Application of High-Resolution Carbon-13, Oxygen-17, and Sodium-23 Nuclear Magnetic Resonance to Study the Influences of Water, Sucrose, and Sodium Chloride on Starch Gelatinization[1]

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ABSTRACT

Nuclear magnetic resonance (NMR) spectroscopy was used to observe molecular changes during thermal transition of wheat starch in free water (D_2O) in the presence of sucrose and sodium using the nuclei of carbon-13, oxygen-17, and sodium-23. A starch-D_2O mixture (40:60) was heated from 25 to 95°C and then cooled back to 25°C. Pulse NMR spectra obtained on heating and cooling showed a drastic increase in the ^{13}C signal intensity and the resolution on gelatinization (55–65°C), indicating an increase in the carbon chain mobility. The ^{17}O NMR spectra showed a relaxation time (T_2) that sharply decreased in this gelatinization temperature range, indicating an increase in "trapped" water; the correlation time indicated that the D_2O mobility was too high to be considered "bound." Added solutes reduced the 17_o T_2 for water. With added sodium chloride, the ^{13}C spectra were broadened during starch gelatinization (55–95°C), accompanied by a decrease in ^{23}Na T_2, indicating a sodium-starch interaction.

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Differential scanning calorimetry (DSC) has provided much information on the amorphous or crystalline nature of starch during gelatinization. However, information is lacking about changes in the molecular mobility of the starch chain and water. Scientists are interested in the effect of water on starch gelatinization because of its plasticizing property (Collison and Chilton 1974, Donovan 1979, Wootton and Bamunuarachchi 1980, Ghiasi et al 1982, Biliaderis 1983, Paton 1987, Levine and Slade 1989). Inhibitory effects of sugar and salt on starch gelatinization have been reported (Wootton and Bamunuarachchi 1980, Evans and Haisman 1982, Ghiasi et al 1982, Spies and Hoseney 1982, Chungcharoen and Lund 1987, Chinachoti et al 1990).

Sugars have been thought to increase the gelatinization temperature of starches (at a constant moisture level) by various means. More than 10 years ago, the competition for water between sugar and starch was proposed as a key factor in reducing water activity of the sugar-starch-water system; thus, less water would be available to gelatinize the starch (D'Appolonia 1972, Labuza 1975, Derby et al 1975). However, some argued that this was not the only factor (Wootton and Bamunuarachchi 1980; Evans and Haisman 1982; Ghiasi et al 1982; Spies and Hoseney 1982; Chungcharoen and Lund 1987; Levine and Slade 1988, 1989). Additional mechanisms have been proposed to inhibit starch gelatinization, such as sugar-starch interaction (Lelievre 1976; Spies and Hoseney 1982; Hansen et al 1987, 1989). Chinachoti and Steinberg (1984) and Carillo et al (1988, 1989) reported that sucrose reduced the water-sorption property in sucrose-starch mixtures. The antiplasticizing effect of sucrose has also reportedly been associated with a decrease in free volume, resulting in a

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less plasticizing effect of the sucrose-water solvent (Levine and Slade (1988, 1989). Effects of salts arise from quite different mechanisms, since salts might affect the water structure (Jane 1990) and Donnan potential because of cation-starch interactions (Oosten 1982, 1983).

With these contrasting viewpoints, it would be of great value to use a technique that monitors the molecular changes on gelatinization as an analysis parallel to the typical DSC. This would allow one to "see" various molecules at the same time.

Nuclear magnetic resonance (NMR) spectroscopy is one of the best alternatives for determining the molecular dynamics of starch (Jane et al 1985, Veregin et al 1986, Richardson 1988, Jane 1990) and its water (Tait et al 1972; Mora-Gutierrez and Baianu 1985, 1989; Richardson et al 1987; Chinachoti and Stengle 1990) by applying ^{13}C and ^{17}O NMR, respectively. ^{13}C NMR spectra for starch powder have shown more than one resonance for each carbon site because of the presence of a number of carbons corresponding to the resonance number in the asymmetric unit (Blanshard et al 1990). The noncrystalline region of a solid sample showed a broad, poorly resolved spectrum due to the large distribution of chemical shifts, whereas the crystalline region showed a narrow spectrum (Veregin et al 1986). Therefore, line narrowing or line broadening of a solid sample was concluded to be a contribution not only of molecular mobility but also of chemical shift distribution (Veregin et al 1986). In a liquid sample with soluble starch, high-resolution ^{13}C NMR with proton decoupling was used to study starch gelatinization and retrogradation (Jane et al 1985, Richardson 1988, J. Jane, *unpublished data*, 1990). In gels, however, high-resolution NMR also showed a typical broad resonance with either dispersion or anisotropy of chemical shifts (Blanshard et al 1990). Although ^{13}C cross-polarized/magic-angle spinning has been superior to high-resolution to study starch chain conformation, the latter could be valuable for observing the overall change in spectrum during gelatinization.

The study of water mobility during starch gelatinization has been limited also. Most work on starch gels and doughs has been done with ^{1}H (proton) or ^{2}H (deuterium) NMR (Jaska 1971, Lelievre and Mitchell 1975, Leung et at 1983, Wynne-Jones and Blanshard 1986). In the study of water mobility by ^{1}H NMR (Jaska 1971), a 40% starch suspension showed a drastic drop in line width (increased relaxation time [T_2]) on starch gelatinization, whereas a 20% starch sample showed the opposite. The former was explained by assuming that water mobility increased suddenly because of the increase in mobility of the starch molecules on gelatinization. In the latter case, the decreased T_2 was explained as being due to the increased water of hydration on gelatinization. However, one of the most serious problems with such ^{1}H NMR studies are the unknown contributions of cross relaxation (Edzes and Samulski 1978, Koenig et al 1978, Shirley and Bryant 1982) and chemical exchange (Mora-Gutierrez and Baianu 1990), both of which should be considered in the analysis of the ^{1}H NMR results. Applying ^{2}H nuclei is an alternative to avoid the problem of cross relaxation due to quadruplarity. However, ^{2}H NMR is subjected to an exchange process that is expected to become promoted when starch is heated and thus is not appropriate for the study of starch gelatinization. Fortunately, water mobility can be measured unambiguously with ^{17}O NMR since it shows little or no chemical exchange and has no cross relaxation because of its different frequency (Richardson et al 1987; Chinachoti, *unpublished data*, Mora-Gutierrez and Baianu 1990). NMR of ^{23}Na could also be used to determine the mobility of sodium cations (which have been proposed to interact with the starch through ionic interaction).

Therefore, the objective of this work was to use ^{13}C, ^{17}O, and ^{23}Na high-resolution NMR to study starch, water, and sodium mobility on heating and cooling during gelatinization in the presence of sucrose and NaCl.

MATERIALS AND METHODS

Wheat starch (Manildra Milling Corp., Minneapolis, MN), deuterium oxide (99%, Wilmad Glass Co., Inc., Buena, NJ), sucrose, and NaCl (Fisher Scientific Co., Fairlawn, NJ), were used. All samples contained starch and free water (D_2O) (40:60). Samples of 10 and 41.25% sucrose (starch basis) and of 1 and 2% NaCl (starch basis) were prepared and left resting overnight before the gelatinization experiment. D_2O instead of H_2O was used to avoid the proton exchange broadening of the ^{17}O water peak (Richardson et al 1987).

The starch sample was heated in the NMR probe from 25 to 95°C and then cooled back to 25°C in a 10-mm NMR tube (Wilmad Glass Co., Inc., Buena, NJ). The NMR probe was equipped with a programmable heating and cooling control. The overall heating and cooling rate was 3.3°C/min, in 10°C steps with a 3-min delay. Temperature variations within the NMR tubes were as follows: ±4.0°C (25–35°C), ±2.5°C (35–45°C), ±1.5°C (45–55°C), ±1.0°C (55–65°C), and ±0.5°C (65–95°C). At the end of each 10°C increase, a ^{13}C, ^{17}O, or ^{23}Na NMR spectrum was obtained. A set of duplicate samples was tested for each nucleus.

^{13}C NMR

^{13}C in natural abundance (1.108%) was used. The spectra were obtained at 75.44 MHz with a Varian XL-300 instrument (Varian Associates, Inc., Sunnyvale, CA). Spectral width was 22,522 Hz; pulse width, 15 μsec (corresponding to a flip angle of 84°); recycle delay, 1.66 sec; number of scans, 128.

^{17}O NMR

^{17}O in natural abundance (3.7×10^{-2}%) was used. The spectra were obtained at 40.67 MHz with a Varian XL-300 instrument. Spectral width was 15,000 Hz; pulse width, 15 μsec (corresponding to a flip angle of 79°); recycle delay, 0.15 sec; number of scans, 4,000. T_2 was calculated from the Fourier transformed spectra from line widths ($\Delta\nu$) at half height by applying the following equation: $T_2 = 1/(\pi\Delta\nu)$.

^{23}Na NMR

^{23}Na in natural abundance (100%) was used. The spectra were obtained at 79.35 MHz. Spectral width was 20,161 Hz; pulse width, 8.7 μsec; recycle delay, 1.24 sec; number of scans, 64. T_2 was calculated as described above.

DSC

The endothermic gelatinization reaction was observed with a differential scanning calorimeter (DSC2, Perkin Elmer Corp., Norwalk, CT). A 10-mg sample was weighed and sealed in a hermetically sealed pan and then heated under the calorimeter from 7 to 160°C at a rate of 10°C/min. The observed endothermic energy was calculated from the peak area. The initial temperature (T_o) and peak temperature (T_p) were also measured (Lund 1983).

RESULTS AND DISCUSSION

^{13}C Results

Starch alone. The ^{13}C NMR spectra for a starch-D_2O mixture (Fig. 1) varied drastically with temperature because of the phase transition of the starch polymer. At 25–55°C, the spectra showed broad lines and thus poor resolution among various carbon groups. As the sample was heated from 55 to 65°C, signal height and resolution increased abruptly. This was due to the glass transition of the amorphous starch, followed by the melting of the crystalline starch that occurs in this temperature range. This was supported by DSC measurement (T_o, 60.9°C; T_p, 66.2°C). This phenomenon involves the disruption of the bonding of starch and starch hydrogen and results in an increased carbon chain fluidity (Lelievre and Mitchell 1975). On cooling (Fig. 1), the spectra remained well resolved and, as described by Reuther et al (1983, 1984), polysaccharide chains at this point aggregated by means of cooperative interactions between the segments of several molecules (called "junction zones").

The observed ^{13}C NMR peaks seemed to be narrow and could lead to a conclusion that carbon T_2 increased during gelatinization. However, T_2 from the line widths was not calculated because

of the possibility of a dispersion of the chemical shifts that may result in a broader resonance, which could be misleading.

Starch-sucrose mixtures. The ^{13}C NMR spectra for mixtures of sucrose, starch, and D_2O showed a number of peaks corresponding to various carbon groups for both starch and sucrose. The typical spectra are shown in Figure 2 for the sample with 20% sucrose (starch basis). The ^{13}C NMR spectra were not well resolved because of the high solid content; thus, most peaks were not identified. However, the peak corresponding to the carbon-1 for starch (Fig. 2) seemed obvious compared with the spectrum for starch alone (Fig. 1). This peak was not observable at 25–55°C; it started to increase in intensity at 65°C and remained well resolved for the rest of the heating and cooling cycle. This indicates an increased starch chain mobility on gelatinization.

Starch-NaCl mixtures. The temperature dependency of ^{13}C NMR spectra for a mixture of starch, NaCl, and D_2O (40:0.4:60) is shown in Figure 3. Only five carbon peaks were observed, and the hidden carbon peak was speculated to overlap in the middle peak range. The overall spectra showed some interesting results. Compared with starch in D_2O (Fig. 1), the unheated starch at 25°C showed a poorly resolved ^{13}C NMR spectrum with a low signal-to-noise ratio, in contrast to the starch-NaCl mixture (Fig. 3, 25°C), which showed a very well resolved ^{13}C NMR spectrum. The increased signal intensity of the starch polymer in the presence of NaCl at room temperature appeared to be due to the amorphous portion of the starch polymer, since the crystalline starch should remain relatively rigid. On heating to 55 and 65°C, a significant increase in the signal intensity was observed; a further increase in temperature beyond the gelatinization temperature caused a significant decrease in the signal intensity (Fig. 3). Consequently, the ^{13}C NMR spectra showed some line broadening at this higher temperature range (above 65°C). This could be due to some chemical shift distribution and/or decreased mobility of the starch chain. We speculated that this was due to some possible interaction between the starch-OH groups and Na cations (Oosten 1982, 1983) that resulted in such modified ^{13}C spectra.

^{17}O Results

Starch alone. A representative ^{17}O spectrum (Fig. 4) indicates a single Lorentzian line shape. A slight asymmetry was observed in some heated samples, indicating possible interference of other ^{17}O nuclei in starch or sucrose molecules. The line widths of all spectra were used to calculate T_2 relaxation times in sec (Fig. 5) against temperature. The T_2 relaxation time was originally high (approximately 3×10^{-3} sec) and, as expected, increased slightly as the temperature increased. When the temperature of the sample rose from 55 to 65°C, however, T_2 decreased drastically (increased in line width), indicating a reduction in D_2O mobility. When the sample was heated further, to 95°C, the ^{17}O NMR data again showed a slight increase in T_2 (Fig. 5). On cooling, the T_2 gradually decreased with temperature, resulting in a final T_2 of approximately 1×10^{-3} sec. The overall reduction in T_2 from the whole process was about two thirds (from about 3×10^{-3} to 1×10^{-3} sec).

Two phenomena may be responsible for the lowering of the T_2: swelling of the amorphous starch and melting of the crystalline starch. On swelling and gelatinization, it is possible that the increased viscosity as a result of aggregation of the polymers could result in decreased water mobility. However, Mora-

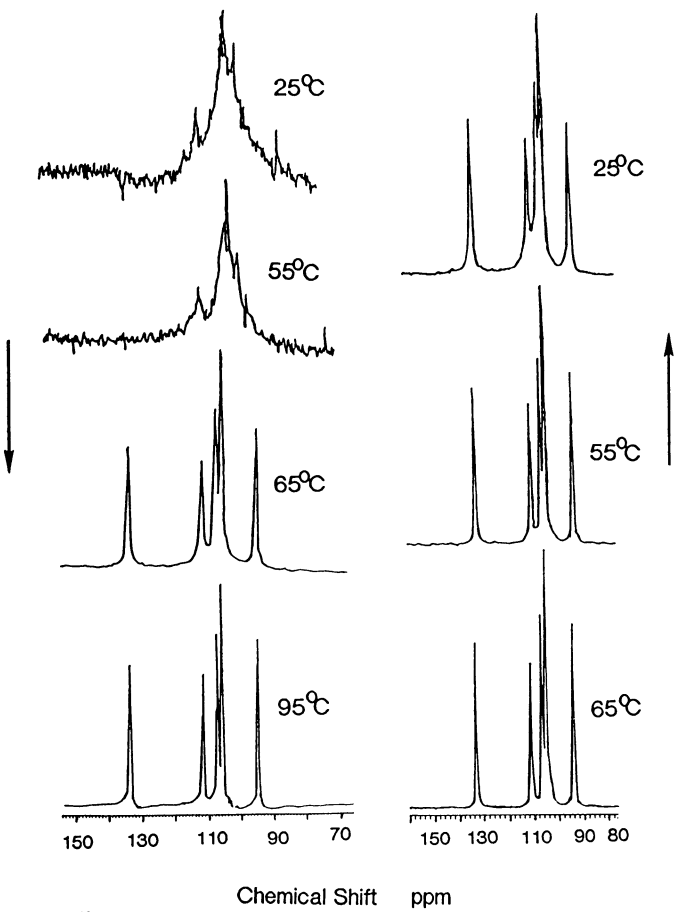

Fig. 1. ^{13}C nuclear magnetic resonance spectra for a mixture of starch and free water (40:60), obtained with proton decoupling, that was heated from 25 to 95°C and then cooled back to 25°C at the rate of 10°C/3 min.

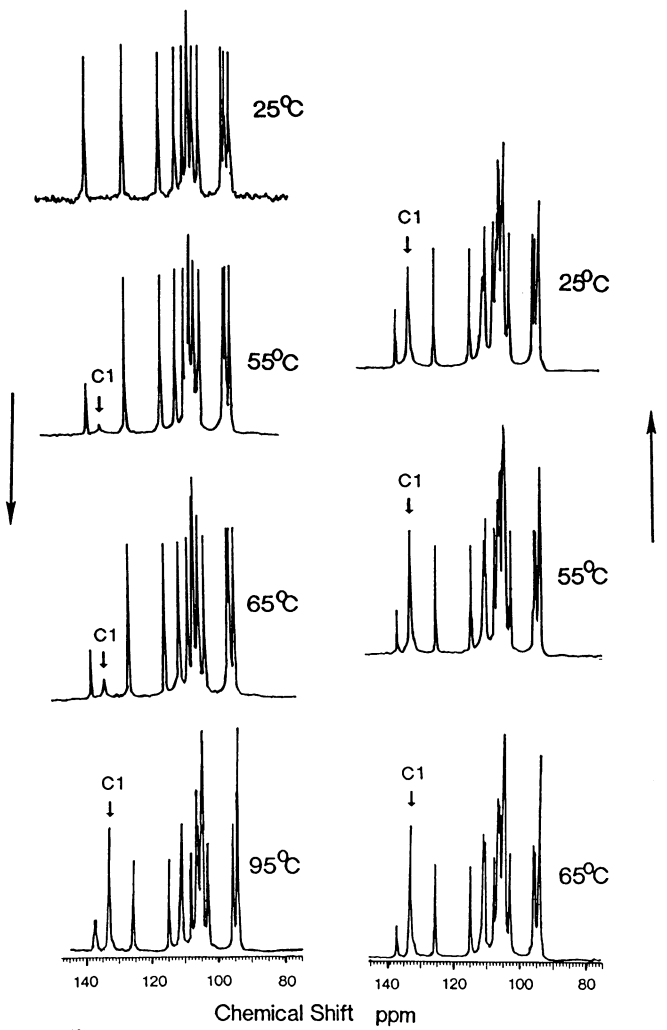

Fig. 2. ^{13}C nuclear magnetic resonance spectra for a mixture of wheat starch, sucrose, and free water (40:8:60) that was heated from 25 to 95°C and then cooled back to 25°C at the rate of 10°C/3 min. Peak with arrow corresponds with carbon-1 for starch.

Gutierrez and Baianu (1989) studied these phenomena in great detail and found no correlation between the increased viscosity and water mobility. Also, they suggested that water in the gel state of amylopectin could be "trapped" between hydrogen-bonded, structured domains.

As described by Levine and Slade (1989), a starch suspension is a nonhomogeneous system. Based on their description, our starch sample was in a granular form, containing only about 30% water (D_2O) hydration; the rest of the D_2O was bulk (100%) water floating on the outside. The two fractions of water (inside and outside of the starch granules) rapidly exchange between each other (Levine and Slade 1989); thus, no distinction in physical properties between the two is observed. This was supported by our result showing an ^{17}O NMR spectrum in a single Lorentzian pattern; T_2 represented an average value between T_2 of both fractions (based on the two-"sites," fast-exchange model). Since most of the water was bulk, and since bulk water has a much higher mobility than the water inside the granules, the measured T_2 for the original (unheated) sample was high. Once heated beyond its gelatinization temperature, the melting of the polymer resulted in a homogeneous matrix (no granular structure) with 60% water (D_2O). The decreased T_2 found at this point could result from an increased hydration of the starch polymers and/or the trapped water between the starch-structured domains (Mora-Gutierrez and Baianu 1989).

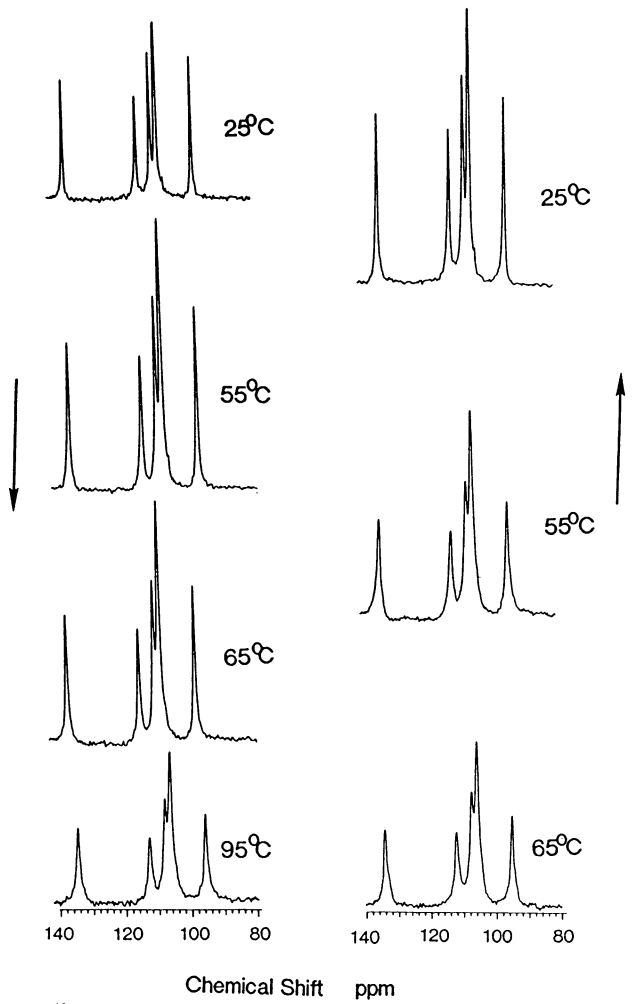

Fig. 3. ^{13}C nuclear magnetic resonance spectra for a mixture of wheat starch, NaCl, and free water (40:0.4:60) that was heated from 25 to 95°C and then cooled back to 25°C at the rate of 10°C/3 min. The chemical shift scale is expressed in arbitrary units.

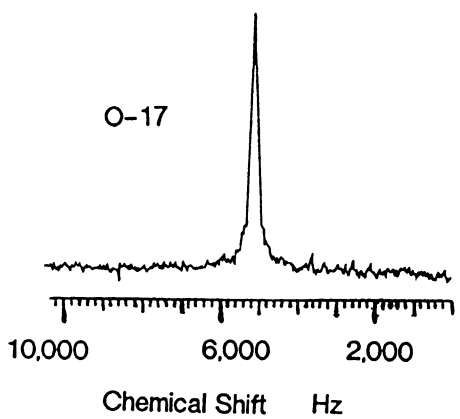

Fig. 4. ^{17}O nuclear magnetic resonance spectrum with proton decoupling for a mixture of starch and free water (40:60) obtained at 25°C.

The suggestion regarding the increased hydration of the starch was complemented by the fact that, on gelatinization, the number of starch-free OH groups that could interact with the D_2O by hydrogen bonding increased greatly. As a result of this increased water-starch interaction, there was more of the less mobile fraction, resulting in an overall decrease in T_2.

However, the calculated correlation time showed that the water presented was not immobile to the degree that it was bound. The correlation time (τ_{cb}) was calculated from the T_2 rate after cooling to 25°C, using the following equation (Richardson et al 1987, Lioutas et al 1986):

$$\frac{R_{2b}}{R_{2F}} \quad \frac{\tau_{cb}}{\tau_{cf}}$$

where R_{2b} is the (^{17}O NMR) relaxation rate for the bound fraction; R_{2f} is the (^{17}O NMR) relaxation rate for free water (D_2O), 195.8 sec^{-1} (Richardson, 1986); τ_{cb} is the correlation time for the bound fraction; τ_{cf} is the correlation time for the free fraction, 3.1 psec (Halle et al 1981) at 20°C.

If R_{2b} was equal to $1/T_2 = 1/1$ msec $= 1{,}000\ sec^{-1}$, the calculated τ_{cb} was 15.8 psec. Although this value was only a rough estimate (because the τ_{cf} used was that for 20°C), the value for τ_{cb} was only about five times higher than that of pure D_2O, too mobile to be considered bound water. This was in agreement with the ^{17}O τ_{cb} of 16.7–45.8 psec for water in wheat flour found by Richardson et al (1986), who reached a similar conclusion. Based on the investigation by Tait et al (1972), only a portion of the water was adsorbed onto the starch; the rest, which was not directly bonded to the starch polymer, was considerably modified. Mora-Gutierrez and Baianu (1989) suggested that this modified water was trapped water.

Comparison of ^{17}O and ^{1}H results. The reduction of T_2 on gelatinization that we observed agrees with the ^{1}H NMR results reported by Lelievre and Mitchell (1975). However, our ^{17}O NMR results did not agree with the ^{1}H NMR results obtained by Jaska

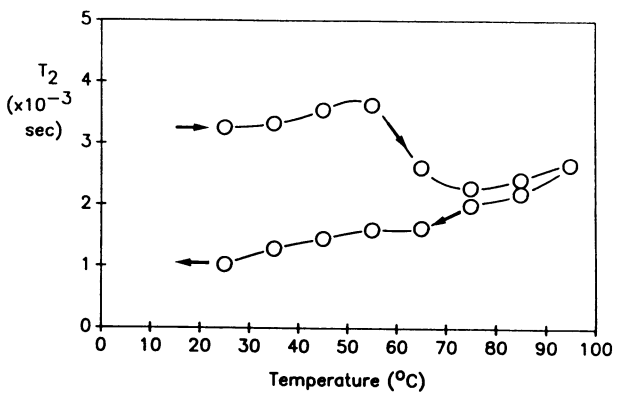

Fig. 5. Spin-spin relaxation times (T_2) for ^{17}O nuclear magnetic resonance spectra of free water in a mixture of starch and free water (40:60) (O) that was heated from 25 to 95°C and then cooled back to 25°C at the rate of 10°C/3 min.

(1971) from starch of same concentration. For comparison, we plotted the T_2 for ^{1}H NMR (Jaska 1971) and our ^{17}O NMR results (Fig. 6).

The proton T_2 was in a much higher range than that for ^{17}O NMR (Fig. 6). This was primarily due to the more efficient relaxation mechanism of ^{17}O nuclei. The trend in T_2 values for the ^{1}H NMR data in this case did not agree with the ^{17}O NMR data. That is, the ^{1}H T_2 gradually decreased as the temperature was raised from room temperature as opposed to the increased T_2 for the case of ^{17}O NMR. The decrease in ^{1}H T_2 could be due to a cross-relaxation process. In addition to the water relaxation mechanism, the ^{1}H nuclei also underwent a cross-relaxation process (Edzes and Samulski 1978, Koenig et al 1978, Shirley and Bryant 1982) between the water protons and starch, which could make a significant contribution to the proton relaxation rate. As a result, the overall T_2 for ^{1}H nuclei appeared lower because of the resulting line broadening from a cross-relaxation process. Thus, water (observed from ^{1}H NMR) might appear more bound than it actually was. Therefore, from the ^{1}H data, it could not be concluded that the water became more bound on heating. Evidently, our ^{17} NMR result showed the opposite.

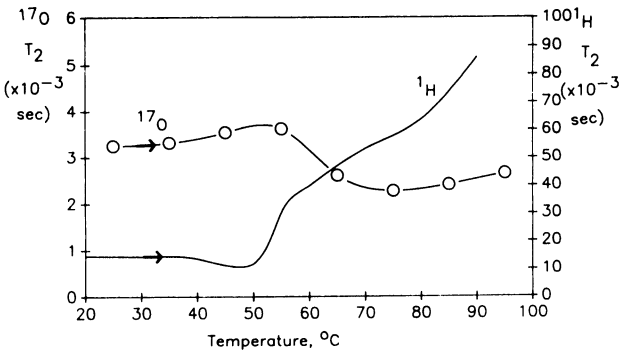

Fig. 6. Spin-spin relaxation times (T_2) obtained from ^{17}O nuclear magnetic resonance data for a mixture of wheat starch and D_2O (40:60) (this work,O), that was heated at the rate of 10°C/3 min, and those from ^{1}H nuclear magnetic resonance data for a mixture of potato starch and H_2O (40:60) (data calculated from Jaska 1971, solid line), heated at a rate of 10°C/5 min.

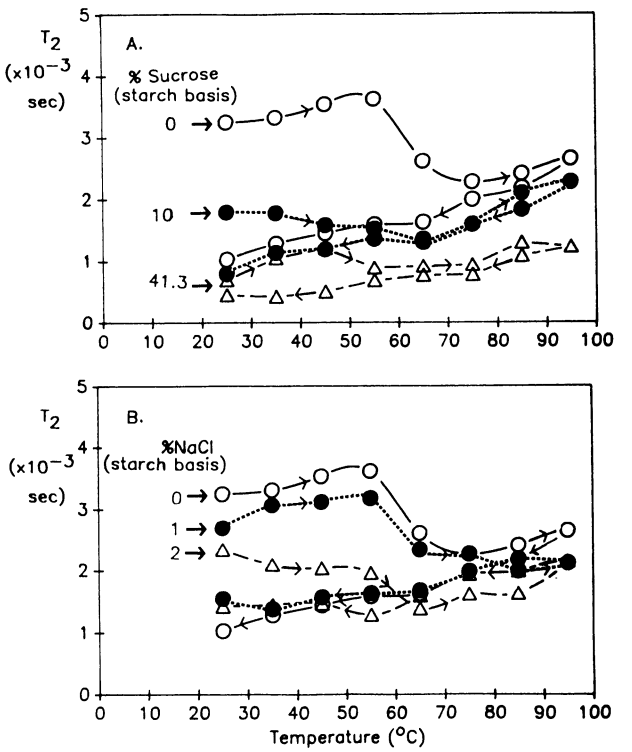

Fig. 7. Spin-spin relaxation times (T_2) for ^{17}O nuclear magnetic resonance spectra for starch in free water that was heated from 25 to 95°C and then cooled back to 25°C. **A,** mixtures of sucrose, starch, and free water (0, 10, and 41.3% sucrose, starch basis); **B,** mixtures of sodium, starch, and free water (0, 1, and 2% NaCl, starch basis).

At the gelatinization temperature range (50–65°C, Fig. 6), the ^{1}H T_2 increased significantly, whereas the ^{17}O T_2 decreased. The increase in ^{1}H T_2, despite the fact that water mobility decreased (as measured from the ^{17}O NMR result), probably occurred because 1) the cross-relaxation process became less significant, 2) the increased starch chain mobility resulted in increased proton mobility, and/or 3) the chemical exchange of the proton became more significant. Therefore, the ^{1}H NMR results could not be interpreted in terms of water mobility alone. Comparing ^{1}H and ^{17}O NMR results helped clarify the relaxation process of each component.

Starch-sucrose mixtures. Figure 7A shows plots of the ^{17}O NMR T_2 relaxation time against temperature for mixtures of sucrose, starch, and D_2O (0:40:60, 4:40:60, and 16.5:40:60). The initial T_2 decreased significantly because of the added crystalline sucrose that dissolved, which decreased D_2O mobility. Also, sucrose-starch interaction might affect water mobility (Chinachoti and Steinberg 1984, Hansen et al 1989). On gelatinization at 50–70°C (Fig. 7A), T_2 in the sucrose-added samples decreased but did so more gradually and to a smaller extent than did the control. It is surprising that the reduction in T_2 started at a lower temperature, whereas the gelatinization temperature of starch in presence of sucrose has occurred at a higher temperature range; this is also supported by the DSC data, which indicate a higher T_p for sucrose samples (Table I). However, the heating rates for NMR experiments in Figure 7A were different from those for the DSC experiment in Table I; thus, the comparison can only be qualitative.

If the early decrease in ^{17}O T_2 of the sucrose samples occurred before the gelatinization temperature of the starch, as described above, then any changes resulting in the decreased T_2 had to be related to sucrose, amorphous starch, and D_2O. A number of points must be considered. First, Duckworth (1981) suggested that water in starch granules acts as a solvent for alcohol and that a sugar molecule can dissolve in such water. If this were the case, heating such a solution should result in increased water mobility (T_2). We found that T_2 decreased with temperature, however (Fig. 7A).

Second, a sugar molecule can interact with the surface of the sorbent (starch) and not dissolve in water in the vicinity, according to the steric exclusion model (Walstra 1973). Since it is not known how this relates to solubilization of sugar and the hydration behavior of sugar-starch-water systems (Duckworth 1981), no conclusion could be made in relation to the ^{17}O NMR results reported here.

The third point to consider has to do with interpretation of the ^{17}O NMR data. A recent ^{17}O NMR study of a similar system (Chinachoti and Stengle 1990) found a significant portion of water in starch exchanging so slowly with the liquid water that the

TABLE I
Results of Differential Scanning Calorimetry for the Endothermic Gelatinization of Wheat Starch in Free Water[a] in the Presence of Sucrose and Sodium Chloride

	Initial Temperature T_o (°C)	Peak Temperature T_p (°C)	Gelatinization Energy ($-\Delta H_G$ cal/g of starch)
Sucrose (%, starch basis)			
0	60.93 ± 0.33	66.15 ± 0.38	2.39 ± 0.07
10	63.01 ± 0.63	68.19 ± 0.73	2.47 ± 0.06
41.3	67.48 ± 0.14	72.88 ± 0.18	2.62 ± 0.06
Sodium (%, starch basis)			
0	60.93 ± 0.33	66.15 ± 0.38	2.39 ± 0.07
1	64.82 ± 0.21	70.45 ± 0.25	2.66 ± 0.24
2	65.96 ± 0.03	71.73 ± 0.10	2.80 ± 0.11

[a]Ratio of wheat starch to free water = 40:60, $-\Delta H_G$ = endothermic energy.

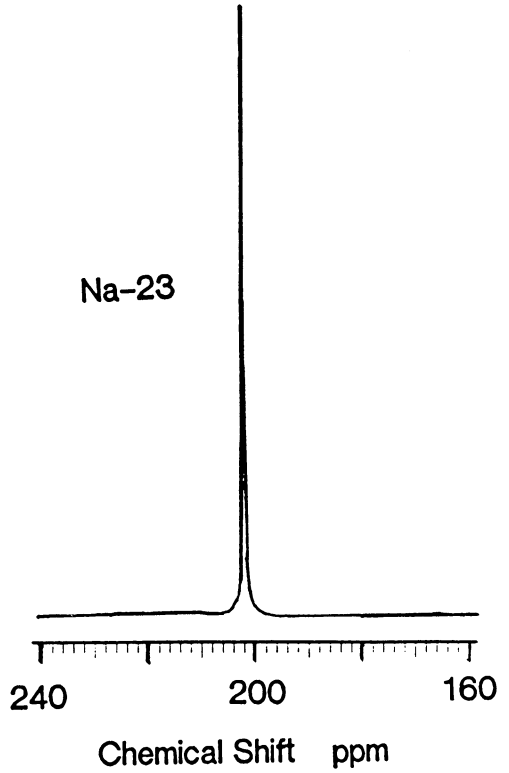

Fig. 8. ^{23}Na nuclear magnetic resonance spectrum obtained for a mixture of starch, NaCl, and free water (40:0.4:60).

NMR instrument could not detect it. This water was described as having much lower mobility. Thus, heating a starch sample could result in an increased exchange rate; therefore, T_2 for the ^{17}O NMR data should decrease. Our samples could have had some nonexchanging D_2O that was not detected at 25°C, but as the starch swelled on heating, the exchanging of D_2O increased. We did not observe a decreased T_2 for the starch-D_2O mixture because the temperature effect predominated. For the sucrose-added samples, the temperature effect was less predominant because of the presence of sucrose. The sucrose could also enter the starch granules, bringing some liquid D_2O, which exchanged with D_2O associated with the starch. This effect causes a decrease in the average mobility of the D_2O observed in the NMR spectrum.

In the gelatinization temperature range, a less drastic drop occurred in T_2 in the presence of sucrose (Fig. 7A). This was not because less starch was gelatinized (in fact, the endothermic energy of gelatinization shown in Table I did not decrease with sucrose content), but rather because the initial T_2 was low when sucrose was present; thus, T_2 decreased less.

Starch-NaCl mixtures. In Fig. 7B, T_2 increased with temperature with 1% NaCl but decreased slightly with 2% NaCl. In the gelatinization temperature range, (peak temperature 70–72°C, Table I), T_2 decreased sharply for ^{17}O, indicating again a decreased water mobility. It was also interesting to note that, in this case, the plot of T_2 versus temperature showed a crossover or a loop in the temperature range above gelatinization.

^{23}Na Results

^{23}Na NMR spectra for mixtures of starch, NaCl, and D_2O showed a Lorentzian line shape (Fig. 8). The T_2 in Figure 9 decreased drastically above 65°C for samples of 1 and 2% NaCl. This temperature corresponded to the change in ^{13}C spectral intensity and line width shown in Figure 3, which seems to support the hypothesis for the Na-starch interaction reported by Oosten (1982, 1983). This interaction was proposed to occur as a result of an ionic interaction between the Na cations and the negatively charged hydroxyl groups on the starch, resulting in an increased Donnan potential and chloride anion exclusion (Oosten 1982).

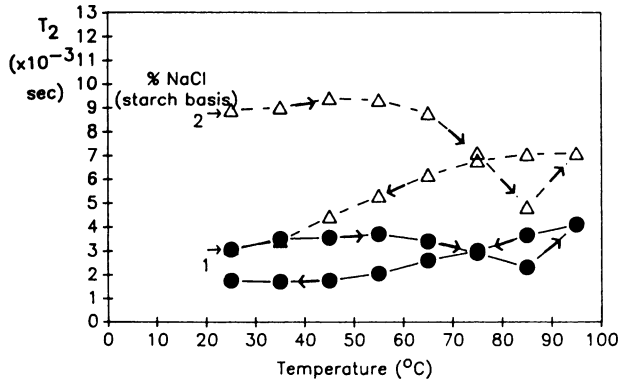

Fig. 9. Relaxation times (T_2) for ^{23}Na nuclear magnetic resonance spectra of sodium cations in mixtures of NaCl, starch, and free water (0, 1, and 2% NaCl, starch basis) that was heated from 25 to 95°C and then cooled back to 25°C.

CONCLUSION

Because the ^{17}O NMR data reported here were subject to little or no influence from chemical exchange and cross-relaxation, they provide much more detailed information about water mobility than do the data for ^{1}H and ^{2}H NMR. Our work also showed that selecting ^{17}O over ^{1}H NMR could result in a contrasting change in T_2. The use of ^{13}C, ^{17}O, and ^{23}Na multinuclear NMR was valuable in observing the effects of ingredients on starch gelatinization on a molecular level as a complement to DSC results.

In a solute-free system, the ^{17}O NMR data show that water mobility was originally high and drastically decreased on gelatinization because of the increasing fraction of trapped water. The line narrowing accompanied by increased intensity of the ^{13}C NMR indicates that the polymer chain increased.

In the presence of solutes, our DSC results agreed with previous reports that solutes increased the gelatinization temperature of the starch. The NMR data also showed that the presence of sucrose and NaCl reduced the mobility of D_2O as determined by the ^{17}O NMR. This could result in lower effectiveness of plasticization of the starch polymer by D_2O. On gelatinization, the ^{13}C spectra in the starch-D_2O and starch-sucrose-D_2O mixtures indicated some line narrowing (i.e., increased mobility) during gelatinization, whereas those in the starch-NaCl-D_2O mixtures showed line broadening (indicating some kind of interaction). The latter phenomenon was supported by the ^{23}Na results, which showed a decrease in sodium mobility on gelatinization.

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