Dynamics of water in strawberry and red onion as studied by dielectric spectroscopy

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We have investigated the microscopic dynamics of strawberry and red onion by means of broadband dielectric spectroscopy. In contrast to most of the previous experiments on carbohydrate-rich biological materials, which have mainly considered the more global dynamics of the "biological matrix," we are here focusing on the microscopic dynamics of mainly the associated water. The results for both strawberry and red onion show that the imaginary part of the permittivity contains one conductivity term and a clear dielectric loss peak, which was found to be similar to the strongest relaxation process of water in carbohydrate solutions. The temperature dependence of the relaxation process was analyzed for different water content. The relaxation process slows down, and its temperature dependence becomes more non-Arrhenius, with decreasing water content. The reason for this is most likely that, on average, the water molecules interact more strongly with carbohydrates and other biological materials at low water content, and the dynamical properties of this biological matrix changes substantially with increasing temperature (from an almost rigid matrix where the water is basically unable to perform long-range diffusion due to confinement effects, to a dynamic matrix with no static confinement effects), which also changes (i.e., reduces) the activation energy of the relaxation process with increasing temperature (i.e., causes a non-Arrhenius temperature dependence). This further changes the conductivity from mainly polarization effects at low temperatures, due to hindered ionic motions, to long-range diffusivity at $T > 250$ K. Thus, around this temperature ions in the carbohydrate solution no longer get stuck in confined cavities, since the motion of the biological matrix "opens up" the cavities and the ions are then able to perform long-range migration.

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I. INTRODUCTION

Water is the foundation of life. It is the medium for biomolecular movements and biological reactions. Thus, in order to understand biological processes, it is essential to elucidate how geometrical confinement and interactions with surfaces and other molecules affect the structure and dynamics of water. Also carbohydrates and their derivatives are widely distributed in living organisms, where they have both structural and metabolic roles [1]. The simplest carbohydrates are small monomeric molecules, the monosaccharides; examples of such sugars are glucose and fructose. Monosaccharides can be linked to each other to form oligosaccharides, which consist of a few monosaccharide units, or polysaccharides, which are polymers of monosaccharides. When two monosaccharide molecules are linked to each other a disaccharide is formed. Sucrose, which is built up of one glucose molecule and one fructose molecule, is an example of a disaccharide. Glucose, fructose, and sucrose are the major carbohydrates in most fruits and vegetables, such as the strawberry and red onion here studied [2,3].

The presence of biological processes that are promoted by water is the reason why cooling and drying are important methods for food storage [4]. The behavior of frozen and/or dried biological materials differs from that of fresh materials and research in this behavior is crucial for the possibility to optimize the stability of the treated food. Several studies [5–8] have been performed on the dynamical behavior of freeze-dried fruits and vegetables. However, most of these studies concentrate on the whole material and very few specifically on the dynamics of its interfacial carbohydrate solution.

Experiments on carbohydrate-rich food, such as vegetables and fruit, reveal a drastic increase in glass transition temperature T_g with decreasing water content [5], suggesting a strong concentration dependence of the dynamics of their carbohydrate solutions. In this study, the microscopic relaxational behavior of strawberry and red onion was studied by means of dielectric spectroscopy. Due to the high dielectric constant of water we mainly probe how the water dynamics is affected by the concentration of carbohydrates in the solution [9]. We observe one clear dielectric loss peak, which therefore is interpreted as a relaxation process of the supercooled water in the carbohydrate solution. The relaxation time τ of this process has a temperature dependence which follows the Vogel-Fulcher-Tammann (VFT) [10–12] behavior,

$$\tau = \tau_0 \exp\left[\frac{DT_0}{T - T_0}\right]. \quad (1)$$

D is a material-dependent constant describing the degree of non-Arrhenius behavior, T_0 is the temperature where τ goes to infinity, and τ_0 is the relaxation time extrapolated to infinite temperature, which usually corresponds to quasilattice and molecular vibrations of the order of 10^{-14} s. Here one should note that this kind of temperature dependence is generally observed also for the viscosity of supercooled liquids. When τ of a main (α-) relaxation process has reached a value of 100 s, the supercooled liquid behaves like a solid and is called a glass. So called strong glass formers, in Angell's strong-fragile classification scheme [13,14], have an α-relaxation time with a nearly Arrhenius temperature de-

pendence (a large D value in the VFT function) in contrast to fragile glass formers, which show a much more rapid increase of the α-relaxation time close to T_g (i.e., a low D value in the VFT function).

The large dipole moment of the water molecule and the unique characteristics of hydrogen bonds are likely the main reasons for the many peculiar properties of water. Most experimental studies [15] of bulk water have indicated that the water molecules tend to form a tetrahedral hydrogen-bonded structure, although these hydrogen bonds have very short lifetimes of the order of picoseconds at room temperature. However, at considerably lower temperatures in the deeply supercooled regime almost all hydrogen bonds should be intact at each moment, which implies that water then forms a permanent tetrahedral network structure [15]. It is therefore reasonable to suspect that the dynamics can be very different for moderately and deeply supercooled water. In the moderately supercooled regime bifurcated bonds are defects in the water network structure that provide large structural rearrangements with low energy barriers. The number of these defects should go to zero as temperature is decreased leaving only regular hydrogen bonds with high-energy barriers against rearrangement. This might be the reason for the proposed change in dynamics that causes water to be anomalous in yet another fashion. Close to the melting point, water seems to be the most fragile of all liquids studied [16], but close to T_g, it may be one of the strongest [16–18]. Thus, it is possible that supercooled water exhibits some kind of dynamic transition somewhere close to $T_s = 228$ K, where the temperature dependence of the α-relaxation time changes from a highly non-Arrhenius behavior at high temperatures to an Arrhenius temperature dependence in the deeply supercooled regime [16–18].

In this study, however, we are not dealing with bulk water since a large fraction of the water molecules in partly dried strawberries and red onion will be directly associated with cell membranes and carbohydrates. This will introduce a confined environment for the water molecules as well as interactions with surrounding carbohydrates and biological surfaces, which will cause alterations in the structure and dynamics of the water molecules. The tetrahedral hydrogen-bonded network structure of bulk water will, for instance, break up and this is, as mentioned above, expected to increase the fragility of the supercooled water and affect the glass transition temperature. Experiments have shown that the relevant length scale for the glass transition is typically a few nanometers for small molecular systems [19]. However, in the case of water this length scale is likely to be shorter since molecular dynamics simulations have shown that the influence of confinement and/or surface interactions on the structural and dynamical properties of water does not exceed a few molecular diameters from the surfaces [20]. The most apparent discrepancies are a lower mobility close to the surfaces [21–25] and, as mentioned above, a distorted hydrogen-bonded network. A surface changes the orientation of the water molecules close to it in a way that depends on the chemical nature of the surface (i.e., whether it is hydrophilic or hydrophobic). This reorientation will in turn affect the interaction between adjacent water molecules and the probability of forming a network structure.

Fresh strawberries and onions contain about 90 wt % water and 9 wt % soluble solids [26], which mainly consist of the carbohydrates fructose, glucose, and sucrose [2,3]. When freezing carbohydrate-rich food material a part of the water will crystallize into almost pure ice, while the remaining part will form a more concentrated carbohydrate solution [5]. This supercooled solution will then transform into a glass at an even lower temperature [5]. Generally, there are many similarities for freezing and melting behavior between sugar solutions and food with high carbohydrate content. It is therefore likely that these processes in biological materials are due to phenomena inherent to the carbohydrate solution. In this context the role of the "biological matrix" is to form small confinements which can obstruct the formation of ice, since freezing and melting of ice as seen in carbohydrate-rich food materials should only occur in larger voids of the biological matrix, provided that the concentration of carbohydrates in the solution is low enough to permit crystallization of the water.

II. EXPERIMENTAL SECTION

Fresh strawberry and red onion were used for the dielectric measurements. In the case of strawberry a scalpel was used to cut out a thin slice perpendicular to the length of the strawberry. The diameter of the slice was 20 mm and to include as much as possible of the behavior of a whole strawberry, the skin and seeds at the edge of the sample were preserved. The red onion sample was cut out of one onion layer. The compact skin of the layer was kept covering one of the sample sides. The samples were cut as thin as possible without destroying their structure or creating an unevenly thick specimen. Initially, both samples were almost 2 mm thick. However, upon installing the samples in the sample holder, the samples were pressed into a width of approximately 1.2 mm. Thus, some water was removed already at this stage.

The dielectric measurements were performed using a broadband dielectric spectrometer, a Novocontrol Alpha System, covering the wide frequency range 10^{-2}–10^{7} Hz. The samples were put between two gold-plated electrodes (diameter 20 mm) and placed in a sample holder. Thereafter, the samples were quickly frozen to 120 K prior to the measurements and then measured at every tenth degree in the temperature range 120–300 K. The temperature was controlled with an accuracy of better than 0.1 K by a nitrogen gas cryofurnace (Novocontrol).

Between measurements, the samples were weighed and, if needed, dried in a vacuum oven. Five measurements were performed for both strawberry and red onion of different water content (see Table I). Before the last measurement on both specimens, the samples were dried for several hours in a vacuum oven. The last measurement was then used as a completely dry reference, representing the biological matrix.

III. RESULTS AND DISCUSSION

In this study the imaginary part of the measured permittivity, the dielectric loss, was analyzed. In this representation

TABLE I. Fit parameters obtained from the VFT fits in Fig. 4. τ_0 is the value to which the relaxation time extrapolates to at an infinite temperature, D is related to the fragility, T_0 is the temperature at which the relaxation time is infinite, and $T_{100\ s}$ is the temperature where the relaxation time has reached 100 s. The water content of the different samples is given in % of the initial water content. Initially, the samples of fresh strawberry and red onion contained 92.7% and 88.8% water, respectively.

% of initial water content	$\log_{10}$ τ_0 (s)	D	T_0 (K)	$T_{100\ s}$ (K)
	Strawberry			
21.6	−9.0	96.0	23.3	112
12.8	−7.4	18.8	64.5	121
10.2	−6.6	8.4	88.8	127
5.5	−6.7	9.1	87.7	128
	Red onion			
50.3	−8.7	37.5	48.4	122
23.0	−7.7	21.1	62.3	121
7.8	−10.2	52.4	48.4	139

conductivity or polarization effects appear as a low-frequency power law while relaxational dynamics give rise to peaks in the response. One clear loss peak was observed in all measurements (see Fig. 1), except for the completely dry samples where no peaks were observed. This suggests that the biological matrix as well as the carbohydrates give a negligible contribution to the imaginary part of the permittivity, which furthermore is supported by the fact that the amplitude of the loss peak strongly increased with increasing water content, but remained almost constant with temperature (in the range 120–230 K). Therefore we have assumed that this process represents the strongest relaxation of the water in the interfacial carbohydrate solution, in agreement with previous findings [9]. At higher frequencies small loss peaks that might be attributed to temporary and possibly random physical changes in the biological matrix could be detected. However, these processes were in general too weak to significantly affect the parameters of the main relaxation process.

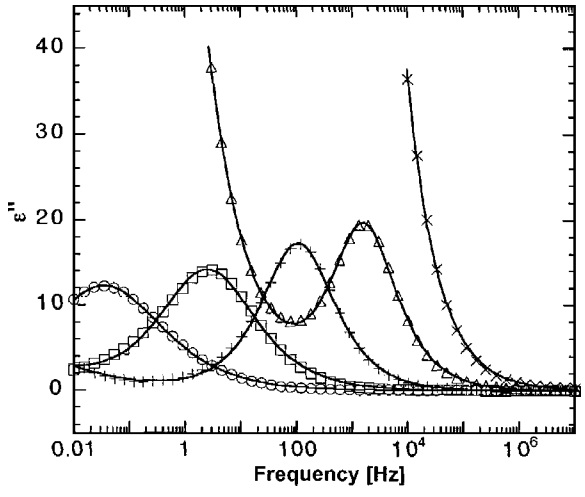

FIG. 1. Imaginary part of the permittivity for strawberry (12.8% of the initial water content) as a function of frequency for the temperatures 130 (○), 150 (□), 180 (+), 220 (△), and 250 K (×). The experimental data have been described by a superposition of a conductivity term and a single dielectric loss peak (lines).

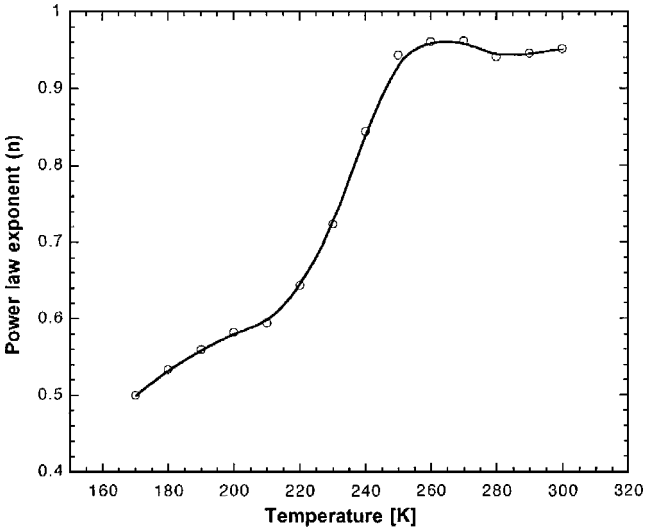

FIG. 2. Temperature dependence of the power-law exponent n of the conductivity obtained for strawberry with 12.8% of the initial water content. (The solid line is a guide to the eye.)

To describe the experimental data shown in Fig. 1 we used the phenomenological Havriliak-Negami (HN) equation together with a conductivity term:

$$\varepsilon''(\omega) = \left(\frac{\sigma}{\varepsilon_0 \omega}\right)^n + \mathrm{Im}\left[\frac{\varepsilon_s - \varepsilon_\infty}{[1 + (i\omega\tau)^\alpha]^\beta}\right], \qquad (2)$$

where ε_s and ε_∞ are the unrelaxed and relaxed values of the dielectric constant, respectively, τ is the relaxation time, ω is the angular frequency, and σ is the conductivity parameter (due to normal dc conductivity and polarization effects). In Fig. 1 it is evident that the magnitude of σ increases with increasing temperature. However, this is true also for the power-law exponent n, which increases from about 0.5 at 170 K to almost 1.0 at 250 K. This is shown in Fig. 2 for strawberry with 12.8% of its initial water content. The gradual increase of the power-law exponent is attributed to a shift from Maxwell-Wagner polarization effects at low temperatures (which are commonly present in inhomogeneous systems, such as biological materials [27]) to mainly normal dc conductivity around 250 K and above. We believe that this transformation is due to an onset of global motions of the biological matrix. This implies that at these high temperatures the cavities open up and the ions in the carbohydrate solution no longer get stuck in confining cavities. The behavior was similar for strawberry and red onion, as well as for different water content (except for the completely dry samples for which the dc conductivity was negligible even at the highest measured temperatures). In fact, only a few percent of the initial water content is needed for ion diffusion; the difference between the completely dried samples and those with the lowest water content is remarkable. Neverthe-

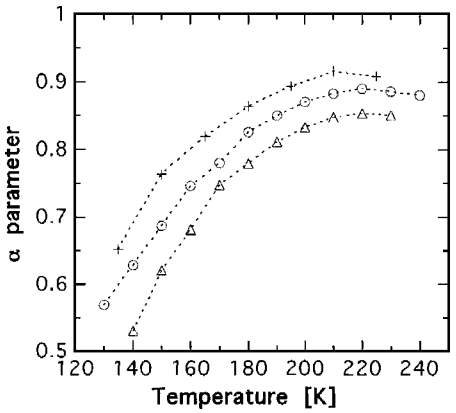

FIG. 3. Dependence of the α parameter in Eq. (2) on temperature and water concentration for strawberry. The different values of water content are (+) 21.6%, (○) 12.8%, and (△) 10.2% of the initial water content.

less, there is only a minor increase of the dc conductivity with increasing water content for the other more water-rich samples. At the highest measured temperatures, from 270 to 310 K electrode polarization is observed, which is shown as a drop in the conductivity at low frequencies (not shown).

The general HN function [Eq. (2)] contains two shape parameters α and γ. However, the special versions of HN with only one shape parameter, the asymmetric Cole Davidson equation ($\alpha=1$) and the symmetric Cole-Cole (CC) equation ($\gamma=1$), have often been used to describe the main α- and secondary β-relaxations, respectively. In this work we find that for both strawberry and red onion the dielectric loss peak is symmetric for all temperatures and concentrations, which suggests that it corresponds to a β-relaxation rather than the α-relaxation. In fact, there are indications that it is the β-relaxation of bulk water that shows a relaxation time of about 100 s at $T\approx 130$ K [28,29], and that T_g (the temperature where the α-relaxation time is approximately 100 s) is located at a considerably higher temperature around 165 K [30–32]. This interpretation would then be in conflict with the common belief in the last decade that T_g for bulk water is in the range 124–136 K [33,34]. Thus, there are indications that the α-relaxation of water is not observed in the present system, as well as in most other types of confined systems and solutions [29]. Although we are in this study unable to determine whether the observed dielectric loss peak corresponds to the α- or β-relaxation of water, these other recent studies [28–32], in combination with the fact that the temperature for which its relaxation time has reached 100 s is considerably lower than the calorimetric glass transition of the samples [5] (see below), suggest that it should be a rather local β-like process.

The width, proportional to $1/\alpha$, of the loss peak decreased with increasing water content and temperature (see Fig. 3). This is an expected behavior for several reasons. First, since there is a difference in the dynamics between rather "free" water molecules (i.e., those interacting only with other water molecules) and water molecules interacting strongly with carbohydrates the peak is expected to be broader for low

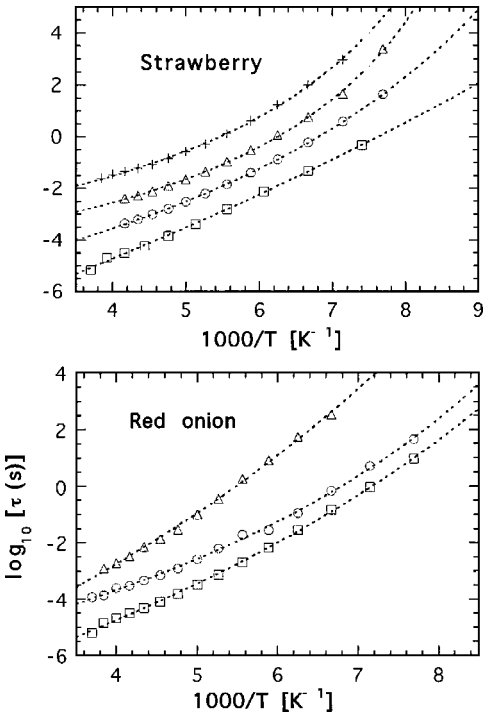

FIG. 4. Temperature dependence of the main relaxation time obtained for (a) strawberry and (b) red onion of different water content. For strawberry the symbols correspond to the following values of water content: (□) 21.6%, (○) 12.8%, (△) 10.2%, and (+) 5.5% of the original water content. In the case of red onion (□) corresponds to 50.3%, (○) to 23.0%, and (△) to 7.8% of the initial water content. The different data sets have been vertically shifted in subsequent steps of one unit, for clarity. Each data set is described by a VFT function and the obtained fitting parameters are given in Table I. $T_{100\ s}$ (see Fig. 5) gives the temperature where the fit function passes $\tau=100$ s.

water content (as also found in Refs. [9,35,36]), where the contribution from water molecules interacting with carbohydrates is stronger. Second, the relaxation function of glass-forming liquids normally shows a more stretched relaxation the deeper in the supercooled regime they are (which can be explained in terms of, for instance, an increased coupling between relaxing units [37]), and third, the pure geometrical confinement effect (which in most cases seems to speed up the dynamics of molecules which are not interacting with the walls of the cavity [38–41]) increases with decreasing water content.

In Fig. 4 we show Arrhenius plots for strawberry and red onion of different water content, where the VFT function [Eq. (1)] has been fitted to the temperature dependence of the relaxation time. The fitting parameters are given in Table I. In the case of strawberry the temperature dependence of the relaxation process changes from a nearly Arrhenius behavior at high water content to a pronounced non-Arrhenius temperature dependence for the lowest water content. The reason for this is most likely that, on average, the water molecules interact more strongly with the carbohydrates and the biological matrix at low water content, and the motion of the biological matrix increases substantially with increasing temperature (from a rigid to a highly flexible matrix), causing a

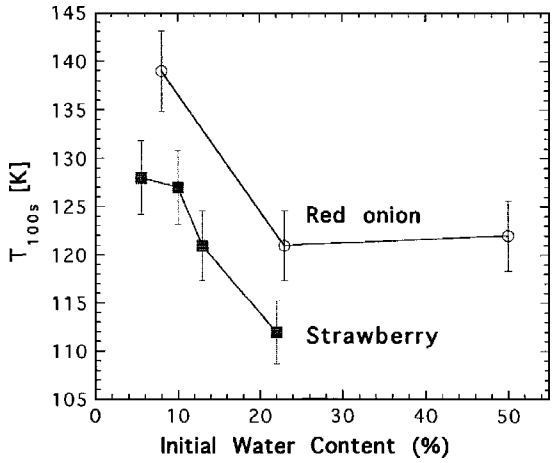

FIG. 5. Estimated temperature for which the relaxation time has reached 100 s, $T_{100\ s}$, as a function of water content in strawberry and red onion. Although the error bars are rather large, the trend is that $T_{100\ s}$ increases with decreasing water content.

reduction of the activation energy of the relaxation process with increasing temperature (i.e., giving rise to a non-Arrhenius temperature dependence). A similar systematic trend is not observed for red onion (probably because the biological matrix of red onion is less flexible and more dependent on the water content). This relaxation process can be considered as frozen when its relaxation time reaches ca. 100 s (in analogy with the result that the glass transition temperature of a glass-forming liquid is commonly defined as the temperature where its α-relaxation time reaches ca. 100 s). The $T_{100\ s}$ values for strawberry and red onion of different water content so obtained are shown in Fig. 5 and Table I. The differences in $T_{100\ s}$ between the different water content were only marginal compared to the divergences in T_g found in the differential scanning calorimetry (DSC) study of Ref. [5], where T_g started at about 190 K for about 10% of the initial water content and finished close to room temperature for the almost completely dried samples. DSC measurements have shown that the glass transition temperature of the whole biologic material changes continuously with the water content from the high glass transition temperature of dry carbohydrates down to that assumed for bulk water [42]. In Ref. [2] the measured T_g values could be predicted by weighing the glass transition temperatures of the pure constituents with the percentages of the constituents in the sample. Since the viscosities of samples with different water content should be related to their glass transition temperatures, this suggests that the viscosity of a biological material should be strongly dependent on its water content. However, in our case we do not necessarily measure relaxational dynamics that is related to the viscosity of the whole biological material. Rather, the observed dielectric process is evidently due to relatively local motions of water molecules that are considerably less affected by the water content. Thus, the local water dynamics is not strongly affected by a dramatic viscosity change of the whole sample. Since the cooperative α-relaxation is generally coupled to the viscosity of the sample this suggests, as mentioned above, that the present relaxation process corresponds to a local β-like process of the water in the carbohydrate solution.

One should also note that for the samples with the highest water content $T_{100\ s}$ is significantly lower than for water confined in more well-defined model systems, such as clays [18], molecular sieves [43], purple membrane [44], and a large number of other model systems [29] where $T_{100\ s}$ normally is in the temperature range 130–140 K. The reason for this might be that in all these systems interactions with surfaces, ions, and other molecules slow down the water relaxation and this effect is unusually low for the present water-rich samples due to their comparably high water content (in most other model systems the interfacial water crystallizes at such high water content). The difficulty in producing reasonably large water clusters and simultaneously preventing them from crystallization in the deeply supercooled regime where bulk water immediately crystallizes is most likely the reason why the cooperative α-relaxation is normally absent in dielectric studies of confined supercooled water [29].

In Fig. 4 and Table I we further note that for both strawberry and red onion, the VFT behavior extrapolate to values between 10^{-10} and 10^{-6} s at infinite temperatures, and not to 10^{-14} s (i.e., the approximate vibration time of single molecules) as normally observed for bulk materials. This fact is of concern but not unheard of. Naturally, the extrapolation over several decades renders τ_0 a difficult value to determine with high accuracy, which is further complicated by the fact that the VFT function normally does not describe the temperature dependence of the relaxation time over the whole relevant temperature range [45]. However, in our case the deviations of τ_0 from 10^{-14} s are so large that this is unlikely the only explanation. A hypothesis is that in networking two-component systems, such as in gels [45] and carbohydrate-water systems of fruits and vegetables, there are collective vibrational modes for the water molecules. The water molecules then move collectively with slower dynamics than that of molecular vibrations. Thus, τ_0 no longer extrapolates to the vibration time of a single water molecule, but rather to these slower collective modes.

In order to elucidate whether the results given above are mainly due to the dynamic properties of water in a carbohydrate solution, or if the confinement effect caused by the biological matrix has a substantial influence on the dynamics, we have studied the dielectric and calorimetric properties of aqueous solutions containing glucose, fructose, and sucrose, respectively. Figure 6 shows the temperature dependence of the relaxation time corresponding to the strongest dielectric process of sucrose aqueous solutions. Similar results were obtained for aqueous solutions of glucose and fructose [46]. These findings should be compared with the corresponding relaxation times for strawberry and red onion of the lowest water content, shown in Fig. 4. It can be seen that the relaxation process in the sucrose aqueous solutions becomes faster with increasing water content, in qualitative agreement with the findings for strawberry and red onion. In the case of the solution containing 30 wt % water $T_{100\ s} \approx 135$ K, which is higher than for strawberry but lower than for red onion at similar water content. Furthermore, the shape of the relaxation process is best described by the symmetric CC equation, as for strawberry and red onion. These findings suggest that it is mainly the interactions with the

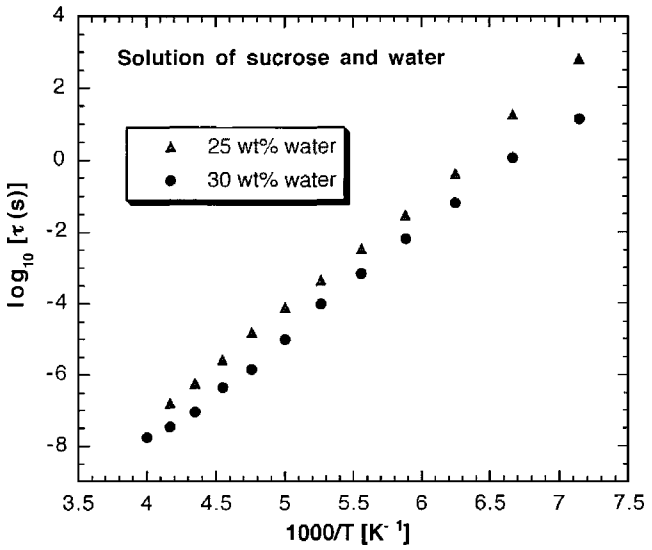

FIG. 6. Temperature dependence of the main relaxation time obtained for solutions of sucrose and water.

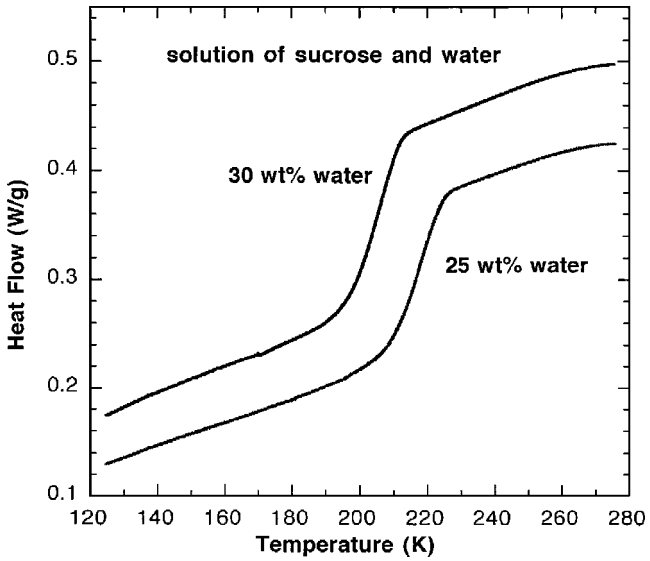

FIG. 7. DSC measurement of exothermic heat flow during cooling (10 K/min) of solutions of sucrose and water.

carbohydrates that affect the water dynamics and that the pure confinement effects are of minor importance. However, one should note that at high temperatures there is a dramatic difference and the bulk carbohydrate solutions show a much faster relaxation process than in strawberry and red onion. The reason for this is most likely the motion of the biological matrix at high temperatures, which reduces the activation energy of the water relaxation process (as discussed above). It is also possible that local motions of the biological matrix can contribute to the dielectric response at high temperatures, or that the water dynamics is coupled to these motions. Such motions are most likely slower than for bulk water and should therefore shift the total relaxation process to lower frequencies.

The calorimetric glass transitions of the same aqueous solutions of sucrose are shown in Fig. 7. In the figure it is evident that the solution exhibits a similar decrease of T_g with increasing water content (the onset temperature of T_g decreases from about 210 to 194 K for an increase from 25 to 30 wt % water) as was found in Ref. [5] for strawberry and red onion. Thus, even in the case of the bulk carbohydrate solutions the calorimetric glass transition temperature is located at a considerably higher temperature (and shows a much greater dependence on the water concentration) than the temperature for which the most pronounced dielectric process has a relaxation time of 100 s, $T_{100\ s}$ (see Fig. 6).

IV. CONCLUSIONS

In the present dielectric study of strawberry and red onion we observe two clear dynamical processes; a loss peak attributed to a relaxation process of water in the carbohydrate solution and ionic polarization, which transforms to long-range diffusion at temperatures above approximately 250 K due to an onset of global motions of the biological matrix. The temperature for which the relaxation time is about 100 s, $T_{100\ s}$, increases with decreasing water content from a lower value to a value similar to what has been found for most model systems of confined water. The increase of $T_{100\ s}$ with decreasing water content is most likely because interactions with carbohydrates and the biological matrix slow down the water dynamics, and the influence of these interactions on the water dynamics increases with decreasing water content. Similar findings are observed for pure solutions of fructose, glucose, and sucrose, indicating that at low temperatures when the biological matrix is essentially frozen it is mainly the concentration of the carbohydrate solution that determines the relaxation process of its water.

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