Carbohydrate Research, 196 (1990) 11–18
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ASPECTS OF THE GLASS TRANSITION BEHAVIOUR OF MIXTURES OF CARBOHYDRATES OF LOW MOLECULAR WEIGHT

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(Received February 22nd, 1989; accepted for publication, June 26th, 1989)

ABSTRACT

The glass transition temperature (T_g) values for carbohydrates alone and in binary mixtures have been determined using differential scanning calorimetry. The T_g of the carbohydrate depends strongly on molecular weight and less on structure. The T_g of the binary mixtures was dependent on composition and, in most instances, was linear with respect to mole fraction. The effect of water on depressing the T_g of the carbohydrates and their binary mixtures was also evaluated. The observed behaviour was compared with that predicted from a thermodynamic approach.

INTRODUCTION

The glass transition behaviour of synthetic polymers is a topic of continuing interest. In the region of the glass transition, polymer diffusion, rate of crystallization, and mechanical properties change markedly and determine the usefulness of a particular polymer. Insights into molecular interactions have also been gained from the study of the glass transition behaviour of mixtures of simple organic molecules[1].

Little has been published on the glass transition behaviour of polysaccharides and carbohydrates of low molecular weight, despite the fact that the glass transition behaviour of amorphous α- and β-D-glucose was described over 60 years ago[2]. Recent work[3] has focussed on the effect of carbohydrates on the freezing behaviour of water and the suppression of its crystallization, *i.e.*, the formation of a water–carbohydrate glass. There has been less interest in the study of the glass transition behaviour of carbohydrates and their mixtures as a function of the contents of water, particularly ≤20% where the glass transition occurs without phase separation of ice. For many applications in the food industry and elsewhere, this composition regime is relevant.

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0008-6215/90/$ 03.50

We now report on the glass transition behaviour of monosaccharides, oligosaccharides, and their mixtures, using differential scanning calorimetry (d.s.c.).

EXPERIMENTAL

Sample preparation. — Crystalline, commercial mono- and di-saccharides were melted by heating to 430 K and then dried *in vacuo* over P_2O_5 at 330 K, and stored thereat prior to use (usually 1–2 days). The recrystallization of the carbohydrate, as evidenced by an endothermic transition in d.s.c., was not detected over this time scale. Mixtures of carbohydrates were prepared by dissolving the required amounts of the carbohydrate in a small quantity of water followed by drying at 330 K.

Differential scanning calorimetry. — Each sample (5–10 mg) was weighed into an aluminium sample pan, using a Cahn 2000 recording electrobalance (sensitivity, 0.1 μg). When required, water was added by exposing the sample to air saturated with water vapour at 25° and the content was determined by drying *in vacuo*. The pan was sealed quickly, and calorimetry was performed using a Perkin–Elmer DSC2 instrument with the data being logged into a microcomputer and subsequently analysed on a VAX 11/785 computer. Each sample was heated to 440 K, cooled to 240 K at 50 K/min, then scanned to 440 K at 10 K/min. A typical trace is shown for D-glucose in Fig. 1. A sharp change in heat capacity, indicative of a glass transition, occurred at 311 K, the heat capacity increment for the transition being 0.88 $J.g^{-1}.K^{-1}$. These data are comparable to accepted literature values[2] for the T_g and ΔC_p of D-glucose of 305 K and 0.8 $J.g^{-1}.K^{-1}$. The observed T_g for D-glucose showed a linear change with scanning rate from 311 K at 10 K/min to 304 K at 1.25 K/min with an extrapolated value for T_g of 303 K at a zero scanning rate. A scanning

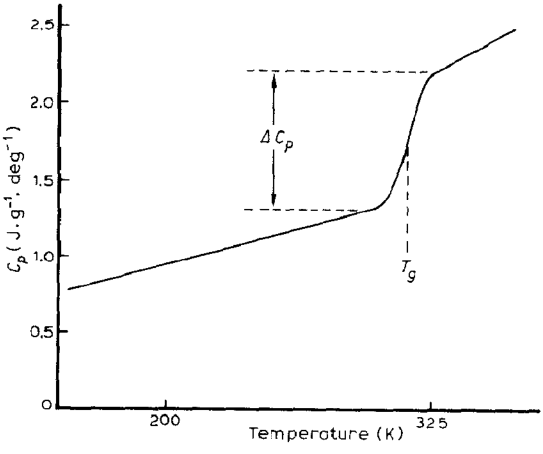

Fig. 1. Plot of heat capacity versus temperature, showing the glass transition temperature (T_g) and heat capacity increment for the transition (ΔC_p) for D-glucose.

rate of 10 K/min was used routinely, and experimental values of T_g were determined at this scanning rate.

RESULTS

The glass transition temperature (T_g), and heat capacity increments for the transition (ΔC_p) of the mono- and oligo-saccharides studied are shown in Table I. For the monosaccharides, T_g spans the temperature interval 254–311 K, with aldopentoses having a T_g lower than that of the aldohexoses. The T_g values of alditols are lower than those of the corresponding aldoses. As the alditols are acyclic, they can adopt more conformations than the corresponding cyclic forms. The results support the general expectation that molecules which have restricted conformational flexibility have a higher T_g. The expectation that T_g will increase with increasing molecular weight is illustrated by the behaviour of the oligosaccharides, with the T_g values being maltose, 368 K; maltotriose, 407 K; and maltohexaose, 448 K. The ΔC_p for the transition showed the reverse trend, decreasing from 0.79 $J.g^{-1}.K^{-1}$ (270 $J.mol^{-1}.K^{-1}$) for maltose to 0.49 $J.g^{-1}.K^{-1}$ (485 $J.mol^{-1}.K^{-1}$) for maltohexaose. The orientation of the hydroxyl groups and the nature of the linkages had a smaller effect on the T_g of oligosaccharides.

The variation of T_g for some mixtures of an oligo- and a mono-saccharide is plotted in Fig. 2 as a function of mole fraction for maltotriose–D-glucose, maltohexaose–D-glucose, and maltohexaose–D-galactose.

For maltotriose–D-glucose and maltohexaose–D-glucose, the variation of T_g is linear in mole fraction, but there is a small positive deviation for maltohexaose–D-galactose. The T_g of some other mixtures (1:1 by weight) are given in Table II. For each mixture, the T_g has a value intermediate between those of the pure compounds. The T_g of maltotriose–alditol mixtures shows significant negative deviations from linearity with mole fraction. The T_g for mixtures of maltotriose with

TABLE I

THE GLASS TRANSITION TEMPERATURES (T_g) AND RELATED HEAT CAPACITY INCREMENTS (ΔC_p) FOR THE MONO- AND OLIGO-SACCHARIDES

Sugar	T_g*(K)*	ΔC_p *($J.mol^{-1}.K^{-1}$)*	*Sugar*	T_g*(K)*	ΔC_p *($J.mol^{-1}.K^{-1}$)*
L-Arabinose	277	120	Maltose	368	270
D-Xylose	286	142	Isomaltose	351	222
Xylitol	254	231	Sucrose	343	263
D-Ribose	262	141	Melibiose	368	222
D-Galactose	305	154	Maltotriose	407	267
D-Glucose	311	158	Maltohexaose	448	485
D-Glucitol	273	251			
D-Mannose	309	175			
L-Rhamnose	300	165			
D-Fructose	280	151			

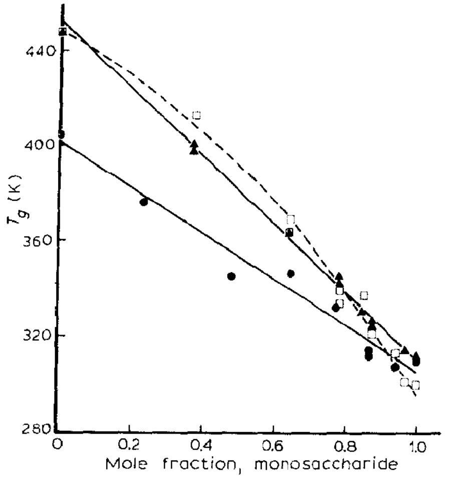

Fig. 2. Plot of T_g versus mole fraction of the monosaccharide for the mixtures maltotriose–D-glucose (●), maltohexaose–D-glucose (▲), and maltohexaose–D-galactose (□).

D-glucitol and xylitol were ~15 K below the temperature expected from linear behaviour.

The glass transition behaviour of carbohydrate–water mixtures was also examined. The strength of the molecular interactions of carbohydrates and water might be expected to have a strong effect on the observed behaviour.

Fig. 3. shows the variation of T_g for maltose–water, maltotriose–water, and maltohexaose–water mixtures. For the maltose–water mixture, the plot is linear over the range 0–0.8 mole fraction of water, with an extrapolated notional "T_g" for pure water of ~240 K. For the maltotriose–water and maltohexaose–water mixtures, the same plot shows strong curvature. The T_g for pure water has been measured[4] as 134 K; therefore, even the plot for maltose–water mixtures must show strong curvature at mole fractions of water >0.8. Experimentally, it is difficult to investigate mixtures where the mole fraction of water is 0.8–1.0 since rapid quenching is needed in order to vitrify aqueous solutions more dilute than those studied.

TABLE II

THE GLASS TRANSITION TEMPERATURES OF SOME MIXTURES OF CARBOHYDRATES (1:1 BY WEIGHT)

Mixture	T_g *(K)*
D-Fructose–D-glucose	286
D-Glucose–D-galactose	305
Sucrose–D-glucose	320
Maltotriose–D-xylose	316
Maltotriose–xylitol	273
Maltotriose–D-glucitol	293
Sucrose–D-fructose	298

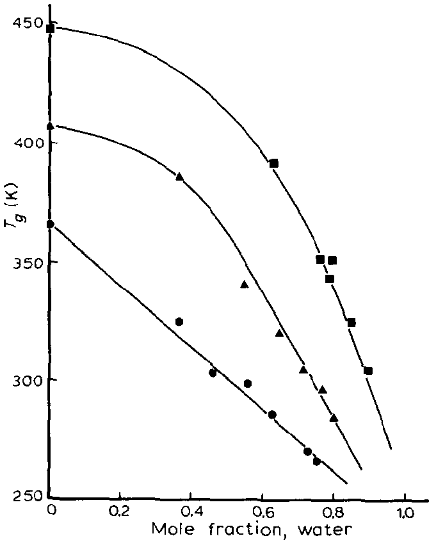

Fig. 3. Plot of T_g versus mole fraction of water for the mixtures maltose–water (●), maltotriose–water (▲), maltohexaose–water (■).

Plots for the maltohexaose–D-glucose–water and maltohexaose–D-glucitol–water mixtures are shown in Fig. 4. The mixtures contained equal weights of each carbohydrate and increasing amounts of water. The T_g of these ternary mixtures varied linearly with the mole fraction of water in the range 0–0.6. The dependence upon mole fraction rather than on the weight fraction means that the components of lower molecular weight have a large influence on the T_g of a mixture.

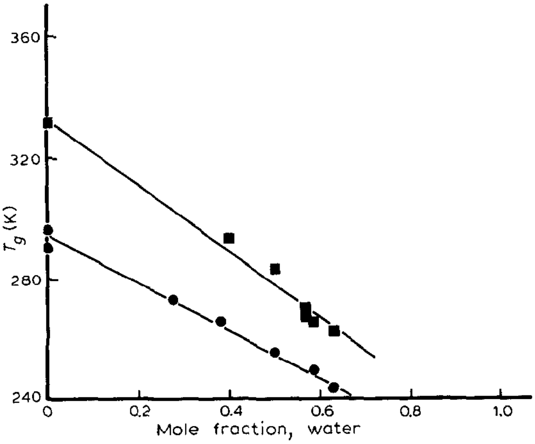

Fig. 4. Plot of T_g versus mole fraction of water for the mixtures maltohexaose–D-glucose–water (■), and maltohexaose–D-glucitol–water (●).

DISCUSSION

For the majority of mixtures of carbohydrates, predominantly linear variations of T_g with mole fraction were obtained. Similar observations have been made on the variation of T_g for binary mixtures of molecular liquids[1], and this implies that there is a relatively simple mixing rule. For systems where strong specific interactions of the species occur, deviations from this simple behaviour have been noted[5].

When water is added either to a carbohydrate or to a mixture of carbohydrates, plots of T_g versus mole fraction become strongly curved or, if linear, cannot be extrapolated to the accepted T_g of pure water. Therefore, it is worthwhile to examine more completely factors which affect the glass transition behaviour.

Several theoretical approaches have been used to describe different aspects of glass transition behaviour, including free-volume theories[6], kinetic theories[7], and both statistical[8] and classical thermodynamic theories[9]. Calorimetric investigations provide all the information necessary to predict the glass transition temperature of mixtures, using the classical thermodynamic theory. In this approach, it is argued that, although kinetic factors can modify the observed behaviour, the underlying phenomenon is a second-order phase transition which can be modelled using a thermodynamic approach. The theory due to Couchman and Karasz[10] leads to the following expression for the T_g of a mixture, T_{gm}, of components 1 and 2,

$$T_{gm} = \frac{x_1 \Delta C_{p1} T_{g1} + x_2 \Delta C_{p2} T_{g2}}{x_1 \Delta C_{p1} + x_2 \Delta C_{p2}}, \qquad (1)$$

where x is the mole fraction. The theory has successfully described the compositional variation of T_g for compatible polymer mixtures[9,10], mixtures of a polymer with a diluent[11], and mixtures of simple alcohols[12]. An equivalent expression has also been obtained using a slightly different thermodynamic approach[13]. Equation *1* is similar to various semi-empirical relationships which have a useful predictive value for polymeric systems.

The use of Equation *1* for aqueous mixtures requires values of the T_g and ΔC_p for water which are a matter of debate[14]. A T_g of 134 K has been obtained in a calorimetric study[4] of a vapour-deposited water glass with a ΔC_p of 34.9 J.mol^{-1}.K^{-1}. Recently, techniques have been developed which make it possible to vitrify liquid water by employing very rapid quenching rates[15]. The structure of this material is very similar to that of the vapour-deposited vitreous water[16]. Calorimetric experiments on vitrified liquid water have failed to yield an unequivocal demonstration of a glass transition[17]. An indirect measurement of T_g can be obtained by the extrapolation of binary aqueous solution data, which yields a value of 139 K for many systems[18]; this value is close to the original calorimetric value used here.

The predicted dependence of T_g on mole fraction for maltohexaose–glucose and maltohexaose–water mixtures is shown in Fig. 5 and compared with the observed behaviour. A similar comparison for the maltohexaose–glucose–water mixture is shown in Fig. 6. The best fit between predicted and observed T_g values is for the maltohexaose–water system. The fit is progressively less good for the maltohexaose–glucose and maltohexaose–glucose–water mixtures. In all instances, theory overestimates the T_g. Kinetic effects could lead to either an elevated or depressed T_g in the mixture by affecting how closely the glass transition approaches the underlying equilibrium second-order phase transition. Couchman and Karasz[10] made two further assumptions that could lead to a discrepancy between theory and experiment. First, ΔC_{p1} and ΔC_{p2} were assumed to be inversely proportional to the absolute temperature. Second, and perhaps more importantly, the two components were assumed to form a regular mixture both in the supercooled liquid and the glassy states. It is known that specific interactions of species can lead to deviations from this idealised behaviour. For example, in mixture of organic chlorides with alcohols, there is evidence for the formation of complexes, which leads to an increase in T_g, with plots of T_g versus mole fraction of halide showing a maximum[5]. It is surprising that the mixtures containing water conform more closely to predicted behaviour than the oligomer–monomer mixtures. More information is needed on the thermodynamics of mixing of these materials in the supercooled liquid and glassy states, in order to establish to what extent they deviate from regular solution behaviour. A more complete understanding would be obtained from dilatometric measurements that would provide the data necessary to apply the free-volume and kinetic theories to the glass transition behaviour of these mixtures.

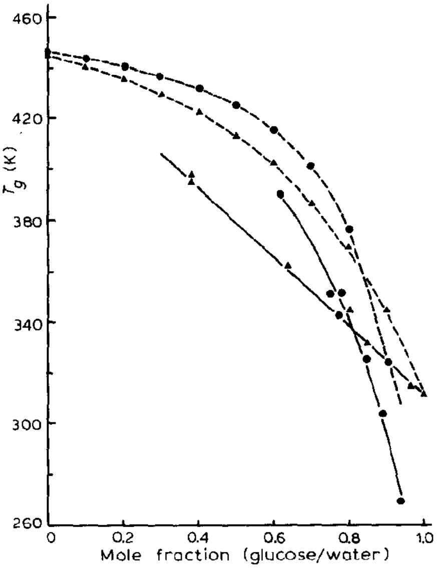

Fig. 5. Comparison of predicted (------) and experimental (—) behaviour for the mixtures maltohexaose–glucose (▲), and maltohexaose–water (●). The mole fraction is for glucose and water, respectively.

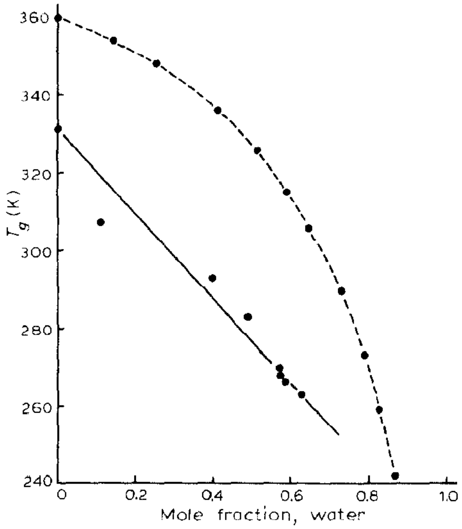

Fig. 6. Comparison of predicted (------) and experimental (—) behaviour for the mixture maltohexaose–glucose–water. The glass transition temperature is plotted versus the mole fraction of water.

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