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A comparative study of the dielectric relaxation behaviour of glucose, maltose, and their mixtures with water in the liquid and glassy states

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Abstract

The dielectric relaxation behaviour of glucose, maltose, and their mixtures with water up to a concentration of 12.0 and 23.0% w/w, respectively, were examined in the frequency range 10^2 to 10^5 Hz. A primary relaxation was observed at temperatures above the glass transition temperature, T_g, and a secondary relaxation at sub-T_g temperatures. The addition of water shifted the primary relaxations to lower temperatures. For the glucose mixtures, water increased the strength of the secondary relaxation and resulted in a merging of the primary and secondary relaxations. The increase in strength of the secondary relaxation was much more marked for the maltose–water mixtures and, in this case, the relaxations remained separate over the range of frequency and water contents studied. For the maltose–water mixtures, the dependence of the strength of the secondary relaxation on the water content was bilinear with a change in gradient at ~ 10.0% w/w water. The sub-T_g relaxations were thought to arise from motions of pendant hydroxymethyl groups attached to the hexose rings and from the reorientation of water molecules. The difference in the secondary relaxation behaviour of glucose and maltose indicates that structural factors, in addition to the presence of hydroxymethyl groups, are also important.

Keywords: Dielectric relaxation; Glass transition; Glucose; Maltose; Water

1. Introduction

Vitreous carbohydrates are widely used to stabilise and encapsulate such labile molecules as food ingredients [1], and therapeutic proteins and peptides [2]. The glass

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transition is also relevant to the use of carbohydrate polymers as structural materials [3]. In both applications water can play a key role since it is a very potent plasticiser [4]. In developing a physico-chemical basis for the preservative and encapsulating action of saccharides and other poly-hydroxy compounds, it is important to understand how molecular structure and water content affect molecular mobility and, more specifically, potentially deleterious chemical reactions [5].

The glass transition temperature, T_g, of carbohydrates is weakly dependent on structure [6], with a much stronger dependence on molecular weight [7]. Undercooled carbohydrate liquids are classified as "fragile" [8], with the dependence of shear viscosity on temperature becoming stronger as the liquid is cooled and T_g is approached [9]. Comparatively little is known about their molecular dynamics, particularly in the glassy state. Dielectric relaxation studies [10] on undercooled pentopyranoses show a primary, α-relaxation associated with molecular reorientation in the viscous liquid. The hexopyranoses [10–12] have, in addition, a clearly distinguishable secondary, β-relaxation, below the calorimetric T_g, which is thought to be associated with the motion of the pendant hydroxymethyl group. The addition of water depresses the calorimetric T_g of glucose and the corresponding dielectric α-relaxations [11], with the α- and β-relaxations merging at high water content (> 30% w/w).

Recent NMR relaxation studies [13,14] on liquid sucrose–water mixtures have shown that the motions of the constituent glucose and fructose rings, their pendant hydroxymethyl groups, and the water molecules decouple at water contents below 40% w/w. ^{13}C NMR relaxation studies [13] found evidence that the pendant hydroxymethyl groups possessed greater mobility than the hexose rings to which they are attached, and that these motions were independent of viscosity. These observations are consistent with predictions [8] of a strong β-relaxation in sucrose glasses based upon the results of a calorimetric study [15]. ESR studies have further probed mobility in sucrose–water [16] and maltodextrin–water [17] systems, and have shown that the probes remain mobile within the glass, with the rotational correlation time and its activation energy being sensitive to composition.

In the present study the dielectric relaxation behaviour of D-glucose, maltose, and their mixtures with water were characterised. The objective was to obtain a measure of molecular mobility in highly viscous amorphous saccharides and to investigate how this was affected by water content and the molecular structure of the saccharide. The work complements earlier calorimetric and viscometric studies [7,18] of malto-oligomer–water mixtures in the glass transition region. Differences between the sugars indicate the initial trend from monomeric to oligomeric behaviour and can give insight into the behaviour of the polymer [7].

2. Materials and methods

D-Glucose and maltose monohydrate were purchased from Sigma Chemical Co. and used without further purification. Chemical structures are shown, in the α form of their pyranose cyclic structures, in Fig. 1. Water was freshly distilled with a conductivity < 1 $\mu S\ m^{-1}$. The T_g values of the amorphous carbohydrates were determined by calorimetry using a Perkin–Elmer DSC2 calorimeter to measure heat capacity as described

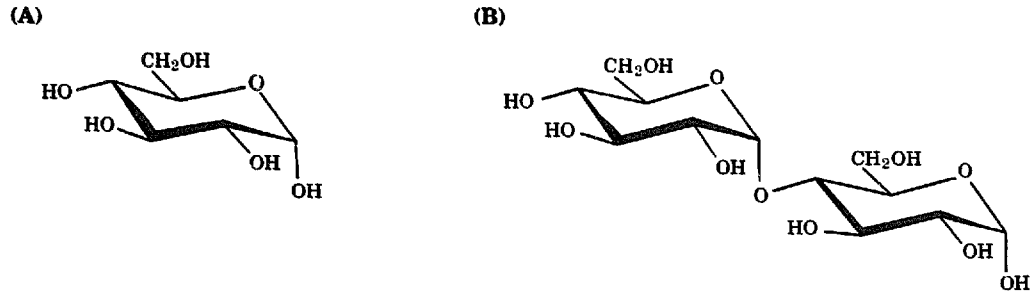

Fig. 1. The cyclic (pyranose) structures of (A) α-D-glucose and (B) α-maltose.

previously [18]. T_g was taken to be the mid-point between the onset and end temperatures. Whereas the dry glucose for dielectric studies could be prepared simply by melting the dry anhydrous crystals, the dry maltose sample was prepared by drying a melt of the monohydrate in a vacuum oven over P_2O_5 at 60 °C. To obtain sugar–water mixtures the samples of the appropriate water content were melted in sealed tubes at 130 °C. The hot liquids were poured onto the lower electrode of the dielectric cell and the upper electrode mounted in place within the cell holder. A dielectric thermal analyser (Rheometrics Scientific, Loughborough) equipped with a General Radio 1689M Precision RLC Digibridge and a stainless steel parallel-plate cell (diameter, 33 mm; typical gap, 0.5 mm) was used for measurements of capacitance and dissipation factor [10]. The temperature was controlled between −130 and 140 °C using a liquid N_2 cryostat and electric heating elements surrounding the sample cell within an enclosure. The bridge was zeroed at 1 kHz on a regular basis to correct for stray capacitances and resistance in the leads and cell. Measurements of the dielectric constant, $\epsilon'(T)$, and dielectric loss, $\epsilon''(T)$, were made at 9 frequencies in the range 100 Hz to 100 kHz, as the temperature was linearly ramped at 1 °C min^{-1}. In this study no attempt was made to characterise any effects of thermal history on the dielectric properties [19–22]. The initial quench of the sample to the starting temperature was at ca. 5 °C min^{-1}, and was followed by a 5 min wait to achieve thermal equilibrium before the upward temperature scan was started. Data were fitted to cubic splines, and isothermal values obtained by interpolation.

At the higher temperatures and water contents, dielectric behaviour was affected by sample conductivity. Dielectric loss data were corrected for conduction, assuming that the conductivity gave rise to an additive contribution of the form, $\epsilon''_c = \sigma/2\pi\epsilon_0 f$, where σ is the conductivity, ϵ_0 is the permittivity of free space, and f is the frequency. At temperatures typical of the α-relaxation the conductivity of pure maltose is a factor of ~ 10 greater than that of glucose, and, in both cases, is greatly increased by the addition of water. Conductivity measurements [23] on maltose–water–KCl mixtures show that the conductivity of nominally pure 12.1% w/w water–maltose is equivalent to a mixture containing 80 ppm KCl.

3. Results

The effect of water content on the calorimetric glass transition temperature of glucose and maltose is shown in Fig. 2. New data are included, together with those of Green and

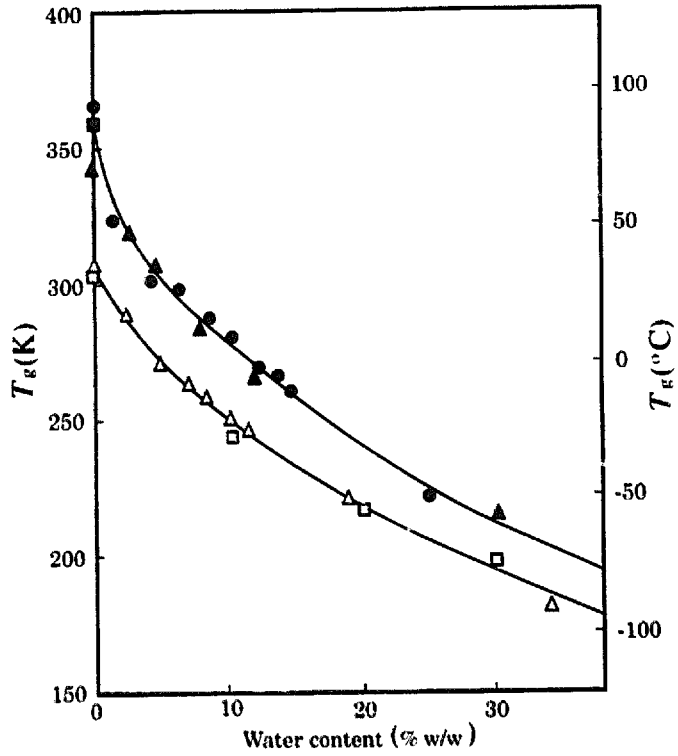

Fig. 2. The variation of glass transition temperature with water content: ○, △, □, ▷glucose; and ●, ▲, ■, maltose; measured by ourselves [7,18], Green and Angell [15], and Roos [24], respectively.

Angell [15], Roos [24] (glucose–water and dry maltose only), and ourselves [7,18]. The values of T_g reported by these other workers are for the onset of the glass transition which is 5–8 °C below the mid-point [24]. The T_g of the dry carbohydrates was 38 °C for glucose and 95 °C for maltose, showing the strong effect of molecular weight. As the water content increased to 30% w/w, the T_g values of glucose and maltose were depressed by 100 and 150 °C, respectively. The data in Fig. 2 were used to interpolate the T_g values of the samples used in the dielectric studies (Table 1).

Table 1
The glass transition temperatures of the sugars and their water mixtures

Glucose–water		Maltose–water	
Water content (% w/w)	T_g (°C)	Water content (% w/w)	T_g (°C)
0.0	30.0	0.0	95.0
5.0	3.0	7.0	19.0
7.0	−8.0	10.0	5.0
12.0	−21.0	11.5	0.0
		15.0	−12.0
		19.0	−27.0
		20.0	−31.0
		23.0	−42.0

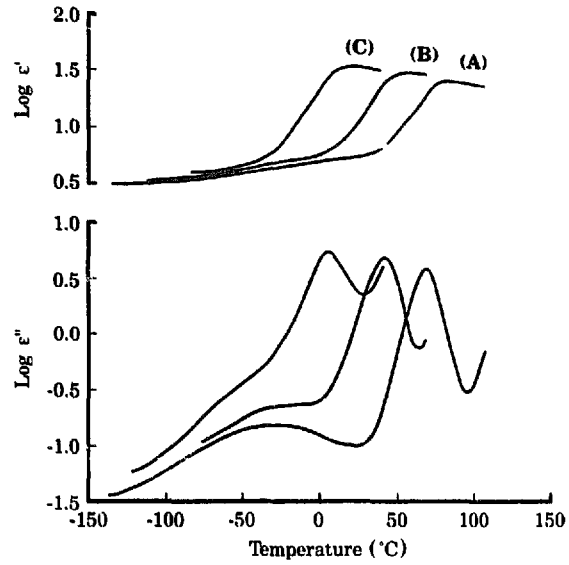

Fig. 3. A plot of the dielectric constant (ϵ') and dielectric loss (ϵ'') against temperature at 10 kHz for (A) pure D-glucose, (B) a 5.0% w/w water–glucose mixture, and (C) a 12.0% w/w water–glucose mixture.

The dielectric constant, ϵ', and dielectric loss, ϵ'', at 10 kHz as a function of temperature for glucose–water and maltose–water mixtures are shown in Figs. 3 and 4, respectively. For the dry carbohydrates, α- and β-relaxations are observed as peaks in ϵ'', at temperatures above and below the calorimetric T_g, respectively. The ϵ' increases to a limited extent with temperature over the range of the β-relaxation, followed by a

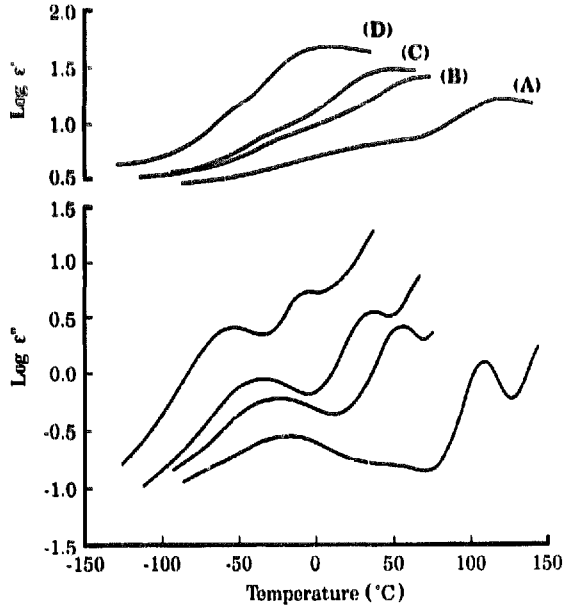

Fig. 4. A plot of the dielectric constant (ϵ') and dielectric loss (ϵ'') against temperature at 10 kHz for (A) pure maltose, (B) a 7.0% w/w water–maltose mixture, (C) a 11.5% w/w water–maltose mixture, and (D) a 20.0% w/w water–maltose mixture.

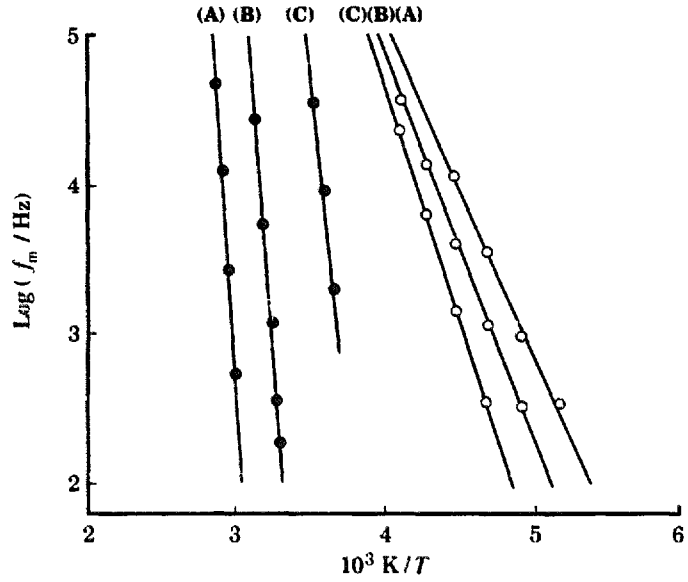

Fig. 5. A plot of the frequency of the maxima in the loss peaks of the α- and β-relaxations against reciprocal temperature: ●, α-relaxation; ○, β-relaxation; (A) pure D-glucose, (B) a 5.0% w/w water–glucose mixture, and (C) a 12.0% w/w water–glucose mixture.

larger increase in the supercooled liquid over the range of the α-relaxation. At higher temperatures, once the α-relaxation is fully relaxed, ϵ' decreases with increasing temperature. On addition of water the α-relaxation is shifted to lower temperature.

A qualitative difference between the two carbohydrates is the effect of increasing water content on the relative positions of the α- and β-relaxations. Whereas for glucose the two relaxations converge, for maltose the two relaxations remain distinct, the β-relaxation shifting to lower temperatures in a similar way to the α-relaxation. This effect can also be seen in the relaxation maps [1,2], Figs. 5 and 6, in which the frequencies of the maxima in the dielectric loss spectra, f_m, are plotted against reciprocal temperature for glucose–water mixtures containing up to 12.0% w/w water, and for maltose–water mixtures containing up to 23.0% w/w water. With the frequency range used in this study the variation of log f_m with $1/T$ is linear, corresponding to (apparent) Arrhenius behaviour for both the α- and β-processes. Data over a wider

[1] It is worth noting that the peaks in Figs. 5 and 6 correspond to $\partial\epsilon''/\partial f = 0$, whereas those in Figs. 3 and 4 correspond to $\partial\epsilon''/\partial T = 0$. The relative positions of these two maxima depend on the shape of the $\epsilon''(f,T)$ surface. Whereas for the α-relaxations in this study the maxima are within a few K of each other, for the β-relaxation they are well separated. Indeed, in Fig. 3, no $\partial\epsilon''/\partial T$ maximum is apparent at 12.0% w/w water though in the ϵ'' spectra a $\partial\epsilon''/\partial f$ peak is observed.

[2] On the basis of more extensive dielectric and calorimetric measurements and a different analysis, Gangasharan and Murthy [12] have recently proposed a different relaxation map in which the β-relaxation is resolved into two overlapping relaxations termed α_2 and β. In order to obtain this resolution it is necessary to assume that the β-relaxation consists of two depressed Cole–Cole arcs. Whilst from a physical point of view the relaxation map gives one possible explanation of their calorimetric results, from a statistical viewpoint no justification in terms of significance is presented for the introduction of further parameters to model the relaxation.

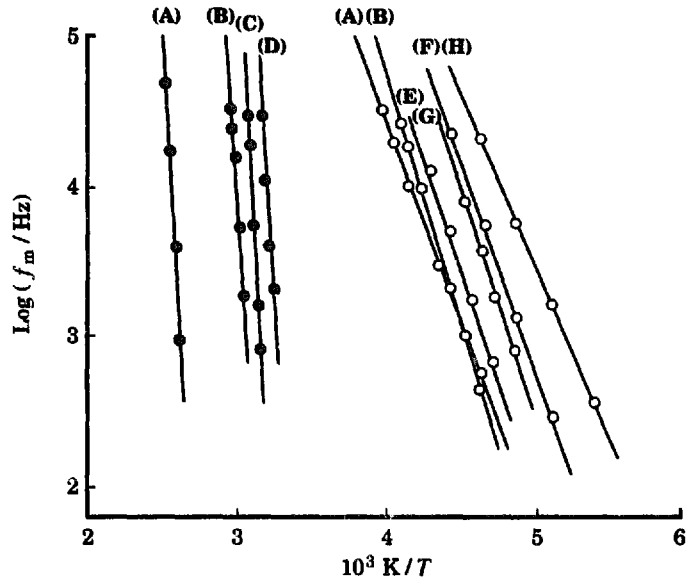

Fig. 6. A plot of the frequency of the maxima in the loss peaks of the α- and β-relaxations against reciprocal temperature: ●, α-relaxation; ○, β-relaxation; water content of maltose–water mixtures: (A) 0.0% w/w; (B) 7.0% w/w; (C) 10.0% w/w; (D) 11.5% w/w; (E) 15.0% w/w; (F) 19.0% w/w; (G) 20.0% w/w; (H) 23.0% w/w. The β-relaxation curves for (C) and (D) overlay those of (B) and were omitted for clarity.

frequency range would be required to characterise the non-Arrhenius behaviour of the α-process [9,11,12]. The convergence of the α- and β-relaxations of D-glucose with increasing water content is clearly seen in the relaxation map, Fig. 5. In contrast the behaviour of maltose is quite different. The initial addition of water shifts the α-relaxation to lower temperatures but has little effect on the position of the β-relaxation. Once the water content exceeds ~ 11.5% w/w, the β-loss peak shifts to lower temperatures on addition of water. For the α-relaxations the values of the activation energy obtained by linear regression ranged from 240 to 330 kJ mol^{-1} and for the β-relaxations from 42 to 63 kJ mol^{-1}. The activation energy of glucose in the region $T/T_g \approx 1.12$ can be compared with the value of 230 kJ mol^{-1} for the activation energy of the shear viscosity [25]. This indicates that the α-relaxation is coupled to the viscosity.

The reduced positions and relative strengths of the loss peaks at 1 kHz for the carbohydrate–water mixtures were also analysed and the results are shown in Table 2. The results for pure glucose were within ~ 10% of previous literature values [11]. On addition of water, the position of the α-relaxation relative to T_g, T_α/T_g, remains relatively constant, whereas T_β/T_g increases from 0.67 for the dry glucose to 0.91 for the sample containing 12.0% w/w water. Similarly, for the maltose–water mixtures, with the exception of the "dry" sample, T_α/T_g remains essentially constant with a relatively smaller increase in T_β/T_g from 0.75 to 0.82 as the water content is increased from 7.0 to 23.0% w/w. The data on the "dry" sample are less reliable as a result of the difficulty associated with maintaining a sample dry during the dielectric experiment. Even a limited sorption of water of 0.5% w/w, with its consequent effect on T_g, would be sufficient to account for the observed deviations in T_α/T_g from a constant value, i.e., independent of water content. A striking difference between the carbohydrate–water

Table 2
Reduced positions and relative strengths of α- and β-relaxations

Water content (% w/w)	T_α / T_g at 1 kHz	T_β / T_g at 1 kHz	$\epsilon''_m(\beta)/\epsilon''_m(\alpha)$ at 1 kHz	$\tan\delta_m(\beta)/\tan\delta_m(\alpha)$ at 1 kHz
Glucose–water				
0.0	1.11	0.67	0.034	0.16
5.0	1.12	0.77	0.030	0.16
12.0	1.12	0.91	0.071	0.41
Maltose–water				
0.0	1.03 [a]	0.59 [a]	0.15	0.59
7.0	1.11	0.75	0.17	0.73
10.0	1.13	0.78	0.18	0.87
11.5	1.11	0.80	0.22	0.98
15.0	–	0.81	–	–
19.0	–	0.82	–	–
20.0	–	0.84	–	–
23.0	–	0.82	–	–

[a] This apparently anomalous result may have arisen from a low water content (about 0.5% w/w).

mixtures is the relative strengths of the relaxations given by the ratios $\epsilon''_m(\beta)/\epsilon''_m(\alpha)$ and $\tan\delta_m(\beta)/\tan\delta_m(\alpha)$. For the maltose–water mixtures these are much larger, and generally large when compared with other molecular glass-forming substances [11].

Normalised loss spectra for pure maltose are shown in Fig. 7. The width at half-height was conveniently estimated by using a least-squares fitting to the data of the Jonscher function [26,27]:

$$\epsilon'' = \frac{\epsilon''_m}{(f/f_m)^m + (f/f_m)^{1-n}} \quad (1)$$

where f_m and ϵ''_m are the peak values of frequency and dielectric loss, and m and $1-n$ are power-law exponents. This functional form can be related to the other commonly used empirical functions [27], and reduces to power-law behaviour on each flank of the relaxation peak, a type of behaviour predicted by generalised models of relaxation processes. The fitting yielded $m \sim 0.61$ and $1-n \sim 0.27$, and a width at half-height of 3.0 decades. A value of $m \sim 1.0$ is equivalent to Cole–Davidson and Kohlrausch–Williams–Watts type behaviour [27] as has been observed for pure glucose [11]. The value of $m \sim 0.61$ for maltose means that this flank of the relaxation falls relatively slowly and gives rise to a wider loss peak than glucose [11] (half-width, 2.3 decades). Inaccuracies which enter through corrections for conduction meant that the loss spectra for the α-relaxations of the maltose–water mixtures were not of high precision and are not presented here. However, the β-relaxations were unaffected by this problem. The effect of water content on the shape of the normalised peak is shown in Fig. 8. As the water content is raised the loss peak narrows, the width at half-height decreasing from 5.4 decades for pure maltose, through 4.8 decades at 10.0% w/w water, to 3.6 decades at 19.0% w/w water. The effect of water content on the strength of the β-relaxation of maltose–water mixtures can be seen in Fig. 9. The loss increases with increasing water

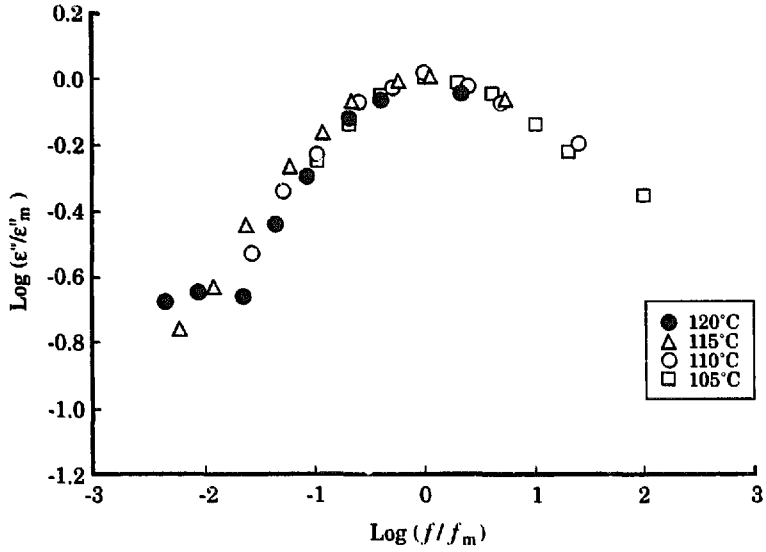

Fig. 7. Normalised plot of the α-relaxation spectrum for pure maltose.

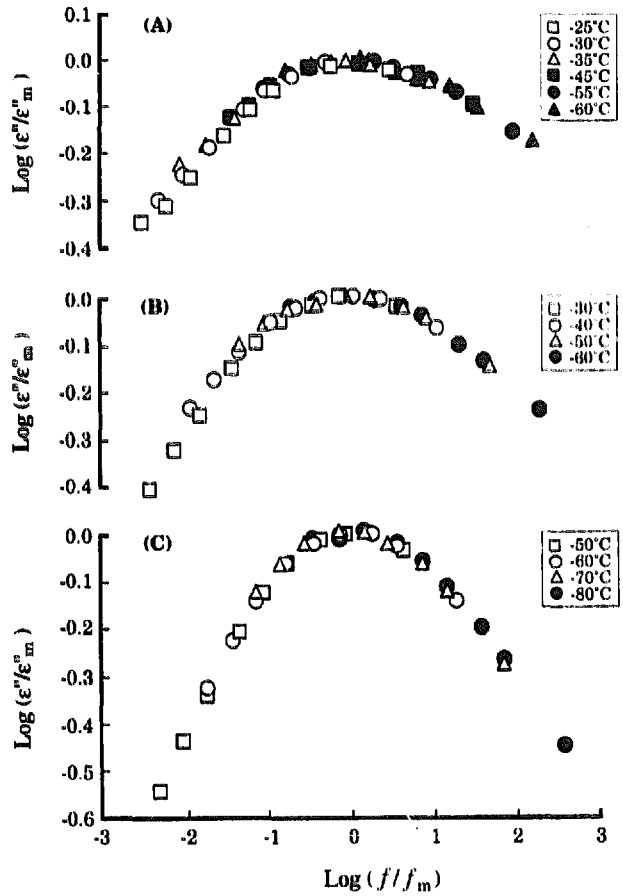

Fig. 8. Normalised plot of the β-relaxation spectrum for (A) pure maltose, (B) a 10.0% w/w water–maltose mixture, and (C) a 19.0% w/w water–maltose mixture.

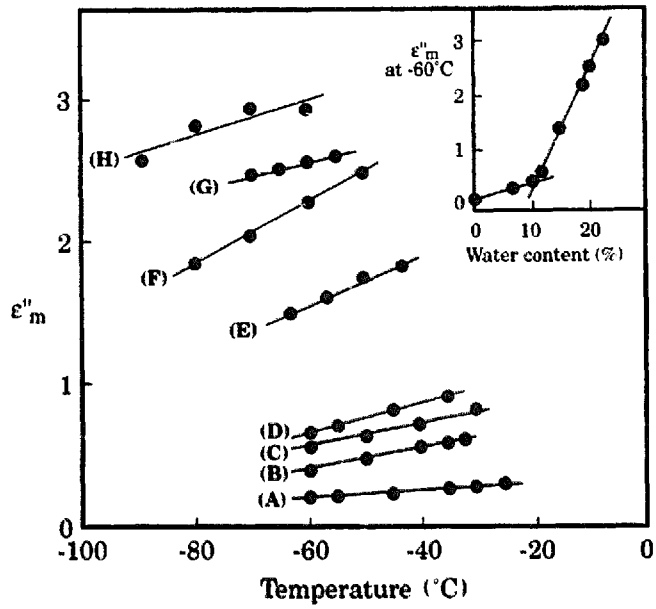

Fig. 9. The β-loss peak maximum plotted against temperature for maltose–water mixtures. The key to water contents is as in Fig. 6. Inset is the β-loss peak maximum at −60 °C plotted against water content.

content. A plot of loss as a function of water content at constant temperature (insert Fig. 9) shows a clear bilinear behaviour with the change in slope at ~ 10.0% w/w water.

4. Discussion

The dielectric relaxation behaviours of glucose and maltose are broadly similar in that both α- and β-relaxations are observed and that the effect of the addition of water is to increase the strength of the β-relaxation and shift the α-relaxation to lower temperatures. However, examining the data in more detail reveals both qualitative and quantitative differences.

At 1 kHz the α-loss peak of glucose is a factor of ~ 2.7 stronger than that of maltose with ϵ''_m ~ 3.7 and ~ 1.3, respectively. The normalised plots (Fig. 7) show that the maltose α-relaxation is broader than that of glucose [11], the main difference being the high temperature, low frequency, "relaxed" flank of the maltose loss peak. These differences may be due to the larger molecular size of maltose, its more extended shape, and more extensive distribution of dipoles. In contrast, the β-loss peak of glucose is a factor of ~ 1.6 weaker than that of maltose, with ϵ''_m ~ 0.12 and ~ 0.20, respectively. The width at half-height for the maltose β-relaxation is ~ 3.0 decades, as compared with ~ 2.3 decades for glucose. The suspicion that the maltose contains a small amount of water (~ 0.5% w/w) means that these results should be assessed with care. While the strength of the β-relaxation may be sensitive to this small amount of water, the results for glucose suggest that the strength of the α-relaxation is relatively insensitive.

The β-relaxations of glucose and maltose show qualitatively different responses to the addition of water. Whereas the addition of water to glucose causes the β-relaxation

to merge with the α-relaxation, in maltose the two relaxations remain distinct in the frequency range examined, with the β-relaxation shifting to lower temperatures at the higher water contents. At water contents in the range 10.0–11.5% w/w, the dielectric results indicate a change in the dynamics of the maltose–water glasses. As the water content is increased through this range, the relaxation map (Fig. 6) shows that the β-relaxation starts to shift to lower temperatures and ϵ''_m (Fig. 9) starts to increase more strongly. The width of the β-relaxation narrows throughout the whole water content range (Fig. 8).

A water content of 10.0% w/w corresponds to a mole fraction of 0.68, i.e., roughly two molecules of water per maltose molecule or one per glucose residue. As water is added the intermolecular hydrogen bonds between the maltose molecules are progressively being replaced by maltose–water bonds. Since the hydrogen-bonding in these systems has not been studied, the significance of this stoichiometry cannot be interpreted. Whilst some of the hydrogen-bonding potential of the sugar molecules may be frustrated, the smaller water molecules are more likely to satisfy their hydrogen-bond requirements. However, whatever the molecular basis of the effect, it is clear that the stoichiometry is critical for the mobilisation of a dipolar species whether it is a water molecule, part of a maltose molecule, or a combination of both.

There is continuing debate surrounding the origin of β-relaxations [28]. Studies of the effect of side group structure on the secondary relaxations of amorphous synthetic polymers have been interpreted in terms of the specific motions of the side groups [29,30]. However, secondary relaxations have been observed in diverse amorphous materials [19,22,31] and it has been argued that they are a universal property of the amorphous state, which originates from cooperative motions in localised loosely packed regions, and, as such, their occurrence transcends the details of molecular structure. In certain cases [32] dielectric, dynamic mechanical, and NMR techniques have been applied; these show convincingly that secondary relaxations can be assigned to the motion of particular groups, though this does not mean that the motion of these groups is not, at least partially, cooperative and/or localised in loosely packed regions. In the present systems, earlier dielectric measurements [10] on D-xylose, in which the pendant hydroxymethyl group is absent, showed no β-process, suggesting that the motion of this group is the origin for the β-process in glucose. This assignment is supported by recent ^{13}C NMR relaxation studies [13] of sucrose–water mixtures. In their studies Girlich and Ludemann reported ^{13}C NMR spin–lattice relaxation times, T_1, for supercooled liquid systems down to about 30 °C for 20% w/w water, i.e., about 80 °C above T_g [15]. Whilst the temperature dependence for the correlation time for the rotational diffusion of the ring carbons could be described by a Vogel–Tammann–Fulcher (VTF) equation, $\tau_c = \tau_\infty \exp(B/T - T_0)$, those for the carbons in pendant hydroxymethyl groups followed Arrhenius behaviour with activation energies ~ 20 kJ mol^{-1}. In the sugar–water mixtures there is also potential for dielectric relaxation due to reorientation of water molecules. Evidence from recently published NMR studies [14] supports the proposals that the progressive increase in the strength of the β-relaxation on addition of water is in part due to the reorientation of water in the carbohydrate mixtures. Using ^{2}H NMR T_1 measurements [14] Girlich and Ludemann studied sucrose–water mixtures across the entire supercooled range down to about 0 °C for a 10% w/w water mixture, i.e., within

~ 10 °C of T_g [15]. Their analysis indicated that, at water contents less than 40% w/w, the rotational mobility of water followed a VTF dependence with a T_0 ~ 120 K which is 15 K below the T_g for liquid water. This value of T_0 is 130 K below the T_0 for the motions of the ring carbons of the sucrose in a 10% w/w water mixture and indicates that the rotations of the water and ring carbons are uncoupled. This also means that the reorientation of the water is not coupled to the viscosity of the mixture. Extrapolating these results into the glass range and to low contents of water suggests that a contribution from the motions of both hydroxymethyl groups and water to the sub-T_g relaxations would be expected. A further contribution to the β-process in oligosaccharides could come from the relative motion of the pyranose rings. The differences in the secondary relaxation behaviour of glucose and maltose suggest that the β-relaxation must be affected by structural factors in addition to the presence of hydroxymethyl groups which are common to both molecules. The maltose–water glasses of low water content represent a further complication since there is a qualitative change in the dipolar dynamics at ~ 10.0–11.5% w/w water. This means that the dynamics of low water (< 10.0% w/w water) systems are distinct and cannot be fully understood by extrapolation from higher water contents.

The qualitative difference between the behaviour of glucose–water and maltose–water mixtures seems surprising given that maltose is a dimer of glucose. The only structural difference is that in maltose two D-glucose molecules are linked by an α-(1 → 4)-D-glucosidic bond. It seems unlikely this would have a large effect on the position of water molecules and the individual dipoles on the sugars. Additionally it is known that the β anomer of maltose forms an intramolecular hydrogen bond between its glucose rings in its crystalline form [33] though this is thought to be absent in dilute aqueous solution [34]. A bond of this type would reduce torsional freedom about the glucosidic linkage and would introduce an intramolecular constraint on the areas of conformational space accessible to the molecule.

The qualitatively different behaviour of glucose–water and maltose–water mixtures could have important practical consequences related to mobility within vitreous carbohydrate matrices. For example, at a water content of 20.0% w/w, a typical concentration for a maximally freeze-concentrated sugar solution [35,36], the dipolar dynamics and, presumably, the molecular dynamics, in general, of the mixtures are quite different. As a sample of glucose–water is cooled through the glass transition region, the dipolar motions are locked up in a single broad transition. By comparison, as a sample of maltose–water is cooled through the transition, while the motions associated with the α-relaxation are locked up there remains the relatively strong β-process allowing dipolar relaxation. The potential practical significance is that, compared to glucose–water glasses, maltose–water mixtures have more substantial mobility within the glass, and that this residual mobility is composition dependent, increasing with water content. Although the relationship of this residual mobility to translational diffusion [37] needs to be examined, this observation does suggest that molecular aspects of vitrification need to be considered, and that vitrification alone is insufficient to immobilise molecules, with potential implications for encapsulation and protection. The question of whether either of these types of dynamic behaviour is anomalous or part of a wider, complex picture of dynamics in sugar–water glasses will have to await further measurements.

5. Conclusions

The dielectric relaxation behaviours of the sugar glasses in this study were qualitatively different, with the secondary relaxation in the maltose–water mixtures being particularly strong. It is proposed that the motion of both water and pendant hydroxymethyl groups contributed to the relaxation. A similar conclusion has recently been reported for the motion of water molecules in highly concentrated solutions of disaccharides as studied using ^{13}C and ^{2}H NMR spectroscopy [13,14]. These experimental approaches are complementary in that dielectric techniques have a larger dynamic range and allow measurements on glassy samples, while liquid-state NMR techniques permit the assignment of particular motions above T_g. The differences in the secondary relaxations of glucose–water and maltose–water mixtures indicate that this relaxation is sensitive to molecular structure and does not arise simply from the additive contributions of independently relaxing hydroxymethyl groups and water molecules.

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