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Water diffusion in glasses of carbohydrates

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Abstract

Diffusion constants of water have been determined at various temperatures, water contents and molecular weights in glassy systems of dried glucose syrups and maltose, with water contents between 3 and 10% (w/w). The diffusion constants were determined from the rate of desorption under reduced air pressure. The initial desorption was shown to be diffusion controlled when sufficiently reduced pressures were applied. The water diffusion was found to be an activated process, with an activation energy that is quite independent of the mean molecular weight and water content of the carbohydrate matrix. The diffusion in matrices of the oligomeric chains of the glucose syrups is faster than in maltose matrices at equal water content. Using an Eyring model for interpretation, this is ascribed to longer jump distances in the activated process in the less densely packed systems containing relatively long oligomeric chains. A strong dependence of the jump distance on the water content was found. © 1997 Elsevier Science Ltd.

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1. Introduction

Glasses of low-molecular-weight carbohydrates are found in nature under circumstances where the activity of biopolymers has to be preserved during severe drought [1] and cold [2]. A possible mechanism of the preserving effect of glassy carbohydrate is the partial replacement of water by carbohydrate molecules as the solvating agent. Like water, carbohydrates have the capacity to form hydrogen bonds with biopolymers. However, the presence of high concentrations of carbohydrate avoids the damaging effect of water crystallisation at low temperatures, while at low water contents, the solvating carbohydrate molecules, that are locked in a rigid matrix, stabilise the higher-order structure of the biopolymers. Preservation and encapsulation in glassy carbohydrate matrices is also used in the pharmaceutical and food industries [3]. In preservation the aim is usually to lengthen the shelf life of unstable compounds such as medicines and enzymes whereas, in encapsulation the role of the matrix is to retain volatile flavours in processed food.

The present work is part of a wider effort to obtain an understanding of the factors which determine the mobility of small amounts (typically below 10% w/w) of small molecules, for example water, in glassy low-molecular-weight carbohydrates. It describes an approach to the problem of measuring the very slow diffusion in glassy and near glassy sys-

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tems. The values of diffusion constants of water in low-molecular-weight carbohydrate–water systems are typically below 10^{-13} m^2 s^{-1} [4]. This is outside the range accessible to Pulsed Field Gradient NMR [5]. Using stimulated echoes and a gradient of 20,000 G m^{-1}, the lowest water diffusion that can be measured in the present systems were found to be about 10^{-13} m^2 s^{-1}. In systems with a slower diffusion, the transverse relaxation rate T_2^{-1} becomes too large in order to generate a (stimulated) echo [6]. Instead, the possibilities offered by desorption rate measurements were explored, using a microbalance. Recently, this method has been used to measure water diffusion constants in maltose–water systems just above the glass transition temperature [4]. Desorption rate measurements are in principle able to provide information on extremely slow diffusion (10^{-17} m^2 s^{-1} and slower) [7] and are therefore suitable for measuring water diffusion in carbohydrate glasses. Sensitivity can be increased through the use of high surface area samples.

Dried glucose syrups and maltose were chosen because they are readily available and relevant to the practical usage of carbohydrates for encapsulation. The availability of glucose syrups in spray-dried form makes them particularly suitable for diffusion experiments, because the high surface to volume ratio accelerates the desorption rate, which would otherwise be difficult to measure. The data reported here complement the water diffusion constants reported in ref. [4] for maltose–water systems above the glass transition.

2. Experimental

The determination of diffusion constants from desorption measurements.—The method of obtaining the diffusion constant of water from desorption rate measurements relies on the assumption that when the water vapour pressure (or, strictly speaking, the chemical potential) in the space surrounding the sample is made sufficiently low, the diffusion of water from the interior towards the surface of the sample determines the rate of desorption (i.e. drying). In the space surrounding the sample, there should be no build up of an interfacial layer or concentration gradient, which would introduce a time dependent chance of water molecules re-entering the sample. Such a time-dependent chance would bring in an additional characteristic time in the drying rate, which would no longer be a simple function of the diffusion constant. Reducing the vapour pressure of water can be achieved by employing a desiccant such as phosphorous pentoxide, which reduces water pressure only. A stronger driving force is achieved by reducing the total pressure with a vacuum pump.

When the desorption rate is determined by diffusion, and the outer water activity is much lower than that at the surface of the sample, the initial decay of the mass of water in the sample, $M(t)$, is described by a linear function of the square root of time [8]:

$$\frac{M(t)}{M(0)} = 1 - k\left(\frac{Dt}{l^2\pi}\right)^{1/2} \quad (1)$$

where $M(0)$ is the initial mass of water, D is the mutual diffusion constant of water and matrix molecules, k is a numerical constant (equal to 2 for a plane sheet, equal to 4 for an infinitely long cylinder, and equal to 6 for a closed surface), and l is the distance that determines the size of the system (half the thickness of a plane sheet, the radius of a cylinder, or the radius of a sphere with the same volume as that enclosed by the closed surface). Since the water concentration is low (usually less than 10% w/w), the matrix molecules move very little during the desorption process, and therefore the mutual diffusion constant is expected to be nearly equal to the tracer or self diffusion constant. For several reasons, the linear dependence of the mass on $t^{1/2}$ fails after long times. Commonly it is found that the mass decay rate decreases as time proceeds. The most obvious reason is the drying out of the centre of the sample, causing a decrease in the volume that contributes to the mass decay rate and higher order terms to become significant. Other reasons are the decreasing equilibrium vapour pressure which causes re-absorption of water (and, consequently, a failure of the assumption that the desorption rate is determined by diffusion) and a concentration dependent diffusion constant which decreases with decreasing water concentration. Unless the definition of the sample geometry is extremely good, it is not possible to interpret the long time decay rate.

Instrumentation.—The desorption rate measurements were carried out on a Cahn 2000 Electrobalance. The balance, mounted in a vacuum bottle, was positioned in a custom-made temperature-controlled cabinet, which was equipped for thermal control with a light bulb supplying heat, a circulating fan and a copper tubing radiator fed with coolant from a thermostatted water bath. The temperature range accessible was 15 to 65 °C, and the temperature could be

controlled within 0.02 °C. Data from the balance was collected by a time logging microcomputer. The pressure was measured with a mercury manometer and controlled with an electronically operated magnetic valve.

Samples.—Samples of glassy maltose–water with a well defined surface area to weight ratio were prepared by mixing molten maltose–water (Maltose monohydrate, Sigma) and olive oil, the latter acting as a dispersion medium and, fortuitously, as a surfactant. The mixtures were made at temperatures between 120 and 150 °C in sealed Pyrex tubes and mixed with a vortex mixer. After vigorous mixing, the suspensions of droplets of molten maltose–water were quickly cooled in an ice–water mixture. The oil was removed by washing with diethyl ether, while fast evaporation of diethyl ether had to be avoided because this gives rise to cooling, condensation of atmospheric humidity, and, consequently, a modification of the water content of the glassy maltose–water beads. Microscopic inspection of the beads, which ranged between 0.1 and 1 mm in diameter, showed that they were homogeneous, transparent and nearly spherical. By sieving, beads with diameters smaller than 300 μm and larger than 500 μm were removed, which resulted in a sample for which the surface area could be accurately estimated.

Spray-dried glucose syrups with a range of dextrose equivalents (DEs) were kindly provided by Roquette-Frères (France). Sieving yielded fractions with a limited range of particle size which allowed the qualitative effects of narrowing the particle size range to be demonstrated. When observed under the microscope, the particles were found to be transparent and apparently homogeneous without pores or bubbles, but often showed fracture surfaces and were generally non-spherical in shape. The irregular non-spherical shape meant that the surface area could not be estimated and so the surface area was determined experimentally from the desorption rates from the powders and a cylindrical tablet compressed from the same material. The tablet which had a well-defined surface area was made by compressing a quantity of powder with a pressure of 10^9 N m^{-2} at about 100 °C, a temperature which is well above the glass transition of the powder (ca. 60 °C). After cooling and slow release of the compression, this resulted in a nearly transparent tablet, of which the drying rate was measured at a relatively high temperature, under experimental conditions at which the desorption from the small surface area of the tablet is easy to measure. By comparison of the initial desorption rates of the powder and the tablet at the same temperature and pressure, the surface area of the powder could be obtained. This procedure to determine the specific surface area was carried for one DE value (47). The other spray-dried glucose syrups used in this work were assumed to have the same specific surface area. The water content was determined by drying under vacuum at 80 °C for two days. Some properties of the dried glucose syrup samples used are summarised in Table 1. The glass transition temperatures (T_g) of all materials used were determined by differential scanning calorimetry, using a Perkin–Elmer DSC 7. The experimental cycle consisted of heating to 160 °C, followed by immediate cooling at 20°/min to 10 °C, and finally measurement of the heat flow during heating at a rate of 10°/min.

Experimental procedure.—In order to make the desorption measurements aluminium cups, ca. 80 mg in weight, 8.0 mm in diameter and 5.0 mm in height, were filled with about 150 mg of sample (dried glucose syrup powder or glassy maltose–water beads). After loading the sample on the balance, a equilibration time of 5 to 10 min was allowed, prior to evacuation. Another 5 min was necessary to reach the final reduced pressure, which was in nearly all cases 26 mb, and then recording of the mass was started. The mass was recorded at 15 s intervals. In order to avoid effects from static electricity, the flasks sur-

Table 1
Composition and glass transition temperatures of dried glucose syrups (Glucidex ®)

	Dextrose equivalent [a]	Water content (% w/w) [b]	T_g (°C)	Glucose content (% w/w) [a]	Disaccharide content [a] (% w/w)	Oligosaccharide content (% w/w) [a]
DE21	20–23	5.2(2)	70.3	3	7	90
DE29	28–31	4.6(2)	64.9	10	9	81
DE39	38–41	4.0(2)	57.4	3	37	60
DE47	43–47	3.2(2)	60.0	5	50	45

[a] Approximate values as reported by the manufacturer.
[b] Determined by drying at 80 °C in vacuum during 2 days.

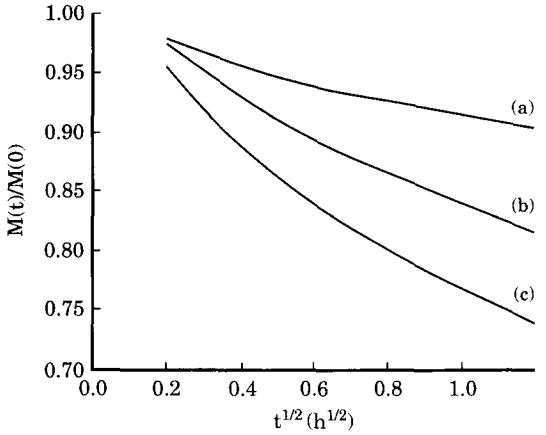

Fig. 1. Examples of the fractional mass loss as a function of time for powders of glassy dried glucose syrup at 26 mb and 35 °C. Dextrose equivalent of glucose syrups: (a) 47; (b) 39; (c) 21.

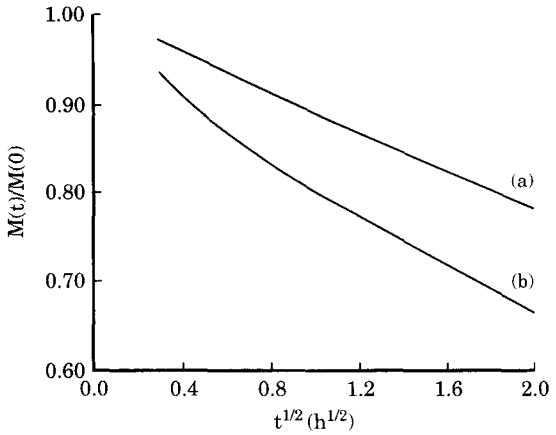

Fig. 2. The effect of sieving on the desorption rate of water from glassy DE47 glucose syrup powder at 27.5 °C. Size fractions: (a) particles with diameters between 300 and 500 μm; and (b) non-sieved powder.

rounding the hang downs of the balance were rinsed on the outside with water before loading the samples.

Data analysis.—Ideally, the diffusion constant of water can be calculated from the linear weight decay on a square root time scale. However, as was mentioned above, for various reasons the decay is often not linear. Fig. 1 is an example of the situation encountered in practice. In order to obtain the diffusion constant, which is contained in the initial slope, a third order polynomial was fitted to the initial part of the mass decay (up to 1 h) and the coefficient of the first order term was assumed to represent the initial slope. The fit to a third order polynomial was in all cases satisfactory.

3. Results

Fig. 1 shows the mass decay at a pressure of 26 mb, due to water loss, of spray-dried glucose syrups of varying compositions. It shows the general tendency of the decay rate to decrease as time proceeds. The reason for this is largely the polydispersity of the material: in Fig. 2, a comparison can be made between the water loss rates of the raw material and material that passed through a sieve of 400 μm. The mass loss from the sieved material, which contains particles between 300 μm and 500 μm, approaches, on a square root time square, a straight line, at times where the raw material data show curvature. This curvature is caused by the presence of many very small particles, that approach their final dry weight faster than larger particles.

Fig. 3 shows the pressure dependence of the drying rate. Except for the highest pressure (200 mb), the initial slopes turn out to be independent of pressure, whereas at longer times the drying is slower the higher the pressure. The point where the drying curve parts from the initial common slope increases with decreasing pressure. It is therefore concluded, that for the drying rate to be governed by diffusion, the vacuum should be as low as is achievable (26 mb) and no data obtained after about one hour should be considered. This test was carried out at 27.5 °C, a temperature at which the diffusion is relatively slow. Most data were obtained at higher temperatures, under conditions when the pressure dependence of the drying rate is more favourable for diffusion measure-

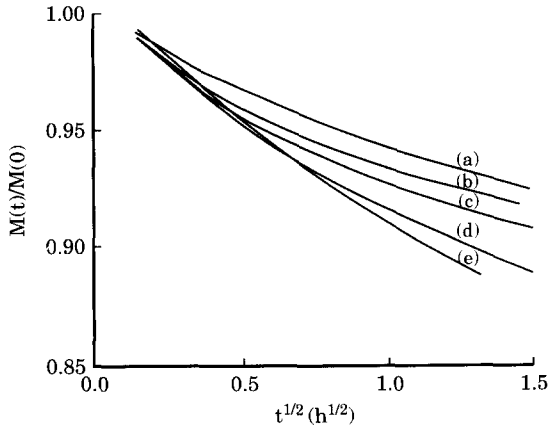

Fig. 3. The influence of air pressure on the desorption rate of water in glassy DE47 glucose syrup powder at 27.5 °C. Air pressures: (a) 216 mb; (b) 125 mb; (c) 79 mb; (d) 38 mb; and (e) 26 mb.

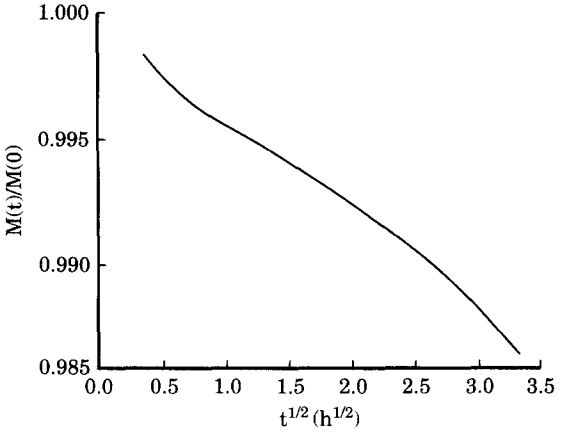

Fig. 4. The drying of a tablet (surface area 0.351×10^{-3} m^2) of glassy DE47 glucose syrup at 26 mb and 55 °C. The initial slope of this curve is used for the determination of the surface area per unit mass of the glucose syrup powders.

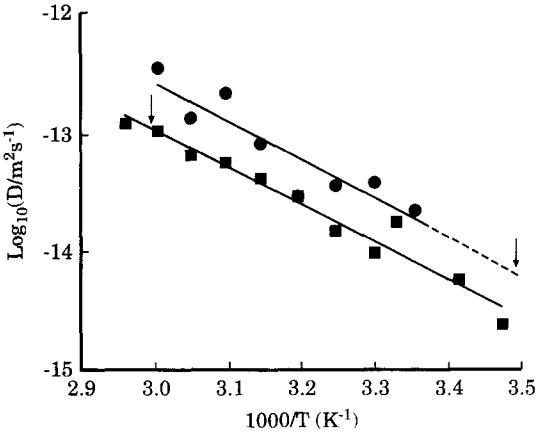

Fig. 5. Arrhenius plot of the diffusion constant of water in maltose at 10% water (w/w), (●) and DE47 glucose syrup at 3.2% water (w/w), (■). The lines are linear least squares fits. The arrows indicate glass transition temperatures.

ments because the equilibrium water vapour pressure above the samples is higher.

The drying rate at 55 °C of a tablet of spray-dried glucose syrup (DE47), with a surface area of 351 mm^2, was used to obtain the surface area per unit mass of the powders. Fig. 4 shows the drying curve of the tablet. An increasing drying rate turned out to be a general phenomenon for carbohydrate tablets, and is probably caused by cracks which result from shrinkage. The formation of cracks results in an increasing surface area and faster drying. To obtain the initial slope the same procedure was followed as for the drying curves of the powders, i.e. a third order polynomial was fitted to the data obtained at times below one hour. The initial slope of $0.063(10) \times 10^{-3}$ $s^{-1/2}$, indicates, when compared with the initial slope for the powder, $6.8(10) \times 10^{-3}$ $s^{-1/2}$, that the area of the powder was reduced by a factor of 108(15) after compressing to a tablet. Consequently, the surface area of the powder as observed by desorption of water could be calculated to be 0.23(3) m^2 g^{-1}. This corresponds to an effective spray dried particle radius of 8 μm, a value which is acceptable on grounds of the microscopic observations. Using Eq. (1), with $k = 6$, the diffusion constant in the tablet is found to be $59(10) \times 10^{-15}$ m^2 s^{-1}.

Temperature dependent measurements of the drying rate show that in the temperature range accessible, 15 °C to 65 °C, the rate increases by two orders of magnitude with increasing temperature. The diffusion constants, calculated using the value of the surface area obtained from the drying of the tablet, are presented in Fig. 5 in a semilog plot vs. $1/T$. The diffusion constants show an Arrhenius dependence, i.e.

$$D(T) = D_0 e^{(-\Delta E_{act}/RT)} \quad (2)$$

characterised by an activation energy ΔE_{act} of 60.3 kJ mol^{-1} and a value for D_0 of 0.34×10^{-3} m^2 s^{-1}. In Fig. 5, the diffusion constants in the maltose/water systems, taken from ref. [4], and those in DE47 glucose syrup are not directly comparable, because of the difference in water content. Unfortunately, the

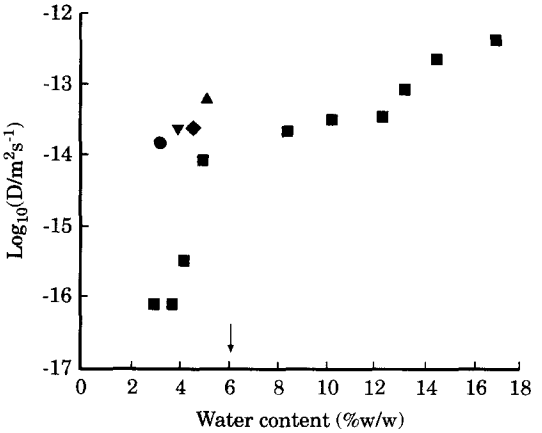

Fig. 6. The diffusion constant of water as a function of water content at 27 °C in maltose (■, taken from [4] except the lowest three water contents) and glucose syrups DE47 (●), DE39 (▼), DE29 (◆), DE21 (▲). The arrow indicates the water content at which the glass transition occurs in the maltose–water systems. The glucose syrup samples are all in their glassy states.

preparation of sufficient quantities of maltose and glucose syrup of identical water content and of a sufficient and known surface area per unit weight could not be achieved. At one temperature, 27 °C, the water diffusion was measured at different mean molecular weights (dextrose equivalents) of the glucose syrups. The results are presented in Fig. 6, together with the water diffusion constants for a maltose–water mixture, partly taken from ref. [4]. It can be seen that the diffusion in higher molecular weight glucose syrups is significantly more rapid than in maltose systems of the same water content.

4. Discussion

The emergence of an Arrhenius behaviour with an activation energy of about 20 times RT (≈ 2.6 kJ mol^{-1} at 35 °C) indicates that the diffusion of water in glassy glucose syrup is an activated process. Very similar findings were reported for Ficoll [9], a sucrose based polymer, and for maltose [4] above the glass transition (see Table 2). The linear Arrhenius behaviour is found both below and above the glass transition temperature (Fig. 5). This demonstrates the total decoupling of the water diffusivity from the macroscopic viscosity. The most probable explanation is a situation in which water molecules, which are much smaller than the carbohydrate units, are able to move through interconnected voids left by the random packing of the matrix molecules. Some support for such an explanation is given by the fact that the diffusivity of water in glucose syrups is, in particular at lower water contents, up to a hundred times greater than in maltose systems (see Fig. 6). Due to the interconnectedness of the carbohydrate units in glucose syrups, the random packing will be less dense, leaving more pathways for water diffusion. As a follow up of the work presented here, experiments are currently being prepared to test this explanation by measuring the diffusivity of small molecules trapped in the carbohydrate matrix as a function of their size.

In Fig. 6 the observation, made in Fig. 5, of decoupling of water diffusion and viscosity is confirmed. Although on increasing the water content of glassy maltose/water towards the point where the glass transition temperature equals the ambient temperature, the water diffusivity shows some deviation from the overall trend, the strong divergence that would be expected from a coupling with the viscosity is not observed. Moreover, this deviation takes place at a water content, at which the system is still glassy, and may well be due to changes in the chemical environment of the water molecules.

Considering the near equality of the activation energies in maltose and glucose syrup systems, the more rapid diffusion in the more highly hydrated maltose (Fig. 5) is necessarily associated with a larger value of D_0, the pre-exponential constant in Eq. (2). A crude quantitative interpretation of D_0 is offered by Eyring's theory [10], according to which D_0 is related to a 'jump distance' λ:

$$D_0 = \frac{kT\lambda^2}{h}\frac{F_{act}}{F} \tag{3}$$

where k is Boltzmann's constant, h is Planck's constant and F_{act}/F is the ratio of the partition functions of a diffusing molecule in its activated and initial states. For the case in which the initial and activitated states differ in the number of translational degrees of freedom, which will be assumed here, this ratio can be shown to be of order unity [10]. In the temperature range studied, 15 to 65 °C, the temperature dependence of D_0 is negligible compared with that of the exponential factor. Using Eq. (3) at 35 °C, the values of λ given in Table 2 are found. The results for glassy glucose syrup (3.2% water) and Ficoll [9] (4.6% water) are probably not significantly different, suggesting a very similar molecular environment of water in these systems. However, in the relatively water-rich maltose system (10.0% water), the jump

Table 2
Parameters from the fit of the Arrhenius expression (Eq. (2)) to the temperature dependence of the water diffusion constant and Eyring jump distances

	Water content	ΔE_{act} (kJ mol^{-1})	D_0 (m^2 s^{-1})	λ (nm)
Maltose	10(2)	64(5)	$2.5(5) \times 10^{-3}$	19.7
Glucose syrup DE47	3.2(2)	61(5)	$0.40(8) \times 10^{-3}$	7.8
Ficoll [5]	4.6(2)	57(5)	0.24×10^{-3}	6.1

distance is nearly three times larger. This is in spite of the fact, that in maltose/water systems with the same water content as glucose syrup/water systems (Fig. 6) the diffusion is slower and, therefore, the jump distance smaller. In all three cases, the values of the jump distances are larger than those expected from the sizes of the carbohydrate units that build the matrix (5–10 Å). A dense random packing of such units is expected to leave voids of the order of a unit size. However, the interconnectedness of the units, and the presence of water molecules may render the packing of the glucose units less dense. To test this interpretation, a rough estimate of the jump distance is made in the simplest and driest of the systems discussed here, that of maltose with 3% water, for which unfortunately no temperature dependent diffusion constant could be measured and, therefore, no value of λ is directly available. In Fig. 6, it is shown that at 27 °C the diffusion constant in DE47 glucose syrup with 3.2% water is about 100 times faster than in maltose with 3% water. It was shown, that the exponential factors in Eq. (2) are quite independent of water content and molecular weights, in the ranges studied. Therefore, the difference in diffusion rate must be due to different values of D_0. Using Eq. (3), it is then concluded that the jump distance in maltose with 3% water is about 10 times smaller than in DE47 glucose syrup, i.e. 0.7 nm. This order of magnitude is in good agreement with the size of a glucose unit. Consequently, the jump distances in the systems with higher molecular weight or higher water content may also be interpreted as distance scales in the systems. In that case, the long jump distances, much larger than a glucose unit, in packed systems of oligomeric chains are not unexpected. More interestingly, the presence of a quantity of water (10%) corresponding to one water molecule per glucose unit gives rise to a 25 fold increase in jump distance and has therefore a dominating influence on the morphology on a molecular distance scale. The strong dependence of the jump distance on the water content may indicate the existence of maltose rich regions and water rich regions, in which the water diffusion is relatively fast. The existence of such inhomogeneities is obviously important when one tries to understand the effectiveness of carbohydrate glasses as encapsulation matrices. To assess the validity of this hypothesis more direct structural information of carbohydrate/water glasses is needed. In particular scattering techniques are expected to be promising in this case, which will therefore play an important role in the continuation of the present work.

5. Conclusions

Water diffusion constants have been determined from desorption (drying) rates of glassy maltose–water and glucose syrup-water systems containing less than 10% (w/w) water. Measuring the very slow diffusion at and below room temperature has been made possible by using large surface areas (powders and samples of submillimeter sized spheres). In order to create a sufficient free energy gradient for the desorption to be diffusion controlled, a reduced air pressure of 26 mb is shown to be necessary. The activation energy of the activated diffusion process turns out not to be significantly different for systems varying in water content and the mean molecular weight of the glucose syrup. The changes in diffusion constants of water as a function of water content and molecular weight is therefore ascribed to changes in the jump distance of the activated diffusion process. This jump distance is larger in systems with higher mean molecular weight. This is explained by a less dense random packing in systems containing longer oligomeric chains. A remarkably strong dependence of the jump distance on the water content is found.

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