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Diffusion of short chain alcohols from amorphous maltose–water mixtures above and below their glass transition temperature

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Abstract

The apparent diffusion coefficient for short chain alcohols in undercooled maltose–water mixtures close to the calorimetric glass transition temperature, T_g, was measured by following desorption using headspace gas chromatography. The plasticising effect of the alcohols on T_g was characterised using differential scanning calorimetry. The initial appearance of alcohol in the headspace showed a linear dependence on the square root of time, allowing it to be modelled as a Fickian diffusive process. The diffusion coefficient decreased with increasing molecular size of alcohol and proximity to T_g. Close to the glass transition the variation of diffusion coefficient with temperature and composition does not follow that of viscosity and, for ethanol, divergence was observed at $T_g/T > 0.88$. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion; Alcohols; Amorphous carbohydrate; Glass transition

1. Introduction

Low water content amorphous carbohydrates are widely used for the stabilisation, and encapsulation of pharmaceuticals [1–3] and flavours [4,5]. Diffusive mobility in these matrices is relevant to water and volatile migration and potentially relevant to rates of chemical reaction [6]. Of particular interest is the relationship between viscosity and diffusivity. As a carbohydrate liquid is undercooled below its crystalline melting temperature, its viscosity progressively increases and is described by the semiempirical Vogel–Tammann–Fulcher (VTF) equation:

$$\eta = A \exp[B/(T - T_0)] \quad (1)$$

where A, B and T_0 are constants. For these ‘fragile’ liquids the viscosity, and associated structural relaxations, show a marked temperature dependence as the viscosity approaches 10^{12} Pa s, in the vicinity of the calorimetric glass transition temperature, T_g [7–9]. For example, for a 10% maltose–water (w/w) mixture with a T_g of 8 °C, the shear viscosity falls from 10^{12} to 10^5 Pa s as the temperature is increased from 8 to 33 °C. Hydrodynamic theories of diffusion predict that this very large viscosity change would have a corresponding effect on translational diffusion [10]. For a spherical particle (or molecule), assuming no ‘slip’ between the moving particle and fluid, the mutual diffusion coefficient, D is

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$$D = kT/6\pi\eta a \quad (2)$$

where k is Boltzmann's constant, T the absolute temperature, and a the hydrodynamic radius. This is the Stokes–Einstein equation. While this type of behaviour may be observed for macromolecular or colloidal particles embedded in a viscous medium, for low molecular weight species in both polymeric [11] and molecular liquids [12] an uncoupling of diffusion from shear viscosity is observed as T_g is approached. While this uncoupling has long been recognised in polymers [13], it is relatively recent that it has been observed in molecular liquids, even occurring for self-diffusion in single component near glassy liquids [14]. It is of theoretical and practical interest to examine the dependence of this uncoupling of viscosity and diffusivity on molecular size.

In an early study on carbohydrate systems, Menting et al. [15] showed that there was a linear relationship between the logarithm of the diffusion coefficient in a 20.1% w/w water content maltodextrin and the molecular diameter of organic volatiles ranging in size from methane (CH_4) to camphor ($C_{10}H_{16}O$). The diffusion coefficient falls from 2.5×10^{-11} $m^2\ s^{-1}$ (methane) to 3.1×10^{-15} $m^2\ s^{-1}$ (camphor) over this range. Unfortunately this research, which predated more recent interest in the relationship between the glass transition of carbohydrates and molecular mobility, does not include measurements of T_g. Recent studies have reported measurements of the diffusion of water in amorphous maltose–water mixtures [16,17], and the conductivity of amorphous maltose–water–KCl mixtures [18] in both the supercooled liquid and glassy states, and the diffusion of permanent gases in starch-based films [19]. For the diffusion of water from a maltose–water glass, a marked uncoupling of diffusion and viscosity is observed, of the order of eight orders of magnitude at T_g.

The present study examines the diffusion of a number of volatile short chain alcohols (methanol, ethanol, propan-1-ol and propan-2-ol) in a low water content amorphous carbohydrate (maltose) of well-defined composition and T_g. The diffusion coefficients were measured using a desorption technique and headspace gas analysis. The main aim was to examine how diffusion was affected by molecular size of the alcohol, and proximity of the matrix to its T_g [20]. Therefore, it was necessary to examine the effect of the alcohol on the T_g of the maltose–water mixture. The observed diffusive behaviour was compared with that found for polymeric and molecular liquids.

2. Experimental

Sample preparation.—Amorphous maltose–water–alcohol mixtures were prepared with water and alcohol contents in the range 3.9–13.4 and 0.2–7.0% w/w, respectively. Several short chain alcohols were examined, including MeOH and propan-2-ol (analytical grade reagents, Fisher Scientific UK, Loughborough, UK), and EtOH (abs) and propan-1-ol (AnalaR, BDH, Lutterworth, UK). The water was 'ultrapure' water taken from a water purifier (Elgastat Maxima, Elga, High Wycombe, UK). The higher water content mixtures were prepared in a series of steps, as follows. Crystalline maltose monohydrate (grade 1, Sigma Chemical Co., Poole, UK) and, if appropriate, water were heated (140 °C) in sealed Pyrex culture tubes until molten and well mixed, the sample was then cooled (60–70 °C) and the alcohol was added to this mixture and carefully reheated. The sample was mixed thoroughly to form a homogeneous mixture. For samples containing $< 5.5\%$ w/w water the mixtures were prepared by heating and mixing dry amorphous maltose (prepared by the evaporation of water from a liquid maltose monohydrate–water mixture, and subsequent drying under vacuum at 60 °C, over P_2O_5, for 24 h) with the required amount of water and alcohol at 140 °C. The sample was loaded, while still warm, into Plastipak syringes (polypropylene, 1 mL capacity, 6.5 mm outside diameter, Becton–Dickinson, Dublin, Ireland) and allowed to cool. Cylinders, typically 4 mm long, with two open ends were cut and then sealed into 22 mL headspace vials with butyl rubber septa, star springs and aluminium caps (Perkin–Elmer, Beaconsfield, UK). The samples were held at constant temperature prior to analysis of the headspace volatiles. A portion of the original mixture was retained for the determination of the water content and initial short chain alcohol content.

Glass transition temperature.—The T_g of the mixtures was determined using a Perkin–Elmer DSC-2 differential scanning calorimeter (DSC) equipped with a liquid nitrogen cooling system. The instrument was calibrated for temperature using the melting of β-naphthyl ether (27.5 °C) and indium (156.6 °C). Typically, 5 mg of the amorphous maltose–water–alcohol mixture was quickly weighed, using a Mettler ME30 microbalance (1 μg sensitivity), and sealed into aluminium DSC pans. The sample was scanned and then rescanned from -40 to 50 °C at a heating rate of 10 °C min^{-1}. The T_g was taken as the temperature at which the heat capacity was midway between that in the liquid and glassy states of the rescanned sample [21].

Water content determination.—The water content of the amorphous mixtures was determined using a Baird and Tatlock AF5 Karl–Fischer titrator with Hydranal Composite 5 (Riedel-de Haen, Gillingham, UK) as the Karl–Fischer reagent [22]. The titrator was calibrated using water and a standard (sodium tartrate dihydrate, Fluka, Gillingham, UK). Prior to titration a sample of each mixture ($\sim$100 mg) was weighed into a screw capped vial (2 mL) and completely dissolved in a mixture of 2:1 MeOH:formamide (1 mL) (formamide: SigmaUltra grade, Sigma Chemical Co., Poole, UK).

Determination of initial short chain alcohol content in amorphous maltose mixtures.—The alcohol content of the matrices was determined using high performance cation exchange chromatography. The samples were analysed using an Aminex HPX-87H column (Bio-Rad Laboratories, Hemel Hempstead, UK) fitted with an RI detector (Gilson, Model 131) and pump (Gilson, Model 305). An aq soln (10% w/w) of the amorphous carbohydrate mixture (20 μL) was injected and eluted with 12 mM sulphuric acid at a flow rate of 0.7 mL min^{-1} and a column temperature of 30 °C [23].

Determination of short chain alcohol desorbed into headspace.—A Perkin–Elmer Autosystem XL GC fitted with a flame ionisation detector and an HS 40XL GC automatic headspace injector (Perkin–Elmer Corp., Beaconsfield, UK) was used to determine the concentration of alcohol that had desorbed from the cylindrical samples into the headspace of the vial. The samples were analysed using a splitless injection and a temperature program from 50 to 65 °C at a rate of 3 °C min^{-1}. A BP1 capillary column was used (25 m × 0.32 mm i.d., 4 μm film thickness, SGE Europe Ltd., Milton Keynes, UK) with He carrier gas (head pressure, 50 kPa), and injector and detector temperatures of 85 and 240 °C, respectively [24]. Calibration standards were analysed for each of the alcohols in the study. The amount of alcohol required to saturate the headspace of the vial was determined from measurements of chromatograph peak areas for a series of vials containing 0–10 μL of alcohol. The saturation concentration was determined from the intersection of the lines fitting the initial linear increase of peak area with amount of alcohol and the section of constant peak area which occurs at higher amounts of alcohol and corresponds to saturation.

Analysis of headspace desorption data.—Diffusion in a cylinder with its ends open and curved surface sealed can be modelled as a one dimensional diffusion problem. Initially the headspace above the surface is free from alcohol, and so, the appropriate boundary condition is that the surface concentration is zero. The cylinder can be viewed as being part of an infinite plane for which the appropriate soln [25] of the diffusion equation at small times is given by,

$$\frac{M_t}{M_0} = 2\left(\frac{\bar{D}t}{l^2}\right)^{1/2}\left\{\pi^{-1/2} + 2\sum_{n=1}^{\infty}(-1)^n \mathit{ierfc}\,\frac{nl}{\sqrt{\bar{D}t}}\right\} \tag{3}$$

where M_t is the mass of volatile in the headspace, M_0 is the total mass of volatile in the cylindrical sample, t is time and $2l$ is the length of cylinder. In practice only the $\pi^{-1/2}$

term in the right hand brackets of Eq. (3) was required. For example, for $(\bar{D}t/l^2)^{1/2} = 0.4$, the leading term ($n = 1$) in the summation in the right hand brackets is $-2ierfc(2.5) = -0.0001$ [25] which is negligible compared with $\pi^{-1/2}$. This value of $(\bar{D}t/l^2)^{1/2}$ corresponds to $M_t/M_0 = 0.45$. In our experiments $M_t/M_0 < 0.45$, and so, the slope of the regression line of the fractional release, M_t/M_0, against $t^{1/2}$ was used to calculate the apparent diffusion coefficient, $\bar{D}$. All regression were performed on PC using MINITAB® (MINITAB® for Windows, release 10.2, Minitab Inc., PA, USA). No attempt will be made here to determine the dependence of the diffusion coefficient upon alcohol concentration [26] and, for this reason, they are reported as apparent diffusion coefficients. Samples that crystallised visibly were excluded from the analysis. The occurrence of crystallisation although not entirely predictable did follow certain patterns. Typical experiments were 6–10 days long. In these, it was only experiments in which $T-T_g$ was > 16 °C and the water content was > 11.6% w/w in which crystallisation was observed. At the end of the desorption experiment, even if maltose crystallisation had occurred, the concentration of the volatile in the headspace was < 25% of the saturation level and, more typically, < 5% of the saturation level.

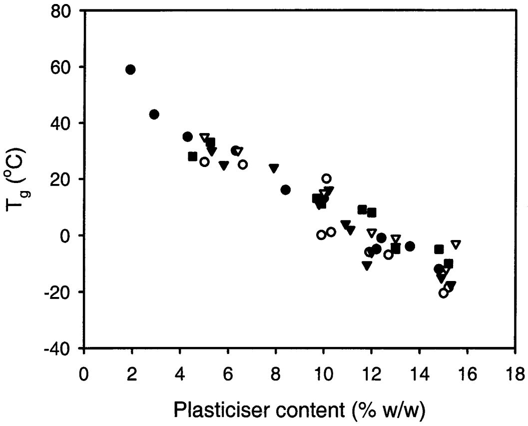

Fig. 1. Glass transition temperatures of amorphous maltose–water–alcohol mixtures with different total plasticiser contents. Alcohol in mixture: ●, none (maltose–water only); ○, MeOH; ▼, EtOH; ▽, propan-1-ol; ■, propan-2-ol. Alcohol contents were in the range 0.1–7.0% w/w.

3. Results and discussion

Glass transition temperatures of the amorphous maltose–water–alcohol mixtures.—The effect of composition on the glass transition temperature, T_g, of the amorphous maltose–water–alcohol mixtures is shown in Fig. 1. Composition is expressed as the total amount of plasticiser, P (% w/w), i.e., the sum of the water, W (% w/w), and alcohol content, A (% w/w). By comparing samples plasticised with water alone with those plasticised with water–alcohol mixtures, it can be seen that, on a weight basis, the plasticising effect of the alcohols is broadly similar to that of water. The T_g of pure maltose is ~93 °C [20] and the T_g of the alcohols is in the range −164 to −180 °C, with no clear effect of molecular size or structure [27]. The reported T_g of water is in the region of −137 °C [28]. A linear regression, of the maltose–water data in Fig. 1, yields the equation T_g (°C) = 61.0–5.03 P (% w/w). The mixtures containing the alcohols show small deviations from this behaviour. Within the composition range examined, methanol and ethanol are more effective, on a weight basis, than water as a plasticising agent (2.1 °C/% w/w methanol and 1.4 °C/% w/w ethanol), while propanol is less effective (0.7 °C/% w/w propan-1-ol). The terms in the brackets were determined using linear regression.

Desorption of alcohols.—Following convention [10,29], the major component in the ternary, maltose–water–alcohol mixture, i.e., the amorphous maltose was regarded as the 'solvent'. The concentration of alcohol in this solvent was dilute to minimise the effect of concentration-dependent changes in chemical potential on the observed diffusive behaviour. Such effects are normally characterised, in systems with high solute concentrations, through the determination of cross diffusion coefficients [29]. For the dilute systems studied these effects were neglected and an apparent diffusion coefficient, $\bar{D}$, determined. Fig. 2 shows the typical dependence of the fractional release, M_t/M_0, upon $t^{1/2}$ for mixtures with 12.1 ± 0.1% w/w water and 2.8 ± 0.1% w/w alcohol at 20 °C. Initially, M_t/M_0 varies linearly with $t^{1/2}$ which is characteristic of diffusive release and this portion of the data was

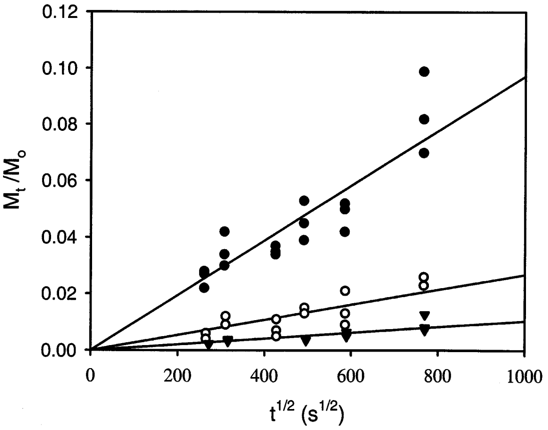

Fig. 2. Fractional headspace release, M_t/M_0, of alcohol from amorphous maltose–water–alcohol mixtures plotted against $t^{1/2}$. Experimental conditions: Temperature, 20 °C; water content, 12.1% w/w; alcohol content, 2.9% w/w. Alcohols: ●, MeOH; ○, EtOH; ▼, propan-2-ol.

used to determine an apparent diffusion coefficient using Eq. (3). At times $> 7 \times 10^5$ s an enhanced release was observed which coincided with a change in appearance of the sample from transparent to opaque as maltose crystallised. During the desorption, the surface layer of the mixture becomes depleted in alcohol, as modelled in the surface boundary condition, however, any concentration dependence of the diffusion coefficient is insufficiently large to give rise to deviations from the $t^{1/2}$ time dependence

Through changes in water and alcohol content, it was possible to prepare mixtures with a range of T_g values (Table 1), and so, coupled with changes in temperature, T, it was possible to examine diffusivity over a range of values of $T - T_g$ (-15 to 60 °C). For the comparison of the diffusivity of the different alcohols their different plasticising ability, characterised above, needs to be recognised. The effect of water content on the diffusivity of the different alcohols is shown in Fig. 3. Following the approach of Berens and Hopfenberg [30] a mean van der Waals diameter, d_b, is used to characterise the size of the alcohols. This is calculated from the van der Waals molar volume, b, using the formula, $d_b/\text{nm} = 1.184\,(b/\text{L mol}^{-1})^{1/3}$. This gives mean diameters of 0.478, 0.525, 0.564, and 0.569 nm for methanol, ethanol, propan-1-ol, and propan-2-ol, respectively [31]. The diffusivity decreases with decreasing water content and is particularly slow ($D < 10^{-19}$ m^2 s^{-1}) in the glassy samples (4.2–4.8% w/w water). For the non-glassy matrices the diffusivity also decreases with increasing molecular size, following the homologous series methanol, ethanol, and propanol.

Mixtures containing ethanol were studied more extensively (Table 1), including a limited investigation of the effect of temperature. Examining the data for linear variations of log $\bar{D}$ with water content, alcohol content and temperature yields the equation:

$$\log(\bar{D}/\text{m}^2\ \text{s}^{-1}) = -21.6 + 0.50\ (W/\%\ \text{w/w}) + 0.35\ (A/\%\ \text{w/w}) + 0.044\ (T/\ ^\circ\text{C}) \quad (4)$$

in which the coefficient for W is significant at the 99% level, A at the 95% level and T at the 90% level. Diffusion increases with increasing water content, alcohol content and temperature. The effect of water content and alcohol content are often assigned to the effects of plasticisation and, as such, are reflected in the T_g of the mixture. Thus the single variable which might be expected to describe the variation of the diffusivity with composition and temperature is the temperature difference, $T - T_g$. Fig. 4 shows the variation of the logarithm of ethanol diffusivity with $T - T_g$. Linear regression analysis shows a significant (at the 95% level) linear behaviour whether the extreme glassy point is included or not. Regressing points above T_g gives

$$\log(\bar{D}/\text{m}^2\ \text{s}^{-1}) = -16.8 + 0.090\ (T - T_g) \quad (5)$$

$\bar{D}$ varies by a factor of ten per 11 °C, in the range 0–60 °C above T_g. A further test of the utility of $T - T_g$ for characterising the diffusivity is shown in Fig. 5. This shows the diffusivities for the alcohols in mixtures with different water contents and temperatures but all with $T - T_g$ in the range 21–31 °C. As before the apparent diffusion coefficient decreases with increasing molecular size. For a particular alcohol the diffusivities are similar indicating that $T - T_g$ is a useful predictor of diffusivity for each of these alcohols.

As the glass transition is approached diffusion slows and it is useful to examine whether the slowing of diffusion is coupled to the increase in viscosity, as might be expected if

Stokes–Einstein type behaviour applied in these systems. In Fig. 6 the expected temperature dependence (expressed as T_g/T) of diffusivity according to the Stokes–Einstein equation (calculated from Eq. (2) using the viscosity of a maltose–water mixture with 12.1% w/w water [7] and a hydrodynamic diameter of 0.525 nm, the van der Waals diameter of ethanol) is compared with the apparent diffusion coefficient of water in a binary maltose–water mixture [16] and the present data on the diffusion coefficient of ethanol in the ternary maltose–water–ethanol mixture. For the water data although there is a slowing of water mobility in the carbohydrate matrix there is a strong divergence of diffusion coefficient and shear viscosity at values of T_g/T in the region of 0.8. For the desorption of ethanol from the ternary maltose–water–ethanol mixture the temperature dependence of apparent diffusion coefficient shows Arrhenius-like behaviour. Within the

Table 1
Composition (W, water content; A, alcohol content), experimental temperature, T, glass transition temperature, T_g, and apparent diffusion coefficient, $\bar{D}$, for amorphous maltose–water–alcohol mixtures

Alcohol	W (% w/w)	A (% w/w)	T (°C)	T_g (°C)	$T-T_g$ (°C)	$\bar{D}$ (m^2 s^{-1})	Figs.
MeOH	13.4	1.8	20	−19	39	5.1×10^{-13}	
	9.2	1.1	20	1 [a]	19	1.4×10^{-14}	
	12.1	2.7	20	−19	39	3.1×10^{-14}	2 and 3
	11.7	1.0	20	−7 [a]	27	1.7×10^{-15}	3 and 5
	4.2	0.8	20	26 [a]	−6	3.0×10^{-20}	3
	5.3	1.3	55	25 [a]	30	4.2×10^{-16}	5
EtOH	12.9	0.9	20	−10	30	5.1×10^{-14}	4
	12.8	2.1	20	−17	37	7.1×10^{-14}	4
	12.6	3.1	20	−22	42	7.1×10^{-14}	4
	12.4	4.6	20	−31	51	1.1×10^{-13}	4
	12.4	5.6	20	−37	57	1.1×10^{-13}	4
	8.5	1.4	20	9	11	6.0×10^{-16}	4
	8.4	2.7	20	2	18	1.0×10^{-15}	4
	8.3	4.0	20	−6	26	2.0×10^{-15}	4
	8.1	5.6	20	−16	36	1.7×10^{-15}	4
	8.0	7.0	20	−24	44	6.0×10^{-15}	4
	13.4	1.3	20	−15	35	1.4×10^{-13}	4
	13.3	2.2	40	−20	60	8.0×10^{-13}	4
	9.3	1.6	40	4	36	6.1×10^{-15}	4
	9.3	1.8	20	2 [a]	18	4.0×10^{-16}	4
	12.1	2.9	20	−18	38	2.1×10^{-15}	2–4
	11.7	1.3	20	−4 [a]	24	2.0×10^{-17}	3–5
	4.8	1.0	20	25 [a]	−5	3.0×10^{-21}	4
	6.3	1.1	55	24 [a]	31	6.8×10^{-17}	4 and 5
Propan-1-ol	11.9	2.9	20	−11	31	1.0×10^{-16}	
	12.2	2.8	20	−13	33	1.2×10^{-14}	
	12.4	2.8	20	−14	34	8.3×10^{-17}	3
	12.5	0.8	20	−5	25	1.2×10^{-17}	
	11.6	1.4	20	−1 [a]	21	7.1×10^{-19}	3 and 5
	4.3	0.7	20	35 [a]	−15	4.4×10^{-21}	3
	5.6	0.8	55	30 [a]	25	6.0×10^{-19}	5
Propan-2-ol	12.2	2.9	20	−12	32	3.2×10^{-16}	2
	11.7	1.3	20	−5 [a]	25	1.3×10^{-18}	5
	3.9	0.2	20	34 [a]	−14	2.4×10^{-20} [b]	3
	4.8	0.4	55	27 [a]	28	6.0×10^{-19}	5

[a] Indicates direct measurement of T_g of mixture. Other values were obtained from composition and regression equations given in text.

[b] Gradient of M_t/M_0 significant at 95% level.

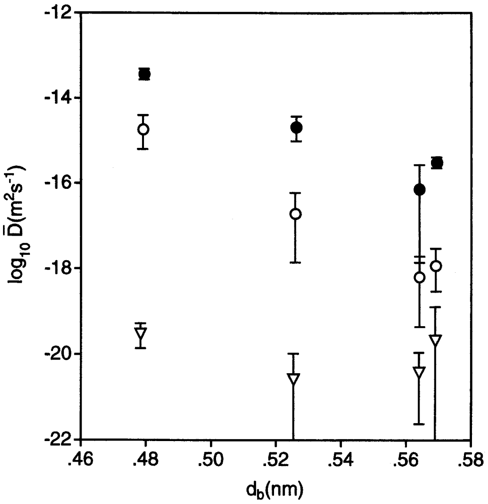

Fig. 3. Logarithm of apparent diffusion coefficient, $\bar{D}$, at different water contents plotted against the van der Waals diameter of alcohol, d_b. Water content ranges: ●, 12.1–12.2% w/w; ○, 11.7% w/w; ▽, 4.2–4.8% w/w. Error bars are 99% confidence limits. See Table 1 for further details.

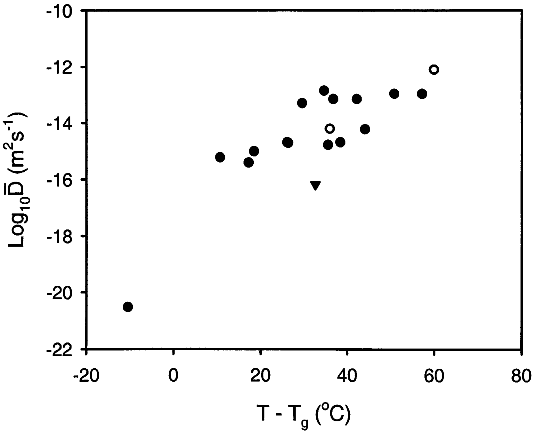

Fig. 4. Logarithm of apparent diffusion coefficient, $\bar{D}$, of EtOH plotted against $T - T_g$. Temperature, T: ●, 20 °C; ○, 40 °C; ▼, 55 °C. See Table 1 for further details.

range of T_g/T of 0.85–0.95 the average diffusion coefficient is in the range 10^{-13} to 10^{-16} m^2 s^{-1}, while the viscosity change is greater than four orders of magnitude from $\sim 10^2$ to $\sim 10^{6.5}$ Pa s. These values of diffusion coefficient compare with a value of $\sim 1.2 \times 10^{-9}$ m^2 s^{-1} for the limiting interdiffusion coefficient in ethanol–water mixtures at 25 °C [10]. Compared with the diffusivity of water in the binary maltose–water mixture the uncoupling of diffusion from shear viscosity is somewhat less marked for ethanol in the ternary, maltose–water–ethanol mixture, (although still many orders of magnitude in the immediate vicinity of T_g), and occurs at values of T_g/T in the region of 0.88. This behaviour is comparable with that observed for a number of organic liquids [12,32] including salol and glycerol. From measurements of self-diffusion and/or tracer diffusion it was observed that an uncoupling of diffusivity from shear viscosity occurred at values of T_g/T in the region of 0.833. The extent of uncoupling of tracer diffusion showed a dependence on size of tracer. As the size of the tracer approached then exceeded that of the solvent, the change in diffusivity with temperature approached and

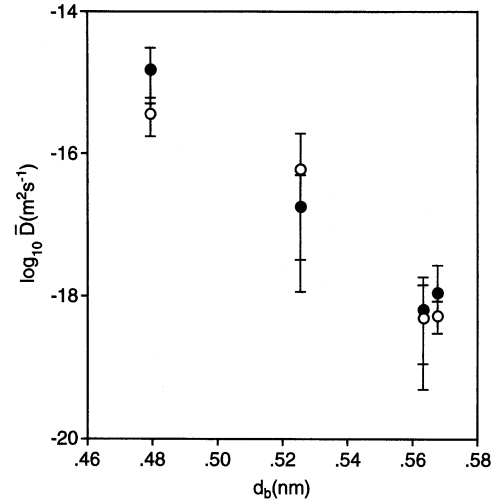

Fig. 5. Logarithm of apparent diffusion coefficient of alcohol in mixtures with similar $T - T_g$ (21–31 °C) plotted against the van der Waals diameter of alcohol. Conditions: water content, 11.6–11.7% w/w, and temperature, 20 °C, ●; water content, 4.8–6.3% w/w, and temperature, 55 °C, ○.

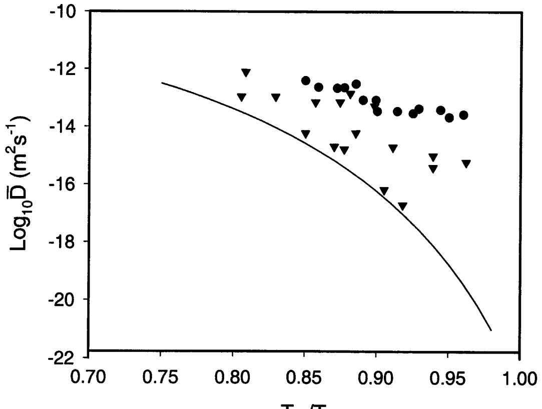

Fig. 6. A scaled Arrhenius plot comparing the observed diffusive behaviour for water in a maltose–water mixture [16], ●; and EtOH in a maltose–water–EtOH mixture (this work), ▼; with that predicted from the viscosity [7] assuming Stokes–Einstein behaviour (—). See text for details.

then, eventually, followed the change in viscosity. In the present study the short chain alcohols are smaller than the maltose solvent and the observation of uncoupling is consistent with these other studies.

It is hoped that this study will stimulate further experimental and theoretical work. For example, there is much interest in the preservation of peptides [33,34], proteins, pollen and seeds [35]. One proposal is that the limited molecular mobility in, for example, low water content amorphous carbohydrates can result in preservation. It is proposed that the mobility of reactants is sufficiently limited to slow deteriorative reactions. The present study shows that the retardation of diffusive mobility in low water content amorphous carbohydrates depends upon molecular structure. This suggests that, while it may be possible to retard the reactions of species which are slowed in glassy and near glassy states, other reactions involving species with motions not coupled to glass formation will not be affected.

Currently measurements of slow dynamics are relatively scarce. Further improvements in sensitivity would extend the range of composition accessible to study. More detailed studies involving both sorption and desorption and probing concentration dependence would give a fuller description of the diffusion process. NMR-based techniques such as the stimulated echo method [14] and stray-field magnetic resonance imaging [36] could usefully be applied. On the theoretical side, the elementary jump processes which give rise to diffusion need to be related to the motions of the other components of the mixture, a link which has been made in polymer–penetrant mixtures [37].

4. Conclusions

The diffusion of short chain alcohols in undercooled maltose–water mixtures decreases with increasing molecular size of the alcohol. The temperature difference between the temperature of observation, T, and T_g is a useful predictor of diffusivity for each of the alcohols examined with diffusion slowing as T_g is approached. Nevertheless the slowing of diffusion is not as great as might be expected from Stokes–Einstein type behaviour, and is in general agreement with observations on diffusivity in other organic liquids in the proximity of T_g.

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