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Effect of molecular structure on the conductivity of amorphous carbohydrate–water–KCl mixtures in the supercooled liquid state

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Abstract

The effect of carbohydrate structure on the conductivity of low water content amorphous carbohydrate–water, and carbohydrate–water–KCl mixtures, has been measured using both direct current and alternating current techniques at temperatures in the supercooled liquid and glassy range, ranging from -40 to 80 °C. The structures included homologous mono-, di- and trisaccharides (glucose, maltose and maltotriose), a monosaccharide with no exocyclic hydroxymethyl group (xylose) and a second trisaccharide (raffinose). The KCl-mixtures contained 9.3% w/w water and 0.74% w/w KCl which resulted in calorimetric glass transition temperatures, T_g, in the range -29–19 °C. At this concentration conduction due to KCl dominated that due to intrinsic conductors originating from the carbohydrates and water. In the supercooled liquid region, as temperature, T, is reduced to T_g, the activation energy of the molar conductivity of KCl, Λ_m, increased as described by a Vogel–Tamman–Fulcher-type equation, $\Lambda_m = \Lambda_{m0}\exp[B/(T-T_0)]$, where Λ_{m0}, B and T_0 are constants. Comparison of the molar conductivity of KCl in the carbohydrate mixtures at T_g with that in aqueous solutions showed that conductivity is, to varying extents, uncoupled from viscosity. The uncoupling increased in the order D-xylose < D-glucose < maltose < maltotriose and raffinose. The results suggest that the primary structural characteristic determining conductivity is molecular weight, though the presence of the exocyclic hydroxymethyl group in the monosaccharide also has an effect. Whilst at T_g the D-xylose mixture had the lowest conductivity, at a particular temperature the trisaccharide mixtures of maltotriose and raffinose had the lowest conductivities.

Keywords: Conductivity; Carbohydrate; Supercooled liquid; Molecular structures

1. Introduction

At low water contents and temperatures amorphous carbohydrates form hydrogen-bonded glasses.[1,2] Glassy and near glassy carbohydrates occur in nature[3] and are also used technologically for encapsulation[4] and preservation.[5,6] The relatively limited molecular mobility in these highly viscous states has been linked to the low matrix permeability necessary for encapsulation and the retardation of deteriorative processes necessary for preservation.[7] The kinetics of these processes depend upon the molecular dynamics in amorphous carbohydrate-rich mixtures.

Measurements of small molecule and probe diffusion,[8–11] ionic conductivity,[12] and dielectric[13–16] and mechanical[17] relaxation combine to give a picture of the various molecular motions. Macroscopic measurements, such as viscosity and dielectric and elastic loss, reveal the main, structural or primary relaxation process which is slowed to experimental timescales (10^2–10^4 s) at the glass transition temperature, T_g.[17] Above T_g the viscosity of carbohydrate–water mixtures exhibit a non-Arrhenian dependence upon temperature, T, which can be described by the empirical Vogel–Tamman–Fulcher (VTF) equation, $\eta = \eta_0\exp[B/(T-T_0)]$ where η_0, B and T_0 are constants.[18,19] Measurements of diffusion[8–11] and ionic conduction[12] show that the translational motion of small molecules and ions in supercooled carbohydrate liquids and glasses are, to various extents, uncoupled from the main structural relaxation and viscosity. Further data on molecular

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mobility, including its dependence upon molecular structure, is required to test whether bimolecular chemical reactions generally become diffusion-influenced in these systems.[20]

In this study, an examination of the effect of carbohydrate structure on the conductivity of amorphous carbohydrate–water–KCl mixtures is presented. Conductivity measurements allow the translational mobility of ions in carbohydrate mixtures to be characterised over a range of 9 orders of magnitude in the supercooled liquid and glassy states.[12] In order to isolate the contribution of KCl to the conduction, both carbohydrate–water and carbohydrate–water–KCl mixtures are studied. The effect of molecular weight was studied by including D-glucose, maltose and maltotriose, the effect of the exocyclic hydroxymethyl group by the inclusion of D-xylose and the combined effects of constituent monosaccharides, different linkages and reducing end group by the inclusion of raffinose. The common disaccharides, sucrose, lactose and trehalose were excluded from the study because of their tendency to recrystallise under the experimental conditions employed.

2. Experimental

2.1. Sample preparation

D-Xylose, D-glucose, maltose monohydrate, maltotriose, raffinose pentahydrate and KCl were obtained from Sigma, Poole, UK. All the materials were SigmaUltra grade except maltotriose which was standard grade. The carbohydrates were crystalline solids except maltotriose which was amorphous (it is not known to crystallise, a behaviour associated with its anomerisation since methyl-α-maltotrioside is readily crystallised[21]). Prior to the preparation of the mixtures the maltotriose was dried in vacuo at 60 °C over P_2O_5 for 24 h and the raffinose was vitrified by freeze-drying a 20% w/w aqueous solution followed by vacuum drying over P_2O_5. Water was obtained from a water purification system (Elgastat Maxima, Elga, High Wycombe, UK) with a conductivity < 1 μS m^{-1}. Amorphous carbohydrate–water (10% w/w water) and carbohydrate–water–KCl (9.3% w/w water, 0.74% w/w KCl) mixtures were prepared from dry carbohydrate, water and aqueous KCl solution, as appropriate, or, in the case of the maltose mixtures, from crystalline maltose monohydrate, water and aqueous KCl solution. The mixtures (typically 4 g) were melted in screw-topped Pyrex culture tubes with occasional agitation and centrifugation to ensure mixing and removal of air bubbles. The molar concentration of the KCl was calculated by assuming volume additivity of the volumes of the components. The partial specific volumes of the carbohydrates (cm^3 g^{-1})[22] are: xylose, 0.656; glucose, 0.651; maltose, 0.640; maltotriose, 0.633; raffinose, 0.633 (assumed to be the same as maltotriose). The volumes of water and KCl were calculated from aqueous KCl densities.[23] The KCl concentration was 145 ± 5 mol m^{-3} in all the KCl mixtures.

2.2. Calorimetry

Glass transition temperatures were determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1} as described previously.[12] T_g was taken to be the temperature at which the heat capacity was midway between the values in the liquid and glassy states measured during a rescan.[24]

2.3. Conductimetry

Conductivity measurements were made using a two-terminal stainless steel parallel-plate cell with circular electrodes (diameter 33 mm, 0.5 mm electrode separation) as described previously.[12] Alternating current (AC) measurements were performed using a General Radio Precision RLC Digibridge (Model 1689M, Quadtech Inc., Bolton, MA, USA) over the frequency range 0.1–100 kHz. The AC measurements were analyzed as in the determination of complex permittivity, i.e., in terms of relative permittivity, ε', and dielectric loss, ε''. The DC conductivity, σ, was determined from the apparent dielectric loss, ε''_{app}, using the relationship:[25]

$$\varepsilon''_{app} = \varepsilon''_{d} + \frac{\sigma}{2\pi\varepsilon_0 f} \tag{1}$$

where ε''_{d} is the dielectric contribution to the apparent dielectric loss, ε_0 is the permittivity of a vacuum, and f is the frequency of the applied voltage. Direct current (DC) measurements were performed on the same samples using a IEEE-programmable electrometer (Model 617, Keithley Instruments Ltd., Reading, UK). Using this method the conductivity is determined from the ohmic resistance of the sample and its dimensions. No signs of sample recrystallization were observed on dismantling the cell after the AC and DC measurements as indicated by the samples remaining transparent with no visible turbidity.

3. Results

3.1. Glass transition temperatures

The glass transition temperatures, T_g, of the amorphous carbohydrate–water and corresponding carbohydrate–water–KCl mixtures were identical within the experimental accuracy. The T_g's of the mixtures were:

D-xylose, − 29 °C; D-glucose, − 17 °C; maltose, 7 °C; maltotriose, 19 °C; and raffinose, 18 °C.

3.2. Interpretation of AC measurements

In order to extract the conductivity from the AC measurements the contributions of conductivity, dielectric relaxation and electrode polarization to the complex apparent permittivity must be distinguished.[12,25,26] Fig. 1(a and b) show the frequency dependence of the apparent relative permittivity and dielectric loss of a amorphous glucose–water–KCl mixture at temperatures in the supercooled liquid region between $T_g + 22$ and $T_g + 67$ °C. At the highest temperatures of 50 and 45 °C ($T_g + 67$, $T_g + 62$ °C), the double logarithmic plot of the apparent dielectric loss versus frequency (Fig. 1(b)) is linear with a slope of − 1 indicating that DC conduction is dominating dielectric relaxation.[12] The increase in apparent relative permittivity at low frequencies (Fig. 1(a)) is due to electrode polarization[26] though, as the slope of the apparent dielectric loss versus frequency shows little deviation from − 1 we conclude that it is not significantly affecting the conductivity. As the temperature is lowered to 35 and 15 °C ($T_g + 52$, $T_g + 32$ °C) the apparent dielectric loss (Fig. 1(b)) shows increasing curvature at high frequencies indicating that conduction is no longer dominant throughout the whole frequency range and dielectric relaxation is contributing to the apparent dielectric loss. Under these conditions the conductivity was determined from the lower frequency portion ($f < 1$ kHz) of the apparent dielectric loss. At the lowest temperature shown, 5 °C ($T_g + 22$ °C), both conduction and dielectric relaxation contribute to the apparent dielectric loss across the whole frequency range and the DC method was used to determine the conductivity.

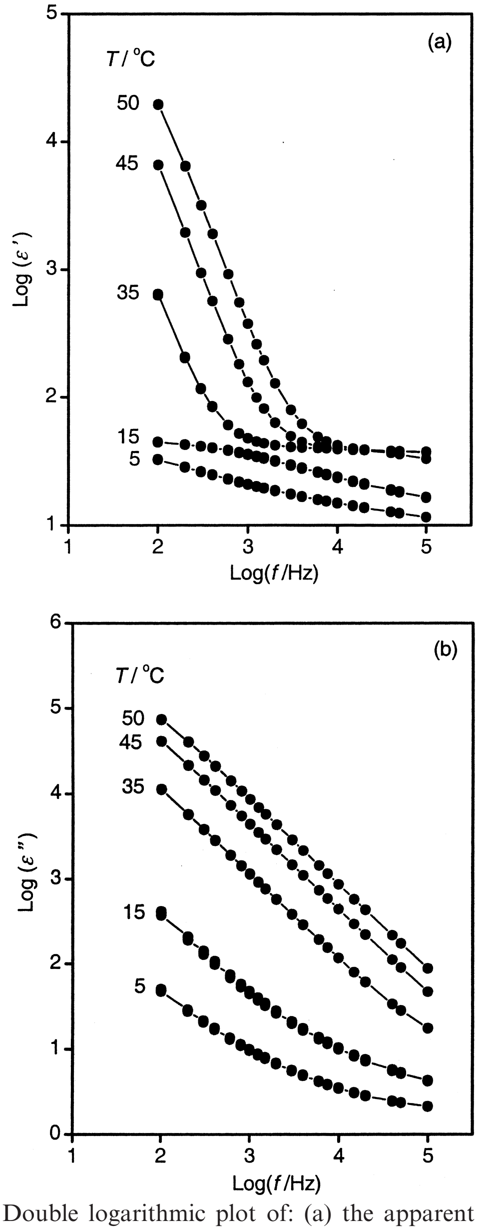

Fig. 1. Double logarithmic plot of: (a) the apparent relative permittivity; and (b) the apparent dielectric loss vs. frequency for a amorphous glucose–water–KCl mixture (9.3% w/w water, 0.74% w/w KCl) in the temperature range $T_g + 22$ to $T_g + 67$ °C.

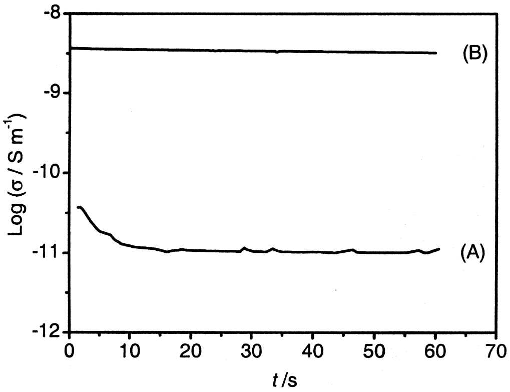

Fig. 2. Comparison of the time dependence of the apparent conductivity of: (A) amorphous glucose–water mixtures (10.0% w/w water); and (B) amorphous glucose–water–KCl mixtures (9.3% w/w water, 0.74% w/w KCl) measured at − 10 °C ($T_g + 7$ °C) using DC method.

3.3. Interpretation of DC measurements

By comparing the DC response of the carbohydrate–water and carbohydrate–water–KCl mixtures it was found that dielectric relaxation does not contribute to the DC response of the KCl mixtures. Fig. 2 shows this comparison for glucose mixtures at $T_g + 7$ °C. In the absence of KCl the apparent conductivity of the glucose–water mixture (A) is over two orders of magnitude smaller and decreases over the duration of the measurement. To establish whether the transient contribution to the apparent conductivity is of the correct order to be due to dielectric relaxation it was modelled as a single exponential relaxation using the expression,[27]

$$\sigma(t) = \sigma_{DC} + (\varepsilon_s - \varepsilon_\infty)\varepsilon_0\tau_0^{-1}\exp(-t/\tau_0) \quad (2)$$

where σ_{DC} is the DC conductivity, ε_s, the static permittivity, ε_∞, the high frequency relative permittivity, and τ_0, the relaxation time. A least squares fitting gives $(\varepsilon_s - \varepsilon_\infty) \sim 16.5$ and $\tau_0 \sim 3.2$ s which are of a physically reasonable magnitude when compared with extrapolated AC measurements of ε_s and ε_∞[15] and τ_0,[13] and so, we conclude that the transient contribution is due to dielectric relaxation. For the glucose–water and xylose-water mixtures in the temperature range T_g to $T_g +$ 10 °C, i_{60}, the current measured 60 s after the voltage is applied, was used to calculate the DC conductivity in order to minimize the contribution of dielectric relaxation to the results.

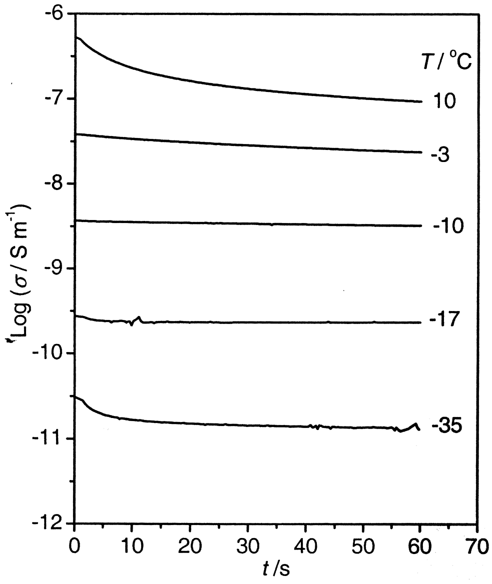

Fig. 3. Effect of temperature on the time dependence of the apparent conductivity of a amorphous glucose–water–KCl mixture (9.3% w/w water, 0.74% w/w KCl) determined using DC method. T_g of the mixture is − 17 °C.

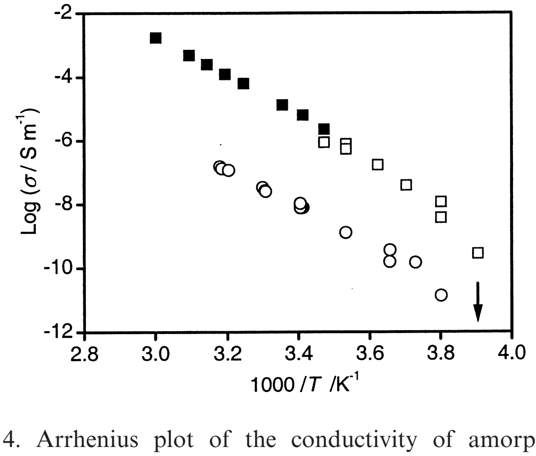

Fig. 4. Arrhenius plot of the conductivity of amorphous glucose–water (DC method, ○) and amorphous glucose–water–KCl (AC method, ■; DC method, □) mixtures at temperatures above T_g (T_g is indicated with arrow).

The DC response of the D-xylose, D-glucose and maltose–water–KCl mixtures were qualitatively similar when temperature was referenced to the appropriate T_g. Fig. 3 shows the transient DC response of a amorphous glucose–water–KCl mixture at a range of temperatures above and below T_g (− 17 °C). At 10 °C the apparent conductivity rises to a maximum in less than 1 s (the first data point is recorded at 0.36 s) and then decays monotonically. This behaviour is characteristic of conduction with electrode polarization.[27] In general, in the supercooled liquid region ($T > T_g$), the maximum current, i_{max}, was used to calculate the DC conductivity in order to minimize the effect of electrode polarization. The conductivities of the glucose–water–KCl mixtures at 15 °C measured using the AC and DC methods were 2.2 and 0.9×10^{-6} S m^{-1}, respectively. The discrepancy we ascribe to electrode polarization. At lower temperatures (− 3, − 10, − 17 °C) the current was relatively constant throughout the 60 s experiment indicating that the time characterizing electrode polarization is longer and has a negligible effect upon the conductivity determined using i_{max}. The maltotriose and raffinose–water–KCl mixtures behaved differently. At T_g the DC results exhibited a transient conductivity which fell to ~ 50% of its maximum value due to electrode polarization effects, however, at lower sub-T_g temperatures (T_g − 40 °C to T_g) this effect was relatively small.

3.4. Conductivity

An Arrhenius plot of the conductivity of the glucose–water and glucose–water–KCl mixtures in the supercooled liquid region is shown in Fig. 4. A comparison of the relative magnitudes shows that the contribution of the KCl to the conductivity of the KCl mixture dominates that of the intrinsic conductors in the glucose–water mixture throughout the supercooled liquid temperature range. Whereas the activation energy of the glucose–water mixture remains constant throughout the temperature range ($E_a \sim 115$ kJ mol^{-1}) that of the glucose–water–KCl mixture increases from 115 kJ mol^{-1} (60 °C $\geq T \geq$ 15 °C) to 150 kJ mol^{-1} (15 °C $\geq T \geq$ − 17 °C) close to T_g. The data in Fig. 4 allow the molar conductivity of KCl in the mixture to be calculated by subtracting the intrinsic conductivity of the equivalent carbohydrate–water mixture (a relatively small value) and dividing by the molar concentration of KCl.

Fig. 5 shows an Arrhenius plot summarizing the molar conductivity of the KCl in the amorphous carbohydrate–water–KCl mixtures. At a given temperature the molar conductivity varies in the order D-xylose > D-

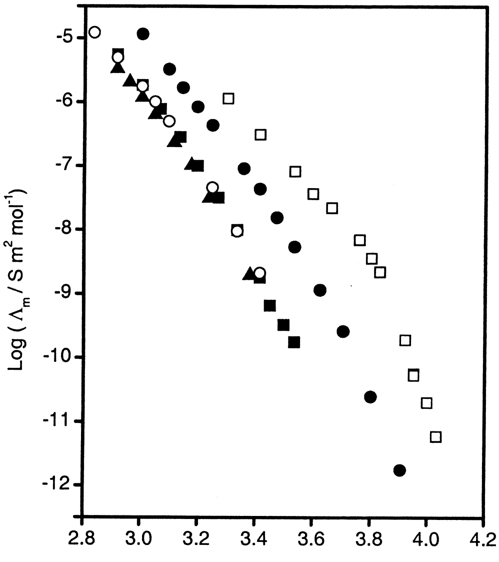

Fig. 5. Arrhenius plot of the molar conductivity of KCl in amorphous carbohydrate–water–KCl mixtures in the supercooled liquid region. Carbohydrates: xylose, (□); glucose, (●); maltose, (■); maltotriose, (▲); raffinose, (○).

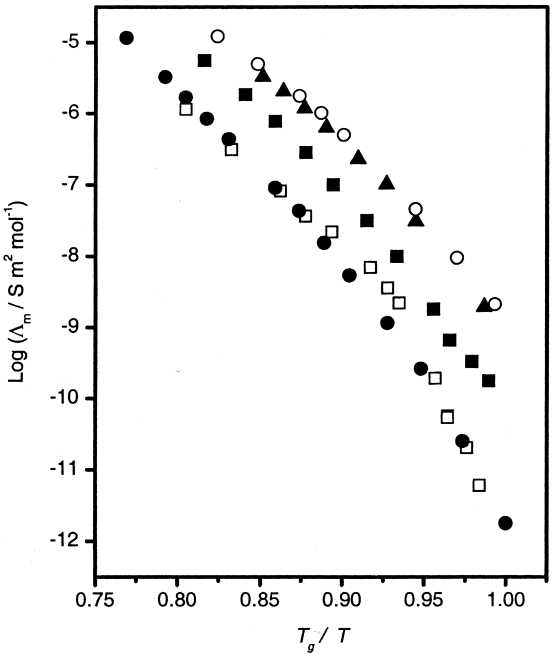

Fig. 6. Scaled Arrhenius plot of the molar conductivity of KCl in amorphous carbohydrate–water–KCl mixtures in the supercooled liquid region. Carbohydrates: xylose, (□); glucose, (●); maltose, (■); maltotriose, (▲); raffinose, (○).

glucose > maltose, maltotriose, raffinose which, when scaled with T_g (Fig. 6) changes to maltotriose, raffinose > maltose > D-xylose, D-glucose. The molar conductivity at T_g, $\Lambda_m(T_g)$, was estimated by extrapolating the data in Figs. 5 and 6 using a VTF-type equation, $\Lambda_m = \Lambda_{m0}\exp[B/(T - T_0)]$. $\Lambda_m(T_g)/S$ m^2 mol^{-1} is: 2.4×10^{-13}, D-xylose; 2.0×10^{-12}, D-glucose; 7.2×10^{-11}, maltose; 1.4×10^{-9}, maltotriose and 1.2×10^{-9}, raffinose.

4. Discussion

The aim was to obtain a measure of the effect of molecular structure on translational mobility in an amorphous carbohydrate in the vicinity of its glass transition, more particularly, to characterise the effects of molecular weight and presence of an exocyclic hydroxymethyl group.

In order to establish that the observed variation in conductivity is largely due to variation in ionic mobility, the potential effects of ion-pairing must be shown to be relatively small. In water at 20 °C, Bjerrum's theory of ionic association[28] predicts that 95% of the K^+ and Cl^- ions are unpaired in 0.145 mol dm^{-3} KCl solutions. Replacing 90% of water by D-glucose reduces the dielectric constant (water, $\varepsilon_s \sim 80$;[23] glucose-10% w/w water, $\varepsilon_s \sim 40$[13]) and increases the fraction of uncharged ion-pairs to 49% with a corresponding reduction of conductivity. However, the effect of temperature on the fraction of ion-pairs is predicted to be relatively small, with a change in the fraction of unpaired ions from 97 to 94% as water is cooled from 60 to 0 °C and from 53 to 45% as glucose-10% w/w water is cooled from 60 to − 20 °C. It can be concluded that, although a fraction of ions is paired, the size of this fraction is relatively insensitive to temperature and the variation in conductivity with temperature is largely due to variation in ionic mobility.

The molar conductivity of a 0.145 M aqueous solution of KCl is 0.013 S m^2 mol^{-1} at 25 °C.[28] Whereas the viscosity of this solution is ~ 1 mPa s, the viscosity of the carbohydrate–water–KCl mixtures at T_g will be about 10^{12} Pa s.[19] Applying the Stokes equation[29] to ionic motions leads to the expectation that $\Lambda_m \propto \eta^{-1}$ and so, if Stokes equation is obeyed the conductivity at T_g should be a factor of 10^{15} lower than in water at 25 °C. Comparison shows that the molar conductivity of KCl in the carbohydrate–water mixtures at T_g is considerably higher than the Stokes prediction, ranging from xylose by a factor of $\sim 2 \times 10^4$, to maltotriose and raffinose by a factor of $\sim 10^8$. The origin of this behaviour is unclear. While the viscosity is intimately linked with the main structural relaxation of the liquid, the translational motions of the ions are experiencing less resistance to their motion. The main structural relaxation is a cooperative motion[30] and so it follows that the ionic motions must be less cooperative, e.g., involving more localised hopping motions which are not present in the main relaxation. The covalent linkages introduced in building di- and trisaccharide molecules from the monomeric monosaccharides must affect the nature of the cooperative motions in a way which leads to increased uncoupling of the ionic motions.

5. Conclusions

In the supercooled liquid region the molar conductivity of KCl in carbohydrate–water–KCl mixtures is uncoupled from the viscosity to an extent which is dependent upon the structure of the carbohydrate. At T_g the magnitude of the molar conductivity varies in the order: maltotriose, raffinose > maltose > D-glucose > D-xylose i.e., in order of decreasing molecular weight or, in other words, increasing uncoupling with increasing molecular weight. Whilst the major variation is between tri-, di- and monosaccharides, at T_g there is also a significant difference between the hexose D-glucose which has an exocyclic group and the pentose D-xylose which does not. In contrast, the trisaccharides, maltotriose and raffinose, show similar behaviour despite their structures differing in constituent monosaccharide units, linkages and end group. The tendency of some supercooled sugars (e.g., trehalose) to crystallise over experimental timescales means that it has not been possible to study the effect of a reducing end group. Estimates of the magnitude of the effect of ion-pairing on the temperature dependence of conductivity predict it to be relatively small compared with the effect of ionic mobility.

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