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Temperature Dependence of the Viscosity of Sugar and Maltodextrin Solutions in Coexistence with Ice

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The viscosities of glucose, sucrose, and maltodextrin solutions coexisting with ice were measured by rotational viscometry. Samples were prepared by forming a shell of pure ice in a stainless steel tube immersed in a cooling bath, then introducing aqueous solutions at concentrations corresponding to the ice-melt equilibrium temperature. Temperature dependence of viscosity was analysed in terms of Arrhenius, VTF, WLF, and power-law models. Two glass transition reference temperatures were used with the WLF and power-law models: (1) T_g *associated with the transition from liquid to glass and (2)* T_g' *associated with the transition to glass from a maximally freeze-concentrated solution. Plots of* Logη *vs* 1/T *were fairly linear for each solution, but each displayed a unique slope with* E_A *ranging from 168 kJ/K mol to 464 kJ/K mol. WLF and power law models gave a linear fit to all solutions when* T_g *was chosen as the reference temperature. Regression analysis gave constants of* $C_1 = 16.5$ *and* $C_2 = 37.5$ *for WLF* ($r = 0.95$)*, and* $\kappa = 10^{18.6}$ *and* $m = 8.5$ *for power-law* ($r = 0.97$) *models.*

Introduction

There has been increased interest in diffusion and relaxation processes in the rubbery and glassy states of food systems. An understanding of such properties is important because they determine such things as texture and the onset of 'collapse phenomena', (1) and may induce diffusion limits to chemical reaction kinetics (2). The primary property that describes mechanical relaxation of mobile components is the viscosity, η. There have been several approaches to describing the temperature dependence of viscosity. The simplest type of temperature dependence is described by Arrhenius kinetics:

$$\eta = A \exp\left[\frac{E_A}{RT}\right] \qquad \text{Eqn (1)}$$

where A is a constant and E_A is an activation energy barrier to flowing molecules. Arrhenius kinetics have been seen for 'strong network-formers' such as SiO_2 and BeF_2, (3) and for many liquids at temperatures far from their glass transition temperature.

Alternatively, the effect of temperature on the volume in which molecules are free to move has been the theoretical framework for the Vogel-Tammann-Fulcher equation:

$$\eta = A' \exp\left[\frac{B}{T - T_o}\right] \qquad \text{Eqn (2)}$$

where T_o represents the temperature at which the free volume would vanish. Williams, Landel, and Ferry (4) developed a related equation:

$$LOG\left(\frac{\eta}{\eta_g}\right) = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)} \qquad \text{Eqn (3)}$$

Here, the viscosity is shown as a function of temperature with respect to that at the glass transition temperature T_g. The constants C_1 and C_2 were determined for a group of glass-forming liquids, with average values of 17.44 and 51.6, respectively. The WLF equation has the advantage that the reference temperature T_g can be measured by techniques such as differential scanning calorimetry (5,6). Alternatively, Hill and Dissado (7) formulated a power law description of relaxation:

$$\eta = \kappa\,(T - T_g)^{-m} \qquad \text{Eqn (4)}$$

where κ and m are constants.

There have been several studies that have looked at the viscosity–temperature relationship in aqueous sugar solutions. These have focused on conditions in which water would not crystallize to form ice. For example, Soesanto and Williams (8) measured the viscosity of non-crystallizing fructose/sucrose mixtures betwen 20 and 80 °C. They found the results were characterized by the WLF equation, although there was no independent check of the constants, C_1 and C_2. Angell *et al.* (9) found that the viscosity of liquid sorbitol was fit by the VTF equation over the temperature range 35 to 100 °C. Ollett and Parker (10) studied supercooled liquid fructose and glucose at temperatures below 90 °C. Using VTF, WLF, and power law equations, they estimated T_g values for fructose to be between 10 and 16 °C.

The viscosities of dilute aqueous solutions at sub-zero temperatures have been less well studied. It is difficult to measure the viscosity in such systems as the formation of ice interferes with traditional types of viscometry. An interesting aspect about these systems is that, as freezing occurs at progressively lower tempera-

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tures, the unfrozen liquid phase becomes increasingly concentrated in solutes until a point is reached (T_g', C_g') (5,20) at which the phase is maximally concentrated. Further lowering of the temperature results in a transition from a rubbery liquid to a brittle glass. There has been some suggestion that relaxation properties in frozen systems should be controlled by T_g (1). Indeed, several rate processes seem to correlate with the temperature difference $T - T_g$ (1). However, some researchers argue that the true reference glass transition temperature (T_g) varies as the solution concentration changes (2,11).

In this study, we measured the viscosity of sugar and food polymer solutions in the presence of ice. Each system was prepared so as to be near equilibrium conditions. The results were analysed in terms of the above equations, using both the measured T_g' and the estimated T_g associated with the given solution concentration. Our aim was to see whether systems at subfreezing temperatures could be described by standard relationships, and if so, which reference temperature is most appropriate for that description.

Experimental

Solution preparation

The following sugar and maltodextrin solutions were prepared in 0 to 700 g/kg concentrations: D-glucose, sucrose (Fisher Scientific, New Jersey, U.S.A.), MD250 (Grain Processing Corp., Muscatine, Iowa, U.S.A.), and MD365. Reagent grade water was used for all solutions (Aldrich, Milwaukee, Wisconsin, U.S.A.). At higher concentrations, vigorous stirring and moderate heating were required to bring the solutes into solution. The concentrations of the solution were checked with an RFM 80 refractometer (Bellingham and Stanley, Kent, England) and agreed to within 1% of the expected values.

Glass transition temperatures

Glass transition temperatures of the maximally freeze-concentrated materials (T_g') were determined using a Perkin-Elmer DSCII differential scanning calorimeter. Approximately 3 mg of each solution was sealed in an aluminium pan and placed in the DSC. Samples were cooled to 220 K (−53 °C) at 80 K/min, then warmed to approximately 1 K above the expected transition point. Annealing in this manner helps ensure maximum formation of ice. After 40 min, the samples were recooled to 220 K. Scans were then taken as each sample was warmed at 10 °C/min up to 300 K. T_g' was found from the onset of the first endothermic transition.

The glass transitions that would occur if ice did not form in the solutions were estimated from the Gordon–Taylor equation (21), as described by Roos and Karel (12). If T_{g1} and T_{g2} are the glass transitions of the pure solvent and solute, respectively, and w_1 and w_2 are the weight per cent of solvent and solute in the solution, then the glass transition of the solution can be estimated as:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad \text{Eqn (5)}$$

State diagrams

Ideally, we wished to measure the viscosity of solutions in equilibrium with ice. As described later, this was only approximated, as a slight temperature gradient (<0.5 °C) existed within the system. It was necessary to know the equilibrium phase diagrams showing the ice-solution equilibrium temperature as a function of concentration. These were developed using the DSC to measure the equilibrium melting points (T_m) of samples over a range of concentrations. Approximately 1 mg samples were sealed in aluminium pans, cooled to 220 K, then scanned at 10 °C/min up to 300 K. The T_ms were extrapolated from the peak temperature of the melting peak after correcting for the finite time required for melting.

Viscosity of solutions in presence of ice

The apparatus used to measure the solution viscosity is shown in **Fig. 1**. A 5 cm diameter, 30 cm long stainless steel tube was capped at one end and placed in a Neslab PCB-4 refrigerated bath containing ethylene glycol. Water was placed into the tube, up to a height of about 5 cm, and allowed to freeze. Solutions of the desired concentration were then poured into the tube over the ice. Prior to this, the bath temperature was adjusted to produce a temperature inside the liquid close to the equilibrium melting point as found from the phase diagrams. In this way, minimal freezing or melting occurred after adding the solutions. In addition, any new ice formed near the periphery and not in the bulk of the solution where the viscosity was being measured. After allowing the system to come to a steady state, the spindle from a Brookfield RVT viscometer (Stoughton, MA, U.S.A.) was lowered into the solution. Viscosity

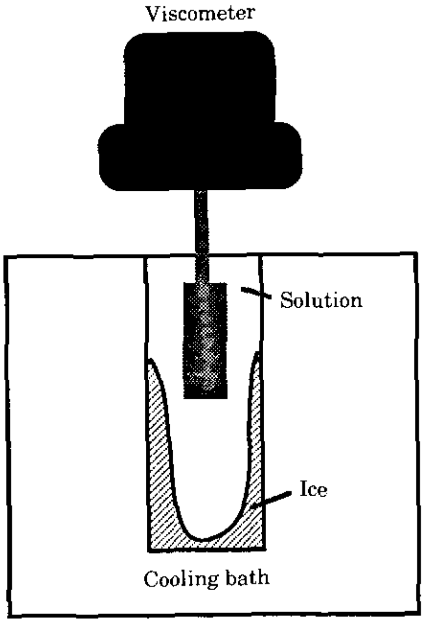

Fig. 1 Apparatus for the determination of viscosities of solutions in equilibrium with ice

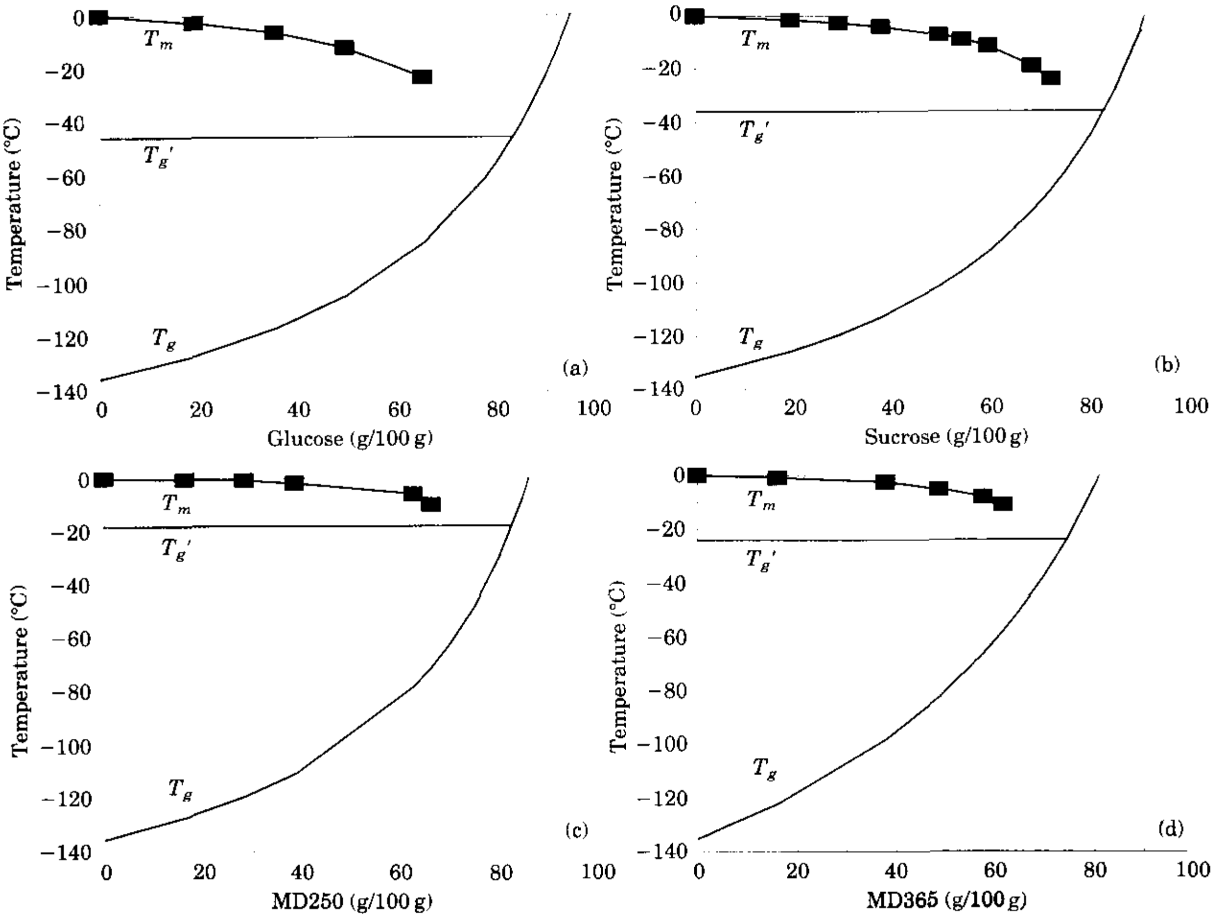

Fig. 2 State diagrams for (a) glucose, (b) sucrose, (c) M250, and (d) M365. Square symbols show phase equilibrium temperature (T_m); T_g'-glass transition temperature of the maximally freeze-concentrated matrix; T_g-calculated glass transition of ice did not form

measurements were taken at several rotational speeds. Up to three different spindle sizes were required to cover all ranges of viscosity. A thermocouple was placed near the rotating spindle to record the temperature, then removed just before viscosity measurement. The temperature throughout the solution varied by 0.5 °C at most. Immediately following viscosity measurements, samples of the solution were withdrawn and the solute concentration redetermined with the refractometer. In most cases, the solution concentration had not changed more than 1–2% from the initial concentration. Estimates of T_g were made from concentrations measured after the system had reached steady state; thus, they corresponded to viscosity measurements of the same steady state system.

Results

State diagrams for each of the solutions studied are shown in **Fig. 2**. T_m values as measured by DSC are shown as square symbols. T_g values were calculated from Equation 5 as a function of solute concentration, and are represented by the lower curve beginning at −135 °C. T_g' values were determined by DSC; T_g' appears as a horizontal line at constant temperature. Measured values for T_g' were −43.5 °C (glucose), −35 °C (sucrose), −22.5 °C (M365), −18.5 °C (M250). These are similar to values shown by Slade and Levine of −43 °C, −32 °C, −22.5 °C, −17.5 °C, respectively (1).

Arrhenius plots of the viscosity data are shown in **Fig. 3**. The data for each sugar or polymer were fairly linear. The data were not, however, colinear. Best fitting lines were determined by linear regression analy-

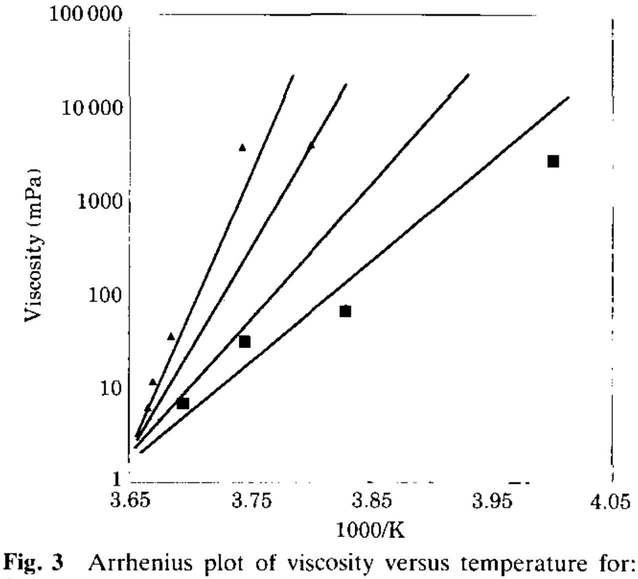

Fig. 3 Arrhenius plot of viscosity versus temperature for: (■) glucose; (□) sucrose; (▲) MD250; and (△) MD365

sis. The apparent activation energies were calculated from the slopes and increased in the order: glucose (E_A = 168 kJ/K·mol, r = 0.98), sucrose (E_A = 270 kJ/K·mol, r = 0.99), M365 (E_A = 435 kJ/K·mol, r = 0.99), and M250 (E_A = 464 kJ/K·mol, r = 0.93).

An iterative computer routine was used to analyse the data according to the VTF equation (Eqn 2). The value of T_0 was varied between 0 °K and 280 °K, then $ln\eta$ was plotted against $1/(T - T_0)$. The correlation coefficient for the best fitting line was determined at each value of T_0. In all cases, the best fit was obtained with T_0 = 0 °K, in which case Equation 2 reduces to the form of Equation 1.

The data were analysed for WLF kinetics as follows. Inverting Equation 3 gives:

$$\frac{1}{LOG\,(\eta/\eta_g)} = -\frac{C_2}{C_1}\frac{1}{(T - T_g)} - \frac{1}{C_1} \qquad \text{Eqn (6)}$$

Thus, a plot of the inverse of the logarithm of viscosity versus $1/(T - T_g)$ should yield a straight line if WLF theory applies. Such a plot is shown in **Fig. 4**, using both the constant T_g' values and the concentration-dependent T_g values. Viscosity data plotted against $1/(T - T_g)$ were colinear and clustered around the solid line describing the WLF equation using the constants C_1 = 17.44 and C_2 = 51.6. Linear regression of all data gave constants of C_1 = 16.5 and C_2 = 37.5 ($\eta_g = 10^{12}$, r = 0.95) (**Table 1**). The fit was slightly better when the data for each sugar were considered individually. C_1 values ranged from 16.1 (M365) to 19.4 (M250); C_2 ranged from 36.4 (M365) to 58.2 (sucrose). The calculated constants for each group are shown in **Table 1**.

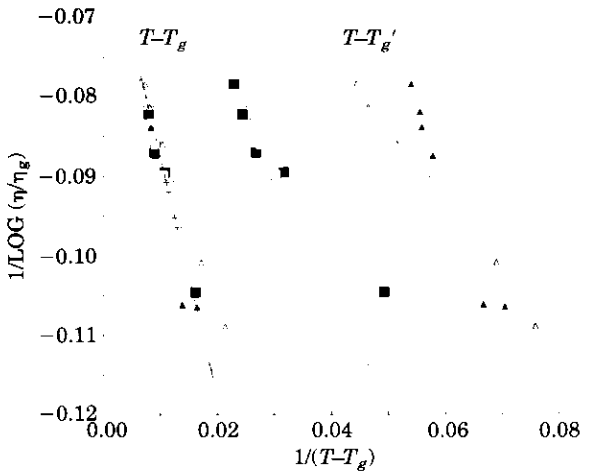

Fig. 4 WLF plot of relative viscosity versus $T - T_g$ or $T - T_g'$ for: (■) glucose; (□) sucrose; (▲) MD250; and (△) MD365

When plotted against $1/(T - T_g')$, the data no longer clustered around a single line. Linear regression of all data gave a correlation coefficient of only 0.55 (**Table 1**). However, when each sugar was considered individually, the curves were highly correlated (r > 0.97). The constants C_1 and C_2 are also shown in **Table 1**. C_1 ranged from 16.7 (glucose) to 57.1 (M250); C_2 ranged from 15.4 (glucose) to 102.9 (M250). The variation among the constants was greater in this case than when the viscosity data was plotted against $1/(T - T_g)$. In addition, there was a greater difference with the 'universal' WLF constants.

In **Fig. 5**, LOGη is shown plotted against LOG$(T - T_g)$ [or LOG$(T - T_g')$]. From this, the power law coefficients of Equation 4 were calculated (**Table 1**). As can be seen, the total data tended to cluster around a single line when plotted against LOG$(T - T_g)$. From linear regression analysis, the constants were calculated as $\kappa = 10^{18.6}$ and $m = -8.54$ (r = 0.97). Linear regression of the data for each sugar or polymer gave a slightly better fit (r > 0.97). Derived constants are shown in **Table 1**. The constant κ ranged from $10^{16.4}$ (M365) to $10^{21.7}$ (M250); m ranged from 7.6 (M365) to 9.8 (M250).

When LOGη was plotted against LOG$(T - T_g')$, the total data were not colinear (r = 0.57). The correlation for each sugar or polymer group was much better (**Table 1**). The range of the constants was larger than when the data were plotted against LOG$(T - T_g)$. Here, κ ranged from $10^{13.2}$ (M250) to $10^{22.8}$ (sucrose); m ranged from 8.9 (glucose) to 13.9 (sucrose).

Discussion

The viscosity data for sugar and maltodextrin solutions coexisting with ice were examined in terms of several existing models describing temperature dependency. The temperature range studied was limited for each system to 0 °C. to that temperature at which the viscosity reached about 10^6 mPa. This lower temperature was related to T_g', in that systems with higher T_g' values showed higher temperatures at which the viscosity measurement was limited. In practice, the ranges were: glucose (0 to −23 °C), sucrose (0 to −18 °C), M 365 (0 to −11 °C), and M250 (0 to −10 °C).

Plots of LOGη versus $1/T$ were fairly linear for each sugar or maltodextrin; however, each showed a unique effective activation energy (E_A) ranging from 168 kJ/K·mol for glucose, to 464 kJ/K·mol for M250. There is no reason that an Arrhenius relationship should apply in this case. The activation energy associated with viscous drag among molecules depends upon both the types of molecules involved and their relative concentrations. In our studies, molecules of various molecular weights were used. In addition, solute concentrations varied with temperature at different sub-freezing temperatures, due to the effects of freeze-concentration.

In contrast, all data could be fit to a single curve using the WLF or power law equations with T_g as the reference temperature. With T_g' as a reference, no single relationship was found. This does not mean that all data must be fit with the same constants. Indeed, better fits were obtained for each sugar or maltodextrin using similar but different constants. However, good fits were obtained for all data using the constants C_1 = 16.5 and C_2 = 37.5 for the WLF model (r = 0.95, $\eta_g = 10^{12}$ Pa.s), and $\kappa = 10^{18.6}$ and m = 8.5 for the power law model (r = 0.97). It is of interest that the C_1 and C_2 constants are of the same order as the average constants of C_1 = 17.4 and C_2 = 51.6, as first described by

Table 1 WLF and power law constants from viscosity data using T_g and T_g' as reference

Sample	Ref. temp.	η_g (Pa)	C_1	C_2	r	κ	m	r
Glucose	T_g	10^{12}	16.8	37.5	0.95	$10^{18.6}$	8.5	0.97
		10^{11}	15.4	69.9	0.94			
		10^{13}	18.6	35.4	0.95			
Sucrose	T_g	10^{12}	18.1	58.2	0.99	$10^{21.4}$	8.8	0.99
		10^{11}	17.7	94.4	0.98			
		10^{13}	19.6	42.2	0.99			
M250	T_g	10^{12}	19.4	74.1	0.98	$10^{21.7}$	9.8	0.99
		10^{11}	19.5	121.1	0.98			
		10^{13}	20.6	53.4	0.98			
M365	T_g	10^{12}	16.1	36.4	0.99	$10^{16.4}$	7.6	0.99
		10^{11}	14.6	53.7	0.98			
		10^{13}	18.0	27.6	0.98			
All	T_g	10^{12}	16.5	37.5	0.95	$10^{18.6}$	8.5	0.97
		10^{11}	15.2	66.4	0.94			
		10^{13}	18.3	33.1	0.95			
Glucose	T_g'	10^{12}	16.7	15.4	0.98	$10^{15.2}$	8.9	0.97
		10^{11}	15.4	22.9	0.98			
		10^{13}	18.6	11.6	0.98			
Sucrose	T_g'	10^{12}	24.1	37.7	0.97	$10^{22.8}$	13.9	0.99
		10^{11}	30.1	77.9	0.99			
		10^{13}	23.9	24.9	0.99			
M250	T_g'	10^{12}	57.1	102.9	0.98	$10^{13.2}$	9.7	0.91
		10^{11}	16.3	48.0	0.98			
		10^{13}	59.5	72.5	0.98			
M365	T_g'	10^{12}	26.8	25.0	0.98	$10^{16.7}$	12.0	0.98
		10^{11}	35.3	53.6	0.99			
		10^{13}	25.8	16.3	0.99			
All	T_g'	10^{12}	13.5	4.9	0.55	$10^{6.8}$	3.7	0.57
		10^{11}	11.4	6.8	0.56			
		10^{13}	15.7	3.8	0.55			

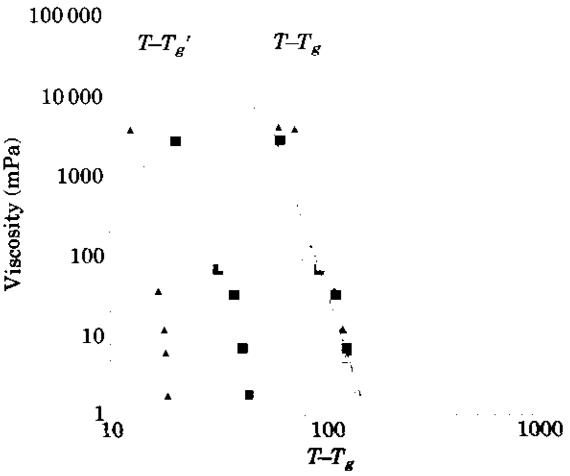

Fig. 5 Power law plot of viscosity versus $T - T_g$ or $T - T_g'$ for: (■) glucose; (□) sucrose; (▲) MD250; and (△) MD365

Williams, Landel, and Ferry (4). These authors found that the viscosities of a variety of organic and inorganic liquids could be described by a single equation. In addition, Ollett and Parker (10) fit the WLF equation to viscosity data for fructose by assuming T_g = 286 °K (13 °C). There is no reason, however, why a single set of constants should apply to all liquids (14). Using data from Ferry (13), Peleg (14) showed that for a variety of polymers, C_1 varied from 11.2 to 16.2 while C_2 varied from 24 to 107.4 °K.

The present data suggest that T_g may be a more universal reference temperature than T_g' for describing relaxation properties in the rubbery liquid at temperatures below T_m. We were not able to measure very high viscosities, and so were restricted to temperatures about 10 to 20 °C above T_g'. As such, we cannot extrapolate our results to temperatures very close to T_g'. It is clear, though, that within the accessible temperature range, using T_g as a reference temperature gave a more uniform fit of all data than did T_g'. When each solution was considered individually, the data were well fit with the WLF and power law equations, with either T_g or T_g' used as the reference temperature. With T_g', however, the range of constants was much greater (**Table 1**).

There have been several attempts to describe diffusion-related processes in terms of WLF kinetics using T_g' as the reference temperature (1). It may be the case that rate processes can be correlated with $T - T_g'$ for particular groups of solutes. For example, Kerr *et al.* (2) found that the log rate of disodium nitrophenol phosphate hydrolysis was a linear function of $T - T_g'$ for a group of maltodextrins and showed a different linear dependence for a group of sugars. Indeed, as shown here, data for glucose and sucrose tend to cluster around one line, as do those for M250 and M365, when T_g' is used as a reference. T_g' is of technological significance in that it describes the transformation from an immobile ice-glass system to a mobile ice-unfrozen liquid system. As such, chemical reactions below T_g' are negligible (15) and T_g' can be correlated with several collapse phenomena such as recrystallization or onset of stickiness (1).

It should be noted that Slade and Levine (1) argue that T_g corresponds to an artificial state, while T_g' offers a 'practical reference state' for frozen systems. We would agree that T_g' is indeed more practical, as it is easier to measure and independent of concentration. In addition, realization of a pure glassy state, with transition temperature T_g, is difficult and not usually attained in high moisture systems. It has been suggested by Simatos *et al.* (22), however, that T_g' is not the appropriate reference temperature for use with the WLF equation. They point out that as a frozen system is warmed above T_g', the viscosity will decrease both according to temperature effects on free-volume (T_g dependent) as well as to decreasing solute concentration).

There have been cautions against using glass transitions as a parameter for describing rate processes at temperatures above T_g (13,14). For example, it is known that T_g depends upon the rates of cooling and heating (23). However, for cooling rates of 0.5 to 120°C/min, and heating rates of 0.5 to 60°C/min, we found no significant differences in the onset of T_g' as measured by differential scanning calorimetry.

It is also a questionable practice to extrapolate viscosity values to temperatures well below that at which viscosity measurements are made. Although we did not extrapolate measurements, we did assume a viscosity at the glass transition of 10^{12} Pa. Some researchers have suggested this value as being characteristic of the transition from rubbery liquid to glass (15–17).

Work such as that by Soesanto and Williams (8) indicates that η_g may not be invariant; for example, they show that η_g varies from about 6×10^{11} Pa to 3×10^{12} Pa as mole fraction of sugar varies from 0.4 to 0.7. By assuming a constant value of η_g, reasonable fits were obtained for the group of sugars and polymers under study. We had tried other assumptions for n_g, such as $n_g = 10^{11}$ or $n_g = 10^{13}$ Pa, as shown in **Table 1**. While such assumptions did result in changes in the derived constants, the goodness of fit was not significantly different than that found when $n_g = 10^{12}$ Pa was assumed. For example, when considering data for all solutions and using T_g as a reference, we found C_1 = 15.2, 16.5, and 18.4 and C_2 = 66.4, 37.5, and 33.1, respectively, for $n_g = 10^{11}$, 10^{12}, and 10^{13} Pa. The correlation coefficients were 0.94, 0.95, and 0.94. Similarly, when T_g' was used as a reference, the correlation coefficients were 0.56, 0.56, and 0.55. Given the observations of Soesanto and Williams (8), it may be more correct to use a reference viscosity n_g that varies with concentration. We were unable to test this idea, as we had no information as to what this function is for each of our solutions.

A slightly better fit was obtained using a power law model. Here, while the relationship between η and $(T - T_g)$ is retained, there is no need to specify η_g. Hill and Dissado (7) show that the WLF equation is an approximation to the power-law description of relaxation. Murthy (19) found that the power-law equation accurately described the temperature dependence of relaxation processes for a wide variety of glass-forming materials.

Each of the models described is a function of either an implicit or explicit reference temperature. For the Arrhenius model, this reference is 0°K (1). For the VTF model, it is T_0, the fictive temperature at which the free volume goes to zero. The WLF and power law models, as described here, use the glass transition temperature as a reference. While both T_g' and T_g could be used as references, we found that T_g came closest to forming a universal relationship for both the polymer and sugar solutions, within the temperature ranges examined. As first noted by Williams *et al.* (4), it is quite possible to use another reference temperature $T_s > T_g$, while retaining the form of Equation 3. We have used the glass transition as a reference because it is a measurable quantity, even though this approach does not allow one to verify the viscosity at the reference temperature. In addition, because we were working with a system in which T_g varied from −135°C to −18°C as solute concentration increased, we could not justify fitting a single reference temperature to the data.

In conclusion, we note that the WLF and power law equations reasonably describe the viscosity–temperature relationship for a small group of carbohydrate solutions in the presence of ice. In future work, we hope to further investigate relaxation processes in other solutions as well as in frozen foods.

Acknowledgements

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