

# Interactions of Starch and Sugar Water Measured by Electron Spin Resonance and Differential Scanning Calorimetry<sup>1</sup>

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## ABSTRACT

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Electron spin resonance (ESR) was used to evaluate the mobility of water in starch-water mixtures (12–50% H<sub>2</sub>O); ESR and differential scanning calorimetry (DSC) were used to study the effect of different sugars on starch-water interactions. TEMPO, a non-hydrogen-bonding hydrophilic probe, was used as the ESR reporter molecule for solution mobility. DSC was used to determine differences in onset temperatures for the starch thermal transitions. Both sugar type and concentration influenced the temperature range over which the events of starch transformations occurred. An increase in ESR correlation time for TEMPO, indicating less mobility in the aqueous phase, generally occurred when the amount

of water was reduced or after heat treatment of starch-sugar-water mixtures. The sugars progressively raised the temperature of starch gelatinization measured by DSC with increasing concentration. ESR results showed differences between the effect of different sugars in the heat treatment temperatures required to increase correlation time. These differences corresponded to differences noted for onset temperature of starch transitions as seen by DSC when different sugars at equal concentration were evaluated. The order of effectiveness of sugars in increasing DSC onset temperatures, as well as increasing ESR correlation time, was fructose, glucose, maltose, and then sucrose.

Sugars have been shown by many different methods to increase the onset temperature where certain events related to starch transitions take place. These methods include microscopic methods such as loss of birefringence and granular swelling, calorimetric methods such as differential scanning calorimetry (DSC), iodine uptake, viscometric techniques, and sedimentation techniques such as swelling power.

A complex sequence of events accompanies thermal starch transitions as defined by Atwell et al (1988). Some methods used to study starch transformations are best described as gelatinization and others as pasting. When comparing methods, it is important to specify any differences in time, temperature, water content, and presence or type of mechanical agitation. Similarities between methods used to characterize these events must be evaluated in relation to what level of starch organization is disrupted (Davis and Gordon 1984).

DSC has become the method of choice to study starch gelatinization (Atwell et al 1988) although others also use the term pasting when discussing measurements made by DSC (Slade and Levine 1988).

Many authors have used DSC to show that sucrose increases the temperature of starch thermal transitions (Donovan 1977, Ghiassi et al 1982, Evans and Haisman 1982, Chungcharoen and Lund 1987). On the other hand, Wootton and Bamunuarachchi (1980) could not detect increased onset temperature for starch transformations in aqueous solutions containing up to 45% sucrose.

More recently, electron spin resonance (ESR) has been used with non-hydrogen-bonding nitroxide spin probes to study starch transformations by measuring changes in the mobility of the probe in the starch-water environment (Pearce et al 1985, 1987; Windle 1985; Nolan et al 1986; Biliaderis and Vaughan 1987). This ESR method has not previously been used to characterize starch systems at low water concentrations down to 11% (wb) or to characterize contributions due to the presence of different sugars on starch transitions.

Individual sugars consistently differ in the degree to which they affect both starch gelatinization and pasting temperatures in cakes and model systems. Most studies are in agreement that the order in which these sugars increase gelatinization or pasting tempera-

ture is fructose, glucose, maltose, then sucrose (Bean and Osman 1959, Miller and Trimbo 1965, Bean et al 1978, Savage and Osman 1978, Koepsel and Hosoney 1980, Spies and Hosoney 1982, Buck and Walker 1988).

The first part of this study investigated the effect of differing amounts of water (12–50% water) in corn starch-water systems on the mobility of the water-soluble probe TEMPO (as an index to overall water mobility) as measured by ESR. The second part of this study investigated the effect of different sugars on regular corn starch-sugar-water systems by ESR, to further evaluate aqueous phase mobility with TEMPO, and DSC, to evaluate onset temperatures of the starch thermal transition.

## MATERIALS AND METHODS

### Starch and Sugars

The starch used was regular corn starch (Melojel, National Starch and Chemical Corp.). Sucrose, glucose, fructose, and maltose were all reagent grade (Aldrich Chemical Company).

### Spin Probe

The nitroxide spin probe TEMPO was obtained from Aldrich Chemical Co. The probe was used as received and prepared for use in a water-TEMPO solution having a probe/water weight ratio of 1:1,000 as described by Pearce et al (1985). The solution was magnetically stirred for 24 hr before use.

### Preparation of Starch-Water-Probe Samples

Samples were prepared by adding cornstarch (11% moisture, wb) to a water-TEMPO solution to give a starch/water weight ratio of 1:2 (70.3% water). The samples were then slurried 24 hr at room temperature in small tightly covered containers.

Starch suspensions were dried back to 12–50% water contents by evaporation at room temperature with periodic sampling, then sealed in 2-mm glass capillary tubes until the ESR spectra were recorded for the first objective. The moisture content at each sampling time was measured by drying samples for 5 hr in a vacuum oven at 25 mmHg vacuum and 98°C (AOAC 1984).

### Preparation of Starch-Sugar-Water-Probe Samples

Samples were prepared by adding either fructose, glucose, maltose, or sucrose to water-TEMPO solution at room temperature. This resulted in a true solution for sucrose and fructose. Dissolved sugar and suspended, undissolved sugar crystals resulted for glucose and maltose at higher sugar concentrations. Cornstarch was then added and the mixture was slurried for 24 hr to give ratios of starch and water + TEMPO solutions of 1:0.5:2, 1:1:2, 1:2:2, and 1:3:2 with respective water contents of 60.3, 52.8, 42.2, and 35.2%.

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## ESR Spectra

Spectra were obtained using a Varian E-3 spectrometer operating at a frequency of about 9.33 GHz. The spectra were recorded at 3.2 kG using a 100 G scan range. Subsamples of the starch slurries were transferred to 2-mm glass capillary tubes and ESR spectra were taken at room temperature without treatment and following 4-min treatments at 55, 75, or 95°C. Three replications were made of each sugar type at each sugar concentration for each heat treatment, resulting in 192 observations.

## Correlation Times

Correlation times,  $\tau$ , were calculated from peak to peak line heights ( $h$ ) from simple three-line spectra of TEMPO with central line width  $T(0)$ , assuming small magnetic anisotropy (Kivelson 1960; Stone et al 1965; Pearce et al 1985, 1987) by the following formula:

$$\tau = \frac{4 \left[ \left( \frac{h(1)}{h(0)} \right)^{0.5} + \left( \frac{h(-1)}{h(0)} \right)^{0.5} - 2 \right]}{b^2 T(0)}$$

where

$$b = \frac{4\pi}{3} \left[ A_{zz} - \frac{1}{2} (A_{xx} + A_{yy}) \right]$$

is a constant of the spectrometer determined by measurement of hyperfine tensors  $A_{zz}$  and  $A_{xx}$ . This formula calculates actual  $\tau$ 's from 0.05 to 1 nsec (Nordio 1976) with an accuracy of about  $\pm 0.3$  nsec (W. G. Miller, University of Minnesota, *personal com-*

*munication*). This error is not due to random experimental error, but rather to systematic errors involving both inherent limits in instrument calibration and in the assumptions used in the formula derivation. Nevertheless, more precision can be extracted from this method than the latter indicates. Correlation times expressed to three decimal places do not have a physical meaning with respect to the actual numerical values but can, as is shown in this study, function in this time range as a useful empirical measurement of motion. Throughout this paper,  $\tau$  refers to this empirical measure of motion as calculated using the above formula.

Analysis of variance for the second objective of the study, using the Statistical Analysis System (SAS 1985), was used to analyze mean value differences. Sugar concentration, sugar type, and heat treatment were independent variables with correlation time the dependent variable. Duncan's multiple range test was applied at the  $P < 0.01$  level to evaluate specific treatment mean differences.

## DSC Thermograms

Subsamples of the starch-sugar-water-probe slurries were transferred into previously weighed aluminum DSC pans (Perkin Elmer kit no. 0219-0062) to yield a total sample size of 12 mg  $\pm 10\%$ . The pans were immediately sealed and exact sample weights determined. Thermograms were obtained on a Perkin Elmer DSC II with the heating rate at 10°C/min and a sensitivity range of 2 mJ/sec. An empty aluminum DSC pan was used as the reference. Thermal transition onset temperatures were determined as the point at which the thermogram first deviated from the baseline. Three to eight replications were made for each sugar concentration combination.

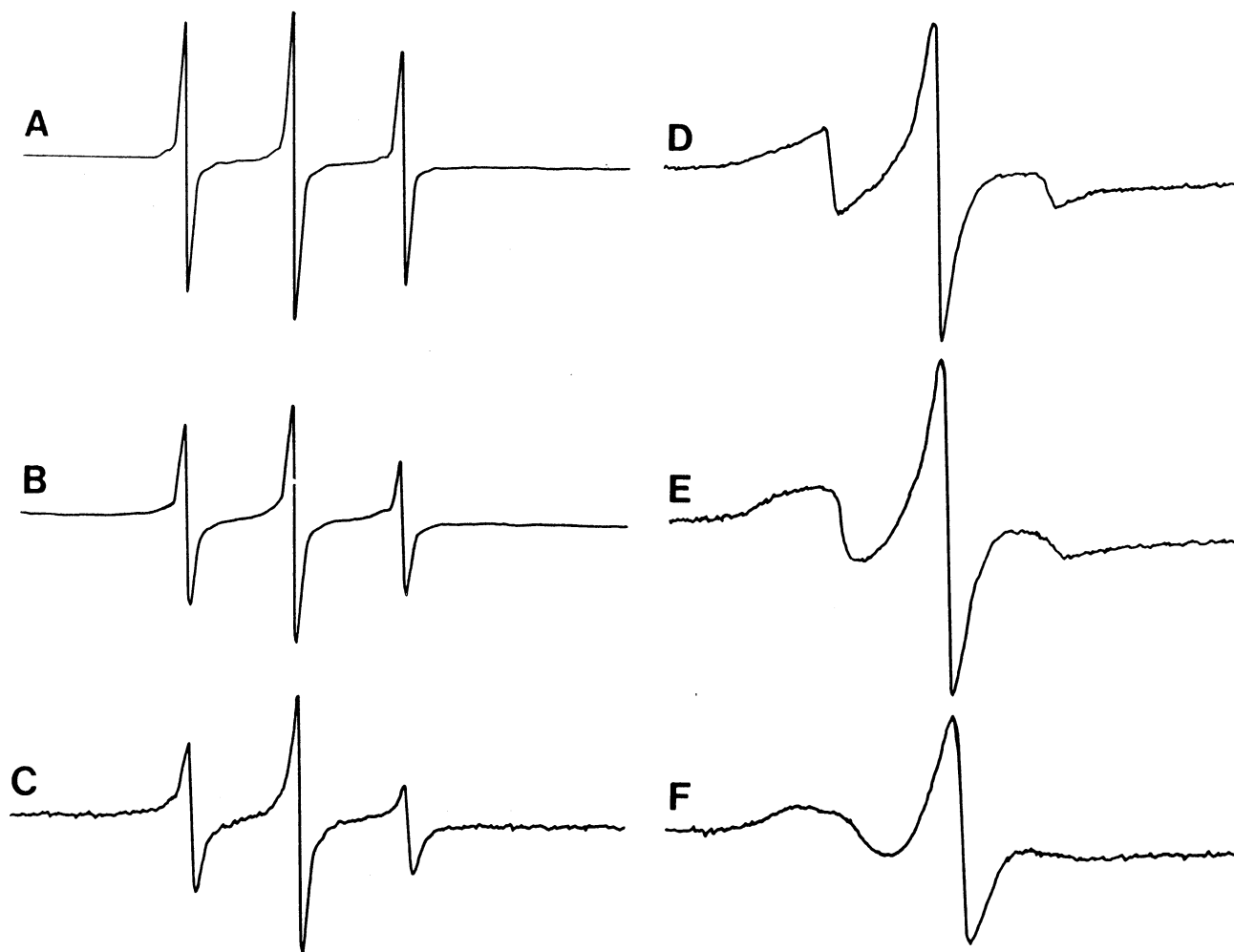


Fig. 1. Electron spin resonance spectra of TEMPO in corn starch with the following water contents: A, 50%; B, 40%; C, 30%; D, 22%; E, 20%; and F, 12%.

## RESULTS

### ESR Spectra of TEMPO in Corn Starch with Diminishing Water Content

The resultant ESR spectra of TEMPO in unheated corn starch slurries were strongly dependent on water concentration. When the water content was decreased gradually from 70.3% (a starch/water weight ratio of 1:2) to 12.0% (wb), the TEMPO spectra gradually changed. At 70.3% water a simple three-line or motionally narrowed spectrum was observed in which the high field line showed only slight decrease in height compared with the spectra of TEMPO in water. Thus starch was found to have a small effect on slowing the motion of the probe from that in water alone. The  $\tau$  of TEMPO in a dilute solution of water was 0.010 nsec and increased to 0.100 nsec at a starch/water ratio of 1:2 in agreement with the findings of Pearce et al (1985). As the amount of water was decreased, a more pronounced effect on the TEMPO spectra was observed as seen in Figure 1A-F for 50, 40, 30, 22, 20, and 12% water, respectively. Figure 1A represents rapid isotropic motion, whereas Figure 1F demonstrates greatly restricted motion. The dependence of  $\tau$  on water concentration is shown in Figure 2. There was a nonlinear increase

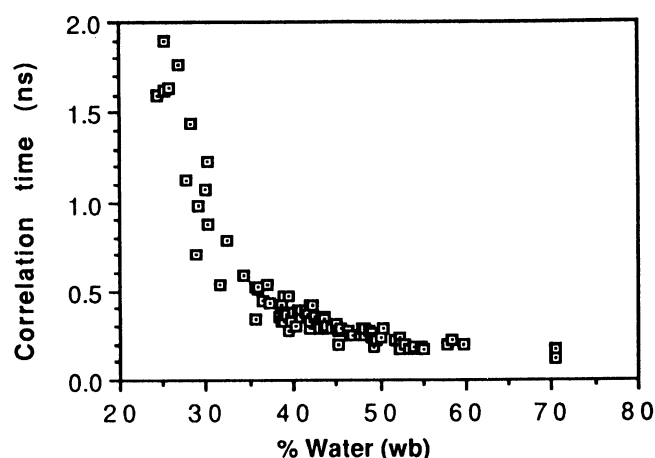


Fig. 2. Correlation time versus % water wb (calculated down to 22% water) for TEMPO in regular corn starch.

TABLE I  
Mean Correlation Times at the Concentration Ratio<sup>a</sup> 1:0.5:2

Heat Treatment Temperature (°C)	Correlation Time <sup>b</sup> (nsec)			
	Fructose	Glucose	Maltose	Sucrose
Room temperature	0.116 a	0.119 a	0.121 a	0.103 a
55	0.148 a	0.154 a	0.142 a	0.148 a
75	0.284 b	0.319 b	0.287 b	0.274 b
95	0.276 b	0.302 b	0.312 b	0.297 b

<sup>a</sup> Ratio of starch to sugar to water + TEMPO.

<sup>b</sup> The letters (read vertically) show significant differences ( $P < 0.01$ ) calculated by Duncan's multiple range test. The standard error of the mean was 0.018.

TABLE II  
Mean Correlation Times at the Concentration Ratio<sup>a</sup> 1:1:2

Heat Treatment Temperature (°C)	Correlation Time <sup>b</sup> (nsec)			
	Fructose	Glucose	Maltose	Sucrose
Room temperature	0.094 a	0.103 a	0.110 a	0.091 a
55	0.136 a	0.141 a	0.151 a	0.129 a
75	0.273 b	0.276 b	0.281 b	0.199 b
95	0.311 b	0.339 b	0.378 c	0.296 c

<sup>a</sup> Ratio of starch to sugar to water + TEMPO.

<sup>b</sup> The letters (read vertically) show significant differences ( $P < 0.01$ ) calculated by Duncan's multiple range test. The standard error of the mean was 0.018.

in  $\tau$  calculated to nearly 2 nsec for the motionally narrowed spectra as the water content decreased.

Correlation times were not calculated from peak to peak line height ratios at less than 22% water because at low water the spectra no longer revealed rapid motion. The concentration of water was decreased until a spectrum similar to 1F, resembling a powder pattern type spectrum, was noted at 12% (wb).

### Effect of Sugar Concentration, Sugar Type, and Heat Treatment on the Correlation Time of TEMPO in Starch-Sugar-Water Samples

The specific effects on  $\tau$  when starch-sugar-water mixtures were first heat treated to different temperatures at set levels of fructose, glucose, maltose, or sucrose are shown in Tables I-IV. A certain minimum heat treatment generally resulted in a larger value, which was associated with starch gelatinization and depended on sugar concentration as well as the type of sugar. With no sugar present,  $\tau$  increased slightly from about 0.1 nsec at room temperature to about 0.3 nsec after a 55°C heat treatment, which confirmed the results found by Pearce et al (1985). After sugar addition, increases in  $\tau$  resulted at higher heat treatment temperatures. From ANOVA, the sugar concentration-sugar type-heat treatment temperature interaction was found significantly different at  $P < 0.01$ .

Table I summarizes differences for the lowest sugar ratio (1:0.5:2) after the sample had undergone heating. All the sugars behaved identically at this concentration, showing a greater increase in  $\tau$  for the 75°C heat treatment, with no further increase in  $\tau$  with subsequent increase in temperature. This 75°C temperature was higher than the 55°C temperature required to increase without sugar.

At the 1:1:2 ratio (Table II) fructose and glucose resulted in significant increases in  $\tau$  for the 75°C heat treatment, whereas maltose and sucrose resulted in increases after the 95°C heat treatment.

At a sugar concentration ratio of 1:2:2 (Table III),  $\tau$  did not increase until the 95°C heat treatment. Also, a small but significant increase in  $\tau$  was seen for maltose after the 55°C heat treatment.

For the 1:3:2 ratio (Table IV), fructose, glucose, and maltose all resulted in increases for the 95°C heat treatment. Glucose and maltose further showed small but significant increases in  $\tau$  at lower heat treatments. Sucrose was the only sugar that did not produce changes in  $\tau$  throughout the heat treatments given.

TABLE III  
Mean Correlation Times at the Concentration Ratio<sup>a</sup> 1:2:2

Heat Treatment Temperature (°C)	Correlation Time <sup>b</sup> (nsec)			
	Fructose	Glucose	Maltose	Sucrose
Room temperature	0.110 a	0.150 a	0.106 a	0.130 a
55	0.124 a	0.146 a	0.178 b	0.181 a
75	0.164 a	0.211 a	0.194 b	0.147 a
95	0.332 b	0.402 b	0.436 c	0.337 b

<sup>a</sup> Ratio of starch to sugar to water + TEMPO.

<sup>b</sup> The letters (read vertically) show significant differences ( $P < 0.01$ ) calculated by Duncan's multiple range test. The standard error of the mean was 0.018.

TABLE IV  
Mean Correlation Times at the Concentration Ratio<sup>a</sup> 1:3:2

Heat Treatment Temperature (°C)	Correlation Time <sup>b</sup> (nsec)			
	Fructose	Glucose	Maltose	Sucrose
Room temperature	0.189 a	0.114 a	0.099 a	0.205 a
55	0.189 a	0.213 b	0.165 b	0.271 a
75	0.193 a	0.233 b	0.261 c	0.258 a
95	0.394 b	0.369 c	0.407 d	0.297 a

<sup>a</sup> Ratio of starch to sugar to water + TEMPO.

<sup>b</sup> The letters (read vertically) show significant differences ( $P < 0.01$ ) calculated by Duncan's multiple range test. The standard error of the mean was 0.018.

Correlation times resulting from the different individual sugars at a single heat treatment temperature can be compared before the  $\tau$  increase associated with starch gelatinization. This type of variation in  $\tau$  was apparent at the 1:3:2 ratio. At room temperature, glucose ( $\tau = 0.114$ ) and maltose ( $\tau = 0.099$ ), which had some suspended undissolved sugar crystals, yielded smaller  $\tau$ 's than fructose ( $\tau = 0.189$ ) and sucrose ( $\tau = 0.205$ ), which were completely dissolved. The presence of sugar crystals reduces the effective concentration of sugar in solution. At 55°C, all sugars were in solution, and differences between sugars were related to differences in local viscosity of the sugar solution as  $\tau$  is directly proportional to viscosity approximated by the Stokes-Einstein relationship. Looking at all the sugar concentrations in Tables I-IV, some differences were noted in the effect on  $\tau$  between sugars compared at a single heat treatment when the temperature was greater than that associated with starch gelatinization. Some of these differences are probably related to local viscosity differences due to the presence of the sugars in the resultant starch suspension or gel. Other differences in the effect on  $\tau$  between sugars are explained by DSC results, which are presented in the next section.

#### DSC Onset Temperatures of Starch-Sugar-Water Samples

As with the ESR results, ANOVA resulted in significant differences for sugar concentration-sugar type for starch thermal transition onset temperatures as measured by DSC. Figure 3 shows typical DSC thermograms of samples containing sucrose. Increasing sugar concentration for all sugars resulted in greater onset temperature for the starch thermal transition. Typical DSC thermograms in Figure 4 further show that the starch transition onset temperature was not increased to the same extent by the individual sugars. The endotherms in the 20–70°C temperature range for samples containing glucose and maltose were due to the dissolution of the portion of undissolved sugar crystals.

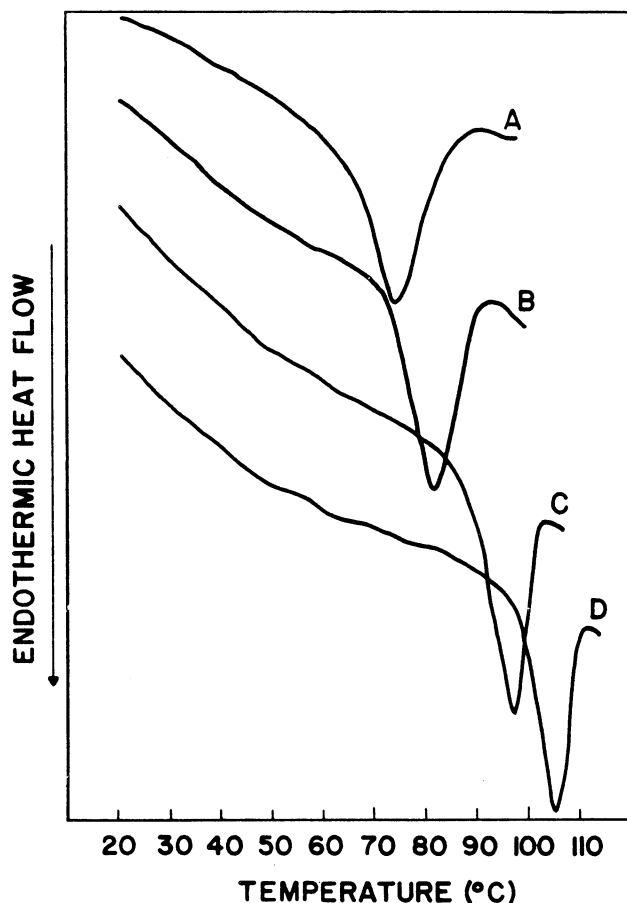


Fig. 3. Differential scanning calorimetry thermograms of sucrose at the following concentrations of starch, sugar, and water + TEMPO: A, 1:0.5:2; B, 1:1:2; C, 1:2:2; D, 1:3:2.

Starch transition onset temperatures are summarized in Table V. Differences between starch transition onset temperatures produced by the individual sugars became more pronounced as the sugar concentrations increased. At the 1:0.5:2 ratio, all sugars resulted in higher starch transition onset temperatures compared with 47°C for regular corn starch and water (1:2) systems. This is a lower value than found in earlier studies due to the slurring step, which reversibly disrupts the granular structure. This step is necessary to prepare samples for ESR measurements (Pearce 1988). Thus, the increase of  $\tau$  at 55°C (Table I) was well after the starch transition onset temperature measured by DSC. At the 1:1:2 ratio, the sugars also resulted in similar increases in starch transition onset temperatures measured by DSC (Table V) as well as similar behavior in the heat treatment dependence of  $\tau$  as seen by ESR (Table II). At the 1:2:2 ratio, differences in DSC onset temperatures between different sugar containing samples became apparent. The onset temperature for samples containing fructose (72°C) fell below the ESR 75°C heat treatment, yet an increase in  $\tau$  was not seen for the slurries containing fructose. The other sugars had onset temperatures of at least 75°C, and all sugars showed an increase in  $\tau$  at heat treatments of 95°C (Table III). The 1:3:2 concentration ratio had the largest starch transition onset temperature differential between sugars. Sucrose had the greatest effect on increasing the starch transition onset temperatures followed by maltose, glucose, then fructose. The starch transition onset temperature for slurries containing sucrose (93.3°C) was slightly less than the 95°C heat treatment given before ESR measurement, yet once again the increase in  $\tau$  was not seen. The onset temperature for samples containing maltose (92°C) was also below the 95°C heat treatment of the ESR

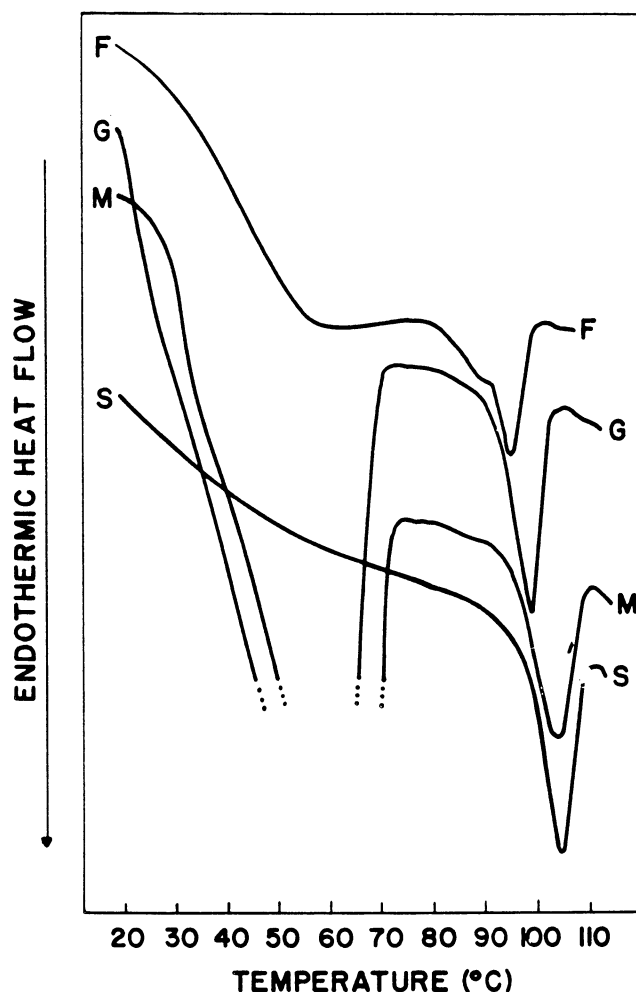


Fig. 4. Differential scanning calorimetry thermograms at a ratio of 1:3:2 for starch, sugar, and water + TEMPO: F = fructose, G = glucose, M = maltose, S = sucrose.

experiments, but in this case an increase in  $\tau$  was seen. Samples containing both fructose and maltose showed an increase in  $\tau$  before the onset temperature of the starch transition as determined by DSC.

## DISCUSSION

### TEMPO Motion, Distribution, and Water Content

The motion of TEMPO in a dilute water solution was slightly slowed when starch was added. Tempo was also slowed down with decreasing amounts of water in a starch-water mixture. After starch was gelatinized, in general the increase in  $\tau$  was small on the ESR time scale, indicating that the gel matrix does not greatly restrict TEMPO mobility in the entrapped solution. Reduced probe mobility is thought to result from the ability of starch to change the local environment experienced by the probe (Pearce et al 1985). The TEMPO solution penetrates the amorphous regions of the starch granules. This region of amorphous starch chains acts as a capillary matrix restricting free motion of the probe. It is conceivable that nonbinding absorption of the probe onto the starch molecular surfaces as it falls out of solution at low water concentrations contributed to the powder pattern type spectrum. Because TEMPO is not thought to hydrogen bond to either polymer or solvent, the composition dependence of correlation time is a measure of the effect of the polymer on solvent properties (Vekslis and Miller 1977).

As is done most often in polymers, the doping of the probe into the starch was done by removing solvent from a starch-probe slurry. Therefore, there is potential for inhomogeneous distribution and partitioning of the nitroxide between different physical regions of the sample (Miller 1979), for example, between the amorphous and crystalline regions of the granule. Pearce et al (1985) suggested that TEMPO in water enters the starch granules, thus the spectrum observed is a composite measure of water properties both within and outside of the granules.

At high water concentration, the three-line spectra are typical of rapid isotropic motion. At lower water concentrations, the powder pattern type of spectrum that began to appear is typical of slow motion of a paramagnetic molecule diluted in a diamagnetic host (Nordio 1976). Due to the non-hydrogen-bonding nature of TEMPO, isotropic motion was assumed for both rapid and motionally slowed spectra. As the shape of the spectra are like neither composite spectra of more than one population of motion nor motionally slowed anisotropic spectra, which look similar in many instances and show a low-field double maxima or high-field double minima (Vekslis and Miller 1977), different microenvironments could not be detected.

There is also the possibility that the probe could be distributed between the starch and lipid portion of the granule because normal cornstarch has 0.6–0.7% total lipid (Morrison 1988). The high-field region, which is most sensitive to changes in polarity, clearly has only one component. Therefore, either ESR measurement of TEMPO is not sensitive to the small amount of lipid present or the lipid does not provide a hydrophobic environment to split the high-field line into two components. Such a high-field split was reported by Pearce et al (1987, 1988).

### Aqueous Phase Mobility of TEMPO

The addition of sugar to a starch-water suspension was not the same as decreasing the weight % water in the starch-water

suspension, as sugars slowed mobility of TEMPO to a lesser extent than did starch. This can be seen by comparing the  $\tau$ 's from Figure 2 with the  $\tau$ 's reported at room temperature in Tables I through IV. The spectra of starch-sugar-water samples at room temperature more closely resembled those of starch-water at equal total starch concentration than those of starch-water at equal total solids concentration. Thus, the addition of sugar does not greatly decrease the motion of the probe.

The idea that sugar competes with starch for water abounds in the literature. The nature of this competition is usually not clearly stated but is discussed in terms of binding of water molecules. This competition is not, however, simply the selective hydration of either the starch or the sugar. It is widely acknowledged that the addition of sugar to a starch-water mixture does not affect starch gelatinization in the same way as lowering the weight percentage of water. In fact, some studies show that sugar addition affects starch gelatinization in a manner similar to that of additional water. For example, Ghiasi et al (1982) gave indirect evidence that the mobility of the entire solution is important to gelatinization properties. They showed that increasing the volume of solution by adding sucrose had an effect on the disappearance of the second starch endotherm as seen by DSC similar to the effect of increasing the volume of the solution by adding water. Correspondingly, in the present study, sugar added to the starch-water suspension did not greatly decrease the initial TEMPO aqueous phase mobility. Thus, the hydration of starch and the hydration of sugar cannot be viewed as competitive, but rather that sugar that is completely solubilized in water results in a sugar-water solution that possesses diluent properties different from those of the original water and sugar components that individually make up the solution. The physical properties of the sugar solution are not additive properties of the contributing components. For example, Brand (1987) showed that the dielectric constants and dielectric loss factors for sucrose solutions are higher than those for pure water even though those values were extremely small for pure crystalline sucrose. The same idea applies to water mobility. Richardson et al (1987) studied the molecular mobility of water in starch-sucrose systems using  $^2\text{H}$  and  $^{17}\text{O}$  nuclear magnetic resonance.  $^2\text{H}$  data showed that water in starch has a greater relaxation rate than in sucrose.  $^{17}\text{O}$  data suggested that water is more tightly bound by sucrose than by starch. The difference in results between the two nuclei monitored was attributed to  $^2\text{H}$  exchange. Initially, the  $^{17}\text{O}$  results seem to contradict the current (ESR) findings that showed more mobility at the same water content in a mixture of starch and sucrose (Tables I–IV) than in starch alone (Fig. 2); but considering water more tightly bound by sucrose than by starch, as shown in  $^{17}\text{O}$  studies, does not preclude the same degree of total solution mobility, as seen by the retention of small  $\tau$ 's when sugars were added to starch-water suspensions. This observation is a result of the complete solubilization of sucrose, in which the resultant solution could retain much of the original mobility of water. The spin probe TEMPO, doped into the system, does not selectively measure the mobility of water molecules, but measures the effect of the starch polymer on the entire solution mobility.

It is important to distinguish between the two contributing factors that affect the mobility of TEMPO when comparing various sugars added to starch-water systems. The first factor is the inherent mobility that individual sugars impart to aqueous regions, giving rise to the local microenvironment. The second factor is the differences in the increase of starch gelatinization temperatures caused by each sugar. As the starch chains separate during gelatinization, they become hydrated, making less total solution available as solvent for the TEMPO and increasing the amorphous capillary matrix, thus increasing  $\tau$ , meaning less solution mobility. The two factors are not related in an obvious way. Both affect  $\tau$ , but only the second is a direct result of starch gelatinization.

### ESR Correlation Times Compared with DSC Onset Temperatures

Comparison of DSC and ESR results must be made carefully, even though preparation for both methods was done in parallel to study starch gelatinization. Only onset temperatures are

TABLE V

DSC<sup>a</sup> Onset Temperatures for Each Sugar at Each Concentration Ratio

Concentration Ratio <sup>b</sup>	Onset Temperature <sup>c</sup>			
	Fructose	Glucose	Maltose	Sucrose
1:0.5:2	60.3	58.0	60.0	60.8
1:1:2	67.3	67.8	67.6	69.7
1:2:2	72.0	75.0	81.3 <sup>d</sup>	82.5
1:3:2	80.7	83.7 <sup>d</sup>	92.0 <sup>d</sup>	93.3

<sup>a</sup> Differential scanning calorimetry.

<sup>b</sup> Ratio of starch to sugar to water + TEMPO.

<sup>c</sup> The average standard deviation was 1.63°C.

<sup>d</sup> Slurries containing undissolved sugar crystals.

reported for DSC endotherms because of the difference in heating procedures from ESR experiments. During the DSC run, samples were heated at 10°C/min to temperatures through the completion of the endotherm, allowing for dynamic transformations to occur at progressively higher temperatures. For ESR experiments, samples were heated at constant temperatures for a length of time sufficient to allow the gelatinization processes to proceed to the degree of completion possible at that temperature and reach a state nearer equilibrium.

Significant differences in  $\tau$  were always seen after maintaining constant heat treatment temperatures well beyond the DSC starch transition onset temperature. When the onset temperature, as seen by DSC, was only slightly less than the ESR heat treatment, a statistically significant difference in  $\tau$  was not seen, because at the onset temperature only a small percent of the population of starch granules have completed the thermal transition. Conversely, statistically significant differences in  $\tau$  were often seen at temperatures well below the DSC starch transition onset temperature. Thus ESR, which gives a measure of mobility in the aqueous phase, is sensitive to changes in the mobility within the starch microenvironment before the DSC endotherms are seen.

Slade and Levine (1988) used free volume theory to explain the relationship between starch gelatinization and the plasticizing effect of diluents in relation to DSC studies. They related free volume, allowing for backbone chain segmental mobility, to glass transition temperature of the amorphous region, which they assumed to immediately precede the melting of crystalline amylopectin. Because, according to free volume theory, a diluent's plasticizing ability is proportional to the inverse number average molecular weight, the free volume theory provides a model to explain the temperature location of starch thermal transitions as affected by sugar solutions. It does not explain changes in the aqueous microenvironment detected by ESR at temperatures below the starch transition onset temperature as measured by DSC. While the ESR spin probe technique used is a measure of the probe's mobility in the system into which it has been doped, the DSC gives a measure of thermal phase transitions of the starch polymers. DSC cannot be used as a measure of mobility of the starch polymers because Blum et al (1984) showed the inadequacy of using calorimetric glass transition measurements as a measure of polymer motion. Also, the ESR results presented in the current study show that DSC is not sensitive to changes in mobility of the aqueous phase.

ESR and DSC both were able to detect differences between sugars and their ability to affect starch gelatinization. Furthermore, ESR alone was sensitive to detecting differences in the aqueous microenvironment as the temperature was increased. This was seen by small differences that were detected when the heat treatment was less than the onset of starch gelatinization as measured by DSC. In the starch-sugar-water system evaluated with different sugars, sucrose had the greatest ability to increase gelatinization temperatures followed by maltose, glucose, then fructose as measured by either method.

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