

The Glass Transition Temperature of Saccharide Aqueous Solutions

Estimated with the Free Volume / Percolation Model

Julian Gelman Constantin¹, Matthias Schneider^{1#}, Horacio R. Corti^{1,2*}

¹Instituto de Química Física de los Materiales, Ambiente y Energía (INQUIMAE), Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Intendente Güiraldes 2160 - Ciudad Universitaria - C1428EGA Buenos Aires - Argentina.

²Departamento de Física de la Materia Condensada, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Av. General Paz 1499, San Martín (1650), Buenos Aires, Argentina.

Present address: Department of Chemistry, University of Southern California, Los Angeles, CA90089-4482, USA.

* Corresponding author. Tel: 5411 6772 7174; Fax: 5411 6772 7121; E-mail address: hrcorti@cnea.gov.ar
(H. R. Corti)

Abstract

The glass transition temperature of trehalose, sucrose, glucose, and fructose aqueous solutions has been predicted as a function of the water content by using the free volume / percolation model (FVPM). This model only requires the molar volume of water in the liquid and supercooled regimes, the molar volumes of the hypothetical pure liquid sugars at temperatures below their pure glass transition temperatures, and the molar volumes of the mixtures at the glass transition temperature. The model is simplified by assuming that the excess thermal expansion coefficient is negligible for saccharide-water mixtures, and this ideal FVPM becomes identical to the Gordon-Taylor model. It was found that the behavior of the water molar volume in trehalose-water mixtures at low temperatures can be obtained by assuming that the FVPM holds for this mixture. The temperature dependence of the water molar volume in the supercooled region of interest seems to be compatible with the recent hypothesis on the existence of two structure of liquid water, being the high density liquid water the state of water in the sugar solutions. The idealized FVPM describes the measured glass transition temperature of sucrose, glucose, and fructose aqueous solutions, with much better accuracy than both, the Gordon-Taylor model based on an empirical k_{GT} constant dependent on the saccharide glass transition temperature, and the Couchman-KarasZ model using experimental heat capacity changes of the components at the glass transition temperature. Thus, FVPM seems to be an excellent tool to predict the glass transition temperature of other aqueous saccharides and polyols solutions by resorting to volumetric information easily available.

Keywords: glass transition; saccharide; water; free volume; percolation; model

1. Introduction

The glass transition temperature of a supercooled fluid represents the temperature, T_g , at which the mechanical relaxation time becomes comparable to the experimental time, conventionally fixed at 100 seconds. It is not a thermodynamic transition, but a dynamic (route-dependent) one, which depends on the technique used to determine it, conventional or modulated differential scanning calorimetry and dynamic mechanical thermal analysis being the more widely used. Even the use of a single technique could lead to different T_g values, depending on the cooling rate.¹

In mixtures the glass transition temperature is a function of the composition, with the component having the lower transition temperature taking the role of plasticizer, as the case of water in aqueous solutions containing carbohydrates or natural biopolymers. The glass transition behavior of these aqueous systems is fundamental to determine their stability during storage of biomolecules, cells or organisms at low temperatures, and the damage of the materials being cryopreserved.² Therefore, the prediction of the glass transition temperature of binary, or more complex, aqueous solutions becomes an useful tool in a number of practical applications related mainly to food and cryopreservation technologies.

In this work we use the free volume/percolation model (FVPM),³ with parameters adjusted using the available information on the trehalose-water system, to estimate the glass transition temperature of simple polyol-water systems and compare the results with the experimental values and those obtained with other theoretical and semiempirical models.

Previously to discuss the FVPM for the estimation of T_g of polyol aqueous solutions, it is worth to analyze the performance of well-known glass transition models applied to these systems.

Generally speaking, the glass transition temperatures of binary aqueous mixtures have been modeled by resorting to theoretical approaches based on the free volume theory of liquids,⁴ and the Ehrenfest second order transition in which the enthalpy, entropy and volume of the mixture are continuous at T_g .⁵

The Gordon and Taylor model (GTM) is a free volume model originally developed to predict the glass transition temperature of polymer blends.⁶ It is also used to calculate T_g of mixtures of water (1) with a second component (2) as a function of its composition if the values of the glass transition temperature of the pure components, T_{gi} , are known. The expression for T_g of the mixture is,

$$T_g = \frac{w_2 T_{g2} + w_1 k_{GT} T_{g1}}{w_2 + w_1 k_{GT}} \quad (1)$$

where w_1 and w_2 are the weight fractions of water and solute, respectively. The coefficient k_{GT} can be calculated from the densities, ρ , of the pure components and the change of the thermal expansibility of the mixture, $\Delta\alpha$, at T_g . By assuming that the product $\Delta\alpha \cdot T_g$ is approximately constant,⁷ the expression of k_{GT} takes the simple form:

$$k_{GT} = \frac{\rho_2 T_{g2}}{\rho_1 T_{g1}} \quad (2)$$

Nevertheless, the application of the GTM is limited due to the lack of information on the volumetric properties of the saccharides in the supercooled regime.

Roos⁸ proposed that k_{GT} could be obtained empirically for saccharide aqueous solutions by fitting the measured glass transition of these systems to equation (1). A linear relationship was found between this parameter and the glass transition temperature of the sugar,

$$k_{GT} = 0.0293 T_{g2} - 4.39 \quad (3)$$

where T_{g2} is the glass transition temperature of the pure saccharide in Kelvin.

Figure 1 shows the experimental T_g for aqueous sucrose,⁸⁻²⁰ and trehalose^{3,8,13,16,18,21-25} solutions, respectively, obtained from differential scanning calorimetry (DSC). The averaged glass transition temperature of pure water reported for amorphous solid water,²⁶⁻²⁸ and for hyperquenched water,²⁸⁻³³ $T_{g1} = (136 \pm 1)$ K, was adopted in the calculations.

The predictions of glass transition temperatures for aqueous sucrose solutions using the empirical k_{GT} given by Eqn. (3) are shown in Figure 1 for $T_{g2} = 343$ K, the mean value of onset and midpoint data. The reasonable good agreement with the experimental data ($\Delta T_g < 10$ K) was expected, taking into account that sucrose was one of the saccharides used in the fit leading to Eqn. (3). In the case of trehalose solutions, the predictions using the empirical k_{GT} (Eqn. (3)), obtained with $T_{g2} = 380$ K for pure trehalose reported by Roos,⁸ underestimate the most recent glass transition measurements in the water-rich region, as shown in Figure 1.

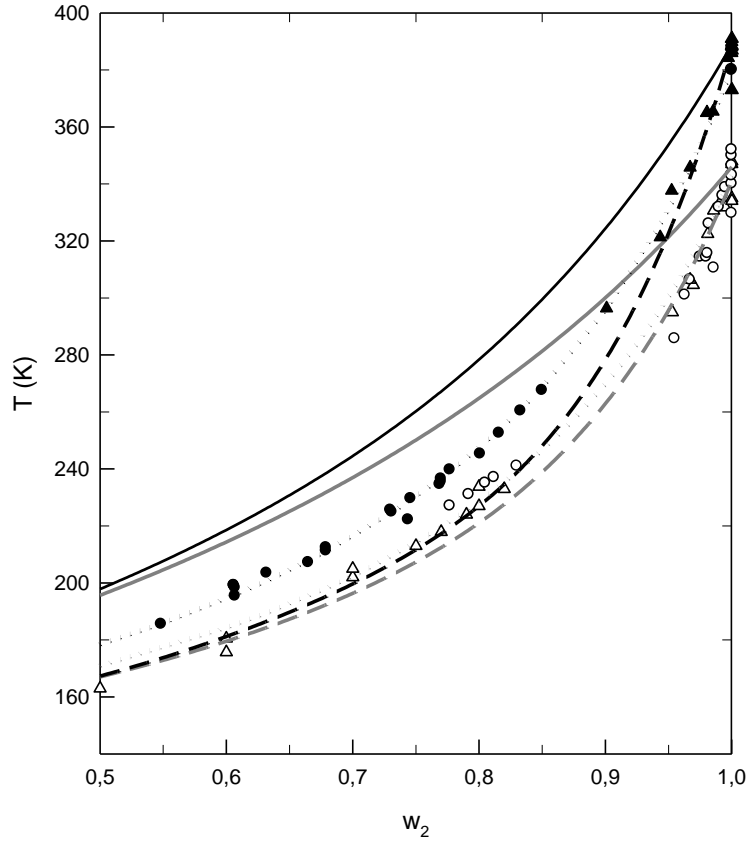


Figure 1. Experimental glass transition temperature of sucrose aqueous solutions: (○) midpoint^{8,11-16} (△) onset^{9,10,17-20}, and trehalose aqueous solutions: (●) midpoint^{3,8,18,21} (▲) onset^{8,13,16,22-25}. Dashed lines correspond to the fits using the GTM (Eqn. 1) with k_{GT} given by Eqn. (3). Solid lines correspond to the fits using the modified CKM (Eqn. 5) with k_{CK} given by Eqn. 6 (3.09 for trehalose, and 2.52 for sucrose). The dotted lines correspond to the GTM (Eqn.1) using k_{GT} as an adjustable parameter ($k_{GT} = 4.76$ for trehalose, and $k_{GT} = 4.94$ for sucrose).

The Couchman-Karasz model (CKM), based on the glass transition as an Ehrenfest second order transition,^{34,35} leads to an expression for T_g of the mixture as a function of composition in terms of the glass transition temperatures of the pure solution components, and $\Delta C_{pi} = C_{pi}(liq) -$

$C_{pi}(\text{glass})$, the heat capacity change at the glass transition. If ΔC_{pi} is assumed independent of the temperature, the following expression holds,.

$$\ln T_g = \frac{w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}}{w_1 \Delta C_{p1} + w_2 \Delta C_{p2}} \quad (4)$$

A similar equation was obtained by Gordon *et al.*³⁶ from the Gibbs-DiMarzio theory of the glass transition.

On the other hand, if the heat capacity changes are assumed to be proportional to the temperature, as proposed by Ten Brinkle *et al.*,³⁷ the following modified CKM expression for T_g is obtained,

$$T_g = \frac{w_2 T_{g2} + w_1 k_{CK} T_{g1}}{w_2 + w_1 k_{CK}} \quad (5)$$

where:

$$k_{CK} = \frac{\Delta C_{p1}}{\Delta C_{p2}} \quad (6)$$

This equation is equivalent to Eqn. (1), excepts that the calculation of k_{CK} requires the thermal experimental properties of the pure components at the glass transition.

The CKM predictions of T_g for the sucrose and trehalose aqueous mixtures, also shown in Figure 1, were obtained using $\Delta C_{p2} = 0.628 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ for trehalose,³ and $\Delta C_{p2} = 0.77 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ for sucrose,³⁸ while for water we adopted $\Delta C_{p1} = 1.94 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$, that is the value reported for H_2O_2 and N_2H_4 aqueous solutions.³⁹ This ΔC_{p1} value agrees with that reported by Sugisaki *et al.*²⁶ for

vapor-deposited amorphous water. Other ΔC_{p1} values reported by Hallbrucker *et al.*²⁷ (0.089 J·K⁻¹·g⁻¹) for hyperquenched glassy water, and by Kohl *et al.* (0.039 J·K⁻¹·g⁻¹),⁴⁰ lead to $k_{CK} < 1$ (according to Eqn. (6)), which would result in convexes curves, instead of the concaves curves experimentally observed.

It is clear from Figure 1 that the modified CKM predictions, Eqn. (5), largely overestimate the glass transition temperature for both disaccharides all over the composition range, as already noted by Blond *et al.*⁴¹ for sucrose aqueous solutions.

Both, GTM and CKM can be used as empirical equations with one (k_{GT} or k_{CK}) or two (T_{g2} , and k_{GT} or k_{CK}) adjustable parameters. In both cases Eqns. (1) and (5) becomes identical and, obviously, the fit of the experimental results is much better, as indicated in Figure 1 (dotted lines) in the case of one adjustable parameter (k_{GT}). Thus, the empirical equations are good for describing the experimental results but the predictive power of the models is lost.

Katkov and Levine⁴² analyzed the predictive power of the CKM expressed by Eqn. (4) using the trehalose-water mixtures as a test system. They concluded that the original CKM fits existing experimental data when $\Delta C_{p2} = 0.55$ J·K⁻¹·g⁻¹ is used.⁸

An empirical equation proposed by Jenckel and Heusch⁴³ expressed in terms of the weight fractions:

$$T_g = w_1 T_{g1} + w_2 T_{g2} + k w_1 w_2 \quad (7)$$

has also been successfully used for different binary mixtures, but it fails when applied to low molecular weight liquids,⁴⁴ as also observed with Eqn. (1) and (5).

2. The Free Volume / Percolation Model (FVPM)

The FVPM is a free-volume approach⁴⁵ that relates T_g to the percolation threshold of a 3-dimensional system. The model requires no adjustable parameters, but only information on the volumetric data of the aqueous system. It was applied for the first time by Miller *et al.*³ to predict T_g of trehalose-water mixtures and details of the model can be found in that work. Nevertheless, we summarize here the main aspect of the model to make clear the assumptions we propose in the present work to estimate T_g of polyols with a minimum of experimental data.

The main idea behind the FVPM is that in the liquid state exists sufficient free volume, V_f , to permit the diffusive motion of its molecules, the fluidity being the consequence of a continuous (percolated) network of “channels and lakes”. With decreasing temperature V_f also decreases and, as the glass transition temperature is reached, this free volume network disintegrates. According to the percolation theory, there is a constant critical volume fraction (0.16) at which the network is not longer percolated, and this universal constant depends of the dimensionality but not of the system composition.⁴⁶ For a 3-dimensional lattice this constant is related with T_g through the expression,

$$\frac{V_f}{V}(T_g) = \frac{V - V^0}{V} = 0.16 \quad (8)$$

where V is the total volume, and V^0 is the hypothetical volume occupied by the molecules at $T = 0$ K. Defining the average thermal expansion coefficient,

$$\langle \alpha \rangle = \frac{1}{T_g} \int_0^{T_g} \alpha dT \quad (9)$$

and taking into account that,

$$V = V^0 \exp[\langle \alpha \rangle T_g] \approx V^0 (1 + \langle \alpha \rangle T_g) \quad (10)$$

we get, replacing Eqn. (10) into Eqn. (8), a relationship between the glass transition temperature and the average thermal expansion coefficient:

$$\langle \alpha \rangle T_g = 0.19 \quad (11)$$

also valid for the pure water and the pure solute. The approximation in Eqn. (10) holds with a accuracy better than 1% if $\langle \alpha \rangle T_g < 0.02$, a condition that is fulfilled for the polyols studied in this work.

It is possible to relate the glass transition temperature of the mixture and those of the pure components by writing the thermal expansion coefficient of the mixture as the sum of the contribution of each pure component (α_i), weighted by its apparent volume fraction in the mixture (φ_i), plus the excess term:

$$\alpha = \varphi_1 \alpha_1 + \varphi_2 \alpha_2 + \varphi^{ex} \langle \alpha^{ex} \rangle \quad (12)$$

In equation (12) $\varphi_i = x_i V_i / V$, where x_i and V_i are the mole fraction and the molar volume of the pure i component, respectively, V the molar volume of the solution, and φ^{ex} and $\langle \alpha^{ex} \rangle$ are the excess volume fraction and the average excess thermal expansion coefficient, respectively.

Combining Eqn. (11) and (12) we obtain the desired relation between the glass transition temperature of the mixture and the volumetric properties,

$$\frac{1}{T_g} = \frac{\varphi_1}{T_{g1}} + \frac{\varphi_2}{T_{g2}} + \frac{\varphi^{ex} \langle \alpha^{ex} \rangle}{0.19} \quad (13)$$

Eqn. (13) is the master equation of the FVPM and it was used in a previous work³ to estimate the glass transition temperature of trehalose aqueous solutions. In order to estimate T_g of a mixture one should be able to calculate the molar volume fraction of the pure components and the excess volume of the aqueous mixture at T_g . Therefore, reasonable assumptions on the volumetric properties of the mixture at low temperature are needed in order to use the FVPM expression for the glass transition temperature.

Regarding the excess term in Eqn. (13), some assumptions related to its magnitude can be formulated. The volumetric properties of aqueous mixtures at low temperatures ($T_{g1} < T < T_{g2}$) are usually available above room temperature, that is, below T_{g2} for most of the saccharides to be considered in this work, but well above T_{g1} . Since the mixtures of interest for practical purposes are concentrated solutions, their glass transition temperature will be much closer to T_{g2} than to T_{g1} .

This is, for instance the case of aqueous trehalose solutions, where $T_{g2} = 389$ K and the glass transition temperatures of trehalose aqueous solutions with concentrations $0.60 < w_2 < 0.83$ lay in the range 193 K $< T < 283$ K.^{3,21} As it is discussed in the Supplementary information, the excess volume of trehalose-water mixtures at 183 K is around 0.36 cm³.mol⁻¹, and then $\varphi^{ex} \approx 0.01$. The value of $\langle \alpha^{ex} \rangle$ is not easy to estimate, but we can consider the value of $\langle \alpha \rangle$ as a reasonable boundary. For the solutes considered in this work the expansivity is close to 10^{-4} K⁻¹ and, consequently $\varphi^{ex} \langle \alpha^{ex} \rangle \approx 10^{-6}$ K⁻¹. Thus, the excess term in Eqn (13) can be neglected.

It is important to note that if the excess term is ignored, then the idealized FVPM model can be expressed as:

$$\frac{1}{T_g} = \frac{\phi_1}{T_{g1}} + \frac{\phi_2}{T_{g2}} \quad (14)$$

This expression can also be obtained from Eqns. (1) and (2), and it can be generalized to multicomponent systems. That is, the idealized FVPM is identical to the GTM, what in turns indicates that the GTM is an special case of the FVPM. Finally, it is worthy note that when the excess term is neglected, the FVPM expression for the glass transition is independent of the critical volume fraction, that is, the ratio between the free volume and the system volume at T_g should be constant but not necessarily 0.16.

Other attempts to apply the FVPM for estimating the glass transition temperature of cryoprotectants in aqueous solutions have been reported.^{47,48} Shah and Schall⁴⁷ used the FVPM to estimate the glass transition temperature of glycerol-water mixtures by assuming that the temperature dependence of the density of water (ρ_1) and glycerol (ρ_2) are constant over all the temperature range down to the glas transition temperature of the mixture. Thus, they obtained the Miller/Fox equation:

$$\frac{1}{T_g} = \rho(T_g) \left(\frac{w_1}{\rho_1(T_g)T_{g1}} + \frac{w_2}{\rho_2(T_g)T_{g2}} \right) \quad (15)$$

where ρ is the density of the mixture. It should be emphasized that the assumption of constant temperature dependence of the pure component densities is not equivalent to the assumptions of this work on the molar volumes of the pure components and the mixture.

Considering the wide deviation of the reported T_g of the glycerol-water mixtures, Shah and Schall⁴⁷ obtained a reasonable prediction with the idealized FVPM. When applied to multicomponent mixtures containing water, glycerol, salts, and polyethylene- glycol, Eqn. (15) yields to better predictions than the Fox equation,⁴⁹ which is similar to Eqn. (14) but with mass fractions replacing volume fractions. In fact Fox equation can be obtained from Eqn. (15) assuming that the density of all pure components and the mixture are equal at all temperatures.

3. Volumetric properties of the pure components

The volumetric properties of water and polyols aqueous solutions are available in literature on a limited range of temperature. It is necessary to made a number of assumptions in order to apply Eqn. (13) to estimate the glass transition temperature of the solutions.

3.1 Molar volume of water in the liquid and supercooled regimes

The molar volume of water of liquid and supercooled water above the homogeneous nucleation temperature ($T_h = 239$ K)⁵⁰ is shown in Figure 2. The assessment of the volumetric properties of water below T_h is not possible experimentally in bulk water due to unavoidable crystallization, but the molar volume of supercooled water confined in nanoporous silica,⁵¹ and of emulsified water under pressure (200 MPa),⁵² could be measured because in both cases the crystallization process can be avoided. These data are also plotted in Figure 2 and exhibited a completely different behavior in the supercooled regime (differences in the liquid region above 273 K can be explained by the effect of pressure).

To complete the information on the volumetric properties of water, molar volume of low-density and high-density amorphous ice at ≈ 120 K,⁵³ are also shown in Figure 2.

The volumetric data for water under nanoconfinement can be discarded as representative of the behavior of bulk water because the expansivity coefficient changes sign twice all over the temperature range. Incidentally, the volumetric properties of low-density amorphous ice at T_g , agrees quite well with that of nanoconfined water, but the slope of the curve V_1 vs. T is much lower than that predicted for the amorphous ice using Eqn. (11).

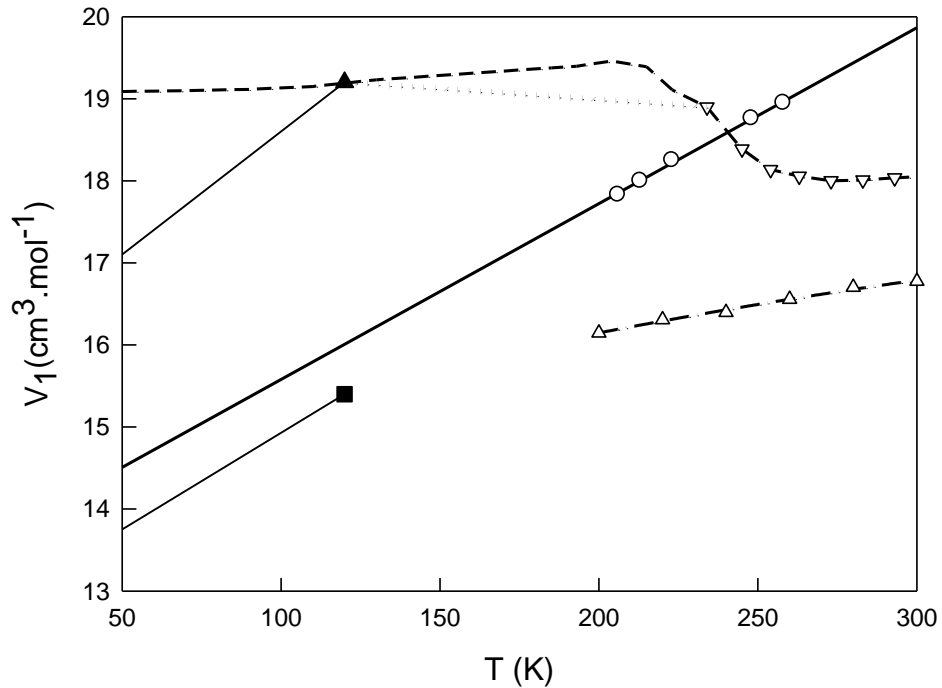


Figure 2. Molar volume of pure water as a function of temperature: supercooled bulk liquid water above the homogeneous nucleation temperature (∇),⁵⁰ supercooled nanoconfined water⁵¹ are indicated by dashed line, low-density (\blacktriangle) and high-density (\blacksquare) amorphous ice [53], and emulsified water at 200 MPa (Δ).⁵² Thin solid lines correspond to extrapolated low temperature molar volumes of low- and high-density amorphous ice calculated using the average thermal expansion coefficient. Solid line correspond to the

linear fit of the molar volume of water (\circ) obtained using FVPM and experimental data for the trehalose-water mixtures.³ Dotted line is the V_1 extrapolation used previously.³

On the other hand, the expansivity coefficient for emulsified/pressurized water does not change sign upon cooling,^{52,54} and the extrapolation down to T_g , seems to correlate rather well with the density of high-density amorphous ice.

It can be concluded that the volumetric properties of nanoconfined and emulsified/pressurized water have a completely different temperature dependence in the interval 200-250 K, and at lower temperatures the molar volumes seems to correlate with the molar volume of low and high density amorphous ice, which differs in more than 20 % each other.

For this reason we decided to adjust the molar volume of water over the entire range of temperature using the FVPM and the experimental data of glass transition temperature for trehalose-water solutions.³ This procedure requires the knowledge of the molar volume of trehalose in the mixtures with water as a function of temperature and composition that will be describe in the next subsection. The adjusted values of water molar volume are shown in Figure 2 on the range of temperature where experimental data for T_g of water-trehalose are available.³

It can be seen in Figure 2 that V_1 is approximately linear with temperature, so the coefficient of thermal expansion is positive and constant all over the temperature range analyzed, and its value is close to that predicted by Eqn. (11). On the other hand, the extrapolation of V_1 at low temperature shows that it is closer to the values corresponding to the high-density amorphous ice.

It has been suggested that the properties of water in supercooled aqueous electrolyte solutions are structurally related to the high-density liquid water, that is the fluid phase correlated to the high-density amorphous ice.^{55,56} We suggest here that something similar occur in polyol

aqueous solutions, and hence the volumetric properties of water are different from that of bulk water (as represented by the linear temperature dependence shown in Figure 2).

3.2 Molar volume of hypothetical liquid trehalose and other polyols

As mentioned above, we calculated the molar volume of water by profiting the experimental data of glass transition temperature for trehalose-water solutions and the FVPM. For this system, volumetric data down to -15 °C is available.³ Densities reported by other authors for the water-trehalose system restrict to very dilute solutions,⁵⁷⁻⁵⁹ or to temperature ranges close to room temperature and above.^{60,61} For this task we used Eqn. (3), and the molar volume of hypothetical liquid trehalose had to be estimated following the procedure described in Supplementary Information.

Briefly, the molar volume of the trehalose solutions, V_m , were plotted at different concentrations as a function of temperature (See Figure S1 in Supplementary Information). It was observed that V_m is a linear function of temperature in the concentration range $0.0890 \leq x_2 \leq 0.0117$, which facilitate extrapolation down to lower temperatures in order to calculate φ_2 .

The molar volume of a hypothetical liquid trehalose, V_2 , at each of temperature was determinate from the linear plots (see Figure S2) of V_m vs. x_2 , by extrapolating to $x_2 = 1$. As explained in Supplementary Information, there is a large error associated to this procedure, and we adopted an alternative procedure consisting in determining V_2 at 10 °C with the former procedure and calculating V_2 at lower temperatures by using Eqn. (11) with $T_{g2} = 389$ K.³

For trehalose aqueous mixtures, the maximum calculated excess volumes was $-0,5 \text{ cm}^3$, which corresponded to excess volume fractions lower than -0.016 . Hence, for simplicity, we could assume here ideal mixture, that is $\phi^{ex} = 0$.

A similar procedure was adopted to calculate V_2 , V_m , and then ϕ_2 for other polyols studied in this work. Table S1 (Supplementary Information) summarizes the parameters used to calculate ϕ_2 for all the solutes. The reference volumes at T_0 were calculated from the reported volumetric properties of the aqueous solutions of sucrose,^{57,60,62,63} fructose,^{59,60,63} and glucose^{57,60,63} using the same procedure described for trehalose.

4. Results and discussion

The calculated glass transition temperatures of the trehalose-water mixtures using FVPM with the adjusted molar volume of water (V_1) are shown in Figure 3. Also shown are the predicted T_g calculated previously,³ using V_1 interpolated from the lines joining the supercooled molar volume of water with the low-density amorphous ice molar volume (see Figure 2). It is clear that the FVPM is very sensitive to the choice of V_1 , and the previous estimation using the extrapolated values of V_1 from T_h to the low-density amorphous ice leads to T_g values that differ from the experimental ones more than 10 K in the water rich region.

Once the molar volume of water in the supercooled region was calculated by using the trehalose-water mixtures as a model system, a validation of the model was attempted by comparing its prediction with experimental data for other saccharide-water systems. We have chosen aqueous solutions of sugars for which volumetric data are available.

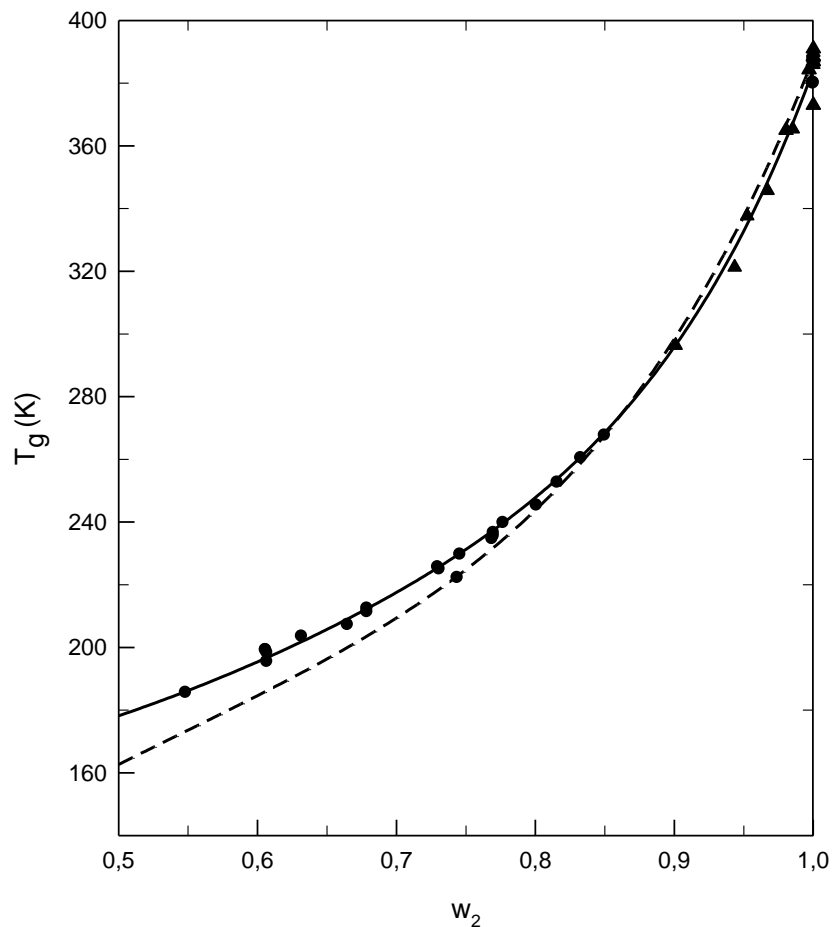


Figure 3. Glass transition temperature of trehalose-water solutions. The symbols correspond to the experimental data as in Figure 1. The predictions of the FVPM using the adjusted V_1 (see text) are indicated by the solid line, whereas the predictions using V_1 interpolated from the lines joining the supercooled molar volume of water with the low-density amorphous ice molar volumes correspond to the dashed line.

Figure 4 shows the predictions of the FVPM for aqueous sucrose solutions compared with the experimental data. Recent results of midpoint T_g by Ruiz-Cabrera *et al.*⁶⁴ were added to the set of experimental data, but it should be noted that the scatter is large at $w_2 > 0.85$. The excess volume

of the sucrose-water mixtures reaches a maximum of $1.0 \text{ cm}^3 \cdot \text{mol}^{-1}$ at $w_2 \approx 0.95$, and the contribution of the excess volume fraction in Eqn. (13) could to be discarded.

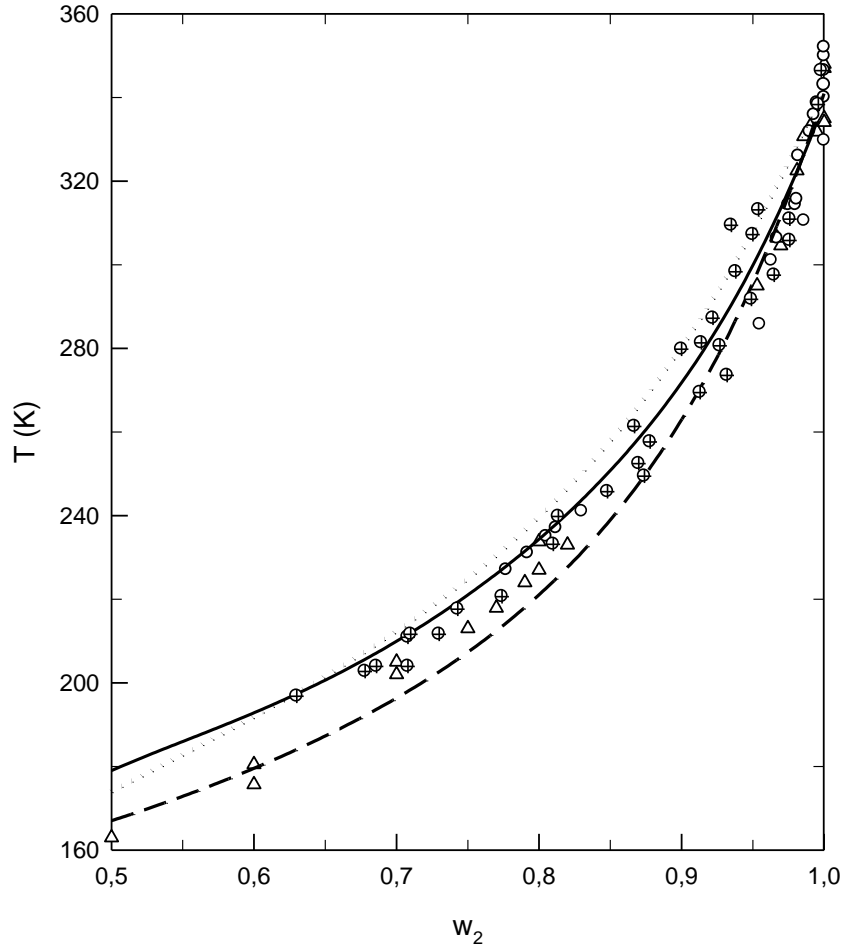


Figure 4. Glass transition temperature of sucrose-water solutions. The symbols correspond to the experimental DSC data as in Figure 1, along with recent midpoint DSC data.⁶⁴ Solid line: prediction by the FVPM; dashed line: GTM with the parameters as in Fig. 1; dotted line original CKM (Eqn. 4) with $T_{g1} = 136 \text{ K}$, $T_{g2} = 343 \text{ K}$, $\Delta C_{p1} = 1.94 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$, and $\Delta C_{p2} = 0.77 \text{ J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$.

The agreement between the experimental data and those estimated with FVPM is quite satisfactory ($R^2 = 0.9779$), and much better than that obtained with the GTM and the k_{GT}

parameter calculated through Eqn. (3) ($R^2= 0.9578$). On the other hand, the original CKM $T_{g2} = 343$ K and $\Delta C_{p2} = 0.77$ J·K⁻¹·g⁻¹, taken from Katkov and Levine,⁴² slightly overestimate T_g of the mixture over an important region of compositions ($R^2= 0.9708$).

The results of FVPM for glucose-water mixtures are depicted in Figure 5, where experimental DSC data.^{8,11,64,65} The excess volume for this mixture has a maximum of 0.6 cm³·mol⁻¹ at $w_2 \approx 0.90$, and again the contribution of the excess term in Eqn (13) was neglected.

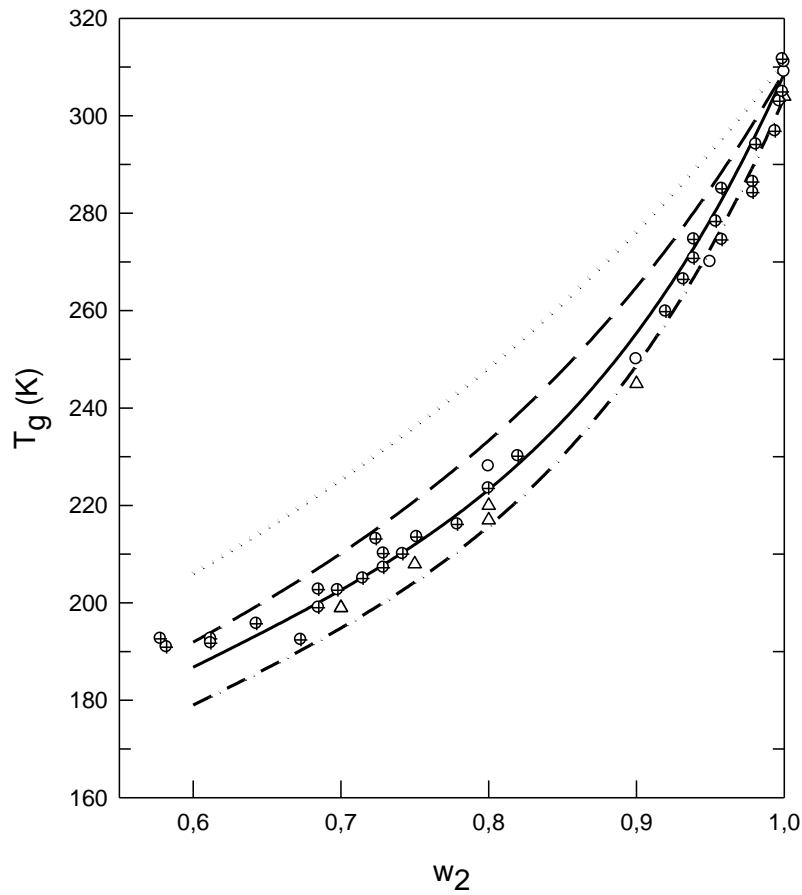


Figure 5. Glass transition temperature of glucose-water solutions. The symbols correspond to experimental onset (Δ)^{8,11} and midpoint (\oplus)⁶⁴, (\circ)⁶⁵, DSC data. Solid line: prediction by the FVPM; dashed-dotted line: GTM with onset $T_{g2} = 304$ K, and $T_{g1} = 138$ K, $k= 4.52$ (Eqn. 3); dashed line: CKM

with midpoint $T_{g2} = 309$ K, $T_{g1} = 135$ K, and $\Delta C_{p2} = 0.63 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$;⁸ dotted line modified CKM with $T_{g1} = 135$ K, $T_{g2} = 311$ K, $\Delta C_{p1} = 1.94 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$, and $\Delta C_{p2} = 0.88 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$.¹⁹

In this case the FVPM predict quite well the experimental data ($R^2 = 0.9867$), which exhibit a considerable scatter. The GTM predictions using the k_{GT} parameter from Eqn. (3) and the onset $T_{g2} = 304$ K with $k_{GT} = 3.08$,⁸ overestimates the experimental values ($R^2 = 0.9682$). CKM with the midpoint $T_{g2} = 309$ K and $\Delta C_{p2} = 0.63 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$;⁸ underestimates the experimental Tg ($R^2 = 0.9486$), whereas the modified CKM with $T_{g2} = 311$ K, and $\Delta C_{p2} = 0.88 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$,¹⁹ largely overestimate ($R^2 = 0.7631$) the glass transition temperature of the mixture.

The glass transition temperature of the fructose-water system, reported in the literature^{8,64-68} as a function of composition, represented in Figure 6, exhibits an even larger scatter than that observed for other saccharides. The maximum excess volume for this mixture is $0.67 \text{ cm}^3\cdot\text{mol}^{-1}$ at $w_2 \approx 0.9$, which allow us to treat the mixture as ideal. In this case the FVPM predictions are closer to the lower boundary of the experimental results, represented by the data by Mehl,⁶⁷ and are quite similar to the GTM predictions with onset $T_{g2} = 278$ K, and $k_{GT} = 3.76$ (Eqn. 3).

On the other hand, CKM with midpoint $T_{g2} = 283$ K and $\Delta C_{p2} = 0.75 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$;⁸ and the modified CKM with $T_{g2} = 280$ K, and $\Delta C_{p2} = 0.84 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$,¹⁹ seems to predict rather well the rest of the data, except for $w_2 > 0.9$, where the experimental results are so disperse that cannot well fitted by all the models. The corresponding values of R^2 for fructose-water are summarized in Table S2 along with those calculated for sucrose and glucose aqueous mixtures.

The validity of the idealized FVPM, as mentioned in Section 2, does not depend on the critical volume fraction. This is an important conclusion because the FVPM predicts that the average expansibility coefficient is given by $\langle \alpha \rangle = 0.19 \cdot T_g^{-1}$, for the mixture and the pure components.

There are no experimental data to test this relationship in the case of the solutes studied in this work, but we can resort to temperature dependence of the volume of sucrose, glucose and trehalose calculated by molecular dynamics simulation.⁶⁹ The volume of the glassy saccharides in the interval between T_{g2} and temperatures 100 - 120 K below T_{g2} yields $\langle \alpha \rangle$ between $(1.43-2.43) \cdot 10^{-4}$ K, which is a factor between 2 and 4 times lower than the values predicted by Eqn. (11). The fail to validate Eqn. (11) should not be taken as conclusive because there are not experimental results supporting the MD simulations, but in any case affect the results obtained with the idealized FVPM.

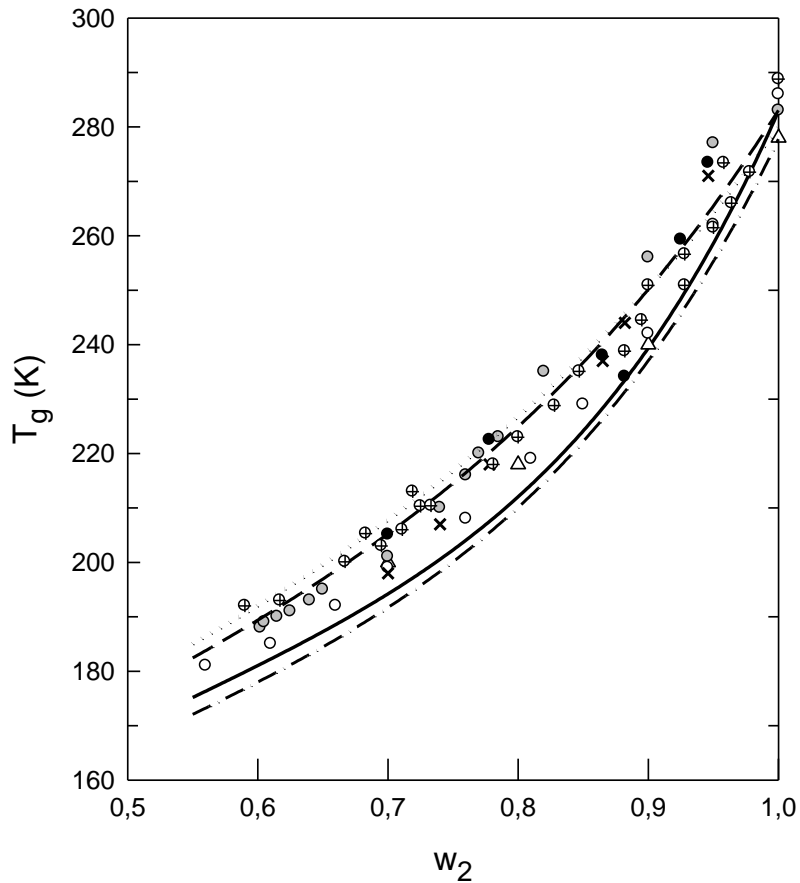


Figure 6. Glass transition temperature of fructose-water solutions. The symbols correspond to experimental onset (Δ)⁸ and midpoint (\oplus)⁶⁴, (\circ)⁶⁶, (\bullet)⁶⁷, (\bullet)⁶⁸, DSC data, and dielectric relaxation data

(X).⁶⁸ Solid line: prediction by the FVPM; dashed-dotted line: GTM with onset $T_{g2} = 278$ K, and $T_{g1} = 138$ K, $k = 3.76$ (Eqn. 3); dashed line: CKM with midpoint $T_{g2} = 283$ K, $T_{g1} = 135$ K, $\Delta C_{p1} = 1.94 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$, and $\Delta C_{p2} = 0.75 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$;⁸ dotted line modified CKM with $T_{g1} = 135$ K, $T_{g2} = 280$ K, $\Delta C_{p1} = 1.94 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$, and $\Delta C_{p2} = 0.84 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$.¹⁹

5. Conclusions

We have employed the FVPM to predict the glass transition temperatures of aqueous solutions of the saccharides trehalose, sucrose, glucose and fructose as a function of the composition in the range $0.5 < w_2 < 1$. The procedure to calculate the needed volumetric properties of the pure components and the mixture is based in calculating the molar volume of water from the partial molar volume of trehalose-water mixtures which is known down to 258 K. The molar volume of water in the supercooled regime seems to resemble that of the high-density liquid water in agreement with the recent hypothesis on the existence of two structure of liquid water, being the high density liquid water the state of water in the these polyols aqueous solutions.

Adopting this water molar volume, and with available volumetric information on the saccharide-water mixtures at temperatures close to room temperature we could reproduce quite well the glass transition temperature of the mixtures with the extra assumption that the excess molar volume of the mixtures are negligible. The idealized FVPM becomes identical to the Gordon-Taylor model when the excess expansibility term is neglected, and it is also independent of the value chosen for the critical volume fraction imposed by the percolation theory. The idealized FVPM reproduce the measured glass transition temperature of sucrose, glucose, and fructose aqueous solutions, with much better accuracy than both, the Gordon-Taylor model using the empirical k_{GT} parameter proposed by Roos⁸, and the Couchman-Karasz model using the

experimental heat capacity changes of the components at the glass transition temperature. Thus, the idealized FVPM can be used to predict the glass transition temperature of other saccharides and polyols solutions by resorting to volumetric information easily available.

Acknowledgments

The authors acknowledge financial support from ANPCyT (PICT Raices 1291), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, PIP 095), and Universidad de Buenos Aires (Project UBACyT 20020100100519). HRC is a member of the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). JGC thanks CONICET for fellowship support. MS acknowledges support from the German Academic Exchange Service for his scholarship.

Supporting Information

This information is available free of charge via the Internet at <http://pubs.acs.org>

References

1. Reid, D. S. Manifestation of Molecular Mobilities in Amorphous Aqueous Systems: the View from Different Experimental Techniques, In: M.P. Buera, J. Welti-Chanes, P.J. Lillford, H.R. Corti (Eds.) *Water Properties of Food, Pharmaceutical, and Biological Materials*; CRC, Taylor & Francis, 2006, pp. 59-76.
2. Corti, H. R.; Angell, C. A.; Auffret, T.; Levine, H.; Buera, M. P.; Reid, D. S.; Roos, Y.; Slade, L. Empirical and Theoretical Models of Equilibrium and Non-Equilibrium Transition

- Temperatures of Supplemented Phase Diagrams in Aqueous Systems. *Pure & Applied Chem.*, **2010**, *82*, 1065-1097.
3. Miller, D. P.; de Pablo, J. J.; Corti, H. R. Thermophysical Properties of Concentrated Aqueous Trehalose Solutions. *Pharm.Res.* **1997**, *41*, 578-590.
 4. Cohen, M. H.; Turnbull, D. Molecular Transport in Liquids and Glasses. *J. Chem. Phys.* **1959**, *31*, 1164-1169.
 5. Callen, H. B. *Thermodynamics*; Wiley: New York, 1960.
 6. Gordon, J. M.; Taylor, J. S. Ideal Copolymers and the Second-Order Transitions of Synthetic Rubbers. I. Non-crystalline Copolymers. *J. Appl. Chem.* **1952**, *2*, 493-500.
 7. Simha, R.; Boyer, R. F. On a General Relation Involving the Glass Temperature and Coefficients of Expansion of Polymers. *J. Chem. Phys.* **1962**, *37*, 1003-1007.
 8. Roos, Y. Melting and Glass Transitions of Low Molecular Weight Carbohydrates. *Carbohydr. Res.* **1993**, *238*, 39-48.
 9. Roos, Y.; Karel, M. Differential Scanning Calorimetry Study of Phase Transitions Affecting the Quality of Dehydrated Materials. *Biotechnol. Prog.* **1990**, *6*, 159-163.
 10. Ablett, S.; Izzard, M. J.; Lillford, J. Differential Scanning Calorimetric Study of Frozen Sucrose and Glycerol Solutions. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 789-794.
 11. Luyet, B.; Rasmussen, D. Study by Differential Thermal Analysis of the Temperatures of Instability of Rapidly Cooled Solutions of Polyvinylpyrrolidone. *Biodynamica* **1968**, *10*, 167-191.
 12. Goff, H. D. The Use of Thermal Analysis in the Development of a Better Understanding of Frozen Food Stability. *Pure & Appl. Chem.* **1995**, *67*, 1801-1808.

13. Saleki-Gerhardt, A.; Zografi, G. Non-Isothermal and Isothermal Crystallization of Sucrose from the Amorphous State. *Pharm. Res.* **1994**, *11*, 1166-1173.
14. Ottenhof, M.-A.; MacNaughtan, W.; Farhat, I. A. FTIR Study of State and Phase Transitions of Low Moisture Sucrose and Lactose. *Carbohydr. Res.* **2003**, *338*, 2195-2202.
15. Shalaev, E. Y.; Franks, F. Structural Glass Transitions and Thermophysical Processes in Amorphous Carbohydrates and their Supersaturated Solutions. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1511-1517.
16. Shamblin, S.; Taylor, L.; Zografi, G. Mixing Behavior of Colyophilized Binary Systems, *J. Pharm. Sci.* **1998**, *87*, 694-701.
17. Elamin, A. A.; Sebhatu, T.; Ahlneck, C. Mixing Behavior of Colyophilized Binary Systems. *Int. J. Pharm.* **1995**, *119*, 25-36.
18. Miller, D.; de Pablo, J. J. Calorimetric Solution Properties of Simple Saccharides and their Significance for the Stabilization of Biological Structure and Function. *J. Phys. Chem. B* **2000**, *104*, 8876-8883.
19. Orford, P. D.; Parker, R.; Ring, S. G. Aspects of the Glass Transition Behaviour of Mixtures of Carbohydrates of Low Molecular Weight. *Carbohydr. Res.* **1990**, *196*, 11-18.
20. Hatley, R. H. M.; Van den Berg, C.; Franks, F. The Unfrozen Water Content of Maximally Freeze-Concentrated Carbohydrate Solutions: Validity of the Methods Used for its Determination. *Cryo-Lett.* **1991**, *12*, 113-124.
21. Miller, D. P.; de Pablo, J. J.; Corti, H. R. Viscosity and Glass Transition Temperature of Aqueous Mixtures of Trehalose with Borax and Sodium Chloride. *J. Phys. Chem. B* **1999**, *103*, 10243-10249.

22. Crowe, L. M.; Reid, D. S.; Crowe, J. H. Is Trehalose Special for Preserving Dry Biomaterials?. *Biophys. J.* **1996**, *71*, 2087-2093.
23. Elias, M. E.; Elias, A. M. Trehalose + Water Fragile System: Properties and Glass Transition. *J. Mol. Liq.* **1999**, *83*, 303-310.
24. Ding, S. P.; Fan, J.; Green, J. L.; Sanchez, E.; Angell, C. A. Vitrification of Trehalose by Water Loss from its Crystalline Dehydrate. *J. Therm. Anal.* **1996**, *47*, 1391-1405.
25. Taylor L.; Zografi, G. Sugar-Polymer Hydrogen Bond Interactions in Lyophilized Amorphous Mixtures. *J. Pharm. Sci.* **1998**, *87*, 1615-1621.
26. Sugisaki, M.; Suga, H.; Seki, S. Calorimetric Study of the Glassy State. IV. Heat Capacities of Glassy Water and Cubic Ice. *Bull. Chem. Soc. Japan* **1968**, *41*, 2591-2599.
27. Hallbrucker, A.; Mayer, E.; Johari, G. P. Glass-Liquid Transition and the Enthalpy of Devitrification of Annealed Vapor-Deposited Amorphous Solid Water. *J. Phys. Chem.* **1989**, *93*, 4986-4990.
28. Johari, G. P.; Hallbrucker, A.; Mayer, E. Two Calorimetrically Distinct States of Liquid Water Below 150 Kelvin. *Science* **1996**, *273*, 90-92.
29. Johari, G. P.; Hallbrucker, A.; Mayer, E. The Glass-Liquid Transition of Hyperquenched Water. *Nature* **1987**, *330*, 552-553.
30. Hallbrucker, A.; Mayer, E.; Johari, G. P. The Heat Capacity and Glass Transition of Hyperquenched Glassy Water. *Philos. Mag.* **1989**, *60*, 179-187.

31. Johari, G. P.; Astl, G.; Mayer, E. Enthalpy Relaxation of Glassy Water. *J. Chem. Phys.* **1990**, *92*, 809-810.
32. Johari, G. P.; Hallbrucker, A.; Mayer, E. Isotope Effect on the Glass Transition and Crystallization of Hyperquenched Glassy Water. *J. Chem. Phys.* **1990**, *92*, 6742-6747.
33. Kohl, I.; Hallbrucker, A.; Mayer, E. The Glassy Water–Cubic Ice System: a Comparative Study by X-Ray Diffraction and Differential Scanning Calorimetry. *Phys. Chem. Chem. Phys.* **2000**, *2*, 1579-1586.
34. Couchman, P. R.; Karasz, F. E. A Classical Thermodynamic Discussion of the Effect of Composition on Glass-Transition Temperatures. *Macromol.* **1978**, *11*, 117-119.
35. Couchman, P. R. Thermodynamics and the Compositional Variation of Glass Transition Temperatures. *Macromol.* **1987**, *20*, 1712-1717.
36. Gordon, J. M.; Rouse, G. B.; Gibbs, J. H.; Risen Jr., W. M. The Composition Dependence of Glass Transition Properties. *J. Chem. Phys.* **1977**, *66*, 4971-4977.
37. Ten Brinkle, G.; Karasz, F. E.; Ellis, T. S. Depression of Glass Transition Temperatures of Polymer Networks by Diluents. *Macromol.* **1983**, *16*, 244-249.
38. Orford, P. D.; Parker, R.; Ring, S. G.; Smith, A. C. Effect of Water as a Diluent on the Glass Transition Behaviour of Malto-Olygosaccharides, Amylose and Amylopectin. *Int. J. Biol. Macromol.* **1989**, *11*, 91-96.
39. Angell, C. A. Insights into Phases of Liquid Water from Study of its Unusual Glass-Forming Properties. *Science* **2008**, *319*, 582-587.
40. Kohl, I.; Bachmann, L.; Mayer, E.; Hallbrucker, A.; Loerting, T. Water Behaviour: Glass transition in Hyperquenched Water?. *Nature* **2005**, *435*, E1.

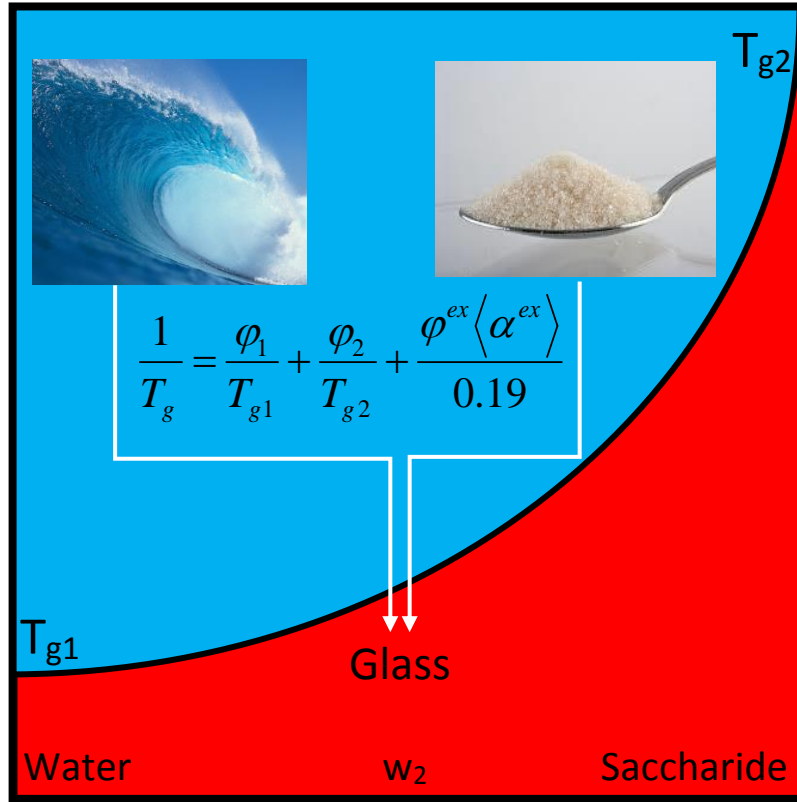
41. Blond, G.; Simatos, D.; Catté, M.; Dussap, C. G.; Gros, J. B. Modeling of the Water-Sucrose State Diagram Below 0 °C. *Carbohydr. Res.* **1997**, *298*, 139-145.
42. Katkov, I.; Levine, F. Prediction of the Glass Transition Temperature of Water Solutions: Comparison of Different Models. *Cryobiology* **2004**, *49*, 62-82.
43. Jenckel, E.; Heusch, R. Die Erniedrigung der Einfriertemperatur Organischer Gläser durch Lösungsmittel. *Kolloidn. Zh.* **1953**, *130*, 89-105.
44. Lesikar, A. V. Glass Transition in Organic Halide Mixtures. *Phys. Chem. Glasses* **1975**, *16*, 83-90.
45. Kolker, A. ; Miller, D. ; de Pablo, J. J. Proceedings of the AIChE Annual Meeting, Miami Beach, Florida, USA, 1995.
46. Zallen, R. *The Physics of Amorphous Solids*; John Wiley & Sons, 1983.
47. Shah, B. N.; Schall, C. A. Measurement and Modeling of the Glass Transition Temperatures of Multi-Component Solutions. *Termochim. Acta* **2006**, *443*, 78-86.
48. Rodriguez Furlán, L. T.; Lecot, J.; Pérez Padilla, A.; Campderrós, M. E. Effect of Saccharides on Glass Transition Temperatures of Frozen and Freeze Dried Bovine Plasma Protein. *J. Food Eng.* **2011**, *106*, 74-79.
49. Fox, T. G. Influence of Diluent and Copolymer Composition on the Glass Transition Temperature of a Polymer System. *Bull. Am. Phys. Soc.* **1956**, *2*, 123-135.
50. Zheleznyi, B. V. The Density of Supercooled Water. *Russ. J. Phys. Chem.* **1969**, *43*, 1311-1312.
51. Mallamace, F.; Branca, C.; Broccio M.; Corsaro, C.; Mou, C.-Y.; Chen, S. H. The Anomalous Behavior of the Density of Water in the Range 30 K < T < 373 K. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 18387-18391.

52. Mishima, O. Volume of Supercooled Water Under Pressure and the Liquid-Liquid Critical Point. *J. Chem. Phys.* **2010**, *133*, 144503.
53. Poole, P.; Essmann, U.; Sciortino, F.; Stanley, H. E. Phase Diagram for Amorphous Solid Water. *Phys. Rev. E* **1993**, *48*, 4605-4610.
54. Holten V.; Bertrand, C. E.; Anisimov, M. A.; Sengers, J. V. Thermodynamics of Supercooled Water. *J. Chem. Phys.* **2012**, *136*, 094507.
55. Mishima O. The Glass-To-Liquid Transition of the Emulsified High-Density Amorphous Ice Made by Pressure-Induced Amorphization. *J. Chem. Phys.* **2004**, *121*, 3161-3164.
56. Corti, H. R.; Nores Pondal, F.; Angell, C. A. Heat Capacity and Glass Transition in P₂O₅-H₂O Solutions: Support for Mishima's Conjecture on Solvent Water at Low Temperature. *Phys. Chem. Chem. Phys.* **2011**, *13*, 19741-19748.
57. Jasra, R. V.; Ahluwalia, J. C. Enthalpies and Heat Capacities of Dissolution, Apparent Molar Heat Capacities, and Apparent Molar Volumes of Some Mono-, Di-, Tri-, and Tetra-Saccharides in Water. *J. Chem. Thermodyn.* **1984**, *16*, 583-590.
58. Banipal, P. K.; Banipal, T. S.; Lark, B. S.; Ahluwalia, J. C. Partial Molar Heat Capacities and Volumes of Some Mono-, Di- and Tri-Saccharides in Water at 298.15, 308.15 and 318.15 K. *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 81-87.
59. Galema, S. A.; H. Høiland, H. Stereochemical Aspects of Hydration of Carbohydrates in Aqueous Solutions. 3. Density and Ultrasound Measurements. *J. Phys. Chem.* **1991**, *95*, 5321-5326.
60. Birch, G. G.; Catsoulis, S. Apparent Molar Volumes of Sugars and their Significance in Sweet Taste Chemoreception. *Chem. Senses.* **1985**, *10*, 325-332.

61. Magazú, S.; Migliardo, P.; Musolino, A. M.; Sciortino, M. T. α,α -trehalose–water Solutions. 1. Hydration Phenomena and Anomalies in the Acoustic Properties. *J. Phys. Chem. B* **1997**, *101*, 2348-2351.
62. Pancoast, H. M; Junk, W. R. (ed.), Handbook of Sugars. AVI Publishing Co., Inc., Westport, Connecticut, USA (1980).
63. Fucaloro, A. F.; Pu, Y; Cha, K.; Williams, A.; Conrad, K. Partial Molar Volumes and Refractions of Aqueous Solutions of Fructose, Glucose, Mannose, and Sucrose at 15.00, 20.00 and 25.00 °C. *J. Solution Chem.* **2007**, *36*, 61-80.
64. Ruiz-Cabrera, M. A.; Rivera-Bautista, C.; Grajales-Lagunes, A. González-García, R.; Schmidt, S. J. State Diagrams for Mixtures of Low Molecular Weight Carbohydrates. *J. Food. Eng.* **2016**, *171*, 185-193.
65. Seo, J.; Kim, S. J.; Oh, J.; Kim, H. K.; Hwang, Y-H. Brillouin Scattering and DSC Studies of Glass Transition Temperatures of Glucose-Water Mixtures. *J. Korean Phys. Soc.* **2004**, *44*, 523-526.
66. Mehl, P. M. Fictive Glass-Transition Temperature and Fragility for the Phase Diagram of the System Fructose/Water. *Termochim. Acta* **1998**, *324*, 215-221.
67. Ablett, S.; Izzard, M.; Lillford, P. J.; Arvanitoyannis, I.; Blanshard, J. M. V. Calorimetric Study of the Glass Transition Occurring in Fructose Solutions. *Carbohydr. Res.* **1993**, *246*, 13-22.
68. Shinyashiki, N.; Shinohara, M.; Iwata, Y.; Goto, T.; Oyama, M.; Suzuki, S.; Yamamoto, W.; Yagihara, S.; Inoue, T.; Oyaizu, S.; Yamamoto, S.; Ngai, K. L.; Capaccioli, S. The Glass Transition and Dielectric Secondary Relaxation of Fructose-Water Mixtures. *J. Phys. Chem. B* **2008**, *112*, 15470–15477

69. Simperler, A.; Kornherr, A.; Chopra, R.; Bonnet, A.; Jones, W.; Motherwell, W. D. S., ; Zifferer, G. Glass Transition Temperature of Glucose, Sucrose, and Trehalose: an Experimental and in Silico Study. *J. Phys. Chem. B* **2006**, 110, 19678-19684.

Grapical Abstract



Supplementary Information:

The Glass Transition Temperature of Saccharide Aqueous Solutions

Estimated with the Free Volume / Percolation Model

Julian Gelman Constantin¹, Matthias Schneider¹, Horacio R. Corti^{1,2*}

¹Instituto de Química Física de los Materiales, Ambiente y Energía (INQUIMAE), Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Intendente Güiraldes 2160 - Ciudad Universitaria - C1428EGA Buenos Aires - Argentina.

²Departamento de Física de la Materia Condensada, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Av. General Paz 1499, San Martín (1650), Buenos Aires, Argentina.

* Corresponding author. Tel: 5411 6772 7174; Fax: 5411 6772 7121; E-mail address: hrcorti@cnea.gov.ar (H. R. Corti)

1. Calculation of the molar volume of pure trehalose at supercooled conditions

The molar volumes, V_m , of the aqueous trehalose solutions in the liquid and supercooled regions were calculated from the volumetric data for aqueous trehalose solutions reported by Miller et al. [1] in the trehalose mole fraction $0.0890 \leq x_2 \leq 0.0117$, and temperatures between 258 K and 293 K. As can be observed in Fig. S1, V_m is linear with temperature all over the concentration range studied.

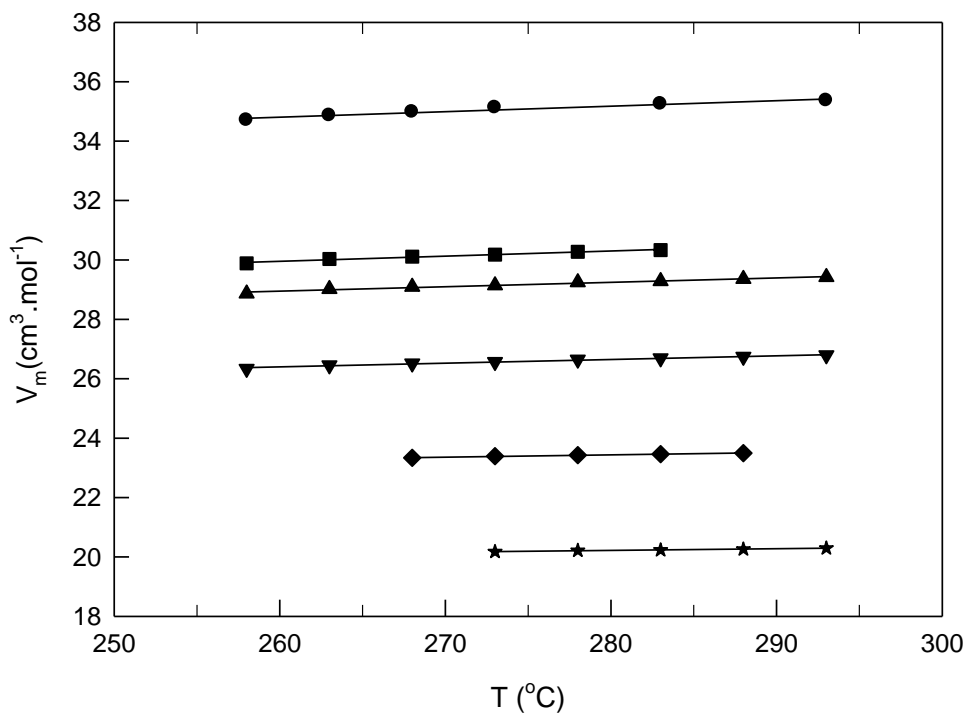


Figure S1: Molar volume of trehalose aqueous solutions as a function of temperature at different solute mole fraction (x_2): 0.0890 (●); 0.0640 (■); 0.0588 (▼); 0.0454 (▲); 0.0287 (◆); 0.0117 (★).

The molar volume of a hypothetical liquid trehalose, V_2 , as a function of temperature between 258 K and 293K can be obtained by plotting V_m vs. x_2 , in the range $0.0890 \leq x_2 \leq 0.0117$ at each temperature, as depicted in Fig. S2 for the data at 283 K. The concentration dependence of V_m is linear, indicating that the excess volume is close to zero in this concentration range.

The same behavior is observed at other temperatures in the studied interval. Therefore, V_2 can be obtained as a function of temperature by extrapolating V_m to $x_2=1$.

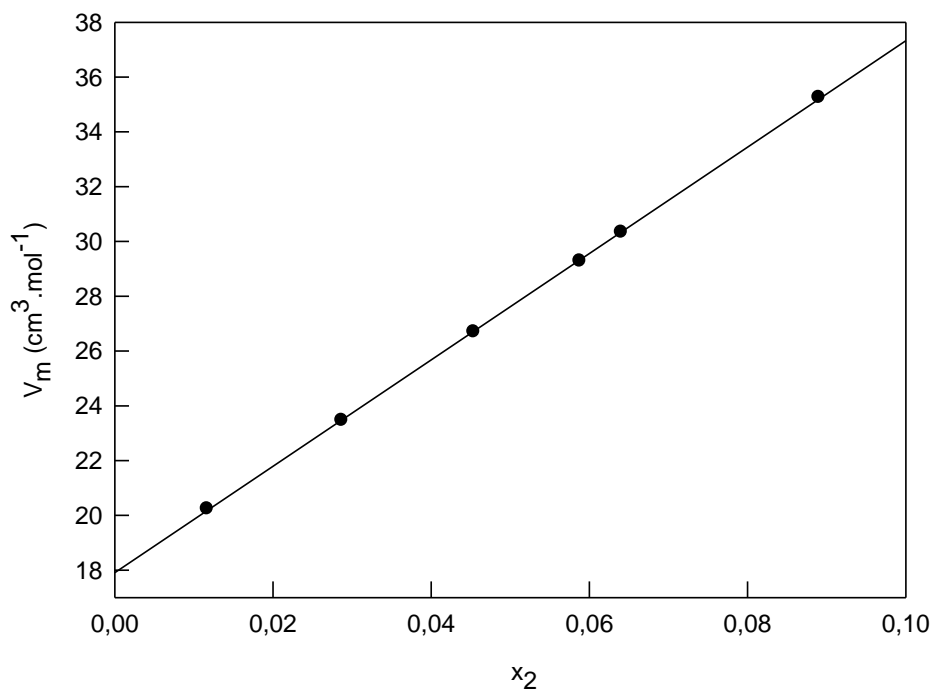


Figure S2: Partial molar volume of trehalose aqueous solutions as a function of trehalose mole fraction at 283 K.

Extrapolation from $x_2 \approx 0.08$ to pure trehalose leads to considerable errors, even when the uncertainties in the slopes of the plots V_m vs. x_2 are small. This is reflected in the results shown

in Fig. S3, where V_2 increases with increasing temperature but the behavior is far of being linear. For this reason we employed an alternative procedure to estimate V_2 .

We adopted $T_0 = 283.15$ K as a reference temperature and extrapolated the data reported in Fig. S2 to $x_2=1$ obtaining $V_2(283.15 \text{ K}) = (212.1 \pm 0.8) \text{ cm}^3 \cdot \text{mol}^{-1}$. Then, we calculated V_2 at all the temperatures by resorting to the expression derived from Eqn. (11) by assuming that the average thermal expansion coefficient does not change with temperature:

$$V_2(T) = V_2(T_0) \left[1 - \frac{0.19}{T_{g2}} (T - T_0) \right]^{-1} \quad (\text{S1})$$

Thus, we obtained the results indicated in Figure S3.

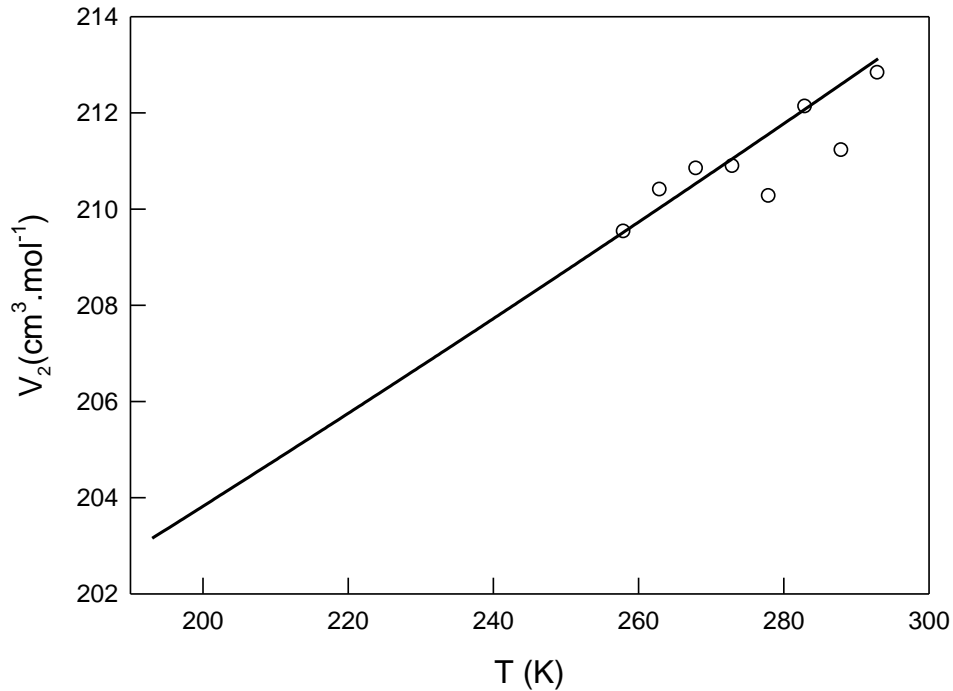


Figure S3: Molar volume of hypothetical liquid trehalose as a function of temperature. Closed circles correspond to the extrapolation of V_m to $x_2=1$, and the solid line corresponds to the calculation based on the V_2 value at 283.15 K and Eqn. S1.

It is observed that, except for the data at 5 °C and 15 °C, the molar volume of liquid trehalose obtained with this procedure agree within the experimental error with the direct procedure.

The molar volume of crystalline anhydrous trehalose ($216.6 \text{ cm}^3 \cdot \text{mol}^{-1}$) at room temperature [2] is close to V_2 (293.15 K) obtained here, which validates the assumption that the excess volume in the water-trehalose mixture is zero all over the concentration range and temperatures considered. The maximum deviation to the ideal behavior is $0.20 \text{ cm}^3 \cdot \text{mol}^{-1}$ at 20 °C and $0.36 \text{ cm}^3 \cdot \text{mol}^{-1}$ at -15 °C.

2. Calculation of the molar volume of other pure saccharides at supercooled conditions

The procedure described for trehalose was also used to obtain the molar volume of the polyols studied in this work by resorting to the volumetric data reported for sucrose [3-6], glucose [4-6], and fructose [5,6]. Table S1 summarizes the parameters used to calculate $V_2(T)$ of the different solutes. The values of the onset and midpoint glass transition temperatures used in the calculations were obtained from reported data for the pure saccharides [7-11].

Table S1: Parameters for the estimation of molar volume of polyols using Eqn. (S1)

Solute	$T_{g,onset}$ (K)	$T_{g,mid}$ (K)	T_0 (K)	$V_2(T_0)$ (cm³.mol⁻¹)
Trehalose	389	389	283.15	212.1 ± 0.8
Sucrose	341	346	273.15	214.1 ± 0.8
Glucose	304	310	293.15	114.0 ± 0.8
Fructose	278	283	293.15	112.3 ± 0.6

3. Comparison of the different glass transition models

We used the R-squared statistical parameters to compare the fit of the different models (FVPM, CKM, and GTM) to the experimental data for the saccharides studied in this work. The results are summarized in Table S2.

Table S2: R-square parameter for the fit of experimental data for sucrose, glucose and fructose aqueous mixtures using the GTM, CKM and FVPM.

Saccharide	GTM	CKM	Modified CKM	FVPM
Sucrose	0,9578	0,9708	-----	0,9779
Glucose	0,9682	0,9486	0,7631	0,9867
Fructose	0,8442	0,9730	0,9603	0,8992

The R-squared confirm that FVPM is the model that better represents the experimental data sets for sucrose and glucose, whereas for fructose CKM and modified CKM perform better (see main article for further discussion).

References

1. Miller, D. P.; de Pablo, J. J.; Corti, H. R. Thermophysical Properties of Concentrated Aqueous Trehalose Solutions. *Pharm.Res.* **1997**, *41*, 578-590.
2. D. R. Lide (ed). CRC Handbook of Chemistry and Physics, 71st ed. Boca Raton, CRC Press Inc., 1990.
3. H.M. Pancoast, H. M.; Junk W. R (ed.). *Handbook of Sugars*. AVI Publishing Co., Inc., Westport, Connecticut, USA (1980).
4. Jasra, R. V.; Ahluwalia, J. C. Enthalpies and Heat Capacities of Dissolution, Apparent Molar Heat Capacities, and Apparent Molar Volumes of Some Mono-, Di-, Tri-, and Tetra-Saccharides in Water. *J. Chem. Thermodyn.* **1984**, *16*, 583-590.
5. Birch, G. G.; Catsoulis, S. Apparent Molar Volumes of Sugars and Their Significance in Sweet Taste Chemoreception. *Chem. Senses.* **1985**, *10*, 325-332.
6. Fucaloro, A. F.; Pu, Y; Cha, K.; Williams, A.; Conrad, K. Partial Molar Volumes and Refractions of Aqueous Solutions of Fructose, Glucose, Mannose, and Sucrose at 15.00, 20.00 and 25.00 °C. *J. Solution Chem.* **2007**, *36*, 61-80.
7. Corti, H. R.; Angell, C. A.; Auffret, T.; Levine, H.; Buera, M. P.; Reid, D. S.; Roos, Y.; Slade, L. Empirical and Theoretical Models of Equilibrium and Non-Equilibrium Transition Temperatures of Supplemented Phase Diagrams in Aqueous Systems. *Pure & Applied Chem.*, **2010**, *82*, 1065-1097.

8. Roos, Y.; Karel, M. Non-Equilibrium Ice Formation in Carbohydrate Solutions. *Cryo-Letters* **1991**, *12*, 367-376.
9. Roos, Y. Melting and Glass Transitions of Low Molecular Weight Carbohydrates. *Carbohydr. Res.*, **1993**, *238*, 39-48
10. Orford, P. D.; Parker, R.; Ring, S. G. Aspects of the Glass Transition Behaviour of Mixtures of Carbohydrates of Low Molecular Weight. *Carbohydr. Res.*, **1990**, *196*, 11-18.
11. Ablett, S.; Izzard, M. J.; Lillford, P. J.; Arvanitoyannis, I.; Blanshard, J. M. V. Calorimetric Study of the Glass Transition Occurring in Fructose Solutions. *Carbohydr. Res.*, **1993**, *246*, 13-22.