

Fictive glass-transition temperature and fragility for the phase diagram of the system fructose/water

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Abstract

The fructose/water phase diagram is determined by conventional DSC. No hydrates are observed and vitrification is achieved at 40 K/min on cooling for concentrations >55%w/w. The Couchman model, the Gordon model and the Jenckel–Heusch model are tested for the compositional variation of the fictive glass-transition temperature. The data fit all these models, except the last, and predict a specific heat change at the glass transition for pure water of 18.9 ± 1.5 and 13.5 ± 0.8 cal/(K mol), respectively, for the first and second models. The fictive glass-transition temperature, T_f , is determined as a function of cooling rate V . The associated activation energy $d(\ln(V)/d(1/T_f))$ is somewhat constant before increasing as the concentration increases above the limiting glass concentration. This concentration is found to be 78 wt%, defining the temperature T'_g at -57°C for fructose. The change of specific heat at the glass transition presents a minimum for the wholly vitrified samples for a stronger thermodynamic glassy state for concentrations between 80 to 95 wt/wt as the kinetic approach, using the fragility factor, leads to a stronger kinetic glassy state close to 75 wt/wt corresponding to T'_g . © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

The knowledge of the glass-transition temperature curves and the limiting glass-transition characteristics for aqueous solutions of mono- and polysaccharides is important for various applications, such as for food science [1] or for protein science and formulations [2], but it is also very useful for basic science for understanding the problem of stabilization or unfolding/folding in proteins using glassy states at low or high temperatures or for biochemical kinetics studies [3]. The example of the fructose–water system is presented following our previous study on trehalose–water system [4]. This system has already been studied

without determining the fictive temperatures of the glass transition and the fragility factor as a function of the concentration [5]. The limiting glass-transition temperature, so-called T'_g , and the non-freezable water content C_w are important parameters for estimating the design of preparation for freeze-drying processes or for assessing the stability of processed products, as examples. These characteristics are determined and compared with previously published reports using other thermal analysis techniques [1] and calorimetry [5]. The results indicated different conclusions on the values of T'_g and C_w , which is what the present study intends to clarify. Fructose is a hexose which is used as sweetener for replacing glucose and is found to be innocuous for diabetes patients, contrary to glucose. Therefore, fructose is a good substitute for glucose in

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food and formulation for possible stabilization of drug or pharmaceutical. The accessibility to direct data from the calorimeter allows for a more flexible and attractive analysis. The phase diagram will be complemented for estimating the vitrification range in the present system. The conventional differential scanning calorimeter is also presently used for the determination of the fictive glass-transition temperature and the associated apparent activation energy, using a whole set of cooling rates. From these data, the fragility of the achieved glassy state as defined by Bohmer et al. [6] can be estimated and compared with previous reports.

2. Materials and methods

2.1. Sample preparations

Fructose (Sigma) and deionized water are used without further purification for preparing samples. A stock solution is initially prepared at a known solute concentration and various concentrations are prepared directly in situ in the DSC pan by drying at room temperature or at higher temperatures at atmospheric pressure or under a mild vacuum. The solute concentration is controlled by weight loss and checked for final weight after complete drying at 360 K. The samples are then warmed to high temperatures to melt and mix. The solubility of fructose is checked using a thermal bath and by observing the fructose crystals melt in the solution through glass vials. The heating rate used is ca. 0.2 K/min. Emulsified samples are prepared as usual by passing through a .22 gage needle the aqueous phase with a 1 : 1 molar methylcyclohexane/ethylcyclopentane mixture containing 4 wt% Span65 as surfactant.

2.2. Calorimetry and analysis

Measurements were performed on a DCS-4 Perkin–Elmer upgraded with a thermal analysis system from Instrument Specialists, allowing for the direct export of the data as ASCII file. This file can be exported to any spreadsheet software such as Excel 5.1 from Microsoft. Baselines are subtracted from measured signals and corrections for the calibrations are included.

The homogeneous ice nucleation temperatures have been recorded, using the emulsified samples, during cooling at 10°C min⁻¹ to know the limitation of the vitrification possibility in the system. The melting temperatures are recorded during warming at 10 K min⁻¹ for bulk samples. These samples are then cooled at various rates from 0.2 to 80 K min⁻¹ to achieve vitrification. The glass transition is recorded during the subsequent warming at the same rate of 10 K min⁻¹. When it is not possible to avoid ice crystallization during the initial cooling, the samples have been annealing or slowly cooled to allow all freezable water to crystallize into ice. The limiting glass transition and its corresponding change in specific heat are also recorded for analysis. Therefore, the variations of the specific heat at the glass-transition and the fictive glass-transition temperatures can be measured as functions of cooling rates. The determination of the fictive temperature T_f is similar to the definition provided by Moynihan [7]:

$$\int_{T \gg T_g}^{T_f} (C_{pe} - C_{pg}) dT = \int_{T \gg T_g}^{T \ll T_g} (C_p - C_{pg}) dT \quad (1)$$

where the integration domain for T is taken far below and above the glass transition and C_{pe} , C_{pg} and C_p are, respectively, the specific heats of the supercooled liquid, the achieved glassy state and of the measured material. Relating the characteristic time for relaxation and the cooling/warming rates, an activation energy as defined by Moynihan [7] is calculated using:

$$d \ln(c) / d(1/T_f) = -E/R \quad (2)$$

This relation is used for the determination of the fragility factor for the various glassy compounds as defined by Bohmer et al. [6]:

$$m = E / \ln(10) RT_f \quad (3)$$

In the present work, the calculation T_f is made by allowing C_{pg} to be equal to 0, as the configurational state of the glassy state can be assumed to be frozen below the glass transition for the considered temperature ranges. Eq. (1) can then be simplified for calculation purposes. A linear variation of C_{pe} with temperature is also assumed for the considered temperature range.

Variation of the glass-transition temperature with concentration of the solute has been modeled by several authors. These models have been the source of discussions, depending on the systems and thermal techniques used for the determination of the glass transition. The present study is an attempt to find out which model is the better indicator for analyzing the data. Four models are investigated. The Couchman theory [8] uses a thermodynamic approach of the glass transition with either the enthalpy or entropy distribution to describe the transition with:

$$\ln(T_g) = \frac{\sum_i X_i \Delta C_{pi} \ln(T_{gi})}{\sum_i X_i \Delta C_{pi}} \quad (4)$$

where T_g , T_{gi} and ΔC_{pi} are, respectively, the glass transition of the sample and of the pure component i and the specific heat change at the glass transition of the same component i . Eq. (4) is the entropic expression as the enthalpic expression is replacing the logarithm of the temperatures T_g , T_{gi} by their natural values that ΔC_{pi} varies as $1/T$. X_i is the weight percent of the component i . The enthalpic expression from Couchman is similar to the model of Gordon et al. The Gordon et al. [9] equation uses the density/specific volume change at the transition:

$$T_g = \frac{X_1 T_{g1} + k X_2 T_{g2}}{X_1 + k X_2} \quad (5)$$

where k is an adjustment to the non-linearity of T_g with the various concentrations. The factor k is equal to the ratio $\Delta C_{p2}/\Delta C_{p1}$. This expression is similar to the enthalpic expression of Couchman. The Jenckel–Heusch equation uses the refractive index measurements in polymers [10], giving:

$$T_g = S_1 T_{g1} + X_2 T_{g2} + K X_1 X_2 \quad (6)$$

where K is proportional to the difference ($T_{g1} - T_{g2}$).

A Gordon–Taylor [11] model equation which has the same expression as Eq. (5) expresses the constant k as equal to $(\rho_1/\rho_2)(\Delta\alpha_2/\Delta\alpha_1)$ with the density ρ_i and the increment of the expansion coefficient $\Delta\alpha_i$ of the pure component i . This model was used for the raffinose/water system [12] and for binary systems of polymers [11] with good agreement. However, the interpretation of the interaction factor k for the raffinose/water system was widely different, being reported as the ratio of the product of the density to the temperature of glass transition of each pure com-

pound. The internal check using published values for the density of the amorphous phases of the sugars and of water do not lead to a right estimate of the glass-transition temperature for pure water. The Jenckel–Heusch equation was used for mono- and polyol/water solutions for the determination of the thermodynamics of the glass transition of pure water [13]. The Gordon et al. model was recently used for the water-sucrose system with a good fit [14].

2.3. Calibration

The DSC-4 was calibrated using indium, ethylene glycol, water, cyclohexane, methylcyclohexane, ethylcyclohexane for temperatures between -160° and 225°C . The energy calibration was also performed simultaneously with the known enthalpy of fusion of each of these transitions. Estimated errors in temperatures and in energies are, respectively, below 0.5 K and 5% of the measured energies.

3. Results

The phase diagram is reported in Fig. 1 with temperatures corresponding to the melting of ice and of pure fructose during warming, to homogeneous ice nucleation and to the glass transition during warming for the totally vitrified samples or for samples after all the ice crystallized during the initial cooling. For these latter samples, two apparent transitions are observed, resembling the glass transitions reported in Fig. 1. In the present study, the lowest temperature transition of these latter is referred to as the glass transition of the remaining solution and the highest temperature to the incipient melting corresponding to a softening of the glassy/rubbery matrix, allowing for the melting of the ice. The vitrification domain is determined by measuring the heat of ice crystallization during the initial cooling. Fig. 2 reports these measures for concentrations at the limit of vitrification corresponding to the concentration limit of the extrapolation of the homogeneous ice-nucleation curve to the glass-transition curve in Fig. 1. This glass-transition curve is reported with the fictive temperature T_f determined using the definition above.

The fitting of the data using the Couchman and the Gordon et al. models (Eqs. (4) and (5)) is in good

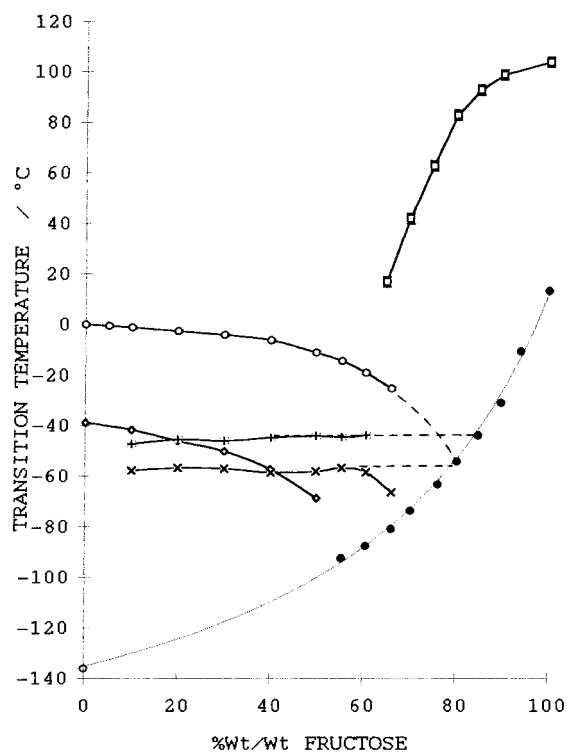


Fig. 1. Phase diagram for the fructose/water system. (O) Ice melting; (□) pure fructose melting; (◇) homogeneous ice nucleation; (*) glass transition for the wholly amorphous state reporting the fictive glass-transition temperature measured during a warming at 10 K/min after a cooling at 5 K/min, (x) glass transition after all the ice crystallized during the initial cooling; and (+) incipient melting. The glass-transition curve is fit using the Gordon et al. model from Eq. (5).

agreement, but fails for the Jenckel–Heusch model (Eq. (6)). The determination of the fit gives the interaction constants with which the change in specific heat at the glass transition for pure water is found to be: ΔC_p (amorphous water) = 18.9 ± 1.5 cal/(mol K) using the Couchman model at $T_g = 135$ K; and ΔC_p (amorphous water) = 13.5 ± 0.8 cal/(mol K) using the Gordon et al. model at $T_g = 138$ K. From the reported experimental values of ΔC_p (amorphous water), the present values are still 40% to twice as high [15–17]. However, other studies on the melibiose–water system [18], ribose–water (unpublished results) and trehalose (unpublished results) give ΔC_p (amorphous water) = 11.8 ± 1.3 Cal/(mol K) at 138 K.

The change in specific heat at the glass transition can be simultaneously measured as the difference

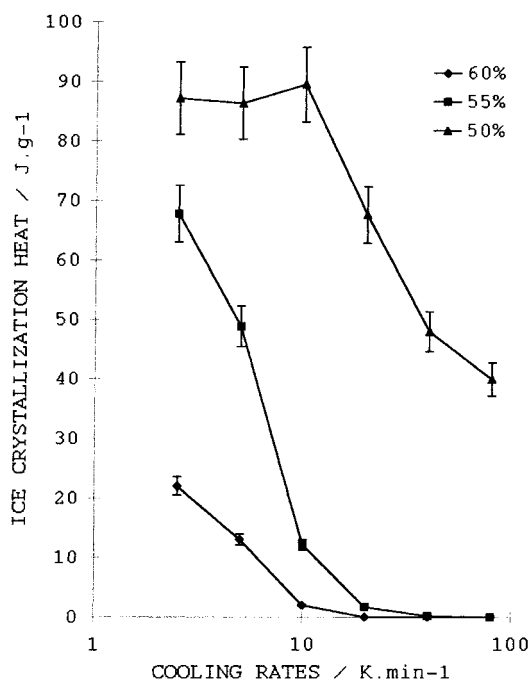


Fig. 2. Heat of ice crystallization as a function of the cooling rate for 50, 55 and 60%wt/wt fructose in water.

between the slope of the enthalpy curve corresponding to the measure thermal curve above, and below, the glass transition and is reported in Fig. 3. Thus, there appears to be a minimum in these changes for a concentration between 80 and 95% corresponding to a minimum in configurational state change to a stronger glass by Angell's definition [19].

The definition of the limiting glass transition can be set by extrapolating the ice-melting curve to the glass-transition curve in Fig. 1 with the inconvenience of some imprecision on account of uncertainty of the extrapolated ice-melting curve. Fig. 1 can also be used for extrapolating the glass-transition curve for samples after all the ice crystallized, thus leading to a value of $T_g' = -57 \pm 1^\circ\text{C}$ and a limiting concentration of 78 wt%. It must be noticed that, for high solute concentrations, ice will not be able to crystallize completely because of its kinetics properties. Therefore, the glass-transition temperature of the remaining glass with incomplete ice crystallization will have a lower solute concentration, and as a result a lower glass-transition temperature, as is observed in Fig. 1 for 65 wt% fructose.

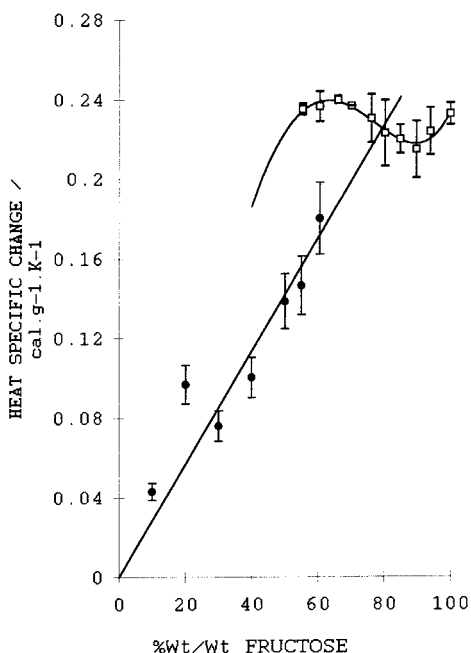


Fig. 3. Variations of the change in specific heat (\square) at T_f as a function of the fructose concentration. The corresponding line is a polynomial fit using a least squares method. Variation of the change in specific heat (\bullet) of the lowest temperature transition reported in Fig. 1 as glass transition after ice crystallized during the initial cooling and the change in specific heat of the vitrified samples. The corresponding straight line is a regression line forced to pass through the origin.

Another approach for the determination of the limiting concentration and T'_g is to consider the thermal curves after all the ice crystallized with the remaining vitrified solution after cooling. The extrapolation of the glass-transition temperature curve for the remaining solution toward the glass-transition curve of vitrified samples gives the same results as the previous method. A quantitative method can also be used, knowing that the contribution to glass transition after complete ice crystallization will come only from the remaining solution, the specific heat change can also be used. Therefore, the ratio $\Delta C_p(T'_g)/X(T'_g)$ of the change in specific heat for the limiting glass state at a concentration $X(T'_g)$ is equal to the ratio $\Delta C_p(T_g)/X_0$ of the change in specific heat for the glass transition of the remaining vitrified solution from a solution of initial concentration X_0 . The application of this observation is reported in Fig. 3, where the inter-

section of the linear regression line for $\Delta C_p(T_g)$ as a function of X_0 with the ΔC_p curve of the wholly vitrified samples leads to a concentration close to 78% wt/wt for $X(T'_g)$. The consideration of the so-called incipient melting from Fig. 1 shows that the corresponding change in specific heat as a function of the fructose concentration is too large compared to that of the totally vitrified samples. This is why this incipient melting has not been considered as a glass transition in the present study. T'_g is, therefore, found using the data from Fig. 1 and this last method to be close to $-57 \pm 1^\circ\text{C}$ at a concentration of $78 \pm 1\%$ wt/wt, contrary to the reported data of -42°C with a concentration of 51% wt/wt [1], or -48° at 79% [5], or else -53°C at 78.6% [20]. A glance at the glass-transition curve shows that a 51% wt/wt fructose solution will not even vitrify during the initial cooling at 40 K/min. For the two other reports, the glass-transition temperatures have been defined as the mid-point of the transition and not, as at present, as the fictive temperature T_f . The limiting concentrations are very close, which apparently excludes the conclusion of the calculation of the limiting concentration using only the amount of crystallized ice as reported in [1].

To complete this study of the glass transition in the fructose/water system, the apparent activation energy, E , is determined with the slope $-E/R$, calculated from the definition of Eq. (2). E is observed to be slightly constant as the fructose concentration increases up to a concentration close to 75%, for which E then increases rapidly as shown in Fig. 4 with $-E/R$ reported in the function for the fructose concentration. From these activation energies and the values of the fictive temperature T_f , it is then possible to calculate the fragility factors defined by Eq. (3) and reported in Fig. 5. A recent study reported the fragility factor for pure fructose as 86 ± 34 when using the fictive glass-transition temperature [21]. Our data is giving a higher value of 146 ± 22 for this fragility factor which might be due to a wider range of cooling rates used in the study. As expected, the fragility factor passes through a minimum for a concentration close to 75% wt/wt for fructose. Above this concentration, the fragility factor increases rapidly as for lower concentrations this factor does not vary as much due to a less effective plasticizing effect of water on the glassy structure of fructose.

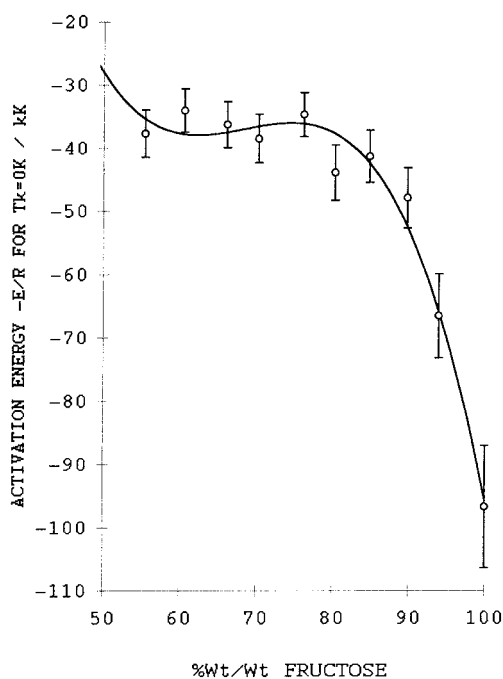


Fig. 4. Apparent activation energy $-E/R$ reported in kK as a function of the fructose concentration. The line is a best polynomial fit using a least squares method.

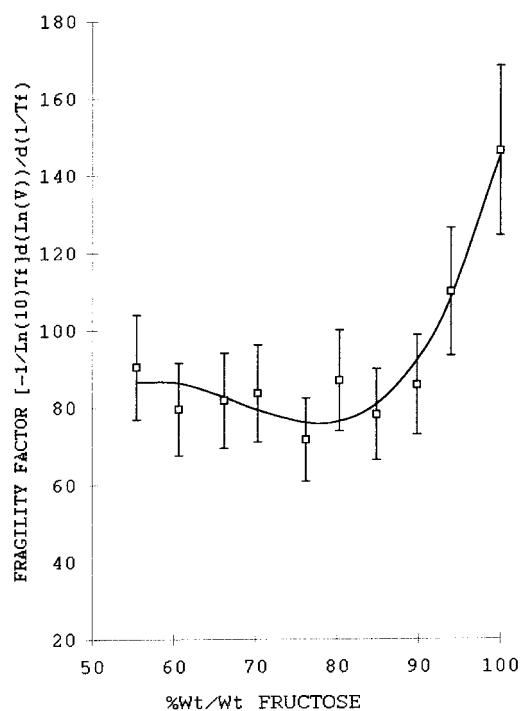


Fig. 5. Fragility factor reported as a function of the fructose concentration. The line is a best polynomial fit using a least squares method.

The phase diagram of the fructose/water system has been complemented with the ice homogeneous nucleation temperature and the fictive glass-transition temperature, T_f , curve. Vitrification can be achieved for concentrations higher than 55% wt/wt. The model of Gordon et al. [9] is providing a good fit for the variation of the fictive glass-transition temperature with the solute concentration. The fit is giving a slightly higher change in specific heat at the glass transition ($T_g=138 K$) for pure water at 13.5 ± 0.8 cal/(K mol). However, this model cannot be used for multicomponent systems with more than two solutes, contrary to the Couchman model which can be generalized to multicomponent systems. The determination of the limiting glassy state at T'_g has been determined to be close to $-58^\circ C$ and to 78% wt/wt fructose in water, using either the extrapolation of the melting temperature curve toward the T_f curve or the linear variations of changes in the specific heat ΔC_p at the glass transition after ice crystallization. The variation of ΔC_p for the wholly vitrified samples shows a stronger glassy state from a thermodynamic viewpoint for concentrations between

80 to 95% wt/wt as the kinetics approach leads to a stronger glassy state close to 75% wt/wt, closely corresponding to the limiting glassy state within the error of determination of the methods.

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