International Journal of Food Science and Technology 1997, **32**, 377–387

The effect of sugars on the diffusion of water in starch gels: a pulsed field gradient NMR study

Imad A. Farhat*, Edouard Loisel, Pedro Saez, William Derbyshire & John M.V. Blanshard

Department of Applied Biochemistry and Food Science, University of Nottingham, Loughborough, UK

Summary The self-diffusion coefficient of water was measured in starch–sugar–water systems of various compositions. The starch was either waxy maize or potato starch and the sugar was either sucrose or xylose. The diffusion results obtained from sugar solutions (i.e. with a zero polymer concentration) suggested that a free water behaviour should only be expected after a bilayer coverage of the sugar molecule. The presence of sugars was found to decrease considerably the translational mobility of water in starch gels. This reduction was proportional to the sugar concentration in the system but showed little dependence on the type of sugar. An attempt was made to relate the self-diffusion coefficients of water in starch–sugar–water gels to those obtained for the individual binary systems (starch–water and sugar–water). A prediction based on the additive effects of sugar and starch only corresponded with experimental results in dilute systems.

Keywords Diffusion, NMR, starch, sugar.

Introduction

The diffusion of water is of major interest in different areas of the food and pharmaceutical industries. It is of primary relevance in hydration/dehydration processes, enzyme activity and drug delivery, etc. Furthermore, there is little doubt that diffusion of water has a direct impact not only on the processing and the sensory perception of foods, but also on the shelf-life of various products (Karel & Saguy, 1991).

Among the various NMR procedures used to investigate biopolymer–water systems, the study of restricted diffusion using pulsed field gradient NMR techniques (Stejskal & Tanner, 1965), first described by Tanner & Stejskal (1968), appears to be particularly valuable in examining the structure of hydrocolloid gels (Ohtsuka *et al*., 1994), the droplet size distribution in water-in-oil emulsions (Callaghan *et al*., 1983) and thus serving as a probe of sample morphology.

Although a considerable amount of work on the self-diffusion of water in biopolymer gels has been reported (Jönson *et al*., 1986; Brosio *et al*., 1994 & Ohtsuka *et al*., 1994), much less is known about relatively concentrated systems (Kimmich *et al*., 1993). Moreover, the effect of added sugars on the diffusion of water has not been investigated. In this paper the translational mobility of water was investigated in ternary starch–sugar–water systems. The first section is concerned with sugar solutions, i.e. a 0:100:w composition of the ternary system (w being the water content). The second section investigates the 100:0:w starch–sugar–water system and the third section illustrates the diffusion of water in 75:25:w and 50:50:w mixtures.

Experimental techniques

Sample preparation

The gels were prepared directly in the NMR tube by heating a starch/sugar suspension to 65–70 °C

---

*Correspondent: Department of Applied Biochemistry and Food Science, University of Nottingham, Sutton Bonington Campus, Loughborough, LE12 5RD, UK. Fax: 44(0)115 9516142. e-mail: Imad.Farhat@nottingham.ac.uk

for 5–10 min in order to obtain a consistent gel.

The samples were sealed and stored at 25 ± 2 °C in a temperature controlled room for a minimum of 24 h to allow for 'full' retrogradation of the system. The optimum storage time corresponding to maximum starch recrystallization, was estimated from the retrogradation kinetics obtained elsewhere (Farhat, 1996) on similar systems.

NMR measurements

Stejskal & Tanner (1965) recognized that magnetic field inhomogeneity could be utilized to investigate the translational mobility of nuclear spins. The nuclei are magnetically 'labelled' by applying a field gradient which phase codes the spins. The phase is then 'decoded' by a second field gradient pulse equivalent to the first one in width and amplitude. The motional history between the coding and the decoding gradients is probed by the study of the magnetization echo. In a pulsed field gradient spin-echo experiment (PFGSE), the following pulse sequence is typically used: $90°_x°$ − delay t_1 − G_z − delay t_2–$180°_y°$ − delay t_1 − G_z where $t_2 = \tau - (t_1 + \delta)$ and δ is the width of the field gradient rf pulse. The intensity of the signal recorded at 2τ, also called echo is given by:

$$A(2\tau) = A(0)\exp\left(-\frac{2\tau}{T_2}\right)$$
$$\exp\left[-\gamma^2G^2\delta^2D\left(\Delta-\frac{\delta}{3}\right)-\frac{2}{3}\gamma^2G_0^2D\tau^3\right] \qquad (1)$$
$$\exp\left[-\gamma^2GG_0\delta D(t_1^2+t_2^2+\right.$$
$$\left.\delta(t_1+t_2)+\frac{2}{3}\delta^2-2\tau^2)\right]$$

Where A(0) is the signal amplitude at the time origin, τ the spacing between the 90° and 180° rf pulses, γ the gyromagnetic ratio for ^{1}H, G the amplitude of the field gradient, Δ the separation between the two field gradients ($\Delta = 2\tau$) and D the self-diffusion coefficient of the molecular species yielding the NMR signal. Equation 1 can be further simplified by replacing T_2 by T_2*, the spin-spin relaxation time reduced by the field inhomogeneities (G_0) other than those applied during the experiment (G):

$$A(2\tau) = A(0)\exp\left(-\frac{2\tau}{T_2*}\right)$$
$$\exp\left[-\gamma^2G^2\delta^2D\left(\Delta-\frac{\delta}{3}\right)\right] \qquad (2)$$

D is obtained from the slope of the *ln* plot of the echo reduction R as a function of G^2 for constant gradient width experiments or as a function of $\delta^2(\Delta\text{-}\delta/3)$ for constant gradient amplitude experiments.

$$\ln(R) = \ln\frac{A(2\tau)_G}{A(2\tau)_{G=0}} + -\gamma^2G^2\delta^2\left(\Delta-\frac{\delta}{3}\right)D \qquad (3)$$

Experimental procedure

A Bruker bench top Minispec NMS120 (Bruker Spectrospin Ltd, Coventry, UK) operating at a resonance frequency of 20 MHz (^{1}H) and a temperature of 40 ± 0.1 °C was used. The samples were sealed in 8 mm diameter NMR tubes and held at constant temperature for 20 min in the spectrometer probe-head prior to measurement. Typically eight scans were accumulated with optimum recycle delays ranging from of 1–10 s depending on the spin-lattice relaxation time (T_1) of the particular system investigated. Both the pulsed field gradient spin-echo (PFG-SE) and stimulated echo (PFG-StE) sequences were used to measure the self-diffusion coefficients. The choice between these two techniques depended upon the NMR relaxation properties of the samples. The general trend is for low water content samples to have reduced T_2 values. This leads to a reduction of the time available to complete the diffusion sequence, and the necessity to increase the amplitudes of the field gradient pulses if sufficient signal attenuation is to be obtained to yield an accurate determination of the diffusion coefficient. This technical problem is further intensified by the feature that diffusion itself is reduced in dry samples, leading to a reduced signal attenuation. Some alleviation is produced if the stimulated echo triplet sequence (PFG-StE) is adopted since, in general, T_1 exceeds T_2.

Due to software limitations on the Bruker NMS120 system, the rf gradient amplitudes are automatically calculated using the self-diffusion coefficient of water ($D_0 = 2.3 \times 10^{-9}$ m^2 s^{-1}) with no possible intervention by the operator. While this value of D_0 is reasonable at 25 °C, it is an underestimate at 40 °C. Therefore, it was preferred to report the diffusion coefficients relative to the bulk self-diffusion coefficient of water (D_0), i.e. D/D_0 rather than the 'absolute' coefficient D. The self-diffusion coefficients can subsequently be calculated using the value of $D_0 = 3.23 \times 10^{-9}$ m^2 s^{-1} reported by Mills (1973) for distilled water at 40 °C.

The standard deviations on the measured D/D_0 values were found to be smaller than 0.04 in the spin echo technique and smaller than 0.09 in the case of the stimulated echo technique.

Results and discussion

Water self-diffusion in sugar solutions and biopolymer gels

Diffusion of water in sugar solutions

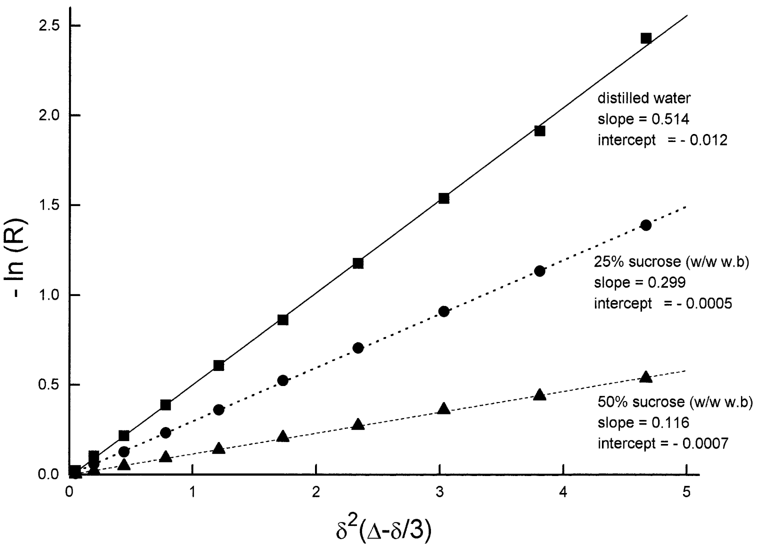
Diffusion coefficients in sucrose solutions were measured using the PFG-SE pulse sequence with a separation between the 90° and the 180° pulses of $\tau = 5$ ms yielding an echo time of 10 ms (2τ). The separation between the 90° and the first field gradient pulse was $t_1 = 200$ μs while the gradient separation Δ was the same as τ (5 ms). The gradient width δ was increased from 0 ms to 1 ms by steps of 0.1 ms. The diffusion coefficient was obtained from the plot of the logarithm of the echo reduction *ln*(R) recorded at different gradient width (δ) as a function of $\delta^2(\Delta\text{-}\delta/3)$ (Fig. 1). The accuracy of the results is illustrated by the coefficient of correlation (> 0.999) and the zero intercept ($-0.012 <$ intercept < 0.007).

The results of the –*ln*(R) vs. $\delta^2(\Delta–\delta/3)$ plots for sugar solutions (sucrose, glucose, fructose, xylose) at various concentrations are listed in Table 1. There was no significant difference between the self-diffusion coefficients of water measured in the presence of the various sugars.

Complexity of the signal recorded on sugar–water mixtures

The recorded NMR signal from a sugar solution is a composite of the contribution of the water and the sugar protons. The situation is complicated by the occurrence of chemical exchange between the water ^{1}H and those on the sugar hydroxyl groups. The NMR signal recorded could therefore be a composite response resulting from, on the one hand the protons of the water and other exchangeable OH protons and, on the other hand, the non-exchangeable ^{1}H of the sugar molecules. In principle, it should be possible to record a second attenuation attributable to the diffusion of the dissolved sucrose molecules. However, in the experimental conditions of limited gradient amplitude ranges and relatively long τ-values, it is believed that the recorded diffusion

Figure 1 A log plot of the echo reduction during pulsed field gradient NMR experiments carried out on sucrose solutions of different concentrations.



	Sugar conc. g sug. g^{-1} water	Intercept	Slope (m s^{-3})	R	D/D_0
Distilled $H_2$0	0	−0.0120	0.514	0.9994	1
Sucrose	0.25	−0.0005	0.299	0.9992	0.582
	0.43	−0.0026	0.248	0.9999	0.483
Glucose	0.25	0.0059	0.297	0.9999	0.577
	0.43	0.0058	0.226	0.9998	0.440
Fructose	0.25	−0.0039	0.319	0.9999	0.620
	0.43	−0.0041	0.251	0.9998	0.488
Xylose	0.25	−0.0007	0.319	0.9996	0.621
	0.43	0.0065	0.258	0.9997	0.501

Table 1 The linear regression results of the log plots of the echo reduction ($-ln[R]$) vs. the $\delta^2(\Delta\text{-}\delta/3)$ parameter for a range of sugar solutions

coefficients were derived principally from the water molecules. The various lines of evidence supporting this hypothesis are reviewed and discussed.

- The spin-spin relaxation times of sugar are expected to be shorter than the T_2 of water, and thus the signal resulting from the sugar non-exchangeable protons is expected, in the experimental conditions, to have decayed significantly at the time of observation (τ = 5 ms). Indeed due to the large field inhomogeneity in the low resolution NMR spectrometer the T_2^* of sugar is anticipated to be smaller than 5 ms.
- There was no evidence of non-linearity in the $-ln$(R) vs. $\delta^2(\Delta–\delta/3)$ plots, with intercept values very close to 0 (Fig. 1). Indeed, unpublished results of Derbyshire & Ablett demonstrated that in glucose solutions over a wide $\delta^2(\Delta–\delta/3)$ range, the same log plot would show two distinct linear regions corresponding to the self-diffusion coefficients of water (large slope) and sugar (smaller slope) (Fig. 2).
- No significant difference was recorded between the D/D_0 values recorded in sucrose solutions (disaccharide) as compared with the glucose, fructose and xylose (monosaccharides) solutions despite the significant difference in the molecular weight of the sugar (~ factor of 2).
- The self-diffusion coefficients (D) of these sugars in solution is expected to be at

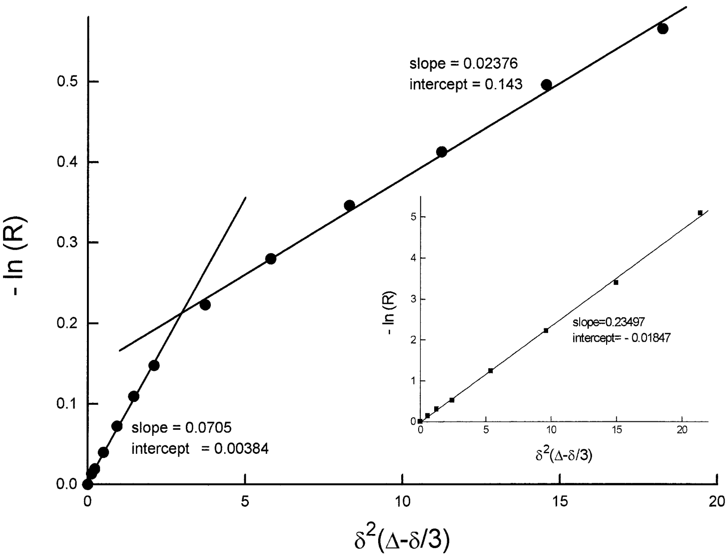
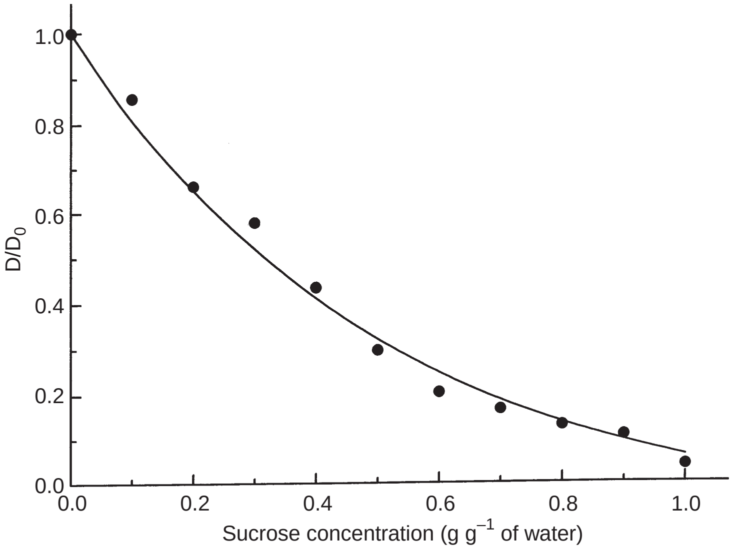


Figure 2 The log plot of the echo reduction as a function of δ^2 $(\Delta–\delta/3)$ for water and glucose/water (33% w/w wet basis) solution. The numerical values should not be compared with those in Fig. 1 since different gradient amplitudes G were used. Graph courtesy of Derbyshire & Ablett (unpublished results).

Figure 3 The relative self-diffusion coefficient (D/D_0) of water as a function of the sucrose/water ratio.



least three times smaller than that of water (Derbyshire & Ablett, unpublished results).

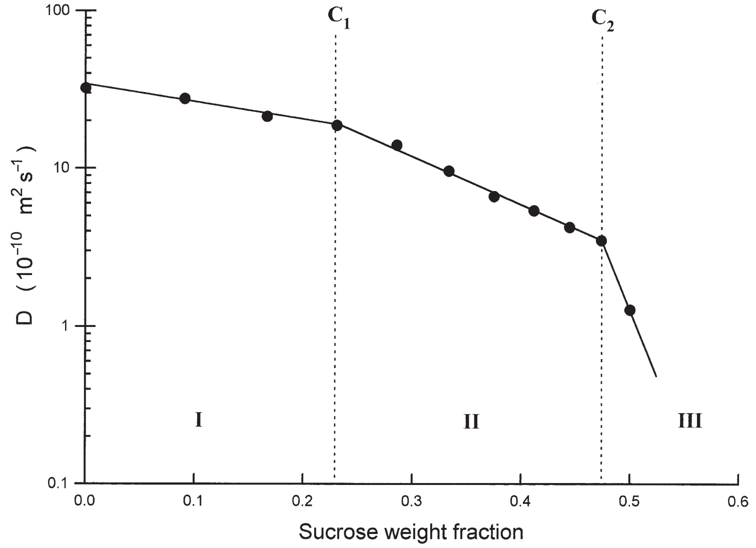
Effect of sucrose concentration

The self-diffusion coefficients were measured for different sucrose contents using the PFG-SE method based on varying the gradient amplitude with the parameters $\Delta = \tau = 6$ ms, $t_1 = 1$ ms and $\delta = 0.5$ ms. As the sucrose concentration was increased, the relative self-diffusion coefficient (D/D_0) decreased rapidly to reach a 'negligible' value at a sucrose concentration higher than 1 g of sugar per g of water (Fig. 3).

Kimmich *et al.* (1993) studied the impact of BSA and gelatin concentration on the self-diffusion coefficient of water. A similar approach was adopted in an attempt to explain the effect of sucrose on the translational mobility of water.

The plot of the self-diffusion coefficient on a logarithmic scale, as a function of the sugar concentration calculated on a total wet weight basis, showed three distinct linear regions (Fig. 4). These observations were interpreted as follows:

Figure 4 The self-diffusion coefficient (D) of water as a function of the weight fraction of sucrose.



- For concentrations below C_1 = 0.25 g of sucrose g^{-1} of solution, the role of sucrose is believed to be principally due to its obstructive effect on the movement of water. Kimmich *et al.* (1993) characterised this concentration as the 'free-water limit' above which the diffusion coefficient values are dominated by those of the molecules in the 'free' water phase and were described using eqn 4:

  $$D = D_0(1 - \beta\Phi) \tag{4}$$

  where Φ is the volume fraction of the obstructing species and β a 'shape' factor.

- At intermediate concentrations (between C_1 = 0.25 and C_2 = 0.48), the fraction of the 'bound' hydration water increases. Assuming a fast diffusion process between the hydration layer and the free water molecules, the diffusion coefficient is given by a weighted average of the diffusion coefficients in the free and the hydration water phases D_f and D_h, respectively.

  $$D = p_hD_h + p_fD_f \quad and \quad p_f + p_h = 1 \tag{5}$$

  It is considered that the depression of D with increased sugar concentration (Fig. 3) is caused by the increasing fraction of the slow diffusing hydration water at the expense of the free water (eqn 5) as the diffusion of water between these two phases is fast relatively to the time scale of the experiment (Belton & Hills, 1987).

- Above C_2 = 0.48, the diffusion coefficient of water decreased dramatically, falling to values below the limits measurable by PFG-NMR methods using the available spectrometer.

Although only one data point was measured in this concentration range, the pattern was consistent with the results reported by Kimmich *et al.* (1993).

A concentration of sucrose of 48% (g of sucrose per 100 g of solution) corresponds to an average of 20.6 molecules of water per molecule of sucrose. Sucrose has 11 potential hydrogen bonding sites and thus 20.6 molecules of water approximates to two water molecules per site. This is in agreement with the hydration numbers (n_h), i.e the number of water molecules found within a given van der Waals distance from the solute molecule, computed by Grigera (1988). Values of 11.45 and 13.23 were reported for sorbitol and mannitol, respectively. These two polyols ($C_6H_{14}O_6$) have six hydrogen bonding sites, which supports the hypothesis that there are ≈2 water molecules per hydrogen bonding site. However, this is only a semi-quantitative estimation of the n_h since the number of available binding sites on the sucrose molecule would also depend on the conformation assumed by the molecule in the experimental conditions (concentration, temperature, etc.).

Hence, a sucrose fraction of 0.48 is consistent with a 'mono-layer' coverage of the sugar molecule and it is not surprising that water molecules in these concentrated sugar solutions exhibit low translational mobility (relative to the time scale of the experiment, namely the echo time of 12 ms). Likewise, the concentration value of 25% corresponds to 3 g of water per g of sucrose, i.e to 57 molecules, which corresponds to ≈2 hydration layers. This suggests that the second hydration layer contains ≈36 water molecules.

According to these calculations, 'free' water type behaviour is only found in water molecules external to two hydration layers. However, diffusional exchange between the various hydration shells, and also between hydration 'free' water, is the determining factor for the observed overall diffusion coefficient. For water contents below the monolayer hydration coverage, the diffusion of water is thought to be very slow.

Water diffusion in starch gels

The self-diffusion coefficients of water were measured in waxy maize and potato starches.

The PFG-SE technique based on the measurement of the echo reduction for different gradient amplitude values with the parameters $\Delta = \tau = 6$ ms (gradient separation) and $\delta = 0.5$ ms (gradient width) was used for short diffusion times (< 10 ms). The stimulated echo (PFG-StE) sequence where the echo reduction was measured for different field gradient widths was adopted for longer diffusion times (up to 90 ms), with the parameters $\tau_1 = 4$ ms (between the first and the second 90° pulses), $\Delta = \tau_2 = 12$–80 ms (gradient separation) and a variable gradient width δ from 0 to 0.5 or from 0 to 1 ms in 10 steps.

D vs. diffusion time – probing the gel structure

One of the advantages of using NMR to study diffusion is that the technique readily permits, within the limitations of the relaxation properties, the variation of the time scale over which the diffusion process is being observed (Δ).

While diffusion in pure water showed the expected independence on the diffusion time and an average value of $D/D_0 \approx 1$ (0.998 ± 0.033) over the whole range of Δ-values investigated (Fig. 4), the D/D_0 values in the gels depended strongly on the diffusion time scale. Indeed, the relative self-diffusion coefficient decreased considerably from its anticipated value of one at $\Delta = 0$ ms to reach a plateau value $(D/D_0)_{min} \approx 0.315$. This corresponds to a diffusion coefficient of 1.02×10^{-9} m^2 s^{-1} calculated relative to the value $D_0 = 3.23 \times 10^{-9}$ m^2 s^{-1} (Mills, 1973). This led to the conclusion that in the time scale considered by the experiment, the starch biopolymers acted as a barrier restricting the diffusion process by means of specific molecular interactions (hydrogen bonding, ^{1}H exchange, etc.) and also by physical, steric obstructions hindering the translational mobility of the diffusing molecule.

Thus, the self-diffusion coefficient of water can be used to probe the structure of the gel in which the diffusion process is taking place. The average one-dimensional displacement $<r>$ of a water molecule with a self-diffusion coefficient D during the diffusion time t is given by $<r> = (2Dt)^{½}$.

For example, for the potato starch gel (1:1) in Fig. 5 $(D/D_0)_{min}$ was reached after a diffusion time t ≈ 50 ms. This leads to an average displacement $<r> \approx 18$ μm. This value yields an average pore size of 36 μm. This value is slightly smaller than the average size of a potato starch granule (12–60 × 15–75 μm). Such a reduction can be attributed to the structure of the gelatinized-retrograded starch system which is thought to be a polymeric network with smaller domains than the colloidal, granular, ungelatinized paste. The Δ value for which the minimum of the relative self-diffusion coefficient reached its maximum, increased when the gel concentration increased. The detailed results of the Δ-dependence of D/D_0 are not reported since the main purpose of this paper is to investigate the role of sugars.

The equilibrium value at long diffusion times $(D/D_0)_{min}$ was selected for the study of the effects of the gel composition on the self-diffusion of water (Fig. 6).

Effect of added sugar on the self-diffusion of water in starch gels

In order to study the effect of the presence of a third component on the diffusion of water in gels, a proportion of the starch was replaced by sugar whilst maintaining the 'solid'/water ratio in the sample constant.

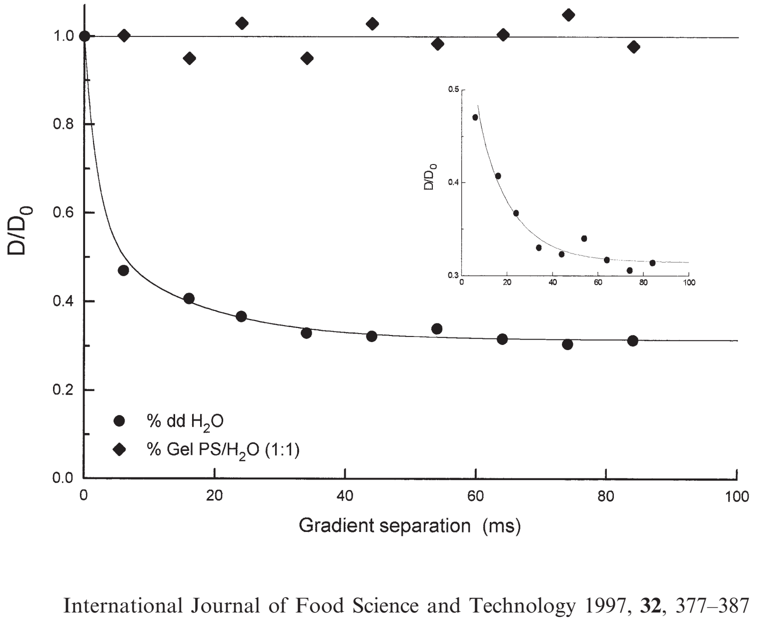


Figure 5 The relative self-diffusion coefficient (D/D_0) of water in distilled deionised water (dd H_2O) and in a 1:1 potato starch gel (PS/H_2O), measured as a function of the gradient separation (Δ). The insert is an expansion of the gel diffusion curve.

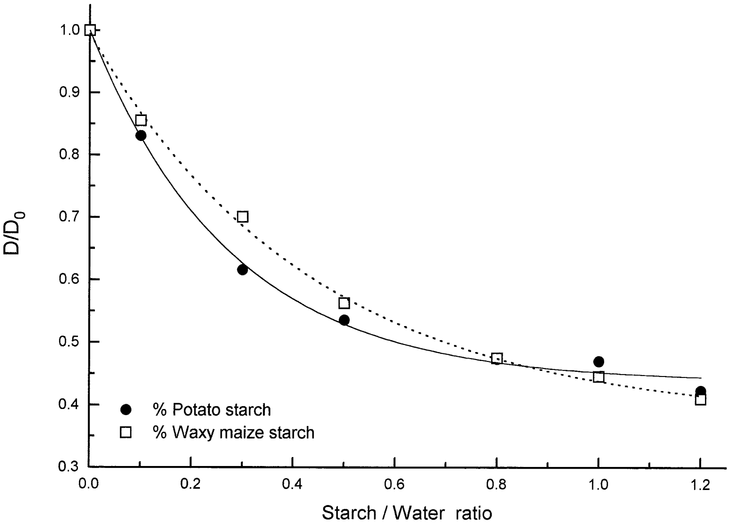


Figure 6 Relative diffusion coefficient of water in waxy maize and potato starch gels as a function of concentration.

In the ternary system, the relative diffusion coefficient of the water D/D_0 was decreased by the presence of sucrose. The effect was directly proportional to the amount of sucrose present in the system (Fig. 7). The values of the water diffusion coefficient in the gels were compared to those calculated using the assumption that the effects of the presence of the biopolymer and the sugar were additive and independent.

For this discussion $(D/D_0)_s$ and $(D/D_0)_p$ are the relative self diffusion coefficients of water in a sugar solution and a biopolymer gel of a particular concentration *c* (sugar/water or polymer/water), respectively. The concentrations used in Figs 7, 8 and 9 are expressed as follows:

(i) a sucrose solution of a concentration *c*, contains *c* g of sucrose per g of water

(ii) a starch gel contains *c* g of starch per g of water

(iii) a starch–sucrose gel contains *c* g of sucrose + *c* g of starch per g of water

If the hypothesis of a simple cumulative reduction of the self-diffusion coefficients applies, then $(D/D_0)_{mix}$ which is the relative self-diffusion

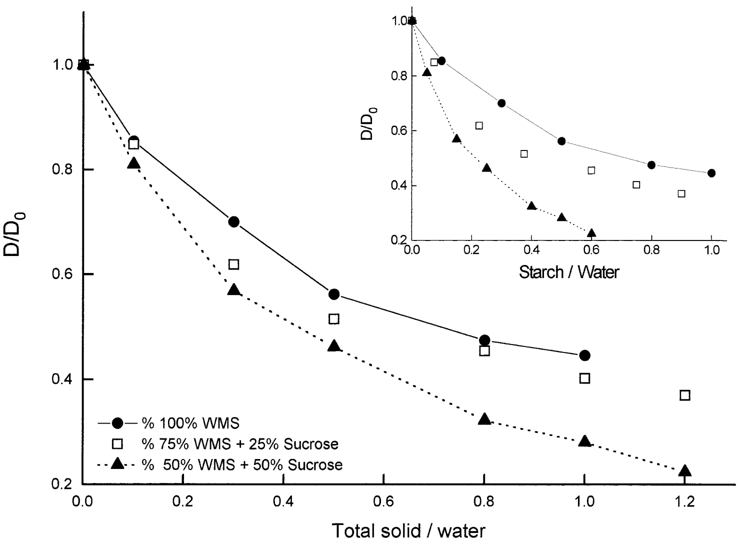


Figure 7 Impact of different sucrose concentrations on the relative self-diffusion coefficient (D/D_0) of water in waxy maize starch (WMS) gels. The insert shows the same results plotted as a function of the total solids concentration.

coefficient of water in a polymer–sugar (1:1) with a polymer/water ratio = c, is given by:

$$\left(\frac{D}{D_0}\right)_{mix} = \left(\frac{D}{D_0}\right)_s \cdot \left(\frac{D}{D_0}\right)_p \qquad (6)$$

The results of this calculation are shown in Fig. 8 where only the lines representing the empirical best fit for the biopolymer–water and the sugar–water systems are shown. The measured relative self-diffusion results followed closely the calculated line of D/D_0 at low starch concentrations. However, when the starch/water ratio exceeded 0.2 (corresponding to a calculated value of ≈0.5 for D/D_0), the measured D/D_0 values became progressively larger than the values predicted on a simple additivity basis. One reason might be that at low water contents, an interaction between biopolymer and sugar molecules leads to a decrease in the number of binding sites (by hydrogen bonding and proton exchange) available on both the sugar and the starch matrix for the water molecules and, thus, the effective population of the mobile water becomes larger than expected increasing the value of the overall

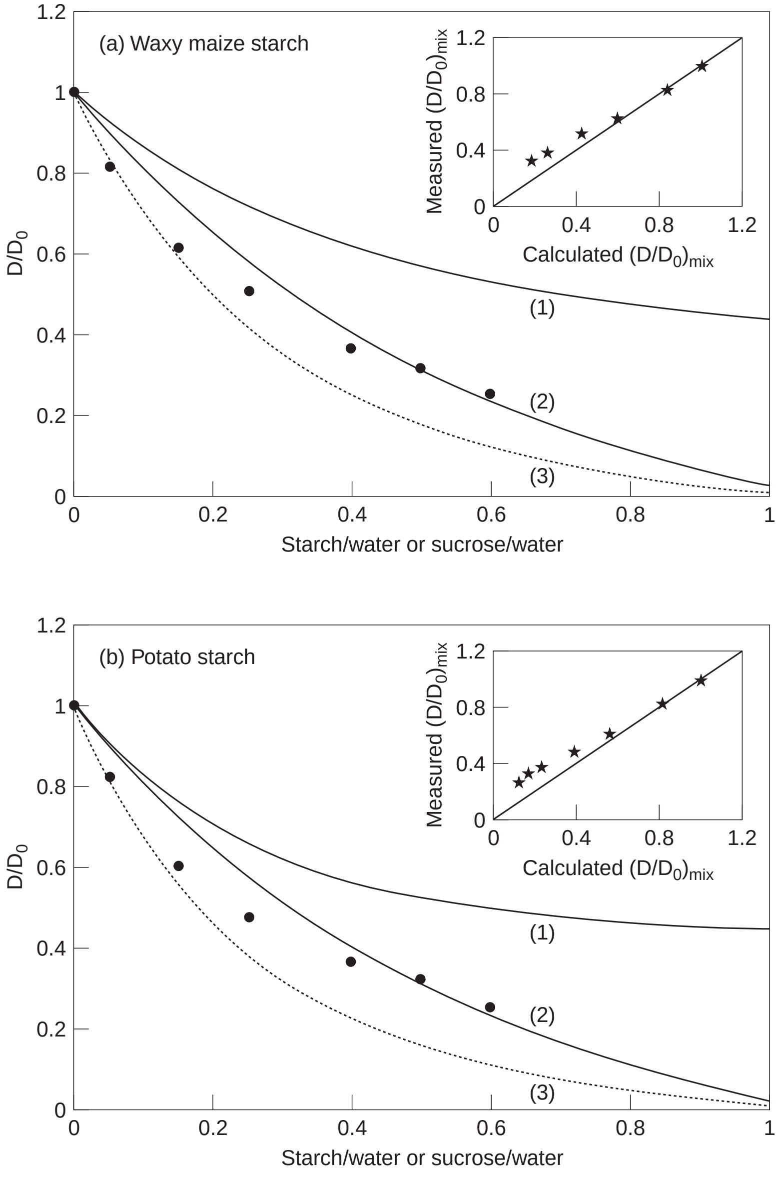


Figure 8 D/D_0 as a function of the polymer/water ratio in (1) starch $(D/D_0)_p$ and starch–sucrose gels $(D/D_0)_{mix}$ and as a function of sugar/water in (2) sucrose solution $(D/D_0)_s$. The experimental results of (D/D_0)mix are plotted in symbols (●) while the calculated data (3) are illustrated by thin dotted lines (- - - -). The inserts show the correlation between the measured and calculated $(D/D_0)_{mix}$ values. Results for (a) waxy maize starch and (b) potato starch are shown.

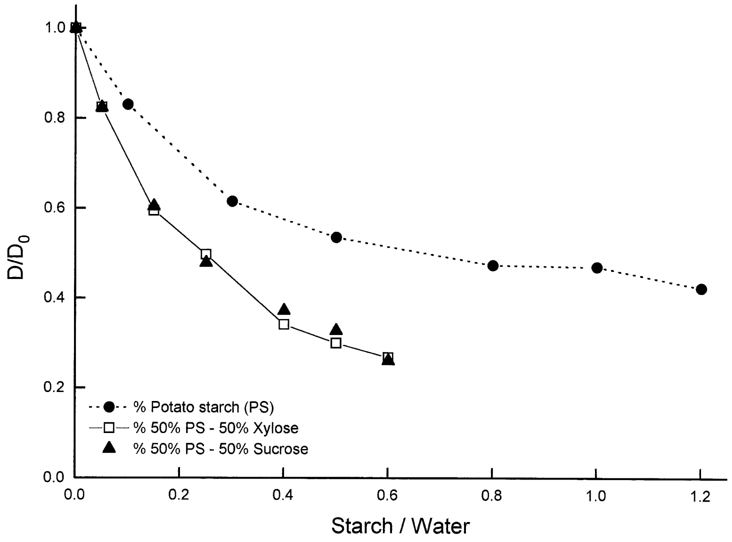


Figure 9 Effect of sucrose and xylose on the relative self-diffusion coefficient (D/D_0) of water in potato starch (PS)–sugar (1:1) gels.

self-diffusion coefficient. Furthermore, the small size of the water molecule would allow diffusion to take place in the free-volume unoccupied by a concentrated starch–sugar phase.

As in the case of sugar solutions, the type of sugar had no significant impact on the relative self-diffusion coefficients of water over the entire range of water contents investigated. An example of this is shown in Fig. 9 where there is no evidence of difference in the water diffusion properties between the 1:1 potato starch/sugar gels prepared with sucrose (disaccharide C12) or with xylose (monosaccharide C5).

Conclusion

The diffusion of water, a physical parameter of great importance in the quality of food products, was reduced by the presence of obstructing molecular species. While the type of the polymer was a determining factor in the diffusion process, the role of the sugar was less specific to the sugar type.

The nature of the effect of sugar and biopolymer molecules on the mobility of water was found to depend on the concentration. While diffusion of water is very slow in the early hydration stages, this process was greatly enhanced as the degree of hydration increased. Above a certain hydration level, an increasing water population started to exhibit a 'free-water' type behaviour. At these low concentration levels, the role of the polymer on the diffusion of water was due to obstructive effects.

Within a relatively narrow range of polymer concentrations, the effect of sugars in depressing the diffusion coefficient of water in gel systems can be anticipated using the diffusion results of the binary systems polymer–water and sugar–water.

Acknowledgements

The authors would like to thank the ACTIF II (Amorphous Crystalline Transitions in Foods) Consortium for financial assistance.

References

Belton, P.S. & Hills, B.P. (1987). The effects of diffusive exchange in heterogeneous systems on NMR line-shapes and relaxation processes. *Molecular Physics*, **61**, 999–1018.

Brosio, E., Dubaldo, A. & Verzegnassi, B. (1994). Pulsed-field gradient spin-echo NMR measurement of water diffusion-coefficient in thickening and gelling agents – guar galactomannan solutions and pectin gels. *Cellular and Molecular Biology*, **40**, 567–573.

Callaghan, P.T., Jolley, K.W. & Humphrey, R.S. (1983). Diffusion of fat and water in cheese as studied by pulsed field gradient nuclear magnetic-resonance. *Journal of Colloid Interface Science*, **93**, 521–529.

Farhat, I.A. (1996). Molecular mobility and interactions in biopolymer-sugar-water systems. PhD thesis. Pp. 165–197. Nottingham University, UK.

Grigera, J.R. (1988). Conformation of polyols in water-molecular-dynamics simulation of mannitol and sorbitol. *Journal of the Chemical Society – Faraday Transactions I*, **84**, 2603–2608.

Jönson, B., Wennerström H., Nilsson P.G. & Linse, P. (1986). Self-diffusion of small molecules in colloidal systems. *Colloid and Polymer Science*, **264**, 77–88.

Karel, M. & Saguy, I. (1991). Effects of water on diffusion in food systems. In: *Water Relationships in Foods* (edited by H. Levine & L. Slade). Pp. 157–173. New York: Plenum Press.

Kimmich, R., Klammler, F., Skirda, V.D., Serebrennikova I.A., Maklakov A.I. & Fatkullin N. (1993). Geometrical restrictions of water diffusion in aqueous protein systems – a study using NMR field-gradient techniques. *Applied Magnetic Resonance*, **4**, 425–440.

Received 18 February, revised and accepted 10 November 1997

Mills, R. (1973). Self-diffusion in normal and heavy water in the range 1–45°. *The Journal of Physical Chemistry*, **77**, 685–688.

Ohtsuka, A., Watanabe, T. & Suzuki, T. (1994). Gel structure and water diffusion phenomena in starch gels studied by pulsed field gradient stimulated echo NMR. *Carbohydrate Polymers*, **25**, 95–100.

Stejskal, E.O. & Tanner, J.E. (1965). Spin diffusion measurements: spin echoes in the presence of a time dependent field gradient. *Journal of Chemical Physics*, **42**, 288–292.

Tanner, J.E. & Stejskal, E.O. (1968). Restricted self-diffusion of protons in colloidal systems by pulsed-gradient spin echo method. *Journal of Chemical Physics,* **49**, 1768–1777.