, for diluted sucrose solutions it was not possible to avoid ice crystallization. Water plasticizes the glassy material and a drastic decrease in the glass transition temperature of the amorphous sucrose can be observed in Fig. 3, in which only the measured  $T_{g_o}$  values for sucrose and sucrose–water glasses are reported.

*Model for the  $T_g$  curve.*—Using the Gordon–Taylor [11,17] equation (1), it is required to select  $T_g$  and  $\Delta C_p$  values for the pure components. For water, these values are still debated [13,22–25]. For sucrose, the variability of data originating from different sources (Table 2) may be attributed to the presence of small quantities of water or to the thermal treatment used to induce vitrification.

The  $T_g$  values calculated using  $\Delta C_p$  values were far from experimental data [26]. We therefore calculated the adjustable parameter  $k$  by fitting eq (1) to our experimental data obtained with sucrose solutions of concentration ranging between 67 and 100%. Calculations were achieved using the two  $T_{g_{water}}$  values, the most frequently found in the literature (Table 3).

The  $k$  values were calculated using both the onset and middle points of the glass transition. All the fitted parameters  $k$  are tabulated in Table 3. They are not significantly different for the two  $T_{g_{water}}$  values used. For the relevant concentration range, i.e. around 80% sucrose, the fitted curves are very close. The results are shown on Fig. 3 (curves a, b), together with the experimental values for the onset tempera-

ture; a similar graph could be drawn with the mid-point temperature.

In another calculation,  $T_{g_{water}}$  and  $T_{g_{sucrose}}$  were also treated as adjustable parameters. In this case, the confidence level for  $k$  is high but the calculated  $T_g$ 's are inaccurate because of the gap between experimental and calculated data.

Taking for  $\Delta C_{p_{water}}$  a value equal to 1.94 J g<sup>-1</sup> K<sup>-1</sup> [22,23], and for  $\Delta C_{p_{sucrose}}$  our experimental values (0.70 J g<sup>-1</sup> K<sup>-1</sup>), the  $k$  values are found to be in the range 0.30–0.40, which are far from the fitted values. It is therefore justified to consider  $k$  as an adjustable parameter. Such deviations are evidence for specific interactions between the components [27]; in the present case, hydrogen bonding is the most likely explanation. By comparison, Roos and Karel [7] obtained a lower value ( $k = 4.7 \pm 0.2$ ) for sucrose solutions between 65 to 80%; the curve drawn with this value gives very similar  $T_g$  values in the 80% range.

Concerning the intersections of the  $T_m$  and  $T_g$  curves, the accuracy of the modified UNIQUAC model [16] suggests that the  $T_m$  curve is acceptable in the concentration range up to 85% sucrose. Similarly, as discussed in the previous section, the  $T_g$  curves fitted by the Gordon–Taylor equation (1) are not significantly different around 80% sucrose whatever the value used for the  $T_g$  of pure water.

On the other hand, the  $T_g - C_g'$  coordinates vary from [228 K – 82.2%] to [232 K – 81.2%] depending on the glass transition temperature taken into account ( $T_{g_{onset}}$  or  $T_{g_{mid-point}}$ ).

More interesting for the interpretation of DSC thermograms obtained with frozen sugar solutions is the comparison of these intersection coordinates with the characteristic temperatures which can be determined from the thermograms, and which are used by different authors to define  $T_g'$ . The onset point  $T_{g_o}$ , the mid-point of the first step  $T_{g_1}$  and the mid-point of the second step  $T_{g_2}$  (Fig. 2) are shown on the state diagram (Fig. 4). The values of  $T_{g_o}$  and  $T_{g_1}$  are close to the intersection of the  $T_m$  curve, with the onset and mid-point glass transition curves despite the significant difference. On the other hand, the value of  $T_{g_2}$  is far from the intersection of the  $T_m$  and  $T_g$  curves and seems to be representative of another process. Indeed, the glass transition, representing an essentially kinetic process, is spread over a large temperature range and may be influenced by compositional changes induced by the melting of ice crystals.

Due to the impossibility of defining a 'true' intersection between the  $T_m$  and one of the  $T_g$  curves, it

Table 3

Calculated values for  $k$  and  $T_g$  from the Gordon–Taylor equation by fitting  $T_{g_{onset}}$  and  $T_{g_{mid-point}}$  of water–sucrose glasses with sucrose concentration varying from 65 to 100%

	$T_{g_{sucrose}}$ (K)	$T_{g_{water}}$ (K)	$k^a \pm ci$
$T_{g_{onset}}$	338	139 [22]	$5.70 \pm 0.18$
	338	135 [23]	$5.46 \pm 0.17$
	$334.1 \pm 7.7^a$	$152.3 \pm 9.8^a$	$6.49 \pm 1.22$
$T_{g_{mid-point}}$	343	142 [24]	$5.35 \pm 0.15$
	343	138 [25]	$5.12 \pm 0.15$
	$339.5 \pm 7.2^a$	$154.6 \pm 8.7^a$	$6.38 \pm 0.66$

<sup>a</sup> Fitted parameters; number of experimental values:  $n = 43$ ; ( $\pm ci$ ) = confidence interval at 95%.

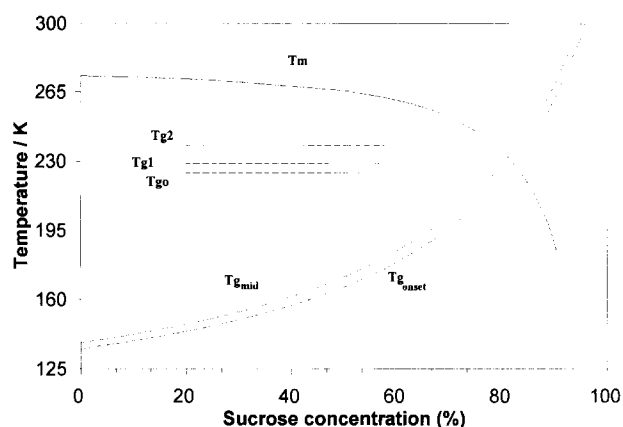


Fig. 4. Partial state diagram of water–sucrose showing the intersections of UNIQUAC calculated  $T_m$  curve with the Gordon–Taylor  $T_{g\text{ onset}}$  and  $T_{g\text{ mid-point}}$  curves. Also shown the regression lines for  $T_{g0}$ ,  $T_{g1}$ , and  $T_{g2}$  values obtained from DSC thermograms of maximally freeze-concentrated sucrose solutions.

appears safer not to consider an absolute value for  $T_g'$ . If the glass transition can be considered as an important stage for the molecular mobility, the important question related to stability is the respective influence of the glass transition and the melting of ice crystals on viscosity and solute mobility. It seems therefore that diffusion measurements must be the objective for further investigations. The FRAP technique has been used to measure diffusion coefficients in highly concentrated sucrose solutions [28]; measurements in frozen systems must be developed. This should allow the determination of the solute mobility and/or the viscosity of the unfrozen phase as a function of the temperature and perhaps to give a better definition of the  $T_g'$  parameter.

#### 4. Conclusion

It is particularly difficult to obtain reliable experimental  $T_m$  values in the range where the solid–liquid equilibrium and glass transition curves intersect, i.e. around the glass transition temperature ( $T_g'$ ) and the concentration ( $C_g'$ ) of the residual amorphous fraction in maximally freeze-concentrated solutions. The use of thermodynamic models is thus an alternative approach and the modified UNIQUAC model for the prediction of the liquid–solid curve of sucrose–water solutions in the high concentration region is a reasonable approximation [16].

Concerning the glass temperature depression with water as a diluent, the Gordon–Taylor equation seems satisfactory for smoothing purposes, although the de-

pendence of the parameter  $k$  on  $\Delta C_p$  values cannot be taken into account, in agreement with the non-regular character of highly concentrated sugar solutions. From the comparison of the temperature range corresponding to the intersection of the UNIQUAC melting curve and the Gordon–Taylor glass transition curves, with the DSC thermograms of maximally freeze-concentrated solutions, we may conclude that the glass transition of the amorphous phase should probably be represented by the first step of the heat capacity increase observed on the thermograms.

Due to the kinetic character of the glass transition, the intersection of the  $T_m$  and  $T_g$  curves cannot be considered as a unique point, so it appears illusory to give an accurate value for  $T_g'$  and  $C_g'$ . Measurements of molecular mobility should be carried out to better define the stability frontier for frozen systems.

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