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Kinetic aspects of the glass-transition behaviour of maltose–water mixtures

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ABSTRACT

The dependence of viscosity on temperature, determined for a range of maltose–water mixtures, is described well by the equation $\eta = A \exp[B/(T-T_0)]$. Predicted values of the glass-transition temperature (T_g), where the viscosity has a value of 10^{12} Pa.s, were within a few degrees of those obtained experimentally by calorimetry. The activation enthalpy for the relaxation processes in the liquid increased on cooling as T_g was approached. The maltose–water mixtures can be considered as fragile in Angell's classification of the viscous and glass-transition behaviour of liquids.

INTRODUCTION

If a crystalline solid is melted, then cooled at a rate which is rapid compared to the rate of crystallisation, the viscosity of the supercooled liquid increases. For some liquids, *e.g.* silica, the increase in viscosity (η) with decrease in temperature (T) shows an Arrhenius dependence on temperature,

$$\eta \propto \exp(E/RT), \qquad (1)$$

where E is the energy of activation for viscous flow and R is the gas constant. More usually, non-Arrhenius behaviour is observed, and the dependence of η on T over many decades is represented[1,2] well by a semi-empirical expression[3–5]:

$$\eta = A \exp[B/(T - T_0)], \qquad (2)$$

where A, B, and T_0 are constants.

As the viscosity increases, the various relaxation processes in the liquid become slower. If relaxation cannot occur within the time scale imposed by the rate of cooling, the liquid-like relaxations are "frozen in", and a brittle, glassy material is formed. Glassy liquids generally have viscosities in excess of 10^{12} Pa.s. If the glass is heated, a sharp increase in the heat capacity or the thermal expansion coefficient occurs at the glass-transition temperature (T_g). The observed T_g is influenced by kinetic factors, principally the rates of heating and cooling through the transition, and moves to lower temperatures as the rate is reduced. It has been suggested[6,7] that, whereas the observed

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transition is influenced by kinetic factors, the underlying transition is an ideal glass transition in the sense of a second-order phase transition which exhibits discontinuities in the second temperature and pressure derivatives of the free energy. Kauzmann[8] pointed out that, if the entropy of the amorphous supercooled liquid is extrapolated from the melting temperature to below the glass-transition temperature, it becomes equal to, then less than, that of the crystalline solid. The temperature at which the entropies of the crystal and supercooled liquid intersect is the Kauzmann temperature (T_k) and is the lower limit of T_g. A glass transition must intervene at a temperature greater than T_k in order to avoid the unlikely occurrence, although not thermodynamically prohibited, of a liquid having an entropy lower than that of the crystal. Experimentally[1,9,10], T_k is similar numerically to T_0 obtained from equation *2*; indeed, the equivalence of T_0 and T_k has been suggested.

The glass-transition behaviour of a wide range of materials has been investigated, including synthetic polymers, and low-molecular-weight inorganic and organic molecules. In a comparison of the relationship of their viscous behaviour with T_g, a useful classification has been developed of strong and fragile liquids[2,11]. Strong liquids are network materials (*e.g.* silica) that are characterised by an approximate Arrhenius dependence of the temperature on the viscosity and a small increment of the heat capacity at the glass transition. Fragile liquids have a much lower energy of activation for viscous flow at temperatures that are high relative to T_g, but a much higher activation energy as T_g is approached. The viscous behaviour is well described by equation *2*, although there is some evidence for a return to Arrhenius behaviour as the glass transition is approached. Fragile liquids exhibit large changes in heat capacity at the glass transition. Examples of fragile liquids include toluene and *o*-terphenyl.

Despite the fact that the glass-transition temperature[12] and viscosity[13] of supercooled D-glucose was investigated over 50 years ago, the glass-transition behaviour of carbohydrates and their mixtures has been investigated little. The industrial relevance of the glassy behaviour of carbohydrates has been highlighted[14], as it affects many aspects of their industrial use, particularly the stability and mechanical properties of carbohydrate-rich materials, and their use as cryopotectants. Recently, there has been renewed interest[15–18] and a need[16] to develop useful empirical and theoretical relationships.

We have reported[19] on the effect of water as a diluent on the glass-transition temperature of malto-oligosaccharides and starch, and compared the behaviour observed with that predicted from a thermodynamic approach. We now consider kinetic aspects of the behaviour of maltose–water mixtures.

EXPERIMENTAL

Maltose monohydrate (Sigma) was used without further purification. Excess of water was removed by vacuum drying at 333 K over P_2O_5. Maltose–water mixtures were prepared by adding a known weight of water to the dry maltose monohydrate, each mixture was sealed in a tube, and heated to 433 K to form a clear homogeneous solution.

In the calculation of water content, allowance was made for the water of crystallisation; the value calculated was in agreement with that found by drying the supercooled liquid *in vacuo* at 333 K over P_2O_5.

Viscosity experiments. — The viscosity of the maltose–water mixtures was measured from the velocity of a falling steel sphere of radius r, in the solution whose viscosity (η) is given by

$$\eta = (2/9)\,(\rho_s - \rho_L)gr^2(t/l)[1 - 2.104(r/R) + 2.09(r/R)^3],$$

where g is the acceleration due to gravity, $\rho_s - \rho_L$ is the difference in density between the steel sphere and the liquid, R is the radius of the wide-bore tube in which the experiment was conducted, and the velocity is given by the distance (l) travelled by the sphere divided by the time (t).

The falling-sphere method has been used to determine the viscosities of organic liquids, including those of glucose and concentrated solutions of sucrose as they are supercooled[13,20,21]. An estimate of the rate of shear, using the formula

$$\gamma = \frac{V}{R - r},$$

where v is the velocity of the sphere, and R and r are the radii of tube and sphere, respectively, gives values in the range 5×10^{-9} to $8 \times 10^{-5}\ \mathrm{s}^{-1}$. At higher viscosities ($> 10^9$–10^{12} Pa.s), there is the possibility that delayed elastic effects can introduce errors. However, these effects did not introduce significant errors at viscosities of $< 10^8$ Pa.s in comparable experiments on supercooled liquid glucose and other organic liquids[13,20].

The wide-bore tube was thermostatted in a water–ethylene glycol bath, the temperature being regulated to 0.001° using a quartz thermometer (Hewlett–Packard 2804A) interfaced to a microcomputer that controlled the power output to the heaters. The quartz thermometer was calibrated against the triple point of pure water and was accurate to $\pm 0.02°$. The motion of the steel ball (radius, 0.1685 cm) in the solution of maltose was monitored using a cathetometer.

Calorimetry. — Samples (5–10 mg) were weighed accurately into aluminium pans, using a Cahn 2000 recording electrobalance with a sensitivity of 0.1 μg. The pans were sealed quickly in order to minimise adsorption of moisture. Differential scanning calorimetry (d.s.c.) was performed with a Perkin–Elmer DSC2 that had an attached cooler unit. Base-line scans were run over the range 230–330 K, using empty sealed pans. Sample scans were performed by initial heating to 330 K, followed by cooling, and reheating at the same rate. Data were logged on a BBC microcomputer, which was then used for base-line subtraction and the calculation of differential heat flow and heat capacity as a function of temperature. After the d.s.c. experiment, the sample pans were punctured and weighed, and the weight of the sample was determined after drying *in vacuo* at 333 K over P_2O_5.

RESULTS AND DISCUSSION

Fig. 1 shows a plot of log η versus $1/T$ for maltose–water mixtures that contained 10, 12.4, 14.7, and 25.3% w/w of water; η decreased with increase in T and content of water. For the range of η studied, Arrhenius behaviour was not observed, but the data were described well by equation *2*. The values of the constants A, B, and T_0, which gave a best fit to the observed data, are represented in Table I. As has been observed for glucose–water mixtures[22], the values of A and B showed no significant trend with increasing content of water. This finding is not surprising, since the values represent an empirical fit of the data and are dependent on the method of analysis[22]. The value of T_0 fell from 240 to 182 K on increasing the content of water from 10 to 25.3% w/w. Included for comparison are values of T_g for each of the samples at which the predicted viscosity reached the accepted value of a glass of 10^{12} Pa.s. The values of T_g ranged from 279 to 223 K and were comparable to the interpolated values of T_g obtained from calorimetric data of the composition-dependence of T_g of maltose–water mixtures. The calorimetric estimate was within the limits of uncertainty of the value obtained from the viscosity experiment and confirmed the view that carbohydrate materials become glassy at viscosities $> 10^{12}$ Pa.s. The value of T_0 (Table I) can be considered as setting a lower limit for T_g and was 30–40 K lower than that of T_g obtained from the sharp change in heat capacity by d.s.c. T_g measured in this way was dependent on the rate of cooling and heating, and moved to lower temperatures as the rate was reduced. This dependence is given by[23]

$$d\ \ln|q|/d(1/T_g) = -\Delta H/R,$$

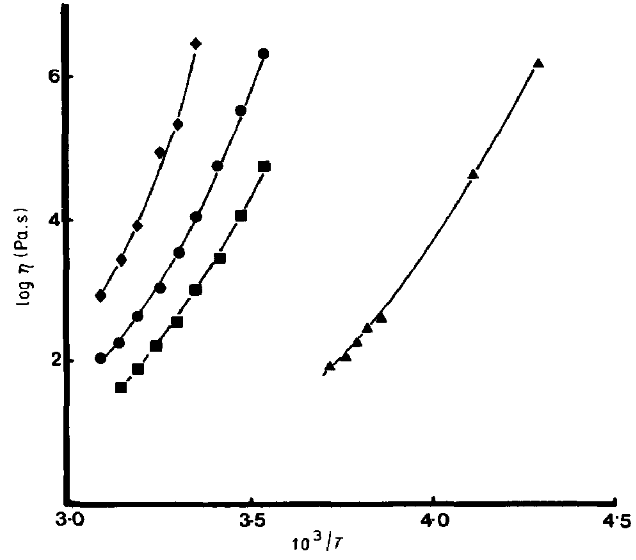

Fig. 1. Graph of log η versus $1/T$ for maltose–water mixtures that contained 10 (◆), 12.4 (●), 14.7 (■), and 25.3% w/w of water (▲).

TABLE I

A comparison of the values of T_g obtained from the fitting of viscosity data to equation *2* and by calorimetry

Content of water (*%w/w*)	*A* (*Pa.s*)	*B* (*K*)	T_0 (*K*)	$T_{g\ vis}$ (*K*)	$T_{g\ cal}$ (*K*)
10.0	1.28×10^{-4}	1195	247	279	281
12.1	4.53×10^{-4}	1083	235	265	268
14.8	6.55×10^{-4}	975	229	257	261
25.3	3.13×10^{-6}	1270	182	216	223

where ΔH is the enthalpy of activation for the relaxation process that controls the structural enthalpy or volume relaxation.

Fig. 2 shows a plot of differential heat input versus *T*, which compares the effect of the rate of heating on the glass-transition behaviour of a maltose–water mixture that contained 12.4% w/w of water. The data were recorded using four rates of heating and cooling (10, 5, 2.5, and 1.25 K/min). The curves have been displaced for the sake of clarity. A sharp increase in the heat capacity occurred in the temperature range 263 to 270 K followed by an overshoot. If a fictive temperature is defined as the temperature at which the observed value of the heat capacity would be that of the supercooled liquid, then the overshoot can be viewed as a delayed relaxation of the fictive temperature towards the ambient temperature, or an enthalpy relaxation. With a reduction in scanning rate from 10 to 1.25 K/min, the mid-point of the rapid heat capacity increment changed from 269.8 to 267.1 K.

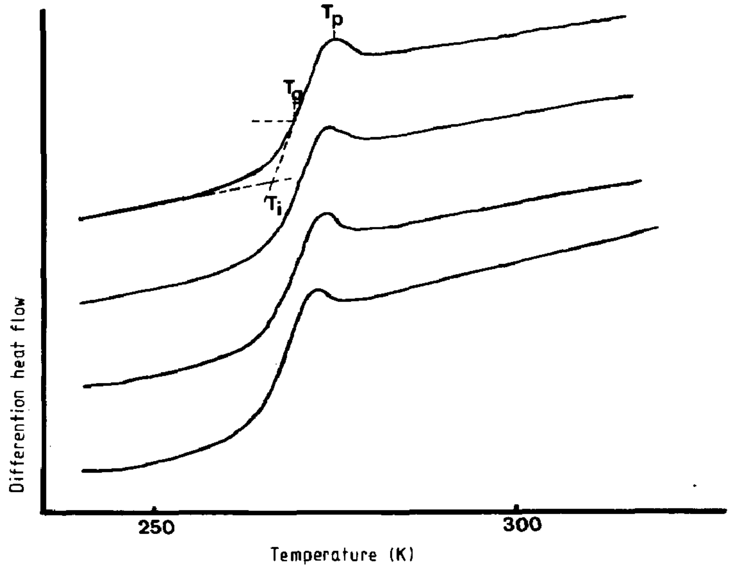

Fig. 2. Graph of differential heat flow versus *T*, showing the glass-transition region for a 97.6% (w/w) maltose–water mixture at heating rates of 10, 5, 2.5, and 1.25 K/min.

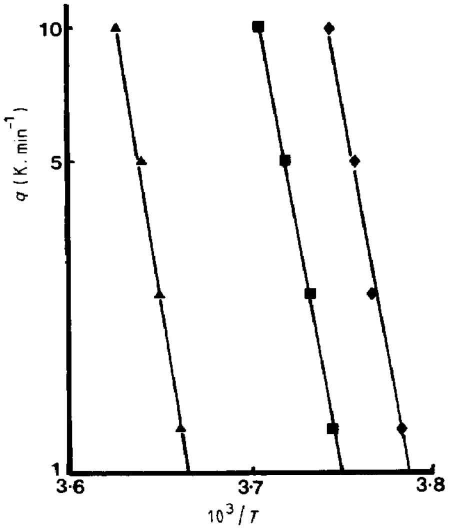

Fig. 3. Graph of scanning rate (q) versus $1/T$, showing dependence of T_i, T_g. amd T_p on the rate of scanning (T_i, T_g, and T_p as in Fig. 2).

Three temperatures were used to characterise the sharp increase in heat capacity which occurs at T_g, namely, the onset temperature, the mid-point temperature, and the temperature of the maximum of the heat capacity overshoot (see construction in Fig. 2). Fig. 3 shows a plot of the log of the scanning rate (q) versus the reciprocal of these temperatures for a maltose–water mixture that contained 12.66% w/w of water. The data show a linear dependence of $1/T$ on log q as predicted from equation *2*, which is consistent with the view that, in the vicinity of T_g, the activation enthalpy for the relaxation process is a constant and the viscosity relationship has an Arrhenius form. Within experimental error, the slopes of the plots shown in Fig. 3 are the same with an average calculated value of ΔH 462 ± 20 kJ/mol. Within the range 12–15% w/w of water, this value of ΔH did not show significant variation.

It is useful to compare this activation enthalpy ΔH_{cal} with that (ΔH_{vis}) obtained from the viscosity experiment, where viscous flow is represented as an activated process. Fig. 4 shows a plot of ΔH versus T for a maltose–water mixture that contained 12.4% w/w of water. Values of ΔH_{vis} were obtained by differentiation of the best fit to equation *2*, and values within the experimental range of the viscosity experiment are shown together with extrapolated values. Included for comparison is the value of ΔH_{cal} with an indication of the range of temperature over which T_g was measured. The extrapolated values of ΔH, obtained from equation *2*, intercept the values from the d.s.c. experiment and indicate that, in the region T_g, a change in viscous behaviour occurred from the dependence in equation *2* to an Arrhenius form. As the value of ΔH_{cal} is consistent with the extrapolated values of ΔH_{vis}, then useful predictions over a wide range of viscosities, approaching at the upper end the viscosity of the glass, can be obtained from equation *2*. Similar conclusions have been drawn for the dependence of η on T for other carbohydrates, including D-glucitol[24] and D-fructose[25].

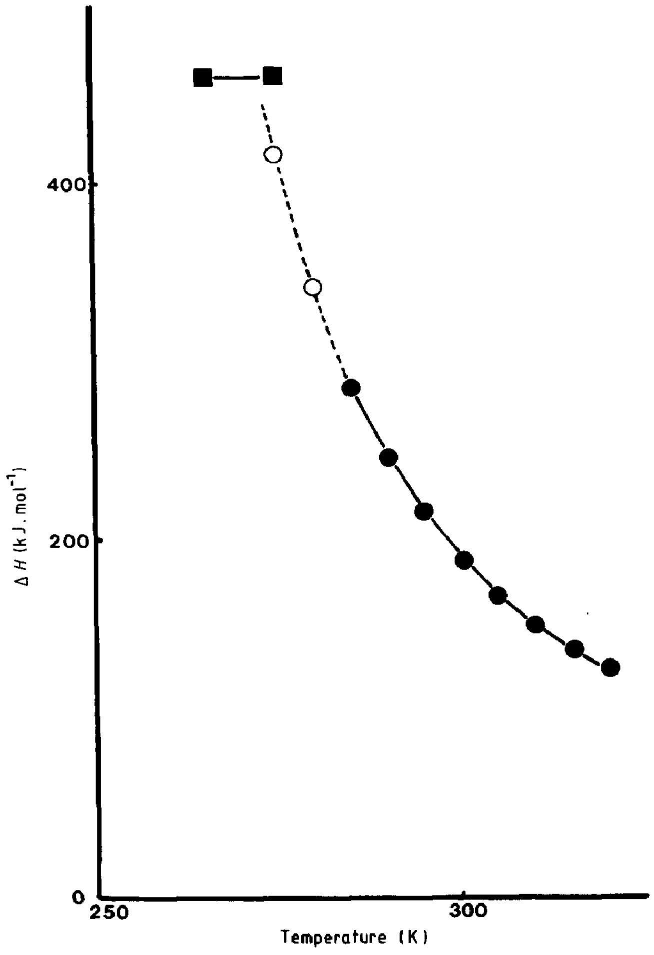

Fig. 4. Graph of activation energy for viscous flow versus T for an 87.6% (w/w) maltose–water mixture.

The values of T_0 obtained by fitting the viscosity data to equation *2* are ~33 K lower than the values of T_g obtained by calorimetry at a scan rate of 10 K/min. If the relaxation process near T_g continues to have a constant activation enthalpy, then scan rates of 10^{-14}–10^{-15} K/min are needed in order to approach T_0, with an experiment lasting 10^{11} years. In practice, most glassy carbohydrates crystallise more rapidly; therefore, the physical significance of T_0 may be questionable.

Fig. 5 shows a plot of log η versus T_g/T, which permits a comparison of the viscous behaviour of supercooled liquids. For "strong" liquids, a linear dependence is observed. For the polyhydroxy compounds that have been studied, the "fragility" of the liquid increases in the order glycerol[26] < D-glucitol[24] < D-fructose[25] < D-glucose[13] < maltose–water. For the maltose–water mixtures, all data points could be fitted to a single curve over the range of water contents studied. For low-molecular-weight carbohydrates, this representation of data holds a useful prospect for predicting the dependence of η on T,

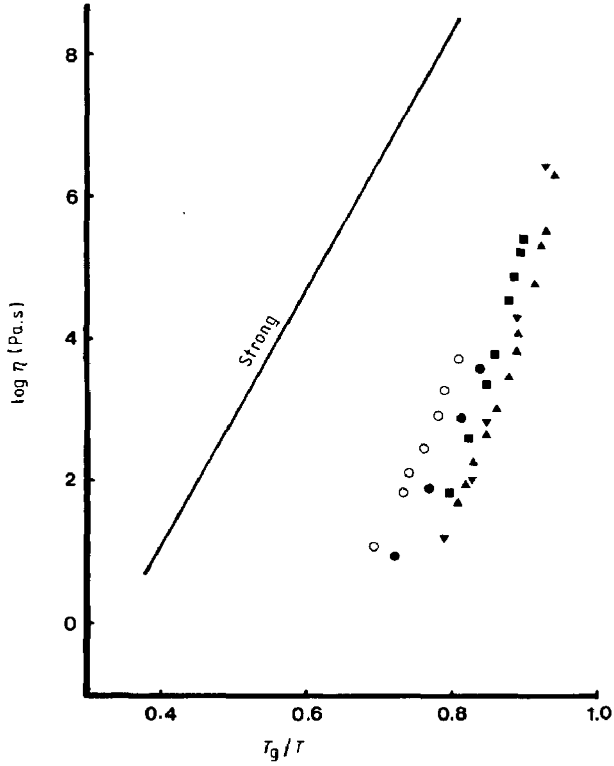

Fig. 5. Graph of log η versus T_g/T for glycerol (o), D-glucitol (●), D-fructose (■), D-glucose (▼), and maltose–water mixtures (▲).

once T_g has been determined. In both, predictions of viscosity will give useful predictions of the characteristic time of the relaxation processes within the liquid, which can be tested experimentally.

One reason for the current interest in the glass-transition behaviour of biological molecules is the effect on stability with respect to crystallisation. In a glassy matrix, diffusion is hindered severely, with the result that glasses do not crystallise for many years. The rate of change of viscosity above the glass transition will affect rates of crystallisation in the supercooled liquid. In order to maximise the rate of crystallisation, a strong driving force favouring crystallisation is required, which implies extensive supercooling, provided that the penalty on the rate of crystallisation, incurred by increasing the viscosity and thus limiting diffusional-encounter, is not too great.

The viscous behaviour of maltose–water mixtures as a function of temperature is described well by equation *2*, which allows extrapolation to the viscosity at T_g. The values of T_g, estimated from viscosity measurements and calorimetry, are comparable, and support two general conclusions. Firstly, the glass-transition behaviour of carbohydrates at low contents of water is affected dramatically by the presence of water, T_g being markedly depressed by the addition of small quantities of water. Secondly, at several degrees above T_g, the viscosity of the liquid changes markedly, so that large changes in the rate of crystallisation would be predicted as a result of relatively small changes in temperature and/or content of water. In Angell's classification[1,11], the carbohydrates studied can be considered as fragile liquids, since the difference in their behaviour showed a relatively small dependence on structure. This classification and description provides a useful basis for comparing the dependence of viscosity on temperature of supercooled liquid carbohydrates and their mixtures with water, and will aid investigation of the relaxation behaviour of these molecules in the vicinity of T_g. For the contents of water studied, it is not possible to isolate the separate contribution to fragile behaviour.

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