^{17}O Nuclear Magnetic Resonance Studies on Wheat Starch-Sucrose-Water Interactions with Increasing Temperature[1]

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ABSTRACT

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Water mobility in wheat starch-sucrose-water dispersions was observed by measuring the transverse relaxation rate (R_2) from ^{17}O nuclear magnetic resonance spectra. Sucrose resulted in an increase in the R_2 or a decrease in the mobility of water and in temperature of the R_2 maximum as temperature was increased from 35 to 81°C. Starch increased the R_2 by decreasing the mobility of water in the sample systems. The results indicated that a sucrose-starch interaction also contributed to the decreased water mobility. The onset temperature of starch gelatinization, as determined by differential scanning calorimetry, appeared to occur shortly after the water reached its R_2 maximum.

Quality of food products is altered by the temperature at which starch gelatinizes in relation to other occurrences and ingredients within the product. During gelatinization of starch, many changes are influenced by the water. The importance of the amount of water to starch gelatinization in a starch-water dispersion has been reported by many researchers using differential scanning calorimetry (DSC) measurements (Collison and Chilton 1974, Donovan 1979, Biliaderis et al 1980, Eliasson 1980, Ghiasi et al 1982, Burt and Russell 1983).

Studying the dynamic condition, or states, of water with nuclear magnetic resonance (NMR) techniques enables understanding of the molecular changes in a system (Jaska 1971, Leung and Steinberg 1979, Leung et al 1979, Lechert et al 1980, Lechert 1981, Nagashima and Suzuki 1981, Lang and Steinberg 1983, Wynne-Jones and Blanshard 1986, Richardson et al 1987b–d, Fanni et al 1989). NMR techniques have been developed to observe molecular mobilities in a variety of food systems, such as instant starch gel, protein, sucrose solution, wheat doughs, breads, and vegetables (Leung et al 1979, 1983; Lechert et al 1980; Halle et al 1981; Lang and Steinberg 1983; Richardson et al 1987c; Richardson 1988). The use of ^{17}O NMR has been shown to be the most effective NMR method for the observation of water mobility (Halle et al 1981; Richardson et al 1986, 1987a–c).

Most NMR studies of starch systems involved heating the system to a defined temperature and investigating the changes associated with heating (Lechert 1981, Richardson et al 1986). New NMR techniques had to be developed to study dynamic changes in wheat starch-sugar-water systems as the heating occurred (Hansen et al 1987, 1989). The temperature range studied corresponded to that used in thermal processing of a food product, and the experiments were designed to elucidate the mechanism(s) operative in the gelatinization of starch in the presence of sucrose.

When sucrose is added to a starch-water dispersion, gelatinization of starch is retarded. Onset temperature of starch gelatinization is increased as sucrose concentration increases. Several mechanisms have been suggested for that phenomenon (Bean et al 1978, Evans and Haisman 1982, Spies and Hoseney 1982, Lelievre 1984). Starch-water interactions, sucrose-water interactions, starch-water-sucrose interactions, or all of these interactions probably are involved in the suggested mechanisms. Therefore, observations of the changes in water mobility as the temperature is increased might give us a better understanding of the starch gelatinization process in terms of water interactions with starch and/or sucrose. The objectives of this study were 1) to observe the mobility or binding of water in wheat starch-sucrose-water systems by measuring the transverse relaxation rate (R_2) from ^{17}O NMR measurements with increasing temperatures of 35–87°C (308–360 K); 2) to study sucrose-water, starch-water, and sucrose-starch-water interactions in the wheat starch-water-sucrose dispersions; and 3) to compare ^{17}O NMR observations with DSC measurements of thermal transitions of the starch-water-sucrose dispersions as temperature was increased.

MATERIALS AND METHODS

Sample Preparation

Wheat starch (Aytex, Olgivie Mills, Minnetonka, MN) was used for all investigations. Reagent-grade sucrose (Fisher Scientific, Fair Lawn, NJ) was used for sucrose-starch systems. Reverse osmosis distilled water with 0.5% enriched ^{17}O water (H$_2$^{17}O; Isotec, Miamisburg, OH) was mixed with 0.15% xanthan gum (Ketrol T, Kelco, San Diego, CA) to make a solution that was used to disperse the starch and prevent sedimentation (Hansen et al 1987). Sucrose solutions of 0.5, 1.0, and 1.5M concentrations were prepared using the enriched water-xanthan gum solution as the solvent. The 10, 20, and 30% (weight basis) starch suspensions were prepared with each pre-prepared sucrose dispersion. The pH ranged between 5.4 and 6.3 for all dispersions. All dispersions were made and stored at 4 ± 1°C overnight and allowed to equilibrate at room temperature (22 ± 2°C) just before making the NMR spectroscopic measurements. For the DSC measurements, each concentration of sucrose solution was injected into the DSC pan containing the starch at 10, 20, or 30% levels (weight basis). The DSC pan was sealed hermetically.

NMR Measurements

A Bruker WM-400 NMR spectrometer (Bruker Instruments, Billerica, MA) was used for the ^{17}O NMR spectra. Samples were injected into a 10-mm (inside diameter) NMR sample tube. Data for enriched H$_2$^{17}O solutions were acquired with the following conditions: a spectrometer frequency of 54.234 MHz, a sweep width of 5,000 Hz, a 90° pulse width of 27.0-μsec 4 K data points, broad band proton (^{1}H) decoupling, and a 205-msec acquisition time with no delay. The ^{1}H decoupling helps to decrease or eliminate proton exchange broadening in the neutral pH ranges (Richardson 1989). Under those conditions, adequate signal to noise was achieved in 128 pulses. Running temperature was 35–87°C (308–360 K), and samples were held 5 min at each 2 K temperature interval before data were acquired. Line shapes were evaluated in terms of fit of least squares of the peaks to a Lorentzian equation after the application of a 10-Hz line broadening. Line widths ($\Delta\nu_{obs}$) were half-height values for the water peak at each temperature. The transverse relaxation rate (R_2; sec^{-1}) was calculated according to Richardson et al (1987b):

$$R_2 \ (\text{sec}^{-1}) = \pi \ (\Delta\nu_{obs}) = 1/T_2$$

The R_2 was determined for each spectrum using the fit of the peak to a Lorentzian line shape, which was confirmed by direct measurements from the plot.

Two primary assumptions were made for the ^{17}O NMR measurements in this study. 1) Line width is the same as T_2.

This is not always true, but the assumption is convenient for small molecules such as water. 2) Only one type of ^{17}O is present; that nucleus was measured.

DSC Measurements

A Perkin-Elmer DSC-4 (Perkin-Elmer, Norwalk, CT) with a FTS Systems Flexi-cooler temperature controller (Stone Ridge, NY) was used for the determination of thermal properties of all sample systems. A sensitivity of 0.5 mcal/sec, a heating rate of 2.5°C/min, and a chart speed of 5 mm/min were used. Samples were heated from 10 to 130°C. An empty pan was used as the reference. Enthalpies (ΔH) of the phase transitions were determined from the areas of the endotherms and were expressed as calories per gram of dry starch. For each wheat starch-sucrose-water system, the mean and standard deviations of least three determinations were obtained.

RESULTS AND DISCUSSION

Comparisons of R_2 at Various Starch Concentrations

In the ^{17}O NMR measurements, R_2 directly monitors water mobility. Therefore, a change of water mobility is detectable based on the extent of hydrogen bonding or interaction with other molecules. As the amount of water associated with the starch changes and the temperature increases, a changing R_2 value is observed. The R_2 changes of 10, 20, 30, and 60% starch-water dispersions with increasing temperature are shown in Figure 1. Results observed for the 30% starch system indicate that R_2 increased from approximately 49°C (322 K) to a maximum value at 53°C (326 K), and then it gradually decreased as temperature increased. After the R_2 maximum (the point of minimum water mobility), the gradual decrease of R_2 indicated a smaller and less rapid increase in water mobility. In a previous study, increasing R_2 in NMR measurements corresponded with the loss of birefringence or swelling of starch granules (Jaska 1971). Starch gelatinization is a continuous process involving the melting of crystallites and the swelling of granules in the presence of water as the temperature is increased. When a starch-water dispersion is stored overnight after preparation, the starch granules will absorb the available water from the system and swell to some extent. As starch granules swell, water is entrapped in the amorphous phase of the starch granule and immobilized. This swelling stage might be reversible (Jaska 1971; C. C. Maningat and P. A. Seib, *unpublished data*). As temperature increases, the granules of starch in the dispersion continuously swell and begin to lose their crystallinity. At the point of R_2 maximum, the water was probably fully entrapped inside the starch granule and had the least mobility in the dispersion. After maximum swelling, water mobility gradually increased as temperature increased. Solubilization of starch granules could cause increased water mobility after maximum swelling (French 1984). Therefore, the increases in water mobility within the granule that were observed after the R_2 maximum probably were caused by an increased mobility of the macromolecules in the system, as Jaska (1971) suggested.

On the other hand, Bean and Yamazaki (1978) noted that the diameter of the starch granules, observed by hot-stage microscopy, correspondingly increased with viscosity as measured by the amylograph between 58 and 70°C. Thus, the increased viscosity that occurred during the swelling of the granules (C. C. Maningat and P. A. Seib, *unpublished data*) possibly contributed to the decreased water mobility observed. Logically, a higher viscosity with increasing starch concentrations would imply a lower water mobility in the system. The dotted line in Figure 1 depicts a water-only (free water) system. The R_2 in the free water and in the 10% starch dispersion were similar. The 10% starch system had less water associated with starch compared with other systems. Therefore, the higher water mobility indicated that more free water was available in the system over the entire temperature range.

A small fraction of water molecules hydrogen-bonded to macromolecules can increase the R_2 (Fung 1977). Generally, water binds to the macromolecules more at higher macromolecule concentrations. Therefore, the 60% starch system probably had more water associated with starch than the other three systems.

Samples were heated to 87°C (360 K) to be certain that all, even the highly concentrated systems (e.g., 30% starch dispersion), were gelatinized completely. The occurrences above 79°C (352 K) were not typical of expectations at high temperatures. However, air bubbles or broken gels were found in most samples after the measurements had been completed. Possibly oxygen was being measured from bubbles that were artifacts of heating.

Comparisons of R_2 at Various Sucrose Concentrations

Figure 2 contains comparisons of R_2 for water at various sucrose concentrations. The overall R_2 gradually increased as the concentration of the sucrose-water solution increased and decreased as temperature increased. In previous work, the NMR lines were broadened by viscosity effects at higher concentrations in sugar solutions and thus decreased the water mobility (Tait et al 1972, Allen and Wood 1974). Generally, molecular motion is faster at higher temperatures. Tait and co-workers (1972) reported that the R_2 from a single spin-echo measurement increased with glucose concentration and showed a linear relationship with η/kT that followed the extended Debye equation ($\tau_r = 4\pi a^3 \eta/kT$). Although they observed a linear relationship over a wide temperature range (2–63°C) for $2.8M$ glucose-water solution, R_2 had an inverse relationship with temperature for sucrose-water solutions in this study (Fig. 2). According to the extended Debye equation, R_2 relates to viscosity proportionally and to temperature inversely.
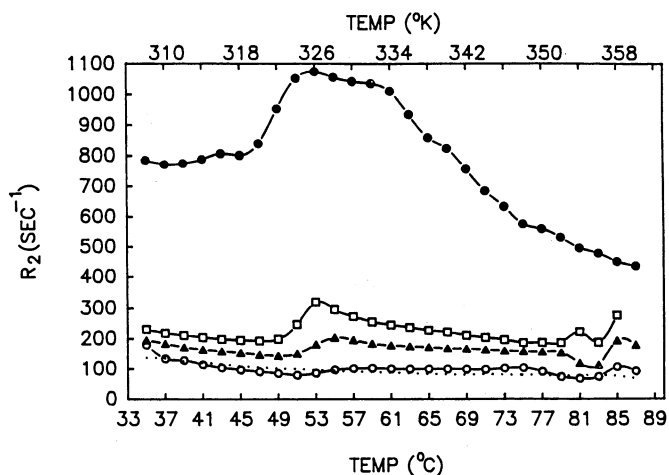

Fig. 1. Transverse relaxation rates (R_2) of starch-water dispersions as a function of increasing temperature. O, ▲, □, and ● = 10, 20, 30, and 60% starch concentrations, respectively.
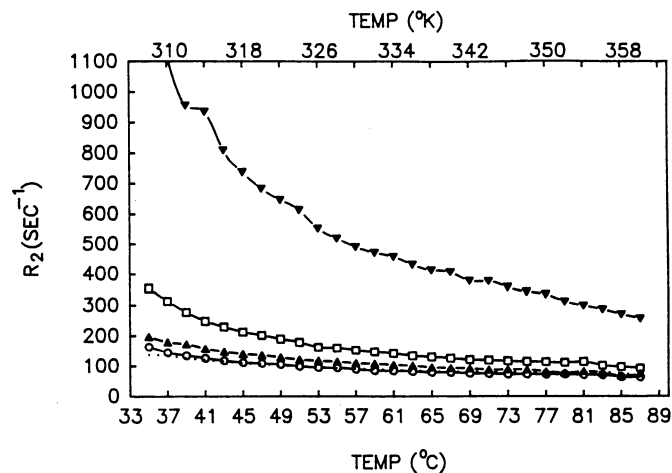

Fig. 2. Transverse relaxation rates (R_2) of sucrose-water dispersions as a function of increasing temperature. O, ▲, □, and ▼ = 0.5, 1.0, 1.5, and saturated sucrose concentrations, respectively.

In measurements of viscosities of sucrose solutions over a temperature range of 5–80°C, Mathlouthi and Kasprzyk (1984) found that intrinsic viscosity demonstrated an inverse relationship with temperature at concentrations of 30–86%.

Furthermore, Suggett et al (1976) suggested that a small fraction of the solvent has a reduced mobility as a result of its interaction with the solute. Actually, the fraction of solvent (hydration water) is decreased as solute concentration is increased. Therefore, the ^{17}O R_2 would be expected to be higher with increasing solute (sucrose) concentrations until the saturated sucrose concentration was reached.

According to Richardson et al (1987a), sucrose solutions at 20°C in concentrations ranging from 5 to 40% (0.5 and 1.0M sucrose systems) showed linear relationships between R_2 and the concentration that was related to the proportion of water more associated with sucrose (solute water) compared with water less associated with sucrose (free water). They assumed nonlinearity in the region from 40 to 60% resulting from formation of inter-

molecular hydrogen bonds between water and sucrose, hydrogen bond-bridging of water and sucrose molecules, and sucrose-sucrose hydrogen bonding. On the other hand, the fact that dissolved sugars enhance the degree of hydrogen bonding in aqueous solutions supports the concept that the sucrose-water interaction is stronger than either the sucrose-sucrose or the water-water interaction (Allen and Wood 1974). Therefore, even though the attraction between sucrose and water increases in the temperature range of 0–25°C (Garrod and Herrington 1970), water mobility could be reduced with viscosity increases as sucrose concentration is increased via sucrose-water interactions and/or other possible interactions, as noted in this study. Thus, the overall tendency of water mobility to increase at the high temperature in each system possibly was caused by the decreasing viscosity of the systems that allowed faster molecular motion.

Wheat Starch-Sucrose-Water Dispersions

Effect of increasing sucrose concentrations. The changes in R_2 with various sucrose concentrations as a function of temperature at 10, 20, and 30% starch concentrations are shown in Figure 3. The overall tendency of R_2 to increase with temperature is similar for 10, 20, and 30% starch concentrations. However, if sucrose was added and the concentration was increased from 0.5 to 1.5M at the same starch concentration, R_2 and the temperature at which the R_2 maximum occurred gradually increased.

Water mobility can decrease with increasing viscosity of the sucrose concentrations through the sucrose (solute)-water interaction as illustrated in Figure 2. The temperature differences for the R_2 maxima among samples at the same starch concentration depended on the sucrose concentration. For example, at the 30% starch concentration (Fig. 3C), the temperatures of R_2 maxima were about 53, 57, 63, and 71°C for starch-water and 0.5, 1.0, and 1.5M sucrose concentrations, respectively.

This result corresponds with the increased onset temperature of gelatinization in the presence of increased sucrose concentrations noted with DSC measurements (Table I). The temperatures observed for R_2 maxima are about 5°C lower than the DSC onset temperatures of gelatinization. These results agreed with Hansen et al (1989). With ^{13}C NMR measurements, they observed major deviations of the chemical shift of sucrose before onset temperature of gelatinization. Changes in chemical shifts of sucrose between sucrose solution and sucrose-starch dispersions were speculated to be an interaction between the sucrose and the starch rather than conformational changes in the sucrose molecules. Sobczynska et al (1990) presumed that sucrose directly interacted with the glucose residues of the starch to increase rigidity before the onset temperature of gelatinization, creating a need for more energy to break the starch-sucrose-water bonds. Thus, the increase in onset temperature of gelatinization observed by DSC measurements (Table I) and the increased temperature for the point of R_2 maxima (Fig. 3) as sucrose concentration
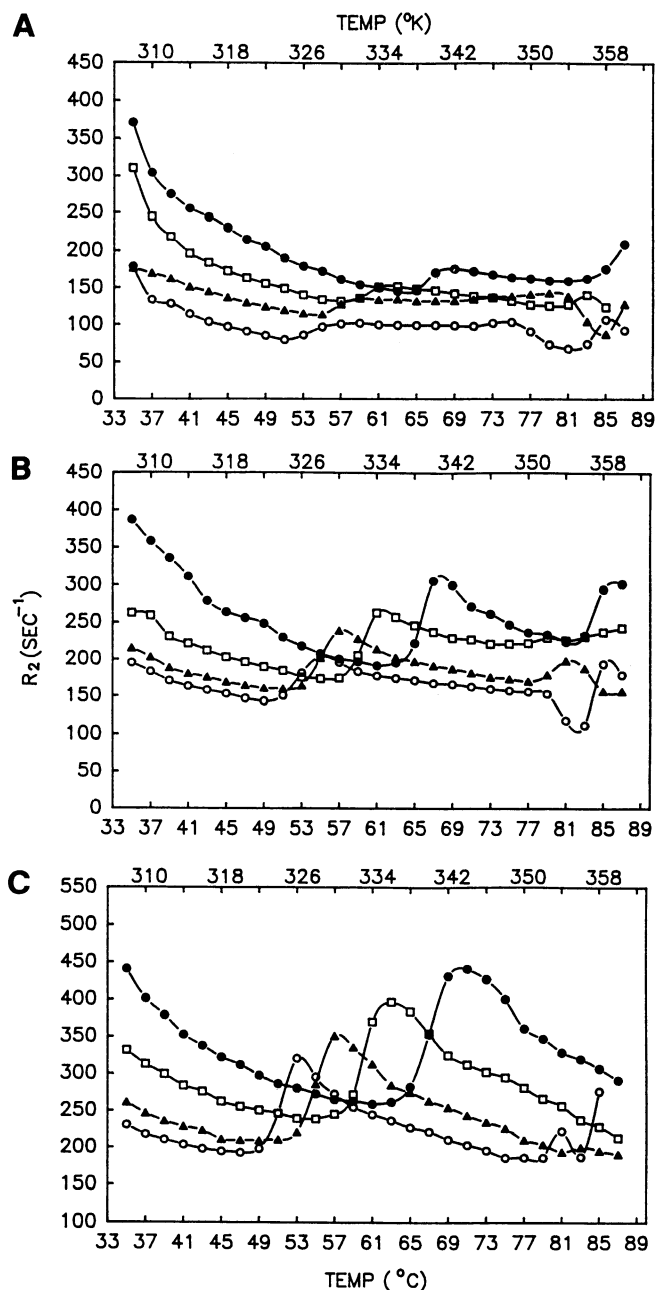

Fig. 3. Transverse relaxation rates (R_2) of 10% (A), 20% (B), and 30% (C) starch-sucrose-water dispersions as a function of increasing temperature. O = No sucrose. ▲, □, and ● = 0.5, 1.0, and 1.5M sucrose concentrations, respectively.

TABLE I
Comparison of Mean[a] Onset Temperatures, Peak Temperatures, and Enthalpies (ΔH) for Various Concentrations of Starch-Sucrose-Water Dispersions

Dispersion[b]	Onset Temperature (°C)	Peak Temperature (°C)	ΔH (cal/g)
10%, 0.0M	55.1	59.2	0.3518
0.5M	60.9 ± 0.56	65.3 ± 0.27	0.1068 ± 0.01
1.0M	67.9 ± 1.40	72.6 ± 0.90	0.1003 ± 0.04
1.5M	76.8 ± 0.37	81.6 ± 0.65	0.1240 ± 0.01
20%, 0.5M	61.3 ± 0.85	65.6 ± 0.32	0.2111 ± 0.01
1.0M	68.3 ± 0.92	72.6 ± 0.40	0.2063 ± 0.03
1.5M	75.9 ± 0.66	80.6 ± 0.66	0.2262 ± 0.02
30%, 0.0M	55.5	60.5	0.5811
0.5M	61.6 ± 1.22	66.0 ± 0.80	0.2943 ± 0.06
1.0M	69.1 ± 0.68	73.4 ± 0.52	0.3100 ± 0.02
1.5M	77.5 ± 0.34	82.0 ± 0.51	0.3099 ± 0.02

[a] Mean of least three measurements.
[b] Amount of starch (%) to sucrose (M).

of the system increased may be explained by this sucrose-water interaction. Two possible mechanisms for the increased energy requirement also were suggested earlier by Spies and Hoseney (1982): 1) Sucrose-starch interactions are the result of sugar molecules bonding with starch in the amorphous region to form a bridge between the chains. Bridges would restrict the flexibility of the chains and delay the gelatinization temperature by requiring more energy to strip the newly created crystallites. 2) When sugar or any small solute is added to water, sucrose-water interactions are indicated by a decreased water activity of the system in the presence of the hydrophilic sucrose molecules. Thus, the ability of water to interact with other components in the system decreases, resulting in higher energy requirements.

Effect of increasing starch concentrations. The change of R_2 with 10, 20, and 30% starch concentrations without sucrose and at the 0.5, 1.0, and 1.5M sucrose concentrations are illustrated in Figure 4. An increase in the proportion of starch relative to the amount of sucrose present in the system resulted in increased R_2 values. The overall water mobility changes with the various starch concentrations at the same sucrose concentration occurred within a relatively narrow temperature range, however. The swelling of starch granules causes large changes in water mobility via a starch-water interaction or changing of viscosity with temperature (Fig. 1). The R_2 differences observed in Figure 4 appear to reflect the differences of starch concentrations rather than of sucrose concentrations. The greater starch (polymer)-water interaction probably resulted in a higher R_2. These results agree with Chinachoti et al (1991), who considered that gelatinization resulted in an increased fraction of trapped water with increased polymer chain lengths. In this study, both the R_2 level and the temperature of the R_2 maximum increased as sucrose concentrations increased at the same starch concentration, and apparently starch and sucrose both were responsible for the decreasing water mobility. Sucrose was responsible for increasing the temperature at which the R_2 maximum (minimum mobility) occurred in comparison with the starch-water system.

All results (Figs. 3 and 4) imply that a wheat starch-sucrose interaction or a starch-sucrose-water interaction influenced the change in water mobility. The starch-water interaction increased the R_2 (Fig. 1), and an increased R_2 also was observed with the sucrose-water interaction via viscosity (Fig. 2). The high starch and sucrose concentrations both resulted in the high R_2 values (Figs. 3 and 4), indicating a lower free water and higher R_2 via both starch polymer and solute effects. Generally, the higher R_2 indicated a greater starch-water or solute-water interaction. This agrees again with the results of Suggett et al (1976), Richardson et al (1987a-c) and electron spin resonance measurements of Johnson et al (1990).

If we consider starch as a partially crystalline, glassy polymer (Biliaderis et al 1980, Maurice et al 1985), water acts as a plasticizer for starch, which depresses the glass transition temperature of the amorphous regions and permits mobility of chains for the crystallites to melt. However, when solutes such as a sucrose are added to the system, the overall water mobility decreases, the water has less plasticizing ability, and the swelling of starch granules can be restrained. Consequently, the gelatinization temperature is increased and enthalpy is decreased (Table I) (Chungcharoen and Lund 1987). Water uptake by the systems is controlled by the chemical potential of water. We assumed that the measurements were made after an equilibrium of the chemical potential of water had been reached. In the starch-sucrose-water dispersions, Sobczynska et al (1990) hypothesized that the sucrose of the solution interacts with starch granules just before starch-water interactions. A lowered chemical potential of water in the sucrose solutions precludes the same extent of granule swelling that occurs in the absence of sucrose (Lelievre 1984, Sobczynska et al 1990). Presumably, sucrose-water interactions or sucrose-starch interactions lowered the chemical potential of water by decreasing water activity (the available water) or by forming bridges between starch chains before starch-water interaction occurred (Spies and Hoseney 1982). Therefore, the starch-water, sucrose-water, sucrose-starch, and starch-sucrose-

water interactions observed in this study all appear to agree with previous results.

The following conclusions seem likely: 1) wheat starch and sucrose both increase the R_2 or decrease the mobility of water
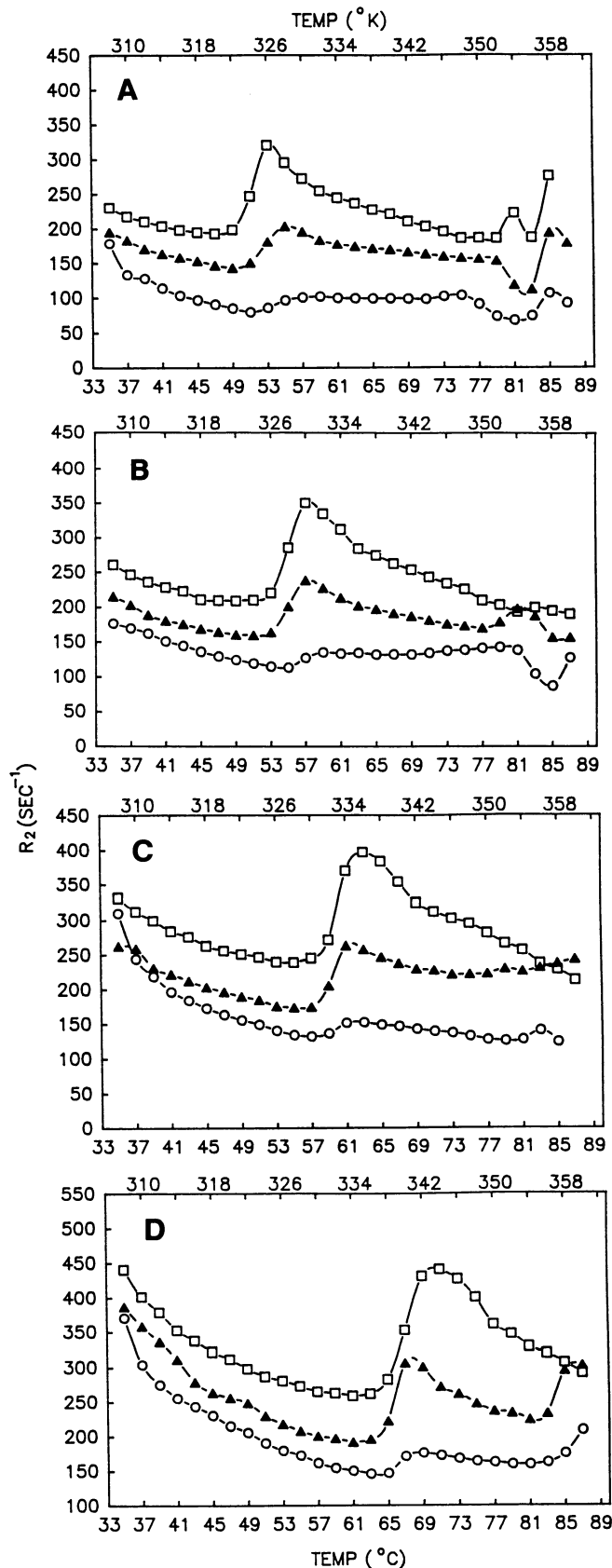

Fig. 4. Transverse relaxation rates (R_2) of starch-water (**A**), starch-0.5M sucrose-water (**B**), starch-1.0M sucrose-water (**C**), and starch-1.5M sucrose-water (**D**) dispersions as a function of increasing temperature. ○, ▲, and □ = 10, 20, and 30% starch concentrations, respectively.

through interactions with water; 2) wheat starch concentrations seem to increase the overall R_2 values; 3) sucrose concentrations seem to increase the temperature at which the R_2 maximum is reached; and 4) the melting of starch or the onset temperature of starch gelatinization as determined by DSC appears to occur after the water reaches its R_2 maximum.

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