Dynamics of Fresh and Freeze-Dried Strawberry and Red Onion by Quasielastic Neutron Scattering

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The microscopic behavior of fresh and freeze-dried strawberry and red onion at different water contents (45 and 20 wt % water) has been investigated by quasielastic neutron scattering (QENS). To distinguish between the dynamics of the water and the biological material isotopic (H/D) substitution was used. The results show that all samples exhibit an onset of anharmonic motions on the experimental time scale (3−100 ps) at about 230−240 K. Above 250 K the dynamics is mainly of translational character and strongly dependent on the hydration level. The diffusion constant increases rapidly with increasing water content and at 280 K it is approximately 20% higher for the hydration water in freeze-dried strawberry than in freeze-dried red onion and around 2 orders of magnitude faster for the hydration water than for the biological material. Moreover, the diffusion constant of the biological part is about 50% faster in freeze-dried strawberry than in freeze-dried red onion. It was also found that the average relaxation time is slightly faster in fresh strawberry than in freeze-dried strawberry. From the results we can conclude that the water dynamics is not only promoting motions in the biological material, it is also affected by the structure (and possibly also the dynamics) of the biological material. Thus, the microscopic properties of the biological materials are interrelated with the properties of their hydration water.

1. Introduction

Sugars and other carbohydrates are biomolecules found in all living systems, where they have structural, metabolic, and cryoprotective roles.[1] The carbohydrates we use as food have their origin in the photosynthesis of plants. They take the form of sugars, which are used directly as energy sources in living organisms, and starches and cellulose, which are used to store energy and make up cell walls in plants, respectively.[1] Fruit and vegetables consist to a large extent of simple sugars and other carbohydrates, and the main sugars in strawberry and red onion, which are the materials investigated in this study, are glucose, fructose, and sucrose.[2,3]

Except for carbohydrates (or sugars) fruits and vegetables contain mainly water, e.g., strawberry and onion contain about 90% water and around 9% soluble solids (which mainly consists of carbohydrates).[4] A large fraction of this water is, as in other biological systems, directly associated with surfaces of different kinds, such as cell membranes and carbohydrates. This will introduce a confined environment for the water molecules as well as interactions with biomolecular surfaces, which will influence both the structure and the mobility of the water molecules.[5−9] The close association of water with biomolecular surfaces leads to a restricted motion of the water molecules and, as a consequence, slower dynamics (about a factor of 10 slower compared to the dynamics of bulk water is commonly observed[10−12]). Thus, the presence of carbohydrate molecules in an aqueous solution has a considerable effect on its surrounding water, i.e., the hydrogen bonds between carbohydrates and water molecules cause a disruption of the hydrogen bonded water network in the hydration layer and the water mobility decreases with increasing concentration of carbohydrates in the solution.[13] The result of the incomplete water network in the vicinity of the carbohydrates is that ice formation is inhibited for such hydration water at all temperatures.[14] Thus, when freezing a carbohydrate-rich food material a part of the water will crystallize into ice, resulting in a more concentrated amorphous carbohydrate solution.[15] This supercooled solution will then transform into a glass when the temperature is lowered below its glass transition temperature T_g.[15] As a result, frozen and freeze-dried food materials behave like highly viscous metastable amorphous materials with either rubber or glass characteristics, depending on the temperature and moisture content.[4] The behavior can be explained by considering the material as a water-plasticized food polymer, with a lowest possible glass transition temperature T_g obtained for the maximum amount of unfozen water.[15] Furthermore, the nonfreezing/unfrozen water in carbohydrate systems is free to move (diffuse) over macroscopic distances in the structure,[16] where the diffusion constant depends on both the water concentration and the geometry of the structure.

In the food industry drying and cooling are of great importance for food storage since they provide environments that reduce chemical and biological processes, and hence, increase the storage stability. The structure and dynamical behavior of frozen and/or dried biological materials differs from that of fresh materials and research on this behavior is crucial for the possibility of optimizing the properties, quality, and stability of the treated food. Structural studies performed by nuclear magnetic resonance (NMR) have shown that when a fruit material is dehydrated both the cell structure and organization of the material are changed.[17,18] The changes are to a large extent irreversible and depend on the method used.[17] Further-

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more, several studies[2−4] have been performed on the dynamical behavior of freeze-dried fruits and vegetables. However, most of these studies concentrate on the more macroscopic properties of the whole material and very few specifically on the microscopic dynamics of the biological material and its hydration water, as is the focus in this study. We present here results from a quasielastic neutron scattering (QENS) study of fresh dehydrated and freeze-dried strawberry and red onion. QENS is a common and suitable technique for investigating the microscopic dynamics of hydrogen-containing materials such as water and biological systems (see, e.g., refs 12 and 19−21) due to the large incoherent scattering cross-section of hydrogen and the possibility of changing the scattering contrast between different parts of the samples by partial deuteration. The results obtained show that the dynamics is strongly affected by the water content, and that the properties of the biological materials and their hydration water are interrelated. The motion of carbohydrates and other biomolecules is probably related to solvent dynamics in a similar way to that observed for proteins.[22,23]

2. Materials and Methods

In this study both fresh and freeze-dried strawberry and red onion (grown in Belgium and Spain, respectively, and bought in an ordinary Swedish supermarket) were investigated. Before the sample preparation procedure started the fresh strawberry and red onion were cut into thin slices. In the case of strawberry, the slices were cut out by a scalpel perpendicular to the length of the strawberry, i.e., as much as possible of the seeds and the skin of each sample was preserved. For each red onion sample, the sample was cut out of one onion layer, where the skin layer was kept on one side of the sample. The major substance in fresh strawberry and red onion is, as mentioned above, water, where the water fraction is 88.7% and 91% for strawberry and red onion, respectively.[2] These materials also contain a large amount of the carbohydrates (sugars) fructose, glucose, and sucrose, with a total fraction of 8.3% and 6% for strawberry[2,24] and red onion,[3,24] respectively. The fiber content is 1.9% and 1.2%, respectively.[24] Apart from carbohydrates strawberry and red onion contain protein (0.5% and 1.2%), fat (0.2% and 0.1%), and small amounts of vitamins and minerals.[24]

To distinguish between the dynamics of the pure biological material and its hydration water isotopic (H/D) substitution was used, i.e., the samples were hydrated in both H_2O (milliQ water) and D_2O. The fresh sample contained 45 wt % water and the freeze-dried samples were prepared with both 20 and 45 wt % water. The fresh strawberry sample in H_2O was prepared by drying the sample in a vacuum oven to the desired water concentration. The freeze-dried samples were first rehydrated by a conventional freeze-drying process, and thereafter soaked in water (H_2O or D_2O) for about 24 h, before they were freeze-dried again. Finally, the samples were rehydrated in 100% relative humidity of D_2O or H_2O to the desired hydration levels. It should here be noted that such a freeze-drying process injures the structure less than "normal" drying,[17] although the cell structure of biological materials is known to be damaged by both drying and freeze-drying.[17]

In a neutron scattering experiment the dynamic structure factor $S(Q,\omega)$, which contains information about the microscopic structure and dynamics of the material studied, is measured. $S(Q,\omega)$ contains both coherent and incoherent scattering contributions, which arise from interparticle and self-correlations, respectively. As mentioned above the main contribution to the scattering cross section of hydrogen-containing materials is the incoherent scattering from the protons. However, since the scattering cross section is not only different for different elements but also different for different isotopes, such as H and D, it is possible to distinguish between motions of the biological material and its surrounding water by use of H/D isotope substitution. Thus, the dynamics of the hydration water of the freeze-dried materials was obtained by subtracting the scattering from the biological material in D_2O from the scattering from the same material in H_2O (since the scattering from D_2O can be considered to be negligible compared to the scattering from H_2O).

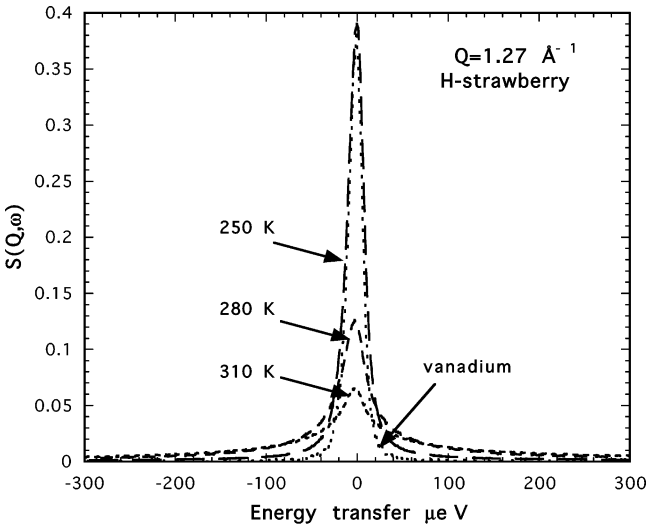

Figure 1. Quasielastic neutron scattering spectra of freeze-dried strawberry with a water content of 45 wt % at 250, 280, and 310 K and $Q = 1.27$ Å^{-1}. Also shown is the instrument resolution of the IRIS spectrometer given by the scattering from a vanadium plate. For comparison, the maximum scattering intensity from the vanadium plate has been normalized to the same intensity as the scattering from the strawberry at the lowest temperature.

The quasielastic neutron scattering (QENS) measurements were carried out on the high-resolution backscattering spectrometer IRIS at the pulsed neutron spallation source ISIS at the Rutherford Appleton Laboratory, UK. The IRIS spectrometer is described in detail in ref 25, so here we will only give some specific details for the present measurements. With use of the PG002 analyzers and an incident neutron wavelength of about 6.6 Å, an energy resolution of 15 μeV [full width at half-maximum (fwhm)] and a total energy window of ±0.5 meV were obtained. For all measurements the samples (i.e., the flat slices of strawberry and red onion) were placed in flat Al containers with an internal thickness of 0.5 mm, and the data were collected with the sample holder (and therefore also the slices of the samples) oriented 135° relative to the incident neutron beam. The 51 detectors, each corresponding to a specific scattering angle and therefore also a specific Q-value (momentum transfer), were grouped into 10 groups of 5 detectors per group, giving a total Q-range of 0.51−1.82 Å^{-1}. The data analysis was performed with the onsite program Modes.[26] Elastic scans were measured on heating from 160 to 310 K and standard quasielastic measurements were performed at 250, 280, and 310 K.

3. Results

In Figure 1 typical quasielastic spectra of freeze-dried strawberry hydrated in H_2O are shown for different temperatures and $Q = 1.27$ Å^{-1}. From the figure it is clear that the elastic scattering decreases rapidly with increasing temperature due to

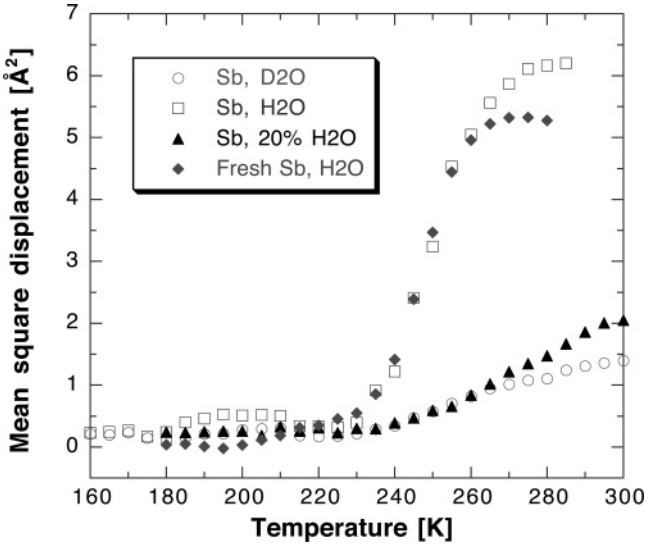

Figure 2. Mean square displacement (MSD) as a function of temperature for different strawberry samples. All samples were freeze-dried except the sample denoted "fresh". The hydration levels are given in weight percent (wt %) water and are 45 wt % for all samples except the one denoted 20%.

an increasing mobility of the hydrogens in the sample. Thus, both the broadening and intensity of the quasielastic scattering increase with increasing temperature.

The approximately elastic incoherent scattering intensity $S(Q,\hbar\omega = 0 \pm 5\ \mu\text{eV})$ was used to obtain the mean square displacement (MSD) of the hydrogens in the sample, by the relation

$$\ln S(Q,\hbar\omega = 0 \pm 5\,\mu\text{eV}) = -\langle u^2\rangle Q^2/3 \qquad (1)$$

where Q is the momentum transfer in the scattering process, $\hbar\omega$ the energy transfer, and $\langle u^2\rangle$ the mean square displacement. In general, at low temperatures when the protons in the sample show pure harmonic (vibrational) motions, the MSD value increases only slowly with increasing temperature due to an increasing amplitude of the vibrations. However, above a certain temperature anharmonic motions are also present on the experimental time scale and the MSD value increases considerably more rapidly with increasing temperature.

Figure 2 shows the temperature dependencies of the MSD values obtained for fresh and freeze-dried strawberry at the two hydration levels. Note here that the samples hydrated in H_2O show hydrogen motions in both the biological material and the surrounding water, whereas the sample in D_2O mainly reflects the motion of hydrogen atoms in the biological material. The results show that there is an onset of anharmonic (i.e., nonvibrational) motions on the experimental time scale at about 230−240 K for all samples. It is, furthermore, seen that the increase in MSD is more rapid for the higher hydration level and for samples hydrated in H_2O (rather than in D_2O). However, it should be noted here that the rapid increase in MSD at about 250 K for the samples hydrated to 45 wt % is partly due to some ice melting. Since there are generally many similarities in the dynamical behavior of sugar solutions and food with high carbohydrate contents (such as the materials investigated here)[15] it is likely that the motions in the biological materials are mainly due to dynamical processes inherent to the carbohydrates in the solution/material. This interpretation is further supported by the fact that similar results have been obtained for sugar solutions,[27,28] where onsets in MSD were observed at about 250 and 230 K for sugars (trehalose, sucrose, and maltose) in D_2O and H_2O, respectively.

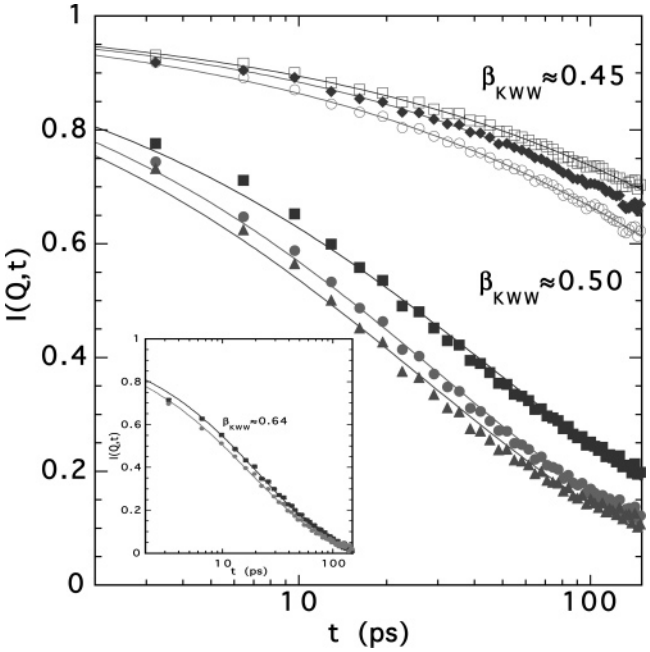

Figure 3. Intermediate scattering functions $I(Q,t)$ obtained at $T = 280$ K and $Q = 0.91$ Å^{-1} for all samples. In the figure open and filled symbols represent samples hydrated in D_2O and H_2O, respectively. Circles (●, ○) and triangles (▲) denote freeze-dried and fresh strawberry, respectively, and squares (■, □) freeze-dried onion, all with a water content of 45 wt %. The strawberry sample with 20 wt % H_2O is denoted by diamonds (♦). The solid lines are fits to the KWW stretched exponential function (eq 2 in the text), which describes the data well for all samples. The stretching parameter β_{KWW} is about 0.5 for the fastest relaxing samples (mainly those with 45 wt % H_2O) and around 0.45 for the other samples. The inset shows the dynamics of the hydration water.

The self-intermediate scattering functions $I(Q,t)$ were obtained by time Fourier transformation of measured incoherent structure factors $S(Q,\omega)$ at $T = 280$ K and $Q = 0.91$ Å^{-1}. Figure 3 shows $I(Q,t)$ normalized to 1 for $t \approx 0$, for samples hydrated in H_2O and D_2O, respectively. The inset in the figure shows $I(Q,t)$ functions for the hydration water (obtained by subtraction of the contribution from the biological material, as described in the Materials and Methods section). The results show that the dynamics of the carbohydrates and the "biological matrix" (e.g., cell membranes), measured in samples hydrated with D_2O, is considerably slower than the water dynamics (by about a factor of 100). In Figure 3 it is furthermore evident that the dynamics must be very complex, with motions on widely different time scales, since the relaxation process is very stretched in time and can be described by the Kohlrausch−Williams−Watts (KWW) stretched exponential function[29,30]

$$I(Q,t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta_{KWW}}\right] \qquad 0 < \beta_{KWW} \le 1 \qquad (2)$$

where τ is a characteristic time of the relaxation function and β_{KWW} is the stretching parameter. From these fits it is possible to determine the average relaxation time $\langle\tau\rangle$ for a particular Q-value and temperature by the relation

$$\langle\tau\rangle = \frac{\tau}{\beta_{KWW}}\Gamma\left(\frac{1}{\beta_{KWW}}\right) \qquad (3)$$

where Γ is the gamma function. Table 1 shows values of β_{KWW} and $\langle\tau\rangle$ for all samples, as well as the hydration water, at $Q = 0.91$ Å^{-1}.

TABLE 1: Relaxation Times and Stretching Parameter Obtained by the Fit to the KWW Function for the Intermediate Scattering Function $I(Q,t)$ at $Q = 0.91$ Å^{-1} for All Samples Investigated as Well as the Hydration Water Obtained by Subtraction of the Biological Material (D_2O Sample) from the H_2O Sample (referred to as H−D)[a]

sample	temp [K]	mean relaxation time $\langle\tau\rangle$ [ps]	stretching parameter β_{KWW}
strawberry D_2O	280	1500 ± 40	0.45
	310	360 ± 5	0.47
strawberry H_2O	280	62 ± 1	0.51
	310	27 ± 1	0.53
strawberry H_2O fresh	280	52 ± 1	0.49
strawberry H_2O 20%	280	2100 ± 60	0.45
red onion H_2O	280	99 ± 1	0.48
red onion D_2O	280	3000 ± 100	0.44
strawberry H−D	280	24 ± 1	0.63
onion H−D	280	27 ± 1	0.65

[a] All samples are freeze-dried except when denoted fresh. The hydration level is 45 wt % in all cases except the one denoted 20% (w/w).

The physical nature of the dynamics is given by the Q-dependence of the average relaxation time $\langle\tau\rangle$. Figure 4A shows how the inverse of the average relaxation time $1/\langle\tau\rangle$ depends on Q^2 for fresh strawberry, and freeze-dried red onion and strawberry with 45 wt % H_2O at $T = 280$ K. Panels B and C of Figure 4 show corresponding values for the freeze-dried D_2O samples and the pure hydration water, respectively. The Q-dependencies obtained have been described by the Gaussian jump-length distribution model[8]

$$\frac{1}{\langle\tau\rangle} = \frac{1}{\tau_{res}}[1 - \exp(-Q^2\langle r^2\rangle/6)] \quad (4)$$

where $\langle r^2\rangle$ is the mean square jump length and τ_{res} is the average residence time between two consecutive jumps in a translational jump process. As can be seen in panels A and B of Figure 4 (H_2O and D_2O samples), the Q-dependencies are well described by the model, which indicates that the average dynamics observed on the experimental time scale is mainly of translational character. In fact, $1/\langle\tau\rangle$ is almost proportional to Q^2, as is the case for ordinary continuous translational diffusion. However, a different behavior is seen for the hydration water, Figure 4C, where the average relaxation time $\langle\tau\rangle$ is almost independent of Q at higher Q-values. Most likely there are two reasons for the reduced Q-dependence in the case of the hydration water. First, the translational diffusion is of jump-diffusion character (which reduces the Q-dependence at high Q) and, second, the Q-independent rotational motion of water molecules contributes to the observed quasielastic scattering. An even weaker Q-dependence of the dynamics was obtained for all samples at the lowest temperature (250 K) suggesting that both the hydration water and the biological material exhibit mainly local and/or rotational motions on the experimental timescale at this temperature.

From the fitting parameters obtained by eq 4 the diffusion constant D can be calculated according to

$$D = \langle r^2\rangle/6\tau_{res} \quad (5)$$

The values of the diffusion constant are given in Table 2, where we note that D of the hydration water is approximately 20% higher in freeze-dried strawberry than in freeze-dried red onion at $T = 280$ K, and that it seems to be even higher in fresh strawberry. A similar trend is observed for diffusive motions in the pure biological part, which are about 50% faster in freeze-dried strawberry than in freeze-dried red onion. Furthermore, in the freeze-dried samples hydrated to 45 wt % the diffusion of the hydration water at $T = 280$ K is approximately 2 orders of magnitude faster than the diffusion of carbohydrates and the "biological matrix".

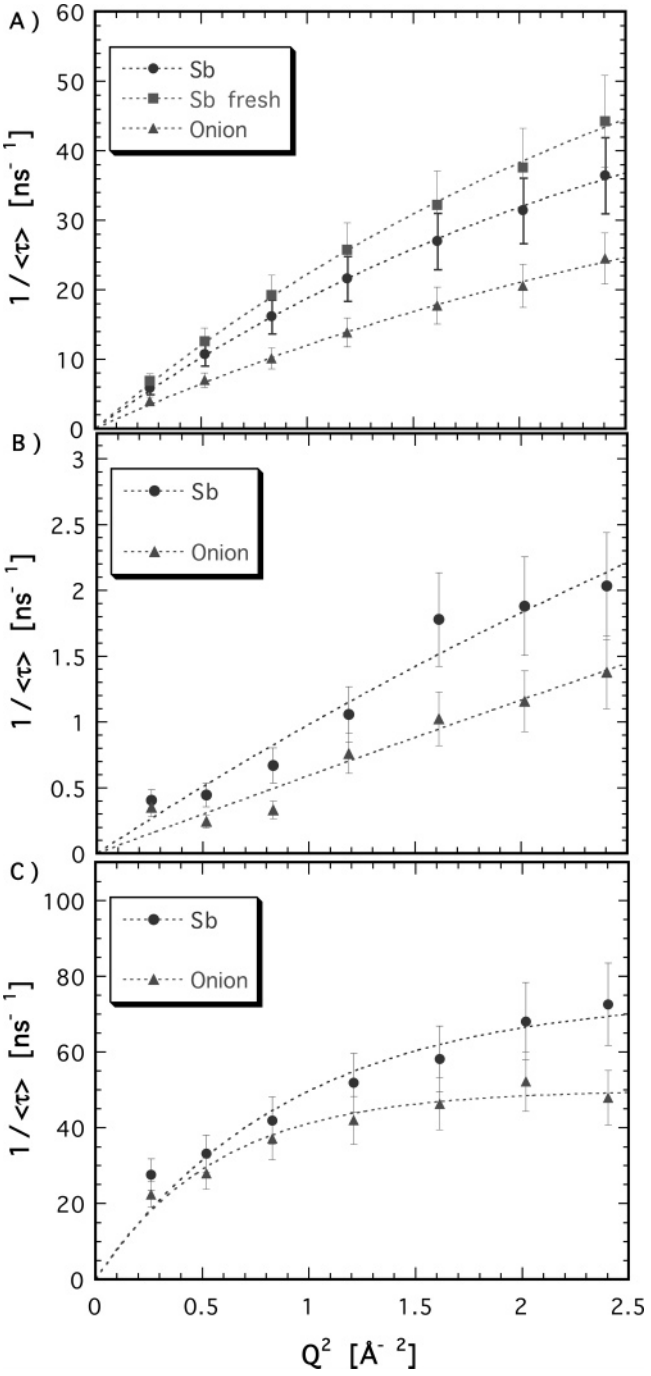

Figure 4. Inverse average relaxation time $1/\langle\tau\rangle$ as a function of Q^2 at $T = 280$ K for fresh (■) and freeze-dried (●) strawberry and freeze-dried onion (▲) with 45 wt % water content: (A) samples hydrated in H_2O; (B) samples hydrated in D_2O; and (C) the hydration water of freeze-dried strawberry and red onion (obtained by subtraction as described in the text). The Q-dependencies are in all cases described by the Gaussian jump-length distribution model.

4. Discussion

In this study we have investigated the microscopic dynamics of fresh (dehydrated) and hydrated freeze-dried strawberry and red onion at different hydration levels by means of quasielastic

TABLE 2: Parameters Obtained from the Fits to the Gaussian Jump-Length Distribution Model (Eq 4), Used for the Characterization of the Translational Diffusion Process of the Samples Here Investigated, Are Shown Together with Corresponding Values in the Literature for Monosaccharide and Disaccharide Solutions, as Well as Bulk Water[a]

ref and technique	sample	wt % water	T [K]	D [m^2/s] water	D [m^2/s] biomaterial	τ_{res} (ps)	$\langle r^2\rangle^{0.5}$ (Å)
this work QENS	Sb/D_2O/Fd	45	280		1.1×10^{-11}	140 ± 6	0.9 ± 0.2
			310		3.6×10^{-11}	21 ± 0.3	0.7 ± 0.1
	Sb/H_2O/Fd	45	280	1.9×10^{-10}*		7.5 ± 0.1	0.9 ± 0.1
			310	4.7×10^{-10}*		5.5 ± 0.1	1.3 ± 0.2
	Sb/H_2O/fresh	45	280	2.2×10^{-10}*		5.2 ± 0.1	0.8 ± 0.1
	onion/D_2O/Fd	45	280		6.0×10^{-12}	55 ± 3	0.5 ± 0.1
	onion/H_2O/Fd	45	280	1.3×10^{-10}*		11 ± 0.4	0.9 ± 0.2
	Sb/H_2O/Fd 20%	20	280	9.6×10^{-12}*		500 ± 30	0.7 ± 0.5
	Sb/H-D/Fd	45	280	8.0×10^{-10}		13 ± 0.4	2.5 ± 0.1
	onion H-D/Fd	45	280	6.6×10^{-10}		17 ± 0.7	2.6 ± 0.1
[8]QENS	bulk water		295	2.37×10^{-9}		2.05	1.7
[37]QENS	sucrose solution	50	303	1.2×10^{-9}		2.9	1.4
[37]QENS			303		1.6×10^{-10}	33	1.8
[21]QENS		≈50	323	1.5×10^{-9}		2.6	
[21]QENS			323		2.1×10^{-10}		
[38]QENS	fructose solution	96	300	2.5×10^{-9}			
[38]QENS		71	300	1.8×10^{-9}			
[38]QENS		40	300	7×10^{-10}			
[39]QENS	glucose solution	85	280	9.8×10^{-10}		1.5	1.0
[40]QENS		85	280		2.5×10^{-10}	0.4	0.2
[39]QENS		85	300	1.6×10^{-9}		0.8	0.9
[39]QENS		85	320	2.2×10^{-9}		0.3	0.7
[39]QENS		67	280	4.5×10^{-10}		3	0.9
[40]QENS		67	280		1.2×10^{-10}	25	1.3
[39]QENS		67	300	6.8×10^{-10}		1.3	0.7
[39]QENS		67	320	1.3×10^{-9}		1.6	1.1
[39]QENS		52	280	1.6×10^{-10}		5	0.7
[40]QENS		52	280		4.5×10^{-11}	78	1.6
[39]QENS		52	300	2.9×10^{-10}		2.8	0.7
[39]QENS		52	320	4.6×10^{-10}		1.7	0.7
[41]NMR	sucrose solution	66	298	6.8×10^{-10}			
[41]NMR					8×10^{-11}		
[41]NMR		53	298	4.5×10^{-10}			
[41]NMR					4×10^{-11}		
[41]NMR	fructose solution	79	298	1.1×10^{-9}			
[41]NMR					3.1×10^{-10}		
[41]NMR		69	298	8×10^{-10}			
[41]NMR					1.8×10^{-10}		
[41]NMR		61	298	5.5×10^{-10}			
[41]NMR					9×10^{-11}		
[41]NMR		47	298	3.5×10^{-10}			
[41]NMR					4×10^{-11}		
[41]NMR	glucose solution	79	298	6×10^{-10}			
[41]NMR					3×10^{-10}		
[41]NMR		74	298	2.3×10^{-10}			
[41]NMR					2.2×10^{-10}		
[41]NMR		62	298	1.4×10^{-10}			
[41]NMR					1.3×10^{-10}		
[13]NMR	glucose solution	60	280	2×10^{-10}			
[13]NMR					7×10^{-11}		
[13]NMR			303	4.5×10^{-10}			
[13]NMR					1.8×10^{-10}		
[13] NMR			315	6.5×10^{-10}			
[13]NMR					2.5×10^{-10}		

[a] In the table, D is the diffusion constant, τ_{res} is the residence time, and $\langle r^2\rangle^{0.5}$ is the mean jump length. In the "sample" column, Sb refers to strawberry, Fd to freeze-dried, and H-D to hydration water obtained from the subtraction of D_2O data from H_2O data. Here it should be noted that in the case of strawberry and red onion hydrated in H_2O (diffusion constants denoted with an asterisk) the weighted average of the motions in both the biological material and hydration water is probed. For the sugar solutions diffusion constants have been measured by both QENS and NMR (as indicated in column 1).

neutron scattering. From the measured data we have calculated parameters for the diffusion process (i.e., in addition to the diffusion constant D, the residence time τ_{res}, and the mean jump length $\langle r^2\rangle^{0.5}$), which are given in Table 2 together with a comparison with corresponding values available in the literature for carbohydrate solutions[21,31−34] and bulk water.[8] Diffusion constants obtained from NMR[13,35] are also given for comparison, and for clarity some of the diffusion constants given in Table 2 are also shown in Figure 5. From Table 2 and Figure 5 it is clear that the diffusion constant D for both the hydration water and the carbohydrates increases with increasing water content and temperature (and that QENS and NMR data are in perfect agreement, although different length scales are probed with the two techniques). This is also true for the carbohydrate-containing samples investigated in the present study. However, the dynamics of both the deuterated and protonated samples in the present study seem to be slower than those in pure sugar solutions, with the largest difference in the diffusion rate seen for samples

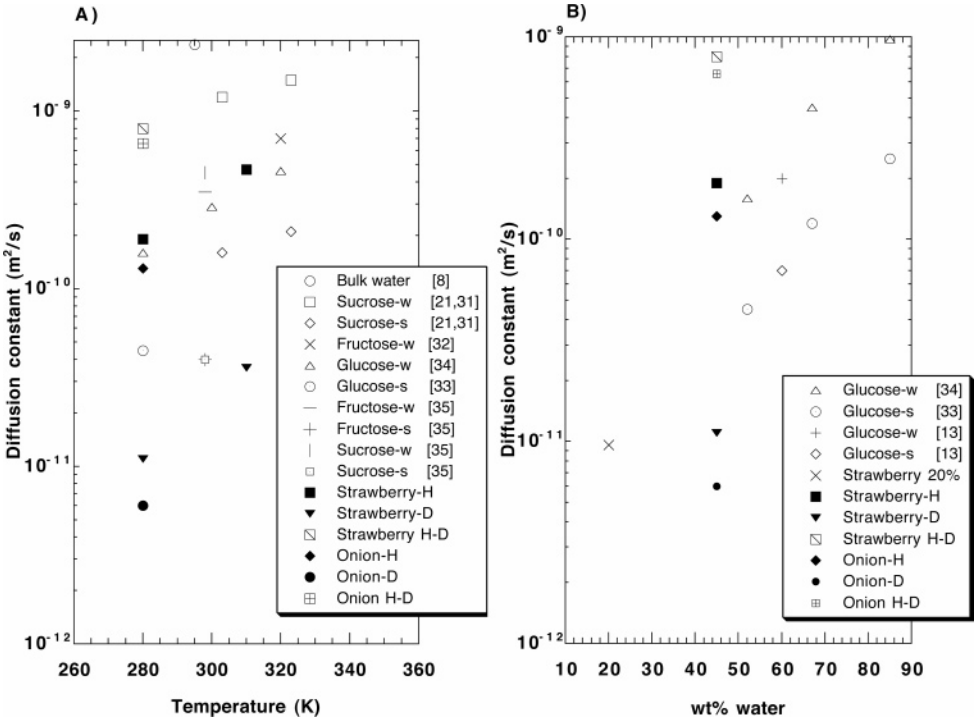

Figure 5. Comparisons of some of the diffusion constants given in Table 2: (A) diffusion constants as a function of temperature for strawberry and red onion hydrated to 45 wt % and carbohydrates solutions hydrated to 45−53 wt % water and (B) diffusion constants at $T = 280$ K given for different wt % water. The diffusion constants for the sugars and water are indicated by s and w, respectively, and references are given in the legend inside the angle brackets. The strawberry and red onion samples hydrated with H_2O and D_2O are indicated by H and D, respectively.

hydrated in D_2O, although one should here note that the literature data on carbohydrate solutions are somewhat inconsistent. Thus, for the carbohydrate solutions the difference in D between the sugar and the water is less than the differences obtained for the water and the biological materials in this study. These differences between the carbohydrate-rich materials studied here and pure sugar solutions are expected since the presence of cell membranes and other constituents is likely to reduce the diffusion rate. Compared to bulk water the difference is even larger, as also expected, since the average diffusion constant for the water in freeze-dried strawberry and red onion hydrated to 45 wt % is about 3 times lower at 280 K than that for bulk water at 295 K. The relatively low value (ca. 0.64) of the stretching parameter β_{KWW} implies that there is a broad distribution of relaxation times and therefore also of local diffusion rates. The likely reason for this is that some of the water molecules are strongly interacting with the biological material while other water molecules are exhibiting considerably faster and more bulklike dynamics.

In a previous study[31] we investigated the microscopic dynamics of water in fresh strawberry and red onion at different hydration levels by means of dielectric spectroscopy. It was found that for high water concentrations the dielectric spectra were dominated by water dynamics and the temperature dependence of the observed main relaxation process showed a similar Arrhenius behavior as water confined in many other types of systems.[19,32−35] However, for the lowest water concentrations a non-Arrhenius behavior was observed for the main process, which was explained by the fact that, on average, the dynamics of the water molecules was more strongly influenced by the motion of the biological material at low water contents. Thus, it seems that the coupling between the water dynamics and the dynamics of the biological material increases with decreasing water content. From the dielectric study it was furthermore found that the conductivity changed its character from low-temperature polarization effects to mainly normal dc-conductivity at about 250 K. This onset of long-range diffusion was suggested to be related to the onset of global motions of the biological matrix, which results in a disappearance of confinement effects for the motion of ions and water molecules. Thus, from both the present and previous studies on strawberry and red onion there are indications of an onset of global motions of the biological material around 250 K, which, for example, is indicated by the onsets of translational motions and dc-conductivity around this temperature. However, a comparison of the average relaxation times $\langle\tau\rangle$ obtained in the present study and in our previous dielectric study[31] is not consistent, which may be explained by the fact that the dielectric data show more global motions than are probed in this study.

The results obtained for strawberry and red onion in the present study, as well as for sugar solutions in other studies,[13,21,31−35] indicate that there is a relationship between the motions in the biological material and the hydration water. For instance, the onset of anharmonic motions on the experimental time-scale occurs at almost the same temperature for the hydration water and the biological material, and the samples with the fastest moving hydration water show also the fastest dynamics in the biological part. Similar findings have been obtained for hydrated proteins, where there is an ongoing discussion on the role of solvent dynamics for protein motions and function. Recently, it has, for example, been suggested that different protein motions are controlled by different motions in the solvent,[22,23] i.e., the protein dynamics is supposed to be slaved by the solvent dynamics. Furthermore, neutron scattering studies on hydrated proteins (see, e.g., refs 27, 28, and 36) have shown an onset of anharmonic motions in the protein at approximately the same temperature as that for its hydration water. Thus, there are indications that the dynamics of strawberry and red onion is related to solvent dynamics in a similar way as hydrated proteins. The question that arises from the present study is, therefore, if slaving is a unique phenomenon for protein motions, or if the solvent dynamics controls motions

of other biomolecules as well. However, it should be noted that the water dynamics is faster in strawberry than in red onion, which suggests that the water dynamics is not only promoting motions in the biological material, it is also affected by the structure (and possibly also the dynamics) of the biological host material. This implies that the properties of the biological material and its hydration water are interrelated.

5. Conclusions

In this study dehydrated fresh strawberry and hydrated freeze-dried strawberry and red onion were investigated by quasielastic neutron scattering (QENS). The results show an onset of anharmonic local motions on the experimental time-scale at 230−240 K for all samples, with an increase in MSD that depends on the hydration level. These local motions transform (at least partly) to translational diffusion at approximately the same temperature (250 K) as an onset in dc-conductivity was observed in a previous dielectric study of the same materials. The appearance of long-range mass and charge transport seems to be caused by an onset of global motions in the biological material that remove long-time confinement effects. At 280 K both the biological material and the hydration water show a broad distribution of relaxation times, although the relaxation rate is slower for the pure biological part. For the freeze-dried samples of the higher hydration level (45 wt % water) the average diffusion rate of water molecules is about 2 orders of magnitude faster than the diffusion of hydrogens in the biological material. The diffusion rates (of the hydration water as well as the biological part) are furthermore faster in strawberry than in red onion. Finally, it should be noted that the present results indicate that there is a similar dynamic relationship between the biological material and its hydration water as previously observed for hydrated proteins, which may suggest that solvent motions control the dynamics of carbohydrates in a similar way as for proteins.

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References and Notes

(1) *Biochemistry*, 3rd ed.; Mathews, C. K., Van Holde, K. E., Ahern, K. G., Eds.; Addison-Wesley Longman: San Fransisco, CA, 2000.

(2) Kallio, H.; Hakala, M.; Pelkkikangas, A. M.; Lapvetelainen, A. *Eur. Food Res. Technol.* **2000**, *212*, 81.

(3) Gennaro, L.; Leonardi, C.; Esposito, F.; Salucci, M.; Maiani, G.; Quaglia, G.; Fogliano, V. *J. Agric. Food Chem.* **2002**, *50*, 1904.

(4) Roos, Y. H. *J. Food Sci.* **1987**, *52*, 146.

(5) Affouard, F.; Bordat, P.; Descamps, M.; Lerbret, A.; Magazu, S.; Migliardo, F.; Ramirez-Cuesta, A. J.; Telling, M. F. T. *Chem. Phys.* **2005**, *317*, 258.

(6) Perez, J.; Zanotti, J. M.; Durand, D. *Biophys. J.* **1999**, *77*, 454.

(7) Bellissentfunel, M. C.; Chen, S. H.; Zanotti, J. M. *Phys. Rev. E* **1995**, *51*, 4558.

(8) Tuck, J. J.; Hall, P. L.; Hayes, M. H. B.; Ross, D. K.; Poinsignon, C. *J. Chem. Soc., Faraday Trans. I* **1984**, *80*, 309.

(9) Magazu, S.; Migliardo, F.; Telling, M. T. F. *J. Phys. Chem. B* **2006**, *110*, 1020.

(10) Denisov, V. P.; Halle, B. *Faraday Discuss.* **1996**, 227.

(11) Gallo, P.; Rovere, M.; Spohr, E. *Phys. Rev. Lett.* **2000**, *85*, 4317.

(12) Dellerue, S.; Bellissent-Funel, M. C. *Chem. Phys.* **2000**, *258*, 315.

(13) Moran, G. R.; Jeffrey, K. R. *J. Chem. Phys.* **1999**, *110*, 3472.

(14) Furuki, T. *Carbohydr. Res.* **2002**, *337*, 441.

(15) Sa, M. M.; Sereno, A. M. *Thermochim. Acta* **1994**, *246*, 285.

(16) Topgaard, D.; Soderman, O. *Biophys. J.* **2002**, *83*, 3596.

(17) Lewicki, P. P.; Gondek, E.; Witrowa-Rajchert, D.; Nowak, D. *J. Food Eng.* **2001**, *49*, 333.

(18) Evans, S. D.; Brambilla, A.; Lane, D. M.; Torreggiani, D.; Hall, L. D. *Lebensm. Wiss. Technol.* **2002**, *35*, 177.

(19) Berntsen, P.; Bergman, R.; Jansson, H.; Weik, M.; Swenson, J. *Biophys. J.* **2005**, *89*, 3120.

(20) Middendorf, H. D. *Physica B* **1996**, *226*, 113.

(21) Magazu, S.; Villari, V.; Migliardo, P.; Maisano, G.; Telling, M. T. F.; Middendorf, H. D. *Phys. B* **2001**, *301*, 130.

(22) Fenimore, P. W.; Frauenfelder, H.; McMahon, B. H.; Young, R. D. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 14408.

(23) Tarek, M.; Tobias, D. J. *Phys. Rev. Lett.* **2002**, *89*.

(24) *Livsmedelsdatabas*, version 04.1.1 (Swedish); National food administration, 2004 (www.slv.se).

(25) Carlile, C. J.; Adams, M. A. *Phys. B* **1992**, *182*, 431.

(26) Howells, W. S. Report No. RAL-TR-96-006, Rutherford Appleton Laboratory, 1996.

(27) Magazu, S.; Migliardo, F.; Mondelli, C.; Romeo, G. *Chem. Phys.* **2003**, *292*, 247.

(28) Magazu, S.; Maisano, G.; Migliardo, F.; Mondelli, C. *Biophys. J.* **2004**, *86*, 3241.

(29) Kolhrausch, R. *Ann. Phys.* (*Weinheim, Ger.*) **1854**, *1*, 179.

(30) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.

(31) Jansson, H.; Huldt, C.; Bergman, R.; Swenson, J. *Phys. Rev. E* **2005**, *71*.

(32) Bergman, R.; Swenson, J. *Nature* **2000**, *403*, 283.

(33) Jansson, H.; Swenson, J. *Eur. Phys. J. E* **2003**, *12*, S51.

(34) Jansson, H.; Bergman, R.; Swenson, J. *J. Non-Cryst. Solids* **2005**, *351*, 2858.

(35) Cerveny, S.; Schwartz, G. A.; Bergman, R.; Swenson, J. *Phys. Rev. Lett.* **2004**, *93*, 245702.

(36) Daniel, R. M.; Smith, J. C.; Ferrand, M.; Hery, S.; Dunn, R.; Finney, J. L. *Biophys. J.* **1998**, *75*, 2504.

(37) Branca, C.; Magazu, S.; Maisano, G.; Telling, M. T. F. *J. Phys. Chem. B* **2004**, *108*, 17069.

(38) Feeney, M.; Brown, C.; Tsai, A.; Neumann, D.; Debenedetti, P. G. *J. Phys. Chem. B* **2001**, *105*, 7799.

(39) Talon, U.; Smith, L. J.; Brady, J. W.; Lewis, B. A.; Copley, J. R. D.; Price, D. L.; Saboungi, M. L. *J. Phys. Chem. B* **2004**, *108*, 5120.

(40) Smith, L. J.; Price, D. L.; Chowdhuri, Z.; Brady, J. W.; Saboungi, M. L. *J. Chem. Phys.* **2004**, *120*, 3527.

(41) Mahawanich, T.; Schmidt, S. J. *Food Chem.* **2004**, *84*, 169.