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Carbohydrate Research 273 (1995) 147–155

CARBOHYDRATE
RESEARCH

Diffusion in maltose–water mixtures at temperatures close to the glass transition

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Received 21 November 1994; accepted 24 February 1995

Abstract

The mean diffusion coefficients, $\bar{D}$, for maltose–water mixtures close to the glass transition temperature, T_g, were measured using a gravimetric method during desorption of water. The mass loss showed a linear dependence on the square root of time, indicating a Fickian diffusive process. At 300 K, an increase in the water content from 5.0 to 17.0% w/w resulted in an increase in $\bar{D}$ from 9.0×10^{-15} to 4.0×10^{-13} m^2 s^{-1}. The variation of $\bar{D}$ with temperature, at a water content of 9.5% w/w, yielded an activation energy of 70 kJ mol^{-1}. The variation of diffusion coefficient with temperature does not follow that of viscosity and diverges when $T_g/T > 0.8$.

Keywords: Diffusion; Water; Maltose; Glass transition

1. Introduction

Recently, there has been increased recognition of the relevance of the glass transition behaviour of carbohydrates to their industrial usage as matrices for the preservation of proteins, food ingredients, and pharmaceuticals [1–4].

As a liquid carbohydrate is cooled below its melting temperature, in many instances crystallization does not result; instead, the viscosity of the liquid progressively increases until, at the glass transition, the amorphous material has solid-like characteristics. The change from liquid-like to solid-like behaviour occurs at the glass transition temperature, T_g, its value depending on thermal history and the time scale of the measurement. It is conveniently determined in calorimetric experiments from the sharp change in heat

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SSDI 0008-6215(95)00120-4

capacity at T_g. Undercooled carbohydrate liquids are classified as "fragile", with a strong dependence of shear viscosity, η, on temperature, T, in the vicinity of T_g [5–9]. This dependence is described by the semi-empirical "VTF" relationship

$$\eta = A \exp\left[B/(T - T_0)\right], \tag{1}$$

where A, B, and T_0 are constants. At T_g, typical values of the shear viscosity are in the region of 10^{12} Pa [5].

If the Stokes–Einstein equation ($D = kT/6\pi\eta a$) for the dependence of diffusion coefficient, D, on hydrodynamic radius, a, and viscosity is applicable to carbohydrate liquids, then diffusion of molecular species in the glass should be enormously retarded. This would, in part, account for the encapsulating and protective ability of these matrices.

Although there is sometimes an expectation that the Stokes–Einstein relationship adequately describes diffusion in molecular liquids, experimental evidence suggests that it is only applicable when the diffusing species is large compared to the size of molecule in the continuous medium [10]. With decreasing size of a probe species, there is a breakdown in this hydrodynamic description. Additionally, on undercooling "fragile" organic liquids there is evidence for a change in diffusive behaviour as T_g is approached, with an uncoupling of diffusion from shear viscosity, with an onset typically in the range of T_g/T 0.8–0.85 [11,12]. Comparable behaviour has been observed for the motion of probe species in synthetic polymer matrices [13–15], particularly if the probe is smaller than the monomer unit of the polymer, or for polymers which retain some mobility in the glass, associated with the motion of side chains, pendant groups, or residual backbone flexibility.

There is also evidence of mobility in vitreous carbohydrates. In dielectric experiments on glucose–water [16] and maltose–water mixtures [17], two main relaxations are observed. The α-relaxation is associated with the reorientation of the whole molecule in the transient electric field, while the β-relaxation, observed at a lower temperature and below T_g, is associated with the reorientation of the pendant hydroxymethyl group [18] and water. This observation suggests that a fraction of water in the glassy carbohydrate matrix retains some orientational mobility. Similarly, in calorimetric experiments, the apparent heat capacity of water in a glassy maltohexaose–water mixture was that of liquid water, suggesting that water in the glassy carbohydrate can explore liquid-like configurations [19]. These observations suggest the need for measurements on diffusion in these systems, over a sufficient length scale to be relevant to practical usage. In this article we examine the effect of undercooling on diffusion in maltose–water mixtures as the glass transition is approached.

2. Experimental

Maltose monohydrate (Sigma) was used without further purification. Concentrated maltose solutions of known water content were prepared as previously described [8]. The crystalline maltose was first melted at 160°C, then cooled to 60°C, and water added to the desired concentration and mixed. Water contents were determined by vacuum drying at 60°C over P_2O_5.

Calorimetry.—Samples (5–10 mg) were weighed accurately into aluminium pans, using a Cahn 2000 recording electrobalance with a sensitivity of 0.1 μg. The pans were sealed quickly in order to minimise adsorption of moisture. Differential scanning calorimetry was performed with a Perkin–Elmer DSC2 calorimeter equipped with a cooler unit. Data were logged on a BBC microcomputer for subsequent analysis. Each sample was scanned twice; the first scan to minimise any differences in thermal history and the second to determine the glass transition temperature. A scanning rate of 10 K min^{-1} was used. After scanning, the water content of each sample was checked by weighing the pan, puncturing it, and reweighing it after vacuum drying at 60°C over P_2O_5. The glass transition temperature was determined from the sharp increase in differential heat flow at T_g. The glass transition temperature was taken to be the mid-point between the onset and completion temperatures.

Diffusion experiments.—Concentrated maltose solutions were transferred to Plastipak syringes (internal diameter, 4.7 mm) at 60°C. These were cut into cylinders of length, $2 \times l$, of between 2.0 and 8.0 mm. A maltose–water cylinder was placed on the pan of a Cahn 2000 recording electrobalance mounted in a chamber containing P_2O_5 which maintained the relative humidity below 2.0%. The relative humidity of the chamber was monitored using a Lee-Integer DHL49 humidity sensor calibrated against saturated salt solutions. The chamber was thermostated in an enclosure regulated to 0.1°C. The amount of water, M_t, lost from the cylinder was recorded as a function of time, t. If M_0 is the original mass of water in the maltose–water mixture, then for a cylinder with its ends open and curved surface sealed, when the surface concentration of water becomes effectively zero, the appropriate solution of the diffusion equation for small time periods is:

$$\frac{M_t}{M_0} = 2\left(\frac{\bar{D}t}{l^2}\right)^{1/2}\left\{\pi^{-1/2} + 2\sum_{n=1}^{\infty}(-1)^n ierfc\frac{nl}{\sqrt{(\bar{D}t)}}\right\} \tag{2}$$

where $\bar{D}$ is a mean value of a concentration-dependent diffusion coefficient [20]. $\bar{D}$ was obtained from measurements of the initial desorption when $M_t/M_0 < 0.01$. Preliminary experiments measured desorption over a 16-h period; during this time M_t/M_0 showed a $t^{1/2}$ dependence. Subsequent experiments lasted 2 h. For the range of water contents and experimental temperatures, the undercooled maltose–water mixtures were stable to crystallisation for at least several days as evidenced by the absence of a melting transition on differential scanning calorimetry. From the dependence of $\bar{D}$ on concentration it is possible by extrapolation to obtain $\bar{D}_0$, the value of $\bar{D}$ at zero concentration of water. Using standard procedures [20] the ratio $\bar{D}/\bar{D}_0$ can be used to estimate D, the interdiffusion coefficient.

3. Results

Fig. 1 shows a plot of T_g versus water content for maltose–water mixtures. The T_g of the mixture falls from 60.0°C at a water content of 1.5% w/w to 0.0°C at a water content of 12.5% w/w. This dependence of T_g on water content is in broad agreement

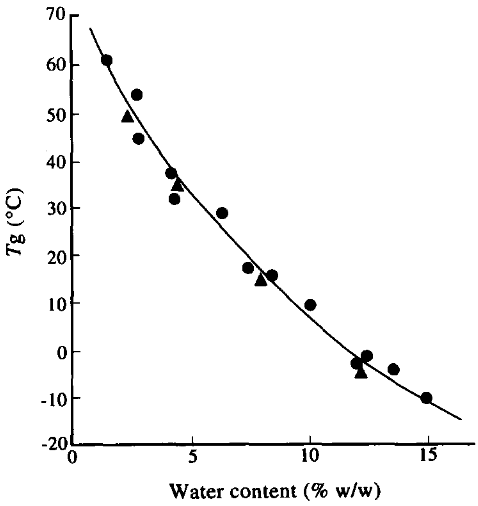

Fig. 1. Graph of glass transition temperature, T_g, versus water content for maltose–water mixtures. Measurements from this laboratory (this work and refs [8] and [21]), ●; measurements of Green and Angell [22], ▲.

with, and extends, earlier studies [8,21,22] and confirms that at low water contents the T_g of the mixture is very sensitive to variations in water content [1].

Fig. 2 shows a plot of the drying of an 86.8% w/w maltose–water mixture at 27.0°C, where M_t/M_0 is plotted as a function of $\sqrt{t}/2l$. The observed linear dependence of this reduced desorption plot shows the applicability of equation (2) for the determination of a diffusion coefficient in these systems [13].

The diffusion coefficient in the maltose–water mixtures was determined as a function of temperature and water content. Fig. 3 shows a plot of log $\bar{D}$ as a function of water

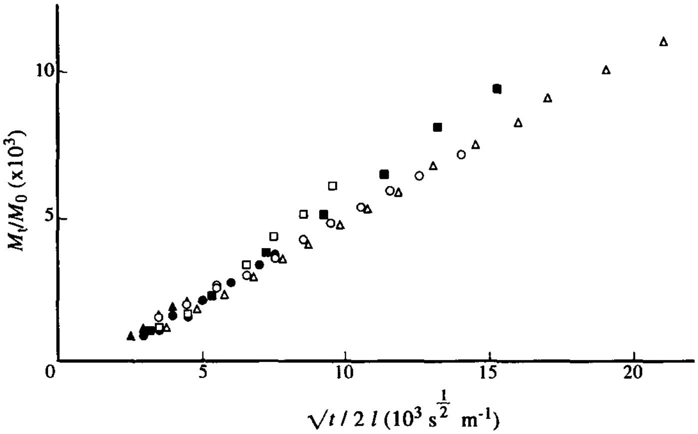

Fig. 2. Reduced desorption plot for an 87.0% w/w aqueous solution of maltose at 27.0°C, where l (mm) is 1.37 (△), 1.70 (□), 1.73 (■), 2.34 (○), 2.55 (●), and 3.64 (▲).

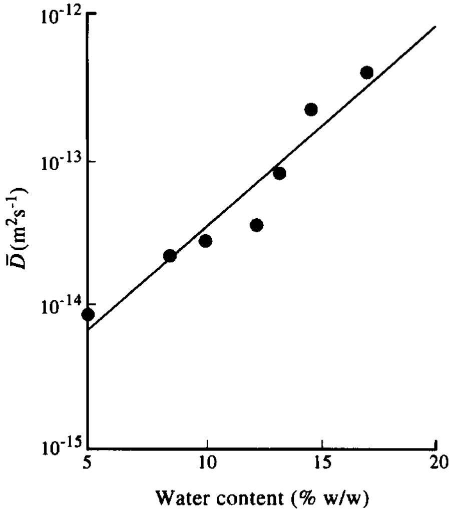

Fig. 3. Graph of mean diffusion coefficient, $\bar{D}$, versus water content for maltose–water mixtures at 27.0°C. The glass transition occurs at a water content of 6.0% w/w at this temperature.

content for maltose–water mixtures at 27.0°C. $\bar{D}$ increases from 9.0×10^{-15} to 4.0×10^{-13} m^2s^{-1} as the water content increases from 5.0 to 17.0% w/w. For this range of water content, the calorimetric T_g ranges from 36.0 to −14.0°C. The deviations from linear behaviour on this log-linear plot suggest that the rate of increase of the mean diffusion coefficient with increasing water content may be faster than exponential.

Crank [20] described approximate methods for extracting the concentration dependence of D from that of $\bar{D}$. In order to proceed, an assumption is made of the underlying dependence of D upon water content. The approximately linear dependence of log $\bar{D}$ upon water content in Fig. 3 suggests an exponential dependence. Extrapolating the data in Fig. 3 gives a value of 1.20×10^{-15} m^2 s^{-1} for $\bar{D}_0$, the mean diffusion coefficient at zero water content. This value is a factor of ~ 6.8 lower than the smallest value of $\bar{D}$ measured at a water content of 5.0% w/w. Applying the corrections computed by Hansen for exponential concentration dependence (tabulated by Crank [20]) to the data at 5.0% w/w water gives a D value of ~ 1.1×10^{-13} m^2 s^{-1}, which is a factor of 12.2 greater than the value of $\bar{D}$. In our experiments a consequence of the concentration dependence of D is that, during desorption, a surface layer of low water content forms in which diffusion is relatively slow. This layer hinders diffusion from sub-surface layers and makes a relatively large contribution to the mean diffusion coefficient. This method of correction is not systematically applied to the results in this paper since, in general, the concentration dependence of D can be discontinuous at the glass transition [23,24], and so the extrapolation to estimate $\bar{D}_0$ may be unreliable. For example, if the variation of D with water content is weaker below T_g, this would result in the estimate of $\bar{D}_0$ being low and an overestimate of the size of the correction.

In Fig. 4, the mean diffusion coefficient of a mixture containing 10.0% w/w water, having a calorimetric T_g of 10.0°C, is shown as a function of temperature in the range

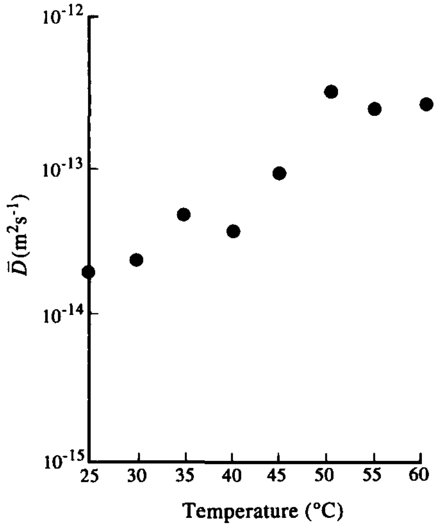

Fig. 4. Graph of mean diffusion coefficient, $\bar{D}$, versus temperature for a 90.0% w/w aqueous solution of maltose.

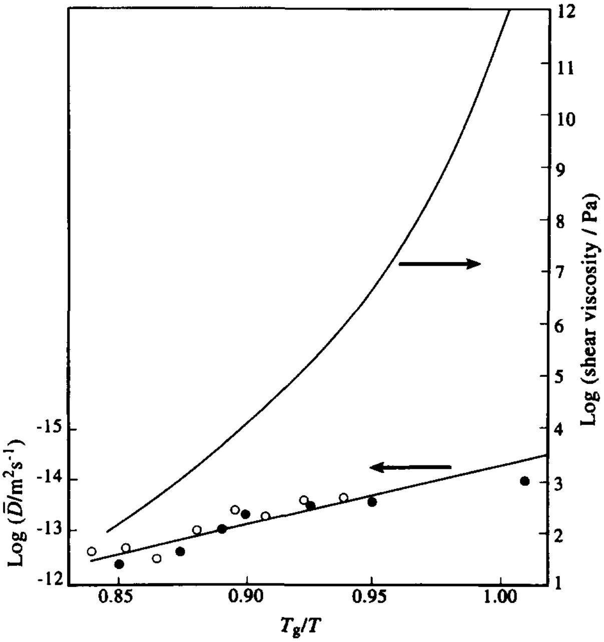

Fig. 5. A comparison of shear viscosity [8] and mean diffusion coefficient, $\bar{D}$, as a function of T_g/T. $\bar{D}$ results from water content study (as in Fig. 3), ●; and from temperature study (as in Fig. 4), ○.

25.0–60.0°C. As the temperature increases from 25.0 to 60.0°C, the mean diffusion coefficient increases from 1.5×10^{-14} m^2 s^{-1} to ca. 2.0×10^{-13} m^2 s^{-1}. The temperature dependence is apparently Arrhenian, with an activation energy of 70 kJ mol^{-1}. These diffusion data are combined in a plot of $\bar{D}$ as a function of T_g/T (Fig. 5), and compared with a VTF fitting of available viscosity data [8] on maltose–water mixtures.

4. Discussion

There have been a number of studies of diffusion in dilute aqueous solutions of low molecular weight carbohydrates. For example, the interdiffusion coefficient, D, at 25.0°C, extrapolated to zero concentration of carbohydrate, was 5.24×10^{-10} and 5.2×10^{-10} m^2 s^{-1} for sucrose and maltose, respectively [25,26]. With increasing concentration of carbohydrate, D slowly decreases, reaching a value of 4.7×10^{-11} m^2 s^{-1} at a concentration of 74.0% w/w maltose at 28.0°C [27]. NMR measurements [28] of the intradiffusion coefficients of water and sucrose in concentrated (70.0% w/w) sucrose solutions gave values of $\sim 1.0 \times 10^{-11}$ and 1.0×10^{-10} m^2 s^{-1} for sucrose and water, respectively, at 40.0°C. As the viscosity of these solutions [29] is still a factor of $\sim 10^{12}$ below that of a glass, these experiments on concentrated carbohydrate solutions do not approach the glass transition region.

There are a few studies of diffusion in biopolymeric materials as they approach dryness and vitrify [30–33]; for example, in a study of diffusion in a gelatinised starch film [31], it was found that the mean diffusion coefficient at 25.0°C fell from 1.0×10^{-12} to 1.0×10^{-14} m^2 s^{-1} as the water content decreased from 9.9 to 0.8% w/w. As an amorphous starch film containing 20.0% w/w water would have a T_g of 25.0°C [34], this indicates a limited retardation of the translational mobility of water in the glassy film. As starch films prepared from particulate dispersions of gelatinised starch are heterogeneous structures with large local variations in polymer concentration, some caution is necessary in the interpretation of the observed diffusive behaviour which could be markedly influenced by the fraction of water present in "pores". In another study [32] of diffusion in maltodextrin–water mixtures, it was found that the mean diffusion coefficient of water in maltodextrin–water mixtures at 21.5°C ranged from 1.9×10^{-11} m^2 s^{-1} at a water content of 26.4% w/w to 1.2×10^{-13} m^2 s^{-1} at a water content of 11.1% w/w. For malto-oligomers the glass transition region would be approached at the lower water contents [21], and these data are further evidence for a rather limited retardation in diffusion in this region. Similarly in a recent, preliminary report of an NMR study [33], it was found that the translational diffusion coefficient of water in a 80.9% w/w pullulan–water mixture was 4.0×10^{-11} m^2 s^{-1} at the calorimetric glass transition.

In the present study of maltose–water mixtures, the measured mean diffusion coefficients are in the range 10^{-12} to 10^{-14} m^2 s^{-1}. While this indicates that there is some slowing of diffusion as the glass transition is approached, it is not associated with the change in shear viscosity, which strongly diverges from diffusion coefficient at values of T_g/T in the region 0.8. The behaviour of this mixture is comparable with that of other organic liquids [11,12]. Further experiments are necessary to identify the effect of differences in molecular size of the two components on the observed change in diffusive behaviour in the region of T_g. The present study demonstrates that, while glassy carbohydrate matrices may have mechanical stability as a result of their very high viscosity and corresponding rigidity, the intuitive view that these matrices similarly ensure protection or encapsulation of low molecular weight species through a dramatic slowing of diffusion is in need of further investigation.

Acknowledgement

The authors thank the Office of Science and Technology for support of this research.

References

[1] L. Slade and H. Levine, in H. Levine and L. Slade (Eds.), *Water Relationships in Foods*, Plenum Press, New York, 1991, pp 29–102.
[2] L. Slade and H. Levine, *Adv. Food Nutr. Res.*, 38 (1994), in press.
[3] Y.M. Newman, S.G. Ring, and C. Colaco, *Biotechnol. Genet. Eng. Rev.*, 11 (1993) 263–294.
[4] F. Franks, *Pure Appl. Chem.*, 65 (1993) 2527–2537.
[5] C.A. Angell, *J. Phys. Chem. Solids*, 49 (1988) 863–871.
[6] C.A. Angell, R.C. Stell, and W. Sichina, *J. Phys. Chem.*, 86 (1982) 1540–1542.
[7] A.L. Ollett and R. Parker, *J. Texture Stud.*, 21 (1990) 355–362.
[8] T.R. Noel, S.G. Ring, and M.A. Whittam, *Carbohydr. Res.*, 212 (1991) 109–117.
[9] C.A. Angell, R.D. Bressel, J.L. Green, H. Kanno, M. Oguni, and E.J. Sare, *J. Food, Eng.*, 22 (1994) 115–142.
[10] H.J.V. Tyrrell and K.R. Harris, *Diffusion in Liquids, a Theoretical and Experimental Study*, Butterworths, London, 1984.
[11] E. Rössler, *Phys. Rev. Lett.*, 65 (1990) 1595–1598.
[12] E. Rössler, *J. Non-Cryst. Solids*, 131 (1991) 242–247.
[13] H. Fujita, in J. Crank and G.S. Park (Eds.), *Diffusion in Polymers*, Academic Press, New York, 1968, pp 75–106.
[14] D. Ehlich and H. Sillescu, *Macromolecules*, 23 (1990) 1600–1610.
[15] B.J. Cauley, C. Cipriani, K. Ellis, A.K. Roy, A.A. Jones, P.T. Inglefield, B.J. McKinley, and R.P. Kambour, *Macromolecules*, 24 (1991) 403–409.
[16] R.K. Chan, K. Pathmanathan, and G.P. Johari, *J. Phys. Chem.*, 90 (1986) 6358–6362.
[17] T.R. Noel, R. Parker, and S.G. Ring, *Carbohydr. Res.*, submitted for publication.
[18] T.R. Noel, S.G. Ring, and M.A. Whittam, *J. Phys. Chem.*, 96 (1992) 5662–5667.
[19] T.R. Noel and S.G. Ring, *Carbohydr. Res.*, 227 (1992) 203–213.
[20] J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1975.
[21] P.D. Orford, R. Parker, S.G. Ring, and A.C. Smith, *Int. J. Biol. Macramol.*, 11 (1989) 91–96.
[22] J.L. Green and C.A. Angell, *J. Phys. Chem.*, 93 (1989) 2880–2882.
[23] V. Stannett, in J. Crank and G.S. Park (Eds.), *Diffusion in Polymers*, Academic Press, New York, 1968, pp 41–73.
[24] I. Arvanitoyannis, M. Kalichevsky, J.M.V. Blanshard, and E. Psomiadou, *Carbohydr. Polym.*, 24 (1994) 1–15.
[25] L.J. Gosting and M.S. Morris, *J. Am. Chem. Soc.*, 71 (1949) 1998–2006.
[26] H. Uedaira and H. Uedaira, *Bull. Chem. Soc. Jpn.*, 42 (1969) 2140–2142.

[27] J. van der Lijn, *Simulation of Heat and Mass Transfer in Spray Drying*, Agric. Res. Rep. 845, Wageningen, 1976, pp 72–85.

[28] D. Girlich, H.-D. Lüdemann, C. Buttersack, and K. Buchholz, *Z. Naturforsch., Teil C*, 49 (1994) 258–264.

[29] M.P. Mageean, J.U. Kriscott, and S.A. Jones, *Physical Properties of Sugars and Their Solutions*, BFMIRA Scientific and Technical Survey No. 172, British Food Industries Research Association, Leatherhead, 1991, p 251.

[30] S. Bruin and K. Ch. A.M. Luyben, in A.S. Mujumdar (Ed.), *Advances in Drying*, Vol. 1, McGraw-Hill, New York, 1980, pp 155–215.

[31] B.P. Fish, in *Fundamental Aspects of the Dehydration of Foodstuffs*, Society of Chemical Industry, London, 1958, pp 143–157.

[32] L.C. Menting, B. Hoogstad, and H.A.C. Thijssen, *J. Food. Technol.*, 5 (1970) 111–125.

[33] S. Ablett, A.H. Darke, M.J. Izzard, and P.J. Lillford, in J.M.V. Blanshard and P.J. Lillford (Eds.), *The Glassy State in Foods*, Nottingham University Press, Nottingham, 1993, pp 189–206.

[34] K.J. Zeleznak and R.C. Hoseney, *Cereal Chem.*, 64 (1987) 121–124.