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Molecular motion in glassy water–malto-oligosaccharide (maltodextrin) mixtures as studied by conventional and saturation-transfer spin-probe e.s.r. spectroscopy

Marcel J. G. W. Roozen*, Marcus A. Hemminga[†], and Pieter Walstra*
Wageningen Agricultural University, P.O. Box 8128, 6700 ET Wageningen (The Netherlands)

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ABSTRACT

Conventional and saturation-transfer e.s.r. spectroscopy have been used to study the rotational behaviour of the spin probe 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (**1**, tempol) around the glass-transition temperature of malto-oligosaccharide–water mixtures. The temperature at which an increase in mobility was observed agreed reasonably well with the glass-transition temperature as determined by d.s.c. The apparent activation energy for rotation in the glassy malto-oligosaccharide increased as the molecular weight became larger, presumably due to a decrease in the free volume of the sample. No influence of the water content of the glassy samples, at temperatures above the freezing point of water, on the apparent activation energy was observed.

INTRODUCTION

The glass-transition behaviour of bio-organic materials, which has become a topic of much interest[1-3], is the phenomenon in which a solid amorphous phase exhibits a discontinuous change in the specific heat on changing the temperature[4]. The mechanical and thermal properties of systems change markedly in the region of the glass-transition temperature[5-7]. Not only is there a sudden change of macroscopic properties around this temperature, but also a change of the translational diffusion coefficient of molecules or segments of polymers[8].

The glass-transition temperature (T_g) for carbohydrate–water mixtures depends strongly on the proportion of water. If the glass transition takes place at temperatures below the freezing point of the solution, a part of the water may crystallise. The viscosity of the remaining solution will become so high that, eventually, freezing of the remaining water is inhibited[9]. The physical state of such a mixture consists of ice crystals embedded in a solid supersaturated matrix. The temperature at which water stops freezing, and where a discontinuous change of the specific heat takes place, is the special glass-transition temperature (T_g'). The amount of water that remains unfrozen is often assumed to be independent of the starting concentration[5]. On rewarming such a mixture, the Stokes viscosity of the amorphous solution starts to decrease strongly above T_g' due to the melting of ice and the increase of the free volume[1].

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[*] Laboratory of Dairying and Food Physics, Department of Food Science.
[†] Author for correspondence: Department of Molecular Physics.

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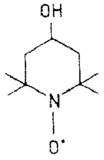

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Spin-probe e.s.r. spectroscopy is a good method for the study of molecular motion in bio-organic glasses[10,11] and gives information on the rotational mobility of dissolved spin probes. The rotational mobility of the probes is expressed by the rotational correlation time (τ_c):

$$\tau_c = (6\, D_{\text{rotational}})^{-1}, \tag{1}$$

where $D_{\text{rotational}}$ is the rotational diffusion coefficient.

By using conventional, as well as saturation-transfer, e.s.r. spectroscopy, τ_c in the range 10^{-11} s $\leqslant \tau_c \leqslant 10^{-3}$ s can be studied. By assuming isotropic rotational motion of the spin probes, a modified Stokes–Einstein theory has been described[11]. In this theory, τ_c of a spin probe is not only a linear function of the Stokes viscosity and the reciprocal of the temperature of its surroundings, but also depends on the coupling between the probe and the solvent. This coupling is affected by specific solvent–probe interactions, such as hydrogen bonds and the geometry of the spin probes[12–14].

By using both conventional and saturation transfer e.s.r. spectroscopy, Ito[15] demonstrated for several organic systems of low molecular weight that the change of the matrix due to the glass transition is reflected in a decrease of τ_c of nitroxide spin probes. Hamada *et al.*[16] showed that τ_c of different nitroxide spin probes in films of nylon-6 decreased with rising water content at a given temperature. We have shown[11] that there is an increase of the rotational mobility of spin probes around the glass-transition temperature on rewarming of a 20% sucrose–water mixture. In addition, it was found that spin probes in concentrated sucrose–water mixtures above and below the glass-transition temperature are present in cavities.

We now describe a study of the glassy state and the glass transition of malto-oligosaccharide–water mixtures.

EXPERIMENTAL

Preparation of solutions. — Dry malto-oligosaccharide (maltodextrin: tri, penta, and hepta, Boehringer) were mixed with an aqueous solution of the spin probe 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (**1**, tempol). The final concentration of the probe was 0.2–0.5 mg/mL. In order to obtain concentrated mixtures, the solutions were dried for 2 weeks over concentrated solutions of salt[17]. The samples were ground in a mortar, dried again for 1 week, then introduced rapidly into capillaries (1-mm diameter), which were sealed. The length of the sample was 4 cm. The water content of the samples was determined by drying for 16 h at 102°.

Spectroscopy. — E.s.r. spectra of the sealed samples in 4-mm e.s.r. tubes were recorded with a Bruker 200D spectrometer with nitrogen-flow temperature control. For conventional e.s.r. spectroscopy, the microwave power was 1–5 mW. The scan range, scan rate, time constant, and modulation amplitude were adjusted so that distortion of the spectra was avoided. The rotational correlation time (τ_c) in the region 10–200 ns was estimated by using the method of Goldman[18] from

$$\tau_c = a(1 - A'_z/A_z)^b,$$

where A'_z is the separation of the outer hyperfine extrema and A_z is the rigid limiting value for the same quantity. Both a and b depend on the nature of the motion of the probe and on the intrinsic line width of the spectra. The Brownian diffusion model was used and gave $a = 1.09\ 10^{-9}$ s and $b = -1.05$[11,19,20].

Saturation transfer e.s.r. spectroscopy was applied in the slow motional region ($10^{-6}\ \text{s} \leqslant \tau_c \leqslant 10^{-3}$ s). Spectra were recorded under saturation conditions (microwave power, 200 mW; modulation amplitude, 1 mT). The e.s.r. signal was recorded in quadrature with respect to the modulation signal. τ_c was estimated by comparing the recorded spectra with spectra for probe **1** in anhydrous glycerol under similar conditions. Values of τ_c between 10^{-7} and 10^{-3} s are accurate[21] to within a factor of 2.

For malto-oligosaccharide–water mixtures to be studied at <0°, the system was cooled rapidly to −70° and rewarmed to the desired temperature, which ensured maximally frozen samples[22].

RESULTS AND DISCUSSION

The glass-transition temperature. — Fig. 1 shows a plot of τ_c versus temperature on rewarming a rapidly cooled 20% maltotriose–water mixture. There is a sudden change in the temperature dependence of the rotational mobility at −23°, which is close

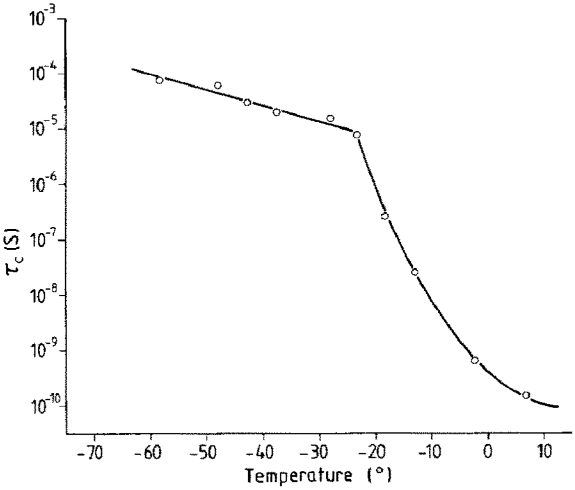

Fig. 1. Rotational correlation time (τ_c) of **1** as a function of temperature in a 20% maltotriose–water mixture.

TABLE I

The special glass-transition temperatures (T_g') for rapidly cooled 20% malto-oligosaccharide water mixtures

Oligosaccharide	T_g'[a] *(degrees)*	T_g'[b] *(degrees)*
Maltotriose	−23	−23.5
Maltopentaose	−18	−16.5
Maltoheptaose	−14	−13.5

[a] Determined by spin-probe e.s.r. spectroscopy (±1°). [b] Determined by d.s.c. by Levine and Slade[22].

to the special glass-transition temperature (T_g' −23.5°) as tabulated by Levine and Slade[22]. Table I shows the results for other 20% malto-oligosaccharide water mixtures and a comparison with the results obtained by Levine and Slade[22].

Fig. 2 shows the rotational mobility of **1** in a concentrated maltoheptaose water mixture (equilibrium relative humidity, 33%). This graph is identical in shape to that in Fig. 1 with T_g at 42°. Due to a higher viscosity, the value of τ_c at temperatures above T_g in Fig. 2 is higher than that for the samples in which ice melts (Fig. 1). Fig. 2 also contains results for an oven-dried sample of maltoheptaose (16 h at 102°). Due to the decrease of the water content, T_g is shifted upwards to ~100°. Table II shows the results for other concentrated malto-oligosaccharide water mixtures. Orford *et al.*[23] studied the glass-transition behaviour of malto-oligosaccharides by means of differential scanning calorimetry (d.s.c.). By minimising the difference between their results and those reported here, the residual water content of the oven-dried samples was estimated to be 2.5%, 4%, and 3.5% for the tri-, penta-, and hepta-saccharide, respectively. It is assumed that

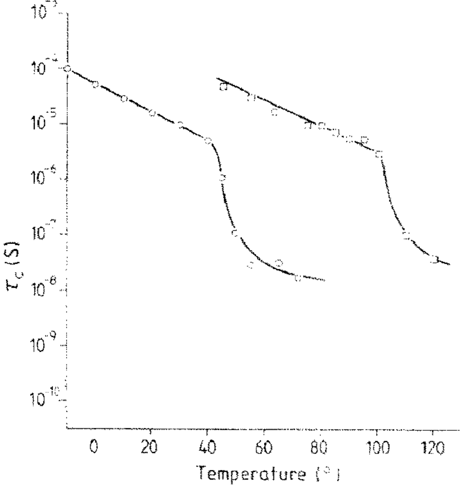

Fig. 2. Rotational correlation time (τ_c) of **1** as a function of temperature in a maltoheptaose water mixture: ○, equilibrium relative humidity 33%, □, oven-dried for 16 h at 102°.

TABLE II

Water content and glass-transition temperatures of malto-oligosaccharide–water mixtures

Mixture	*Humidity*[a]	*Corrected water content*[b] (%)	*Glass-transition temperature* (°)		
			E.s.r.	*D.s.c.*[c]	*Equation 2*[d]
Trisaccharide	O.d.[e]	2.5	85	90	108
	33	10.0	45	24	52
	57	11.5	15	16	42
	75	19.5	10	N.d.[f]	1
Pentasaccharide	O.d.	4.0	90	100	119
	33	12.5	45	37	48
	57	13.5	35	31	42
	75	18.5	15	7	13
Heptasaccharide	O.d.	3.5	100	109	138
	33	11.5	42	42	64
	57	14.5	40	25	44
	75	18.5	22	7	20

[a] Relative humidity of the air above the solution of salt over which the sample was dried. [b] Determined by drying at 100° overnight; corrected by +2%, +4%, and +3.5% for tri-, penta-, and hepta-saccharide, respectively (see text). [c] From Orford[23]; for the penta- and hepta-saccharides, the results for the hexasaccharide were taken. [d] Calculated from equation *2* (see text). [e] Oven-dried for 16 h at 102°. [f] Not determined.

the drying procedure described by Orford *et al.*[23] (which consists of freeze-drying followed by vacuum-drying over P_2O_5 at 60°) is more reliable than drying at 102°.

Couchman[24,25] developed a thermodynamic model for the glass transition. The relation (equation *2*) for the compositional variation of T_g derived from entropy can be used generally.

$$\ln T_g = \frac{X_1\,\Delta C_{p,1}\ln T_{g,1} + X_2\,\Delta C_{p,2}\ln T_{g,2}}{X_1\,\Delta C_{p,1} + X_2\,\Delta C_{p,2}} \qquad (2)$$

where X is the mol fraction, ΔC_p is the heat capacity increment (J. mol^{-1}.K^{-1}), which is assumed to be temperature independent, and the subscripts 1 and 2 refer to the two components. In equation *2*, which has been used[26,27] successfully for plasticised organic polymers, the values for T_g and ΔC_p of the malto-oligosaccharides estimated by Orford *et al.*[23] were applied. The glass-transition temperature and heat-capacity increment of water were taken to be 134 K and 1.2 kJ.kg^{-1}.K^{-1}, respectively, based on the study by Angell and Tucker[28]. The value for ΔC_p as used by Orford and Ring[23] (1.92 kJ.kg^{-1}.K^{-1} as reported by Sugisaki *et al.*[29]) is less adequate, due to the formation of ice in the samples[30].

Table II shows a comparison of the e.s.r. results and those calculated using equation *2*. Differences between the experimental and calculated glass-transition temperatures cannot be attributed solely to uncertainties in the data. Specific interactions of the malto-oligosaccharide and water molecules may account for the deviations, since the latter break or weaken the hydrogen bonds between the former. This results in experimental values for T_g that are lower than those calculated using equation *2*. This effect is shown clearly in Table II for the oven-dried samples. The restricted applicability of the random mixing effect, on which equation *2* is based, may be an additional source of differences between the experimental and calculated values of T_g.

Commercial maltodextrin. — In order to compare the above results with those on materials used in the food industry, such as enzymically converted starch, which is a mixture of oligosaccharides with various molecular weights, a commercial sample of maltodextrin was examined, namely, Passelli SA 2, which has an average molecular weight of 8000. Fig. 3 shows the rotational mobility of **1** in this sample (equilibrium relative humidity, 57%) as a function of temperature. Apart from a sudden change in the temperature dependence of the mobility at 30°, τ_c becomes constant at 70°. This phenomenon was also observed with other commercial maltodextrin mixtures (results not shown), but not for the smaller malto-oligosaccharides, which could indicate that the interaction of the polymer chains and **1** increases (due to the softening of the chain molecules) to the same extent as η/T decreases.

Fig. 3 also shows that the addition of 8% (by weight) of D-glucose to the polymer results in a decrease of T_g by 5°, possibly because of a small increase of the water/malto-oligosaccharide ratio or a plasticiser effect of the glucose, although water molecules that interact with glucose molecules may not be able to plasticise the polymer chain.

Rotational mobility in glassy systems. — The temperature dependency of the correlation time of spin probes is frequently described by the Arrhenius-type equation

$$\tau_c = \tau_a \exp(E_a/RT), \qquad (3)$$

where τ_a is a temperature-independent factor, R and T have their usual meaning, and E_a is often interpreted as an activation energy for rotation[15,16,32,33]. The values of E_a for **1** in glassy malto-oligosaccharide/water mixtures are shown in Tables III and IV.

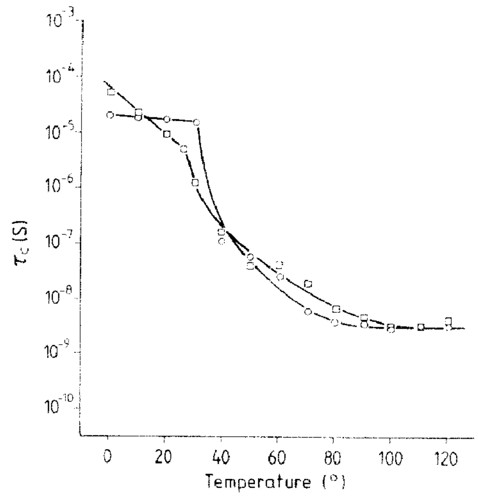

Fig. 3. Rotational correlation time (τ_c) of **1** as a function of temperature in a heterodisperse commercial maltodextrin (Passelli SA 2): ○, 12.7% of water; □, 12.7% of water and 8% of D-glucose.

TABLE III

Apparent activation energy for rotation (E_a) of probe **1** in glassy 20% malto-oligosaccharide–water–ice mixtures

Oligosaccharide	E_a *(kJ/mol)*
Tri	17
Penta	14
Hepta	26

TABLE IV

Apparent activation energy for rotation (E_a) of **1** in concentrated glassy malto-oligosaccharide–water mixtures

Oligosaccharide	*Corrected water content* (%)[a]	E_a *(kJ/mol)*
Tri	2.5	35
	10.0	49
	11.5	35
	19.5	41
Penta	4.0	35
	12.5	26
	13.5	26
	18.5	43
Hepta	3.5	21
	11.5	29
	14.5	34
	18.5	34

[a] Determined by drying at 100° overnight; corrected by +2.5%, +4%, and +3.5%, respectively, for the tri-, penta-, and hepta-saccharide (see text).

It was concluded[11] that the spin probes in glassy sucrose–water mixtures were present in cavities in the lattice of the amorphous solution. The value for τ_c in glassy maltotriose (Fig. 1) also indicated the presence of cavities. However, the absolute values for τ_c and E_a clearly show that **1** did not rotate freely in such cavities.

Two important factors have been proposed to determine the rotational mobility of probes in glassy systems: (*a*) the free volume of the "host" systems[8], and (*b*) the specific interaction of the spin probe and the chain molecule[16]. Hydrogen bonds often are the most important interaction[8,11]. These factors not only influence the absolute value of τ_c, but also the change of τ_c as a function of temperature (as expressed by E_a). Table IV shows that the values of E_a for the trisaccharide samples are somewhat higher than those for the penta- and hepta-saccharide samples, which may reflect an increase of free volume with increasing molecular weight[34]. The same effect is more pronounced in Fig. 3. The addition of glucose to the polymer presumably results in a decrease in the free volume of the system, which may explain the strong increase of E_a from 8 to 60 kJ/mol.

The value (11–49 kJ/mol) for E_a in glassy malto-oligosaccharide–water mixtures is relatively high compared to the results from studies of spin probes in glassy nylon–water films[32,35]. In the latter system, the probes appear to rotate in local defects with a low E_a (2–8 kJ/mol) and a τ_c between 10^{-8} and 10^{-7} s. The relatively high values for E_a and τ_c noted above probably reflect the difference in number and strength of hydrogen bonds formed between the probe and its surrounding. Also the relatively small free volume of the malto-oligosaccharide, due to its small molecular weight as compared to that of nylon, may add to this effect.

Taking into account that the uncertainty in E_a in Table IV is at least 10%, no significant influence of the water content of the samples on E_a can be observed. For the mobility of probes in glassy nylon, two effects of water have been described. (*a*) The effect of water molecules on the micro-environment around the probe molecule. According to McGregor *et al.*[35], water may be able to reduce the mobility of spin probes in glassy systems due to an obstruction effect (lowering of the free volume). The addition of a little water to dry glassy nylon causes τ_c to increase by a factor of 1.6. Reduction of the local viscosity, and thus an increase of mobility of the spin probes by water, can be detected[32,33] only at temperatures above T_g. (*b*) The effect of water molecules on the interaction of the chain and the probe. According to Hamada[32], water molecules can break the hydrogen bonds between the chain and the probe molecules, which may result in a decrease of E_a for rotation. The two factors have opposite effects on E_a and may be small, so that no significant influence of the water content of the samples on E_a is observed.

The values for E_a in frozen malto-oligosaccharide–water mixtures as shown in Table III are smaller than in the concentrated samples (Table IV). The presence of ice crystals may increase the free volume or reduce the interaction with the spin probe.

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