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Studies of water mobility and determination of polymer, solute, and free water in wheat starch-sugar-water dispersions by using ^{17}O nuclear magnetic resonance spectroscopy

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Kansas State University, 1990

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STUDIES OF WATER MOBILITY AND DETERMINATION OF POLYMER,
SOLUTE, AND FREE WATER IN WHEAT STARCH-SUGAR-WATER
DISPERSIONS BY USING ^{17}O NUCLEAR MAGNETIC RESONANCE
SPECTROSCOPY

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A DISSERTATION

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Major Professor

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REVIEW OF LITERATURE

WATER MOBILITY STUDIES USING NMR MEASUREMENTS

Water probably is the most critical component in the biological system. In foods, water is not just a medium for reaction, but it is an active ingredient to control reactions, texture and general physical and biological behavior (Whistler and Daniel, 1985). The amount of each different water state present in a food can profoundly affect the chemical, physical, biological and rheological properties of foods (Chinachoti and Steinberg, 1986).

Pulsed NMR spectroscopy was used to study water mobility in various food systems such as instant starch gel, sucrose solution, starch-sucrose system, starch powder, wheat flour suspensions, wheat doughs and breads, and vegetables (Leung et al., 1979, 1983; Lechert et al., 1980; Richardson et al., 1986a,b, 1987a,b; Hansen et al., 1987).

Characterization of water

Lang and Steinberg (1981) showed differences in sorption behavior between macromolecules (starch, casein) and solutes (sucrose, NaCl) by using the Smith linear sorption isotherm. They reported that each of these sorbed a different type of water over a broad a_w range. The water sorbed by the macromolecules was termed 'polymer' water while that sorbed by solutes was termed 'solute' water.

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Later Lang and Steinberg (1983) reported variable time decay responses from longitudinal relaxation time (T_1) and transverse relaxation time (T_2) measurements of a pulsed ^{1}H NMR with the same a_w (0.91) of starch, sucrose and 90:10 starch:sucrose systems. They concluded that polymer and solute water show different NMR signal responses and can coexist in a food.

Nagashima and Suzuki (1981) also tried to characterize bound water in a variety of systems (amino acids, beef, condensed milk, and starches) with pulsed ^{1}H NMR. They measured the variation of free induction decay (FID) amplitude with changing temperature, and obtained the variation of liquid or unfrozen water content as a function of temperature by using freezing curves. Long relaxation reflects the liquid state and converts to unfrozen water, differentiating 'weakly bound water' and 'tightly bound water' at -20C. They postulated that different freezing curves indicate different states of components.

Water mobility

Water mobility and binding are closely related to each other. Water that is tightly bonded to a substrate is highly immobilized, and T_2 is reduced. If a small fraction of water molecules are hydrogen bonded to macromolecules, water mobility decreases (Fung, 1977; Wynne-Jones and

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Blanshard, 1986). According to this, we can detect a change in the extent of hydrogen bonding or water interaction and calculate the amount of bound water from the mobility data (Lechert, 1981).

Leung et al. (1976) reported that the amount of water bound to macromolecules (sodium alginate, pectin, corn starch, casein, and cellulose) was consistent in the pulsed NMR measurements. Although T_1 increased with moisture content for all the macromolecules, T_2 values were different among samples with the same moisture contents. The T_2 values also provide a measure of the strength of water binding: a short T_2 indicates strong water binding. In contrast to Leung's results, Brosio et al. (1983) reported that water-binding values using low resolution pulsed ^1H were not constant but increased as total water increased with powdered milk system.

<u>Starch-water systems.</u> Proton NMR T_1 (Leung et al., 1976) measurements showed single phase water, and T_2 measurements indicated two phases of water. Two-phase behavior reflects the existence of two water fractions with different mobilities and has been reported by others (Henning and Lechert, 1974; Lelievre and Mitchell, 1975; Henning, 1977). Lelievre and Mitchell (1975) obtained a two-state model for concentrations with up to 40% starch-water dispersions. Multiple phases of water were reported

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in starch-water dispersions with differing degrees of mobility for each different phase by Kashkina et al. (1979).

Lechert et al. (1980) studied mobility of bound water on starch with ^{2}H resonance reorientation. Deviations from isotropic motion cause a splitting of the ^{2}H resonance line, which is a measure of anisotropic motion. The bound water of potato starch showed distinct anisotropic water motion, whereas wheat starch had weak anisotropic motion, and corn starch showed isotropic motion. Therefore, they concluded that different starches show different water reorientation rates (Lechert and Henning, 1976; Henning, 1977; Lechert and Schwier, 1982).

Richardson et al. (1987a) reported four different regions of water mobility by using high field ^{17}O and ^{2}H NMR with corn starch suspensions and powders ranging from 10-96% starch concentration. They applied a standard isotropic two state model for the high moisture region (region I and II, 10-40% and 40-60% solids concentrations, respectively), with fast exchange. A plot of relaxation rate vs corn starch concentration showed three regions of decreasing mobility. The relaxation rate was linear with chemical activity over the entire concentration range. Two regions of mobility, trapped (III) and monolayer (IV) water, were shown in the low moisture region (III and IV, 60-92% and 92-96% solids concentrations, respectively). Richardson et al. (1987a)

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also found that ^{17}O NMR relaxation rate was affected only by the concentration of corn starch in water.

Callaghan et al. (1983) studied water diffusion of wheat starch pastes by adapting the pulsed field gradient technique. They observed no significant difference in water diffusion coefficients among different rheological pastes and concluded that the paste did not restrict diffusion.

Sugar-water systems. Some carbohydrate solutions, such as glucose, sucrose, and maltose solution, were observed using dielectric or nuclear magnetic relaxation spectroscopy (Tait et al., 1972; Allen and Wood, 1974; Suggett, 1976; Suggett and Clark, 1976; Suggett et al., 1976). Tait et al. (1972) observed monosaccharide solutions (hexose and pentose) with ^{17}O NMR using enriched ^{17}O water ($H_2^{17}O$). Relaxation rate was greater in hexose (glucose, galactose, and mannose) solutions than pentose (ribose) solutions. The transverse relaxation rate (R_2) of glucose increased with concentration in a nonlinear manner. Nonlinearity decreased as temperature increased. Viscosity dependence of R_2 was linear if plotted against $\eta/\rho T$, where η is viscosity and ρ is the density. They concluded that glucose increases the hydrogen bonding of aqueous solutions based on a significant decrease of the quadrupole coupling constant in glucose solutions compared to pure water. Suggett (1976) and Suggett et al. (1976) reported a single correlation time for

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sugar solutions. A slow exchange process was the result of coupled motion of the hydrated side chains and sugar ring, which implied solute-solvent interaction.

Richardson et al. (1987b) studied molecular mobility of water associated with 5-80% sucrose solids concentrations by using ^{2}H and ^{17}O high field NMR measurements. They observed three regions of successively decreasing water mobility with increasing solute concentrations and suggested solute-solvent and solute-solute interactions via hydrogen bonding as the mechanism to explain the observed decrease in water mobility. Harvey and Symons (1978) investigated the hydration of glucose, mannose, galactose, ribose, sorbose and fructose based on chemical shifts as a function of temperature by using ^{1}H high field NMR. They concluded that each hydroxyl group of the monosaccharide bonds with the water molecules.

Starch-sucrose-water systems. A system of more than one or two components becomes complex and the possible interactions increases. The rate of water exchange among components and microhomogeneity of the system needs to be considered (Richardson and Steinberg, 1987). Richardson et al. (1987b) studied the mobility of water in a polymer-solute system of freeze dried starch:sucrose (FSS; 90:10) in D_2O or $H_2^{17}O$. Solid concentrations of 10-93% were evaluated using ^{2}H and ^{17}O high field NMR. The ^{17}O data showed one and

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two Lorentzian peaks from 10-72.4% and 73.0-83.3% solids concentration, respectively, and a single Lorentzian peak appeared beyond 83.3% solids concentration. They hypothesized that two peaks resulted in the FSS-D_2O system because two distinct water phases appeared that do not exchange at a rate greater than that of NMR frequency. The starch system showed a sharp increase in R_2 with concentration increases because of the water trapped between the starch granules (Richardson et al., 1987b). The FSS system showed little increase in R_2. Solvated sucrose has the ability to create channels between starch granules that allow the water to continue to move freely in the system. They postulated that two peaks appeared when sucrose-water interaction are no longer able to provide a 'communication network'.

Other multi-component systems. Leung et al. (1979) measured T_2 of ^2H NMR and found non-exponential decay of the signal indicating two or more species of water with slow exchange in a wheat flour dough system. Even though the variation is small between two fractions, long and short relaxation curves represent more and less mobile fractions of water, respectively. Later Leung et al. (1983) could not resolve the two fractions of water in soft and hard wheat doughs and breads. They concluded that ^1H or ^2H relaxation does not reflect different rheological properties. Bread

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staling resulted in decreases in T_2 and T_1 with time indicating an overall decrease in water mobility and an increase in water binding during the process.

Temperature effects

Proton NMR measurements by Jaska (1971) indicated a decrease in water mobility during the reversible hydration or swelling stage and an increase in the mobility of absorbed water at the onset temperature of gelatinization. Jaska (1971) postulated that the decrease in water mobility was caused by an increasing number of water molecules being absorbed in the solid starch and later by an increasing mobility of the starch molecules which associated with the water. Lelievre and Mitchell (1975) followed T_2 vs temperature with wheat starch suspensions ranging from 2 to 40%, w/w. Water mobility decreased as hydration of the starch occurred at the onset temperature of gelatinization. As heating progressed, T_2 went through a minimum and then increased as starch chain mobility increased. The transition suggested that starch gelatinization was a melting process. Wynne-Jones and Blanshard (1986) reported an overall decrease in mobility of water molecules in wheat starch gels ranging from 25-60% water. This decrease in water mobility was accompanied by an increase in the fraction of 'bound' water in the gel although the formation

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of hydrogen bonds and the rate and extent of this change exhibited a positive temperature dependence.

Windle (1985) used electron resonance spin to study potato starch granules in excess water systems. They exhibited three distinct starch-water stages at approximately 25-50C, 50-70C, and 70-90C, corresponding to a pre-gelatinization, gelatinization, and post-gelatinization stage, respectively. The mobility of the absorbed water and the starch-water interaction in the first two stages depended strongly upon the initial granule hydration state. Hansen et al. (1987) investigated possible sugar-starch interactions as a function of increasing temperature by using ^{13}C NMR. Their results suggested that sugar-starch interactions were occuring during heating of starch and appeared to occur just prior and within the temperature range of starch gelatinization as measured by DSC. Hansen et al. (1989) also reported that as the molar concentration of sucrose was increased, the number of carbon atoms involved and the strength of interactions appeared to decrease.

Determination of different states of water

Different environmental states are characterized by different relaxation times. In previous NMR measurements, no single exponential behavior of the spin-echo decay curve

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of water was interpreted as the presence of different types or states of water molecules. Different relaxation times corresponded to different molecular mobilities (Leung et al., 1976, 1979; Di Nola and Brosio, 1983).

Brosio et al. (1978) attempted to determine moisture content in starch-rich food products by applying the low resolution pulsed NMR technique. They measured the water content of samples from the liquid to solid ratio, which were converted to percentage weights. They assumed that most of exchangeable hydrogens in starch contribute to the liquid phase signal. Di Nola and Brosio (1983) reported that the amount of bound water determined by pulsed NMR agreed with the amount of unfreezable water as determined by other techniques. They claimed that ignoring the exchange process resulted in disagreement between the amount of bound water determined by pulsed NMR and unfreezable water determined by wide-line NMR (Leung et al., 1976, 1979). Apparent relaxation rates vary with the moisture content of the sample, and the values differ from those of bound or free water when an exchange process is present. However, those studies considered only two states--bound and free.

Chinachoti and Steinberg (1986) tried to determine polymer and solute waters quantitatively in a starch-sucrose model system by using model equations. The equations were developed for calculating solute water and polymer water

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from T_1 of a low field (10MHz) pulsed ^{1}H NMR and a_w. They reported high correlation ($r^2 > 0.97$) between T_1 and a_w. The T_1 increased with increasing sucrose content and a_w. Sobczynska et al. (1990) calculated the free, solute and polymer water in starch-sucrose-water dispersions as polymer-solute-water model systems using ^{17}O NMR relaxation rates. Each portion of observed water was compared to a theoretical value. Sobczynska et al. (1990) considered relaxation rates of saturated solutions of solute (sucrose) and polymer (starch) as intrinsic relaxation rates for solute water and polymer water, respectively. The theoretical values of each state of water did not show much change, while the observed values showed dramatic changes over the temperature ranges (33-71C) studied.

^{17}O NMR measurements in food systems

Quadrupolar relaxation is the primary mechanism of ^{2}H or [17]O relaxation and changes in hydration states are reflected directly in the T_1 and T_2. If water interacts strongly, the relaxation rates are shortened (Leung et al., 1983). In any quadrupolar nucleus of spin greater than 1 ([17]O=5/2), recovery of longitudinal magnetization is no longer monoexponetial if slow motion occurs. Whenever a small molecule or an ion is bound to a macromolecules, its dynamics are slowed and the extreme narrowing condition is

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not satisfied. The T_1 is shortened and becomes frequency dependent (Fanni et al., 1989). Although T_1 is neither affected by line width nor dependent on line width, T_1 is considered the same as T_2 in solutions of small molecules. To get consistent line widths, lineshapes are analyzed in terms of the equation for a Lorentzian peak

$$1/I = 4(v_o - v)^2/I_{max} \ (\Delta v)^2 + 1/I_{max}$$

where v_o is the midpoint of the signal, v is the width of the signal at the half height, I_{max} is the peak height, and I is the height of the signal at a point v. The equation to obtain consistent line widths for a nucleus undergoing quadrupolar relaxation that gives a Lorentzian lineshape is:

$$T_2^{-1} = T_1^{-1} = K\pi(e^2qQ/h)^2 \tau r$$

where e^2qQ/h is the quadrupolar coupling constant and $K=3/125$ for ^{17}O (Tiet et al., 1972). Therefore, to explain line width in terms of relaxation phenomena, T_2 or transverse relaxation rate (R_2) can be used

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

where Δv_{obs} is half height of width.

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The ^{17}O nuclei are affected by coupling from neighboring protons. Decoupling of protons is necessary to increase accuracy at the line width (Earl and Niederberger, 1977). Halle et al. (1981) reported extensive proton exchange broadening of ^{17}O resonance at and near the pH of neutral water. Richardson (1989) almost eliminated proton exchange broadening in ^{17}O NMR transverse relaxation even in the neutral pH range for water and corn starch-water systems by using proton decoupling.

Several advantages of ^{17}O relaxation are: 1) Strong quadrupolar interaction leads to large relaxation effects, thus, permitting studies at reasonably low concentrations. 2) The intramolecular origin of the electric field gradient at the water oxygen nucleus makes the quadrupolar interaction virtually independent of the molecular environment, which greatly facilitates the interpretation of relaxation data. 3) The ^{17}O relaxation is not influenced by proton (deutron) exchange with prototropic residues on the starch and sucrose except for a narrow pH range around neutral, a serious problem in ^{1}H and ^{2}H relaxation. 4) Cross-relaxation, which contributes significantly to ^{1}H relaxation, is unimportant for ^{17}O (Halle et al., 1981).

Therefore, the oxygen nucleus is considered the best probe for studying water-binding by solid components and the molecular motion of water (Richardson et al., 1987a).

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Varying the $D_2O:H_2O$ ratio had no effect on the longitudinal (T_1) or transverse (T_2) relaxation times of deuterons (Leung et al., 1983). It is been reported that all the water in a starch gel (Wynne-Jones and Blanshard, 1986) or all the OH groups in defatted wheat starch granules (French, 1984) was available for exchange and can be replaced with heavy water or deuterium (D_2O). Because of the extremely low natural abundance of its one magnetically active isotope (^{17}O, 0.037%), enriched ^{17}O water ($H_2^{17}O$) can be used to obtain more sensitive measurements (Kintzinger, 1983). The $H_2^{17}O$ in NMR measurements is not sensitive to proton or deuteron exchange with the solute, and the nuclear relaxation rate is at least two orders of magnitude more sensitive to molecular motion (Tait et al., 1972). The $H_2^{17}O$ does not exchange with oxygen atoms of sucrose or starch, so it is not affected by chemical shifts. Therefore, strengthening the concentration of water's oxygen by 15 using 0.5% $H_2^{17}O$ allows measurement of mobility of only water's oxygen rather the sucrose's or starch's oxygen in the sucrose-starch-water dispersion.

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STARCH GELATINIZATION

Structure of starch granule

The main source of starch is cereal grains, tubers and roots. Starch is chemically heterogeneous and mainly composed of two kinds of polysaccharides molecules: amylose and amylopectin. The amylose molecule has almost all α-1,4 bonds with 9-20 chains per molecule (Hizukuri et al., 1981) and amylopectin has around 96% α-1,4 bonds and 4% α-1,6 bonds. Native starch granules are organized into quasicrystalline macromolecular aggregates (Hood, 1982). In general, starch granules are birefringent and show a characteristic "Maltese cross" pattern under the polarizing microscope. The partially crystalline, glassy polymers have characteristic x-ray diffraction patterns (Maurice et al., 1985).

Currently, amylose is considered a mixed chain of linear and branched polymers with a limited amount of long chain branching that allows amylose to behave like a linear polymer (Lineback, 1984). For the amylopectin, the 'cluster' model is widely accepted (French, 1972; Robin et al., 1974; Nikuni, 1978; Manners and Matheson, 1981) to account for crystalline and amorphous regions in starch. The branch points are located in less organized amorphous regions, while the chains can associate into crystalline

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regions. In the starch granule, amylose can exist in a random or helical configuration depending upon the presence of lipids, which occur in most cereal starches and amylopectin probably is present in a helical form (Lineback, 1984).

Biliaderis and coworkers (1984) mentioned three phases of starch granules for understanding starch behavior; 1) crystalline, 2) a continuous bulk amorphous phase (amylose), and 3) intercrystalline amorphous phase within amylopectin. Highly organized crystalline regions and amorphous or gel-like regions exist almost equally in starch granules. The gel phase, which is thought to be the continuous phase in starch, is comprised of the noncrystalline regions of amylopectin molecules and, presumably, amylose molecules. The amorphous phase of starch is most readily penetrable by water and low molecular weight, water-soluble solutes, such as sucrose, glucose, or urea (Maningat and Seib, 1987).

Gelatinization

If starch granules are heated in excess water, gelatinization of starch occurs. However, gelatinization characteristics differ in starches (Lund, 1984), and the mechanism of the gelatinization process is not clearly understood. The importance of gelatinization is in the changing of the physical, chemical and biological properties

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of starches. Futhermore, the gelatinization process alters
the quality of food products. For example, if starch
gelatinization and granule swelling do not occur
concurrently with maximum batter expansion in cake baking,
obtaining high volume and symmetry in a cake will not be
possible (Bean et al., 1983).

During gelatinization, some changes proceed
collectively and sequentially with heating (French, 1984;
Maningat and Seib, 1987; Slade and Levine, 1987). According
to the definition, which was chosen based on survey at the
Carbohydrate Symposium of American Association of Cereal
Chemists in 1986, starch gelatinization is "the collapse
(disruption) of molecular orders within the starch granule
manifested in irreversible changes in properties such as
granular swelling, native crystallite melting, loss of
birefringence and starch solubilization. The point of
initial gelatinization and the range over which it occurs is
governed by starch concentration, method of observation,
granule type, and heterogenities within the granule
population under observation" (Atwell et al., 1988).
The definition pointed out the disruption of molecular order
as the primary change occurring in gelatinization.

Granular swelling occurs to some extent without heating
when starch granules are in excess water. Swelling begins
in the least organized, amorphous, intercrystallite regions

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of the granule (French, 1984). The gel phase of the starch granule is hydrophilic and after immersing in water, it undergoes limited reversible swelling, with subsequent swelling of the entire granule (Maningat and Seib, 1987). Starch granules heated in excess water swell continuously to the irreversible state from the reversible state. Increased molecular mobility in the starch granule results in a redistribution of molecules at the maximum resistant granular swelling condition, and the smaller, linear amylose molecules diffuse out of the swollen granules (Jaska, 1971; French, 1984). The temperature at which swelling starts is called the initial gelatinization temperature (Lineback, 1984). Bean and Yamazaki (1978) reported that initial granule swelling observed microscopically related to the viscosity increase at the first-stage of gelatinization. The rapid increase in viscosity observed during the initial swelling of the granules occurred before all birefriengence was lost, and the temperature range for viscosity increases corresponded with the starch granule diameter ratio increases. Sometimes the swelling temperature of starch granules could be limited by lipid-amylose complexes, polymer entanglements, and in some cases by incompletely disrupted crystalline regions of the original starch particles (Lelievre, 1984).

Loss of birefringence means that the hydrogen bonding

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that causes crystallite formation was broken by the gelatinization process. This bond cleavage resulted in ordered amylopectin branched chains (Chinachoti and Steinberg, 1984). About 98% loss of birefriengence under a Kofler electrically heated hot stage microscopie or a polarizing microscope (Watson, 1964) is the point considered as the gelatinization endpoint. Major structural changes occur beyond the birefriengence end-point according to DSC studies. Therefore, Zobel (1984) claimed that a temperature range is needed to provide maximum disruption of structure to achieve swelling and high viscosities in a hot starch paste.

Native crystalline melting occurs concurrently with swelling of granule. As the gel phase swells, it exerts a tension on the neighboring crystallites and tends to distort them. Consequently, uncoiling or dissociation of double helical regions occurs with further heating and the amylopectin crystallite structure is disrupted (French, 1984). The crystallites in the granule disappear as noted by loss of birefringence and x-ray diffraction studies (Maningat and Seib, 1987). The x-ray diffraction pattern of starch provides useful information regarding molecular organization of starch as well as changes in starch crystallinity. An x-ray pattern does not provide quantitative values for starch gelatinization (Lineback,

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1984).

DSC measurements have become a major means of studying melting concept for gelatinization. DSC is a thermoanalytical technique for monitoring changes in physical or chemical properties of materials as a function of temperature by detecting the heat changes associated with such processes (Biliaderis, 1983). Actually the temperature of melting crystallites and the level of water are closly related in DSC measurements (Zobel, 1984).

In DSC measurements, the importance of the amount of water on starch gelatinization in a starch dispersion has been reported by many researchers (Collison and Chilton, 1974; Burt and Russell, 1983). Variations in water:starch ratios produce endotherms with single and multiple peaks in DSC measurements (Donovan, 1979; Biliaderis et al., 1980; Eliasson, 1980; Ghiasi et al., 1982). In excess water systems (>67%) a single, sharp endothermic transition results. This transition respresents the melting of crystallites (Ghiasi et al., 1982; Zeleznak and Hoseney, 1987). When starch was heated 10C/min in excess water, strong gelatinization endotherms were observed with half-widths of 8-10C. The intensity of the gelatinization endotherms diminished, as starch was heated with progressively less water, and a new endotherm appeared at higher temperatures as water was decreased. Thus, wheat

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starch does not gelatinize below 30-32% moisture (wet basis) while at 42% moisture it 'gelatinizes' at approximately 100C (Derby et al., 1975; Donovan, 1979; Wootton and Bamunarachchi, 1980). However, the condition or states of water in starch and water dispersion also influence starch gelatinization.

Maurice et al. (1985) reported DSC measurements of starch heated in the presence of an intermediate level of water caused both the amorphous and crystalline structure of starch to undergo transitions. In excess water, water acts as a plastisizer depressing the glass transition temperature of the amorphous regions permitting sufficient mobility of chains for the crystallites to melt. Thus, the glass-transition temperature (T_g) of the amorphous phase would be slightly lower than the 'melting' or endothermic transition of the crystallites (T_m). When water becomes limiting, higher temperatures are required to exceed T_g. In limited water systems, T_g could control where T_m occurs.

ROLE OF SUGARS ON STARCH GELATINIZATION

The effect sugars on starch gelatinization is increasing the temperature of gelatinization rather than inhibiting the process. In cake baking, altering the

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gelatinization temperature is influential to the cake structure, especially the volume and contour (Osman, 1975; Bean et al., 1978). Bean et al. (1978) reported that optimum cake structure was obtained at starch gelatinization temperature of approximately 90C. Inhibiting starch granule swelling, decreasing available water, lowering water activity and forming of bridges (or interactions) are proposed mechanisms of sugars by many researchers for increasing the temperature of the starch gelatinization process (Glicksman, 1969; D'Appolonia, 1972; Derby et al., 1975; Lelievre, 1976; Bean and Yamazaki, 1978; Donovan, 1979; Wootton and Bamunuarachchi, 1980; Evans and Haisman, 1982; Spies and Hoseney, 1982; Lelievre, 1984).

Inhibition of starch granule swelling by sugars was hypothesized based mainly on viscosity changes (Bean and Yamazaki, 1978; Lelievre, 1984). The viscosity of a starch dispersion increases as starch granules swell. A higher temperatures of maximum viscosity with the addition of sucrose implies that the swelling of starch granule is inhibited by the presence of sucrose.

Cheers and Lelievre (1983), however, reported that sucrose in the range 0-20%, w/w, caused an increase in the swelling volume of wheat starch. If the sucrose concentration was greater than 20% (w/w), a decrease in swelling volume occurred. Bean and Yamazaki (1978) observed

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microscopically that faster and more apparent swelling of granules occurs in 30 and 50% sucrose solutions than in water alone. Glicksman (1969) stated that sucroses's high solubility could tie up the water and inhibit granule swelling by rendering water unavailable to the starch.

Less available of water in the system was considered to result because sucrose easily hydrogen bonds with water in solution and, thus, lowers the amount of free water in the system (Lelievre, 1976). Therefore, less water is available for the starch and the gelatinization process is delayed.

However, if sucrose limits the available water with hydrogen bonding, Donovan (1979) noted that the DSC endotherms would be broadened at the same onset temperature and the enthalpy (ΔH_g) of gelatinization should change with sugar concentration. But Spies and Hoseney (1982) found that the onset temperature increased with increasing sugar concentrations and the endotherms were broadened with a single sharp peak. A nonlinear relationship between ΔH_g and the available water was reported by Wootton and Bamunuarachchi (1980). Therefore, increasing of the gelatinization temperature by sugars is not simply from lowering the available water in the system, but water binding might be involved in causing the increased gelatinization temperature.

Water activity (a_w) changes by sugars was proposed by

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Evans and Haisman (1982). Solutes such as sugars are known to decrease water activity. Decreasing water activity by adding sugars in water changes the ability of water or chemical potential of water to interact with other components in the system (Spies and Hoseney, 1982). They suggested that a lowered water activity required more energy for any chemical or physical reactions involving water and thus, the gelatinization temperature was increased. However, increased gelatinization temperatures with different sugars at the same water activities implied that water activity alone was not responsible for the increased temperature of gelatinization.

Interaction of sugars and starch were hypothesized with the assumption that sugars were able to penetrate the starch granule (Spies and Hoseney, 1982; Lelievre, 1984). Spies and Hoseney (1982) assumed that the sugars form bridges within the starch granule and these bridges stabilize the amorphous regions of the granules. Longer chains, up to molecular weight of 800 (Brown and French, 1977), can bridge more gaps and increase the number of the hydrogen bonds than shorter chains. As more bonds are formed, the flexibility of chains decreases and more energy is required to pull the crystallites apart. Thus gelatinization temperature is increased requiring more energy to destabilize the starch granules. Sugar-sugar interactions could result in longer

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bridges or act as longer molecular weight compounds, which can increase the gelatinization temperature (Mathlouthi et al., 1980; Mathlouthi and Luu, 1980; Richardson et al., 1987b).

Antiplasticizing effects of sugars on starch gelatinization with decreasing free water volume was noted by Slade and Levine (1987). Water alone is a plasticizer in the amorphous regions of starch granules. The mobility of the polymer chains increases and the free volume also increases. However, when sugar/water cosolvent exists, the plasticizing effect is decreased. As the molecular weight and volume of the solvents increase, the ability to act as a plasticizing agent and free water volume decreases. Thus, the temperature of starch gelatinization increases.

Generally, lower molecular weight and smaller molecules have lower mobilization points. All substances with especially low mobilization points have small highly polar molecules each with groupings capable of forming firm hydrogen bonds (Duckworth, 1981). Solutions of the monosaccharides, glucose or fructose raised the gelatinization temperature of starch, but to less extent than the disaccharides, sucrose or maltose (Osman, 1975; Bean et al., 1978; Hansen et al., 1989). On the contrary, Spies and Hoseney (1982) reported that sucrose raised onset temperature of gelatinization to a greater extent than

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maltotriose, a molecule of greater molecular weight. Slade
and Levine (1987) reported the following order: water alone
< galactose < xylose < fructose < mannose < glucose <
maltose < lactose < maltotriose < 10-DE maltodextrin <
sucrose as the order of elevation of gelatinization
temperature of native wheat starch with a series of 1:1:1
sugar:water:starch mixtures studied with DSC. This increase
in gelatinization temperature was not in accordance with an
increase in molecular weight. Therefore, the molecular
weight of solvent and differences in free volume alone have
not explained the increased gelatinization temperature.

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CHAPTER 1

^{17}O NMR STUDIES ON WHEAT STARCH-SUCROSE-WATER INTERACTIONS WITH INCREASING TEMPERATURE

ABSTRACT

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

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INTRODUCTION

Quality of food products is altered by the temperature at which starch gelatinizes in relation to other occurences and ingredients within each product. During gelatinization of starch, many changes are influenced by the water. The importance of the amount of water on the gelatinization of starch in a starch-water dispersion has been reported by many researchers using 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 one to understand the molecular changes in a system (Jaska, 1971; Leung et al., 1979; Leung and Steinberg 1979; Lechart et al., 1980; Lechart, 1981; Nagashima and Suzuki, 1981; Lang and Steinberg, 1983; Wynne-Jones and Blanshard, 1986; Richardson et al., 1987a,b,d; Fanni et al., 1989).

NMR techniques have been developed to observe molecular mobilities in a variety of foods systems such as instant starch gel, protein, sucrose solution, wheat doughs, breads, vegetables (Leung et al., 1979, 1983; Lechart et al., 1980; Halle et al., 1981; Lang and Steinberg 1983; Richardson et al., 1987a; Richardson, 1988). The ^{17}O NMR has been shown to be the most effective of NMR methods for the observation of

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water mobility (Halle et al., 1981; Richardson et al., 1986, 1987a,b,c).

Most NMR studies on starch systems involved heating the system to a defined temperature and investigating the associated changes from the heating (Lechert, 1981; Richardson et al., 1986). New NMR techniques had to be developed to study dynamic changes in the 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 gelatinization process 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 those interactions are probably involved in the suggested mechanisms. Therefore, observations of changing water mobility as the temperature is increased might give us a better understanding of the starch gelatinization process

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regarding 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 temperature from
35 to 87C (308-360K); 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 is increased.

METHODS AND MATERIALS

Sample preparation

Wheat starch (Aytex^a, Olgivie Mills, Inc.) was used for
all investigations. Reagent grade sucrose (Fisher
Scientific) was used for sucrose-starch systems. Reverse
osmosis distilled water with 0.5% enriched ^{17}O water ($H_2^{17}O$;
ISOTEC INC., A Matheson Co.) was prepared with 0.15% xanthan
gum (Ketrol T, Kelco) solution that were used to disperse
the starch to prevent sedimentation (Hansen et al., 1987).
Sucrose solutions of 0.5, 1.0, and 1.5 M concentrations were

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prepared using the enriched ^{17}O 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 $4\pm1C$ overnight and allowed to equilibrate at room temperature $(22\pm2C)$ just prior to making the NMR spectroscopic measurements. For the DSC measurements, each concentration of a sucrose solution was injected into the DSC pan containing the starch at either a 10, 20, or 30% level (weight basis). The DSC pan was sealed hermetically.

NMR measurement

A Bruker WM-400 NMR spectrometer was used for the ^{17}O NMR spectra. Samples were injected into a 10mm (id) NMR sample tube. Data for enriched ^{17}O water $(H_2^{17}O)$ solutions were acquired with the following conditions: a spectrometer frequency of 54.234 MHz, a sweep width of 5000 Hz, a 90° pulse width of 27.0 us, 4K data points, broad band proton (^1H) decoupling and a 205 msec acquistion time with no delay. The ^1H 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

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was from 35 to 87C (308-360K) and samples were held 5 min at each 2K temperature interval before data was acquired. Lineshapes were evaluated in terms of least squares fit of the peaks to a Lorentzian equation after application of a 10 Hz line broadening. Linewidths (ΔV_{obs}) were half-height values for the water peak at each temperature. Transverse relaxation rate (R_2; sec^{-1}) was calculated according to Richardson et al. (1987b):

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

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

The primary assumptions made for the ^{17}O NMR measurement in this study were: 1) Line width is the same as T_2; this is not always true but is convenient for small molecules such as water. 2) Only one type of ^{17}O present; that nuclei was measured.

DSC measurement

A Perkin-Elmer DSC-4 with a Fis Systems Flexicooler temperature controller was used for the determination of thermal properties of all sample systems. A sensitivity of

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0.5 mcal/sec, heating rate of 2.5C/min and chart speed of 5mm/min were used. Samples were heated from 10 to 130C. 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 cal/g dry starch. For each wheat starch-sucrose-water system, the mean and standard deviation of least three determinations were obtained.

RESULTS AND DISCUSSION

Comparisons of R_1 at various starch concentrations

In the ^{17}O NMR measurements, transverse relaxation rate (R_2) directly monitors water mobility. According to this, a change of water mobility is detectable based on the extent of hydrogen bonding or interaction with other molecules. As the amount of water associatied with the starch changes and the temperature increases, a changing R_1 value is observed. The R_1 changes of 10, 20, 30, and 60% starch-water dispersions with increasing temperature are shown in Fig. 1. Results observed on the 30% starch system in Fig. 1 indicate R_2 increased from approximately 49C (322K) to a maximum value at 53C (326K) and then gradually decreased as temperature increased. After the R_2 maximum, the point of

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minimum water mobility, the gradual decrease of R_2 indicated a smaller and less rapid increase in water mobility was obtained. In a previous study, increasing R_2 in NMR measurements corresponded with the loss of birefrigence or swelling of starch granules (Jaska, 1971). Starch gelatinization is a continuous process involving the melting of crystallites and 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 inside of the granule. This swelling stage might be reversible (Jaska,1971; Maningat and Seib, 1987). 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, probably the water was 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

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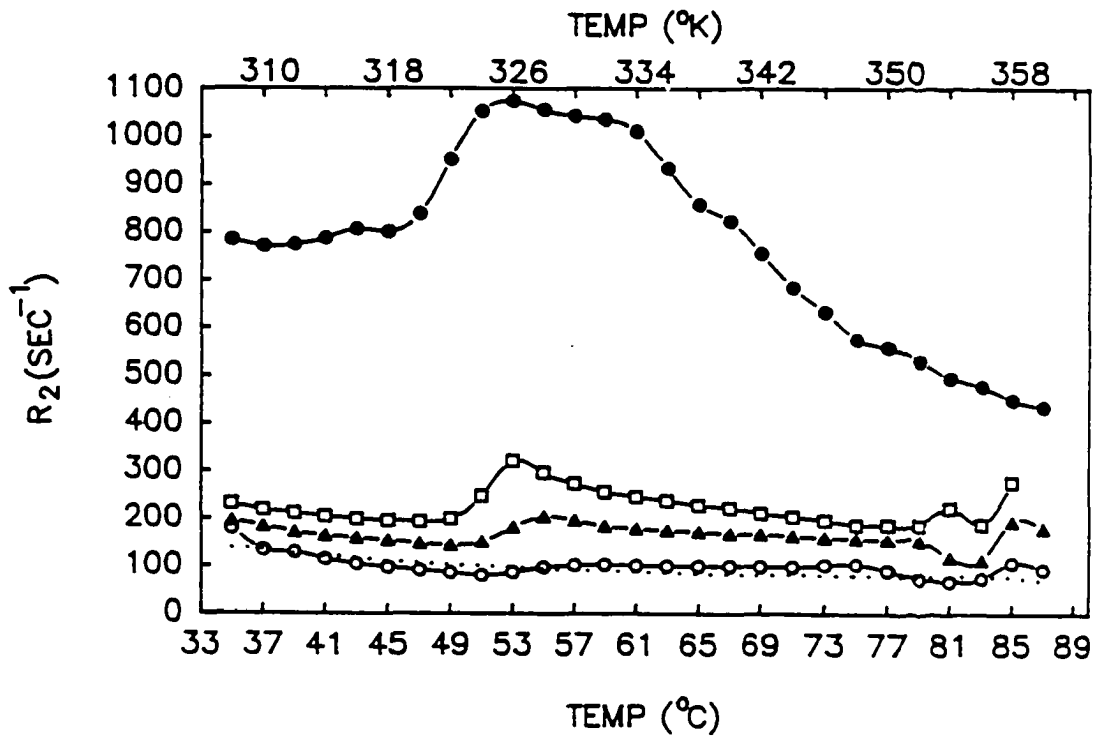
Fig. 1 - Transverse relaxation rates (R_2) of the starch-water dispersions as a function of increasing temperature (O——O ; 10%, ▲——▲ ; 20%, □——□ ; 30%, and ●——● ; 60% starch concentration).

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in the system as Jaska (1971) suggested.

On the other hand, Bean and Yamazaki (1978) mentioned that the diameter of the starch granules using hot stage microscopy correspondingly increased with viscosity as measured by amylograph between 58 and 70C. Thus, the increased viscosity that occurred during the swelling of the granules (Maningat and Seib, 1987) 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 Fig. 1 depicts a water only (free water) system. The R_1 in the free water and the 10% starch dispersion were similar. The 10% starch system had less water associated with starch compared to other systems. Therefore, the higher water mobility indicate the more free water available in the system over the entire temperature range.

A small fraction of water molecules hydrogen bonded to macromolecules increases 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.

The main reason of running samples up to 87C (360K) was to make sure all samples, even high concentration systems (eg. 30% starch-1.5M sucrose-water dispersion), were

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measured in high enough temperature ranges for the complete
gelatinization process. In all Figures in this study,
inexplainable curves were noted above 79C (352K). Air
bubbles or broken gels were found in some samples after
measurements. Possibly the instrument measured oxygen of
not only in sample system but also of bubbles as an artifact
of heating.

Comparisons of R_1 at various sucrose concentrations

Fig. 2 contains comparisons of R_1 for water at varied
sucrose concentrations. The overall relaxation rate (R_1)
gradually increases as concentration of sucrose-water
solution increases and decreases as temperature increases.
In previous work, the NMR lines were broadened by viscosity
effects at higher concentrations in sugar solutions and thus
decreased the water mobility (Tiat et al., 1972; Allen and
Wood, 1974). Generally molecular motion is faster at
higher temperature. Tiat and co-workers (1972) reported
that the R_1 from a single spin-echo measurement increased
with glucose concentration and showed a linear relationship
with / T that followed the extended Debye equation
($_r$ = $4\pi a^3$ / T). Although they observed a linear
relationship over wide temperature range (2-63C) for 2.8 M
glucose-water solution, R_2 had an inverse relationship with

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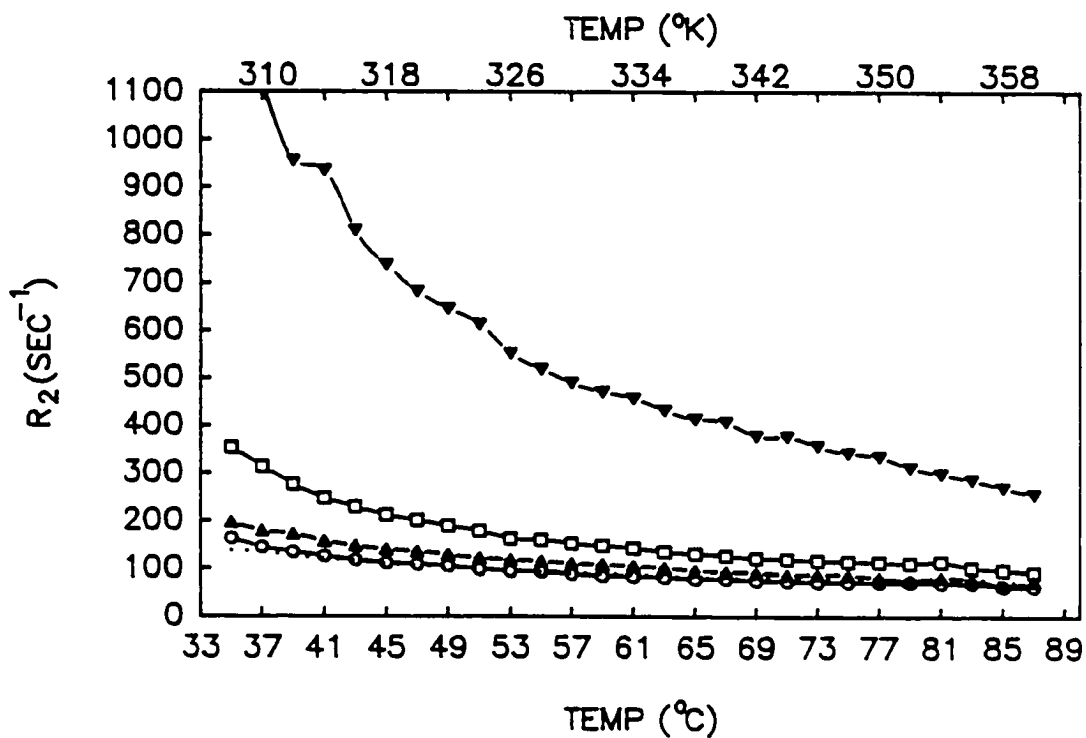
Fig. 2 - Transverse relaxation rates (R_2) of the sucrose-water solutions as a function of increasing temperature (O——O ; 0.5M, ▲——▲; 1.0M, □——□ ; 1.5M, and ▼——▼ ; saturated sucrose concentration).

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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. Schneider (1963) found that intrinsic viscosity
showed an inverse relationship with temperature at 30% and
up to 86% concentrations in the measurements of sucrose
solution viscosities over a temperature range of 5-80C.

Futhermore, 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, it would be expected
that the ^{17}O transverse relaxation rate (R_2) was higher with
increasing solute (sucrose) concentrations until the
saturated sucrose concentration was reached.

According to Richardson et al. (1987c), sucrose
solution at concentrations ranging from 5 to 40% (0.5 and
1.0M sucrose systems) showed linear relationships between R_2
and concentration based on the population of water
associated more with sucrose ('solute water') and water less
associated with sucrose ('free water') in the 20C system.
They assumed nonlinearity in the region from 40 to 60% that
resulted from: i) formation of intermolecular hydrogen bonds
between water and sucrose; ii) hydrogen bond bridging of
water and sucrose molecules; and iii) sucrose-sucrose

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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 0-25C (Garrod and Herrington, 1970), water mobility could be reduced with viscosity increases as sucrose concentration is increased via sucrose-water interaction and/or other possible interactions as was noted in this study. Thus, the overall tendency of water mobility to increase at the high temperature in each system possibly was from the decreasing viscosity of the systems that allowed faster molecular motion.

Wheat starch-sucrose-water dispersions

<u>Effect of increasing sucrose concentrations</u>   The changes in R_2 with the varied sucrose concentrations as a function of temperature at 10, 20, and 30% starch concentrations are graphed in Fig. 3, 4, and 5, respectively. The overall tendency of R_2 to increase with temperature is similar for 10, 20, and 30% starch concentrations. However, if sucrose concentration was

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TEMP (°K)
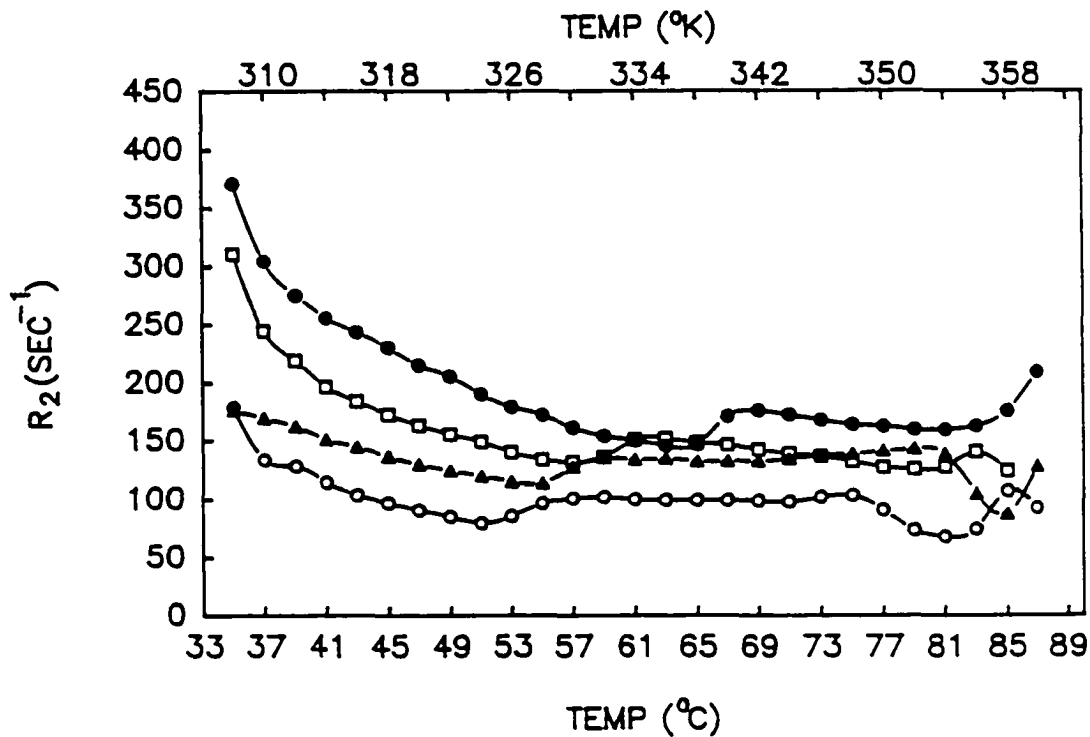
Fig. 3 - Transverse relaxation rates (R_2) of the 10%
starch-sucrose; O—O -0.0M, ▲—▲ -0.5M, □—□ -1.0M, and
●—● -1.5M concentration-water dispersions as a
function of increasing temperature.

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Fig. 4 - Transverse relaxation rates (R_2) of the 20% starch-sucrose; O—O -0.0M, ▲—▲ -0.5M, □—□ -1.0M, and ●—● -1.5M concentration-water dispersions as a function of increasing temperature.

50

TEMP (°K)
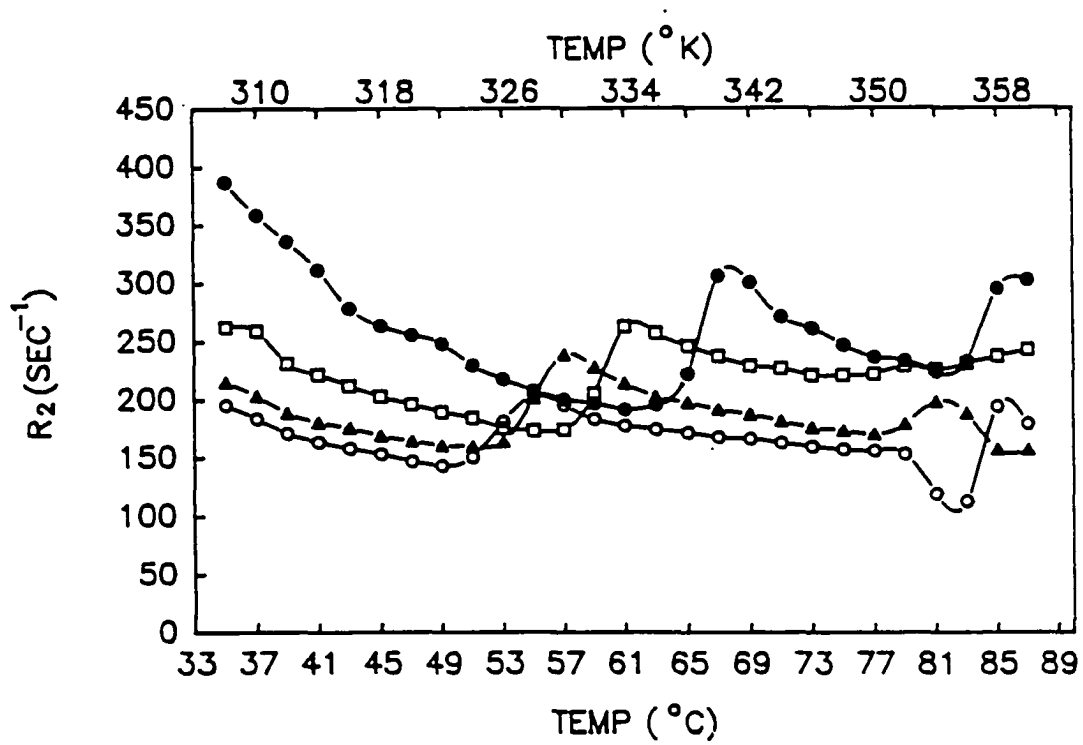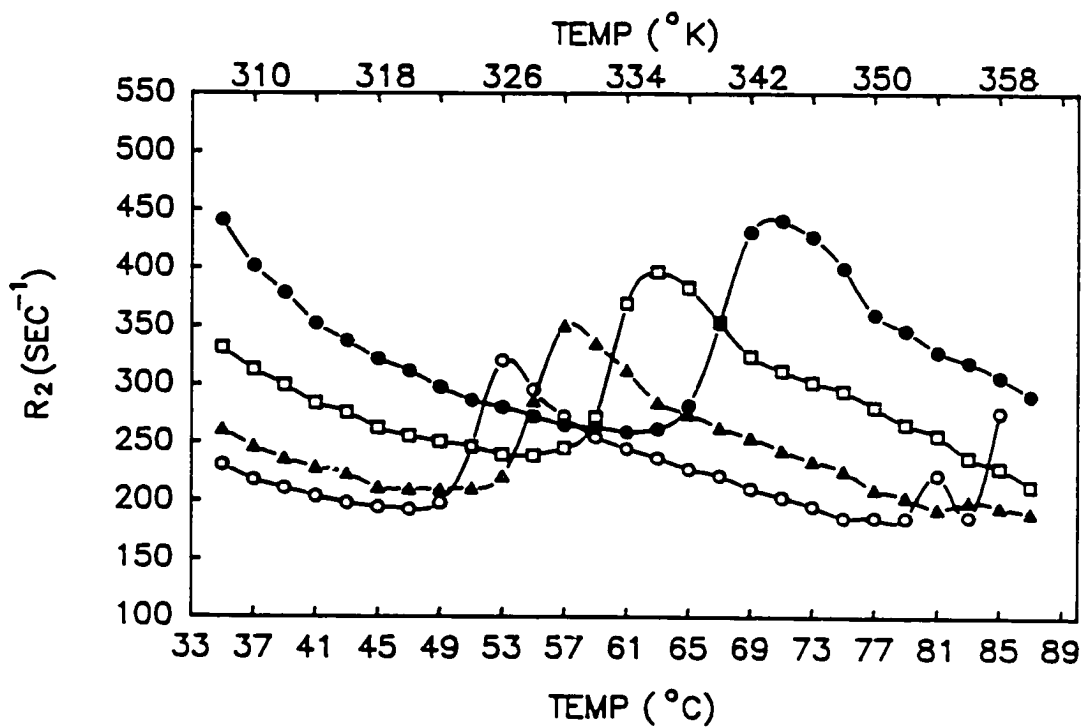
Fig. 5 - Transverse relaxation rates (R_2) of the 30%
starch-sucrose; O——O -0.0M, ▲——▲ -0.5M, □——□ -1.0M, and
●——● -1.5M concentration-water dispersions as a
function of increasing temperature.

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increased from 0 to 1.5M at the same starch concentration, R_2 and the temperature at which R_2 maximum occurred were gradually increased.

Possibly water mobility decreases with viscosity from the sucrose concentration through the sucrose (solute)-water interaction as observed in Fig. 2. The temperature differences for the R_2 maximum among samples at the same starch concentration depended on the sucrose concentration. For example, at the 30% starch concentration (Fig. 5), the temperature of R_2 maximum appeared at about 53, 57, 63, and 71C for 0, 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 1). The temperatures observed by R_2 are about 5° earlier than the DSC onset temperature of gelatinization. These results agreed with Hansen et al. (1989). They observed major deviations of chemical shift of sucrose prior to onset temperature of gelatinization with ^{13}C NMR measurements. Changes in chemical shifts of sucrose between sucrose solution and sucrose-starch dispersions were speculated as an interaction between the sucrose and starch rather than as conformational changes in the sucrose molecules. Sobczynska et al. (1990) presumed that sucrose directly interacted with

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Table 1 - Comparison of mean* onset temperature, peak
temperature and enthalpies (ΔH) for various
concentration of starch-sucrose-water dispersions

Dispersion	Onset temp(°C)	Peak temp (°C)	ΔH (Cal/g)
10% starch	55.1	59.2	0.3518
10% - 0.5M	60.9±0.56	65.3±0.27	0.1068±0.01
10% - 1.0M	67.9±1.40	72.6±0.90	0.1003±0.04
10% - 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
20% - 1.0M	68.3±0.92	72.6±0.40	0.2063±0.03
20% - 1.5M	75.9±0.66	80.6±0.66	0.2262±0.02
30% starch	55.5	60.5	0.5811
30% - 0.5M	61.6±1.22	66.0±0.80	0.2943±0.06
30% - 1.0M	69.1±0.68	73.4±0.52	0.3100±0.02
30% - 1.5M	77.5±0.34	82.0±0.51	0.3099±0.02

* Mean of least three measurements

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the glucose residues of the starch to increase the rigidity prior to 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 1), and the increased temperature for the point of R_1 maximum (Fig. 3, 4, and 5) as sucrose concentration of the system increased are noted in this regard. This possibility was also suggested earlier by Spies and Hoseney (1982) in two ways: 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) Sucrose-water interactions are indicated if sugar or any small solute is added to water 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 decreased, resulting in higher energy requirements.

Effect of increasing starch concentrations   The change of R_1 with 10, 20 and 30% starch concentrations at the 0, 0.5, 1.0, and 1.5M sucrose concentrations are illustrated in Fig. 6, 7, 8, and 9, respectively. Increasing the proportion of starch relative to the sucrose

resulted in increased R_2 values, but the water mobility
changes at the various starch concentrations at the same
sucrose concentration occurred within a relatively narrow
temperature range. 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 Fig. 6 through 9
appear to reflect the differences of starch concentrations
rather than sucrose concentrations. The greater starch
(polymer)-water interaction probably resulted in a higher
R_2. Both the R_2 level and the temperature of the R_2 maximum
increased as sucrose concentrations increased at the same
starch concentration, but apparently starch was more
responsible for the decreasing water mobility and sucrose
was more responsible for increasing the temperature at which
the R_2 maximum (minimum mobility) occurred.

All results (Fig. 3 through 9) imply that a wheat
starch-sucrose interaction or a starch-sucrose-water
interaction influences 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 resulted in the high R_2 values (Fig.
3 through 9), indicating a lower water concentration and
higher R_2 via both polymer and solute effects. Generally,

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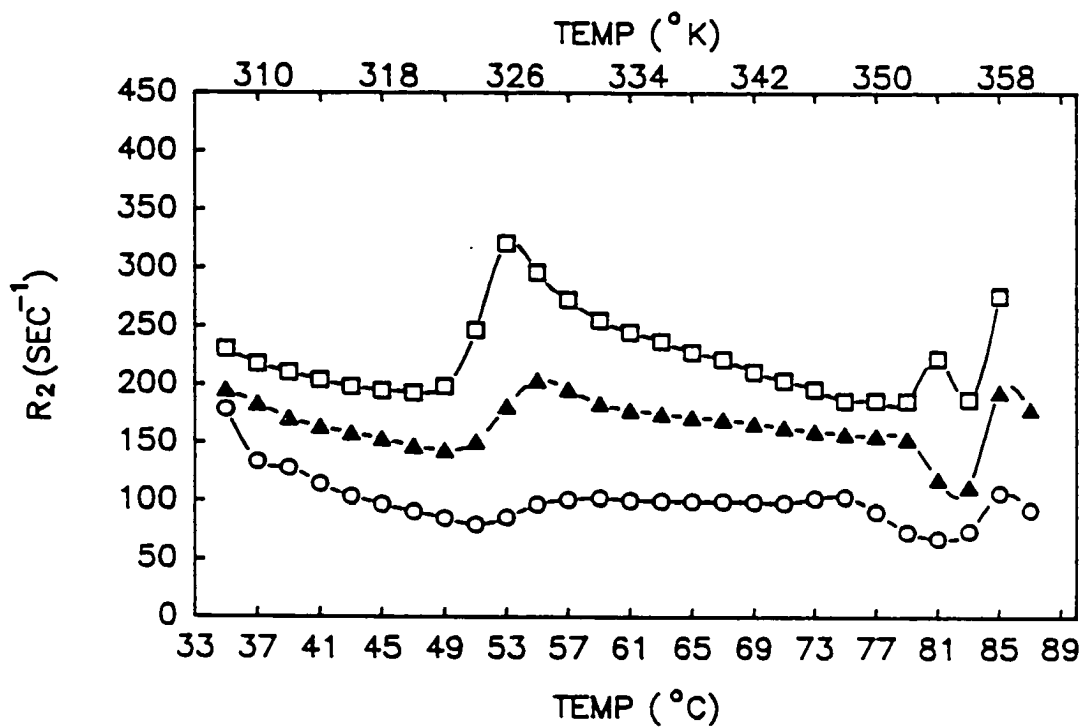
Fig. 6 - Transverse relaxation rates (R_2) of the starch;
O——O -10%, ▲——▲ -20%, and □——□ -30% starch
concentration-0.0M sucrose-water dispersions as a function
of increasing temperature.
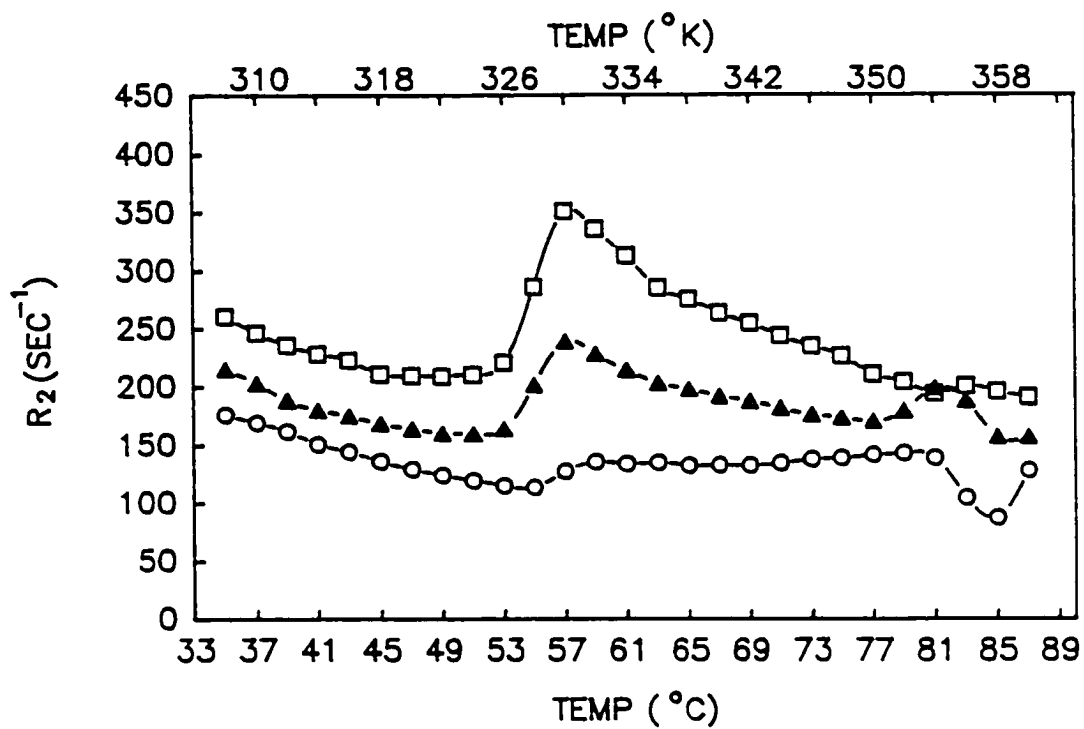
Fig. 7 - Transverse relaxation rates (R_2) of the starch;
O——O -10%, ▲——▲ -20%, and □——□ -30% starch
concentration-0.5M sucrose-water dispersions as a function
of increasing temperature.
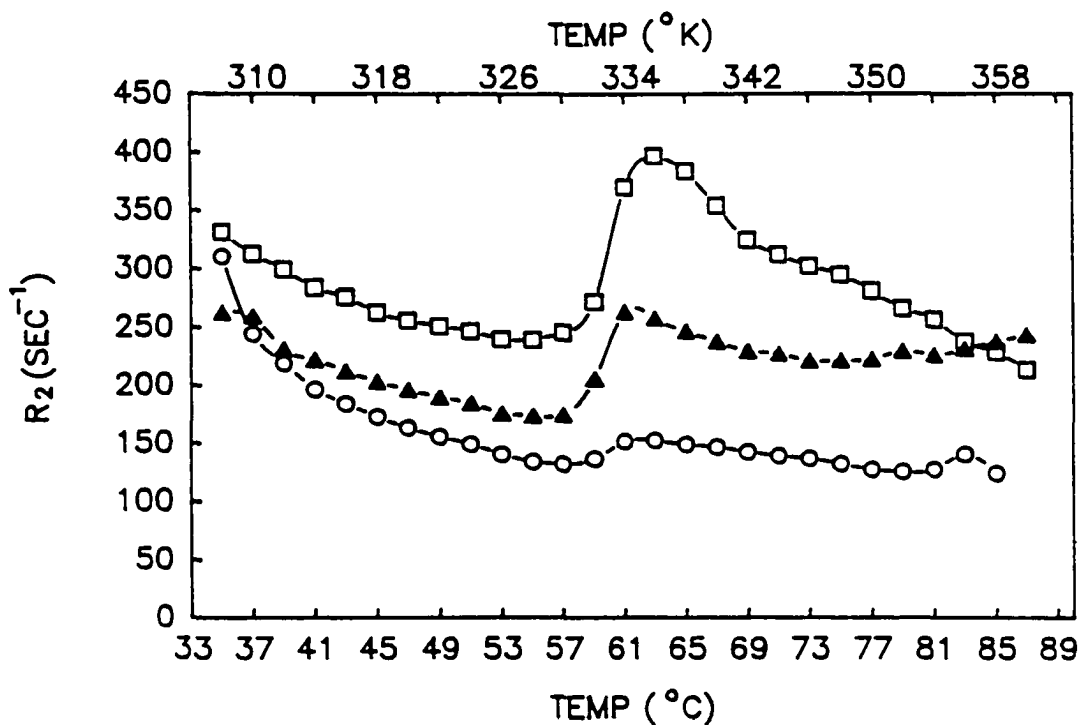
Fig. 8 - Transverse relaxation rates (R_2) of the starch;
O——O -10%, ▲——▲ -20%, and □——□ -30% starch
concentration-1.0M sucrose-water dispersions as a function
of increasing temperature.

TEMP (°K)

R$_2$(SEC^{-1})

TEMP (°C)
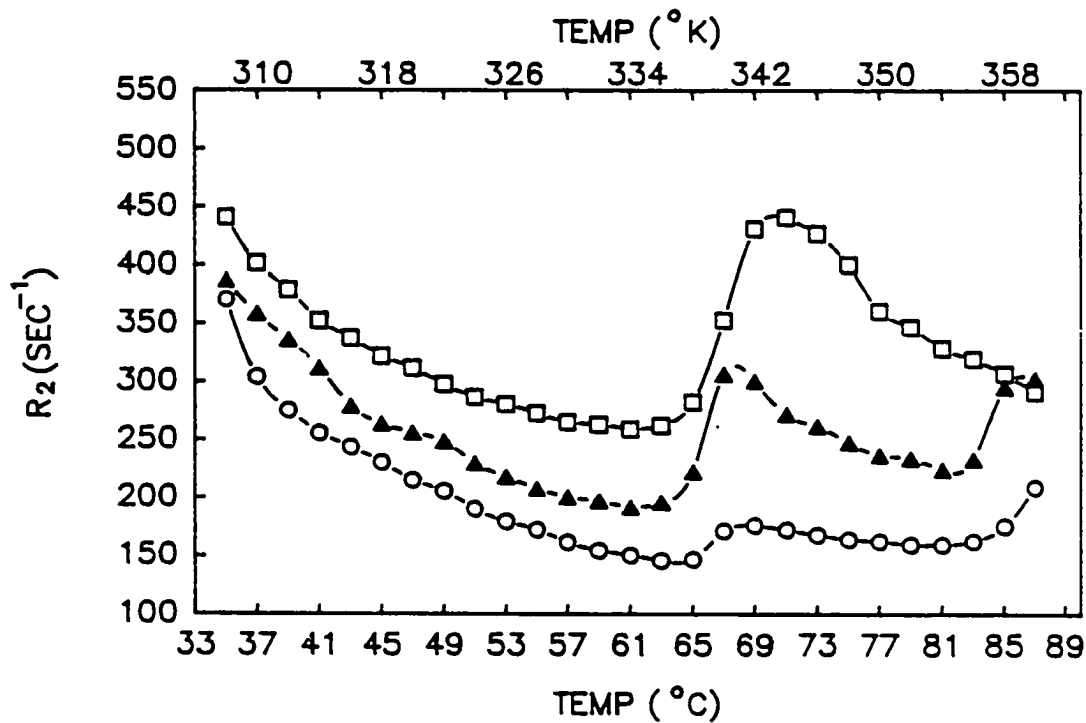
Fig. 9 - Transverse relaxation rates (R$_1$) of the starch;
O——O -10%, ▲——▲ -20%, and □——□ -30% starch
concentration-1.5M sucrose-water dispersions as a function
of increasing temperature.

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the higher R_2 indicated a greater polymer-water or solute-water interaction. This agrees again with the results of Suggett et al. (1976) and Richardson et al. (1987a,b,c).

If we consider starch as a partially crystalline, glassy polymer (Maurice et al., 1985; Bilaideris et al., 1980), water acts as a plasticizer for starch to depress the glass transition temperature of the amorphous regions and permit sufficient mobility of chains for the crystallites to melt. However, when solutes such as a sucrose are added to the system, less water is available to act as a plasticizer and the swelling of starch granules could be restrained. Consequently, the gelatinization temperature is increased and enthalpy decreased (Table 1) and the overall water mobility is decreased (Chungcharoen and Lund, 1987). Water uptake by the systems is controlled by the chemical potential of water. The assumption was made 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 granules just prior to 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

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sucrose-starch interactions lowered the chemical potential of water by decreasing water activity (the available water) or 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.

CONCLUSIONS

1. Wheat starch and sucrose both increased the R_2 or decreased the mobility of water 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.

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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CHAPTER 2

COMPARISONS OF WATER MOBILITY AMONG FOUR DIFFERENT SUGARS;

GLUCOSE, MALTOSE, MALTOTRIOSE, AND SUCROSE

ABSTRACT

Water mobility in wheat starch-sugar (glucose, maltose, maltotriose, and sucrose)-water dispersions was observed as temperature was increased from 35 to 87C by measuring the transverse relaxation rate (R_2) from the ^{17}O nuclear magnetic resonance (NMR) spectra. The changes of water mobility with different sugar dispersions exhibited similar patterns. The increased temperatures at which the R_2 maximum occurred and the magnitude of the R_2 maximum increased as molecular weight and concentration of sugar dispersions were increased. Structural differences appeared to influence the rate of water mobility changes at the same molecular weight. Limited starch granule swelling seemed to occur with the 20% starch-1.5M maltotriose-water dispersion and to influence the changes of R_2.

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INTRODUCTION

Some work has indicated that a water's ability to act as a plasticizing agent during starch gelatinization generally decreases as molecular weight and concentration of sugar solution is increased (Chungcharoen and Lund, 1987; Slade and Levine, 1987). Longer sugars up to molecular weight of 800 (Brown and French, 1977) can bridge a larger space and induce more bonding with starch chains than shorter sugars. The flexibility of the starch chains would be diminished, and the gelatinization temperature increased requiring more energy to pull the crystallites apart (Spies and Hoseney, 1982).

Solutions of monosaccharides, such as glucose and fructose, increased the gelatinization temperature of starch but to a lesser extent than disaccharides, such as sucrose or maltose (Osman, 1975; Bean et al., 1978; Hansen et al., 1989). Spies and Hoseney (1982) reported, however, that sucrose raised onset temperature of gelatinization to a greater extent than maltotriose, a molecule of greater molecular weight. Slade and Levine (1987) measured 1:1:1 sugar:water:starch mixtures using DSC. They reported increasing gelatinization temperature with varied sugars in the following order: water alone < galactose < xylose < fructose < mannose < glucose < maltose < lactose <

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maltotriose < 10-DE maltodextrin < sucrose. This increase in gelatinization temperature did not follow an increase in molecular weight for all cases. Therefore, involvement of other factors was suggested.

The ability to penetrate the starch granule and to interact with starch chains also increases gelatinization temperature (Spies and Hoseney, 1982; Hansen et al., 1989). Brown and French (1977) reported that oligosaccharides with molecular weights less than 800 are able to penetrate the starch granules along with water. In addition, sugars' ability to interact with itself and/or with water also affects water mobility and could reduce plasticizing effects and increase gelatinization temperature (Richardson et al., 1987; Hansen et al., 1989; Sobczynska et al., 1990).

The sucrose study reported in Chapter 1 showed that water mobility of a starch-sucrose-water dispersion was closely related to the starch-sucrose-water interaction. The major water mobility changes with NMR measurements occurred prior to the onset temperature of gelatinization as observed by DSC measurements in the same type starch-sucrose-water dispersions. Lower molecular weights and smaller molecules, in general, had lower mobilization points (Leung et al., 1976, 1979; Duckworth, 1981). The molecular weight, structure and chain length of glucose, maltose, maltotriose and sucrose are different. Glucose, maltose, or

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maltotriose-starch-water dispersions were compared to the sucrose system in this study 1) to observe whether glucose, maltose, and maltotriose have similar effects on water mobility as sucrose and, 2) to determine if any factor can be isolated that causes changes of water mobility in wheat starch-sugar-water model systems as temperature is increased from 35 (308K) to 87C (360K) by comparing glucose, maltose, and maltotriose .

MATERIALS AND METHODS

All materials and methods were the same as given in Chapter 1 unless otherwise specified. The D-glucose (dextrose) and maltose were purchased from Fisher Scientific Co. and maltotriose was purchased from Sigma Chemical Co. Only 20% (weight basis) wheat starch with 0.5, 1.0, and 1.5M of each sugar system was measured.

RESULTS AND DISCUSSION

Glucose-starch-water dispersion

Changes of water mobility for 20% starch with 0, 0.5, 1.0, and 1.5M glucose concentrations (glucose dispersions)

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with increasing temperature are shown in Fig. 2. Glucose
dispersions (Fig. 2) showed similar changes when compared to
sucrose-starch-water dispersions (sucrose dispersions) (Fig.
1). The transverse relaxation rate (R_2) and R_2 maximum
temperature increased with increasing glucose concentrations
but to a lesser extent than did the sucrose dispersions
(Fig. 1). For example, the maximum R_2 at 59C (332K) of the
1.5M glucose dispersion was about 250, whereas for the 1.5M
sucrose dispersion this value was about 320 at 67C (340K).
Likewise, the 1.0M and 0.5M glucose dispersions were lower
than the values of the corresponding sucrose dispersions.
These results agree with the supposition that a lower
molecular weight results in a lower water mobility (Leung et
al.,1976, 1979). Glucose ($C_6H_{12}O_6$) has six hydrogen bonding
sites for water molecules compared to sucrose's eleven
($C_{12}H_{22}O_{11}$). Fewer hydrogen bonding sites probably results in
more free water and less restricted water mobility in the
glucose dispersions that were reflected in the lower overall
R_2 changes and increased temperatures of the R_2 maximum with
glucose dispersions.

The DSC measurements for each system are given in Table
1 and support the NMR results. The water mobility changed
prior to onset temperature of gelatinization as it did for
the sucrose dispersions, and the onset temperatures of 0.5,
1.0, and 1.5M glucose dispersions were lower than for the

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Fig. 1 - Transverse relaxation rates (R_2) of the 20% starch-sucrose; O—O - 0.0 M, ▲—▲ - 0.5M, □—□ - 1.0M and ●—● -1.5M concentration-water dispersions as a function of increasing temperature.

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Fig. 2 - Transverse relaxation rates (R_2) of the 20%
starch-glucose; O——O - 0.0 M, ▲——▲ - 0.5M, □——□ -.
1.0M and ●——● -1.5M concentration-water dispersions as
a function of increasing temperature.

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same concentrations of sucrose dispersions. For example, onset gelatinization temperature of the 1.5M glucose system was about 62C (335K) and, for the 1.5M sucrose dispersion, onset temperature was about 76C (349K). The pattern of the overall R_1 changes of glucose dispersions was similar to that of sucrose dispersions, but all changes were to a lesser degree.

Maltose-starch-water dispersion

Changes of water mobility for 20% starch with 0, 0.5, 1.0, and 1.5M maltose concentrations (maltose dispersions) with increasing temperature are given in Fig. 3. The changes and overall patterns again were similar to the sucrose dispersion. The overall R_1 values and the temperature at which the R_1 maximum occurred were slightly lower compared to the sucrose dispersions (Fig. 1). The R_1 maximum for the 1.5M maltose dispersion was about 200 at 65C (338K) and about 220 at 67C (340K) for sucrose. Likewise, the DSC results were similar as indicated in Table 1; onset temperature of maltose gelatinization was slightly lower than for sucrose at each concentration, an effect that was less noticeable at the high concentration.

The molecular weight and the number of hydrogen bonding sites of maltose ($C_{12}H_{22}O_{11}$; M.W. 342) are the same as sucrose
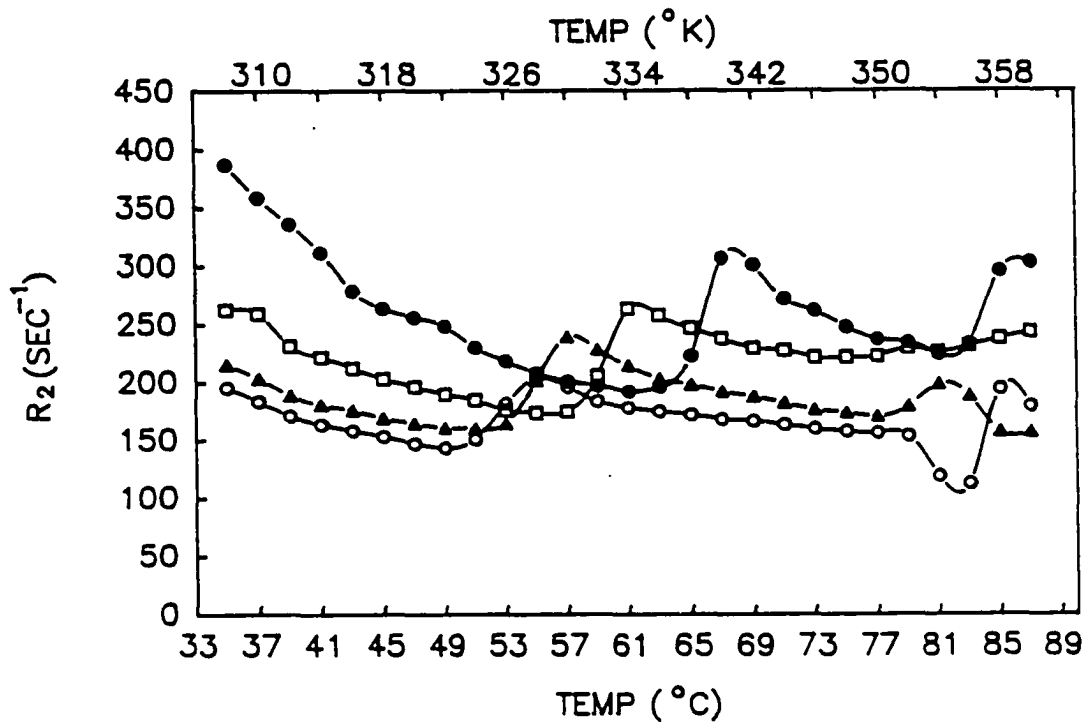
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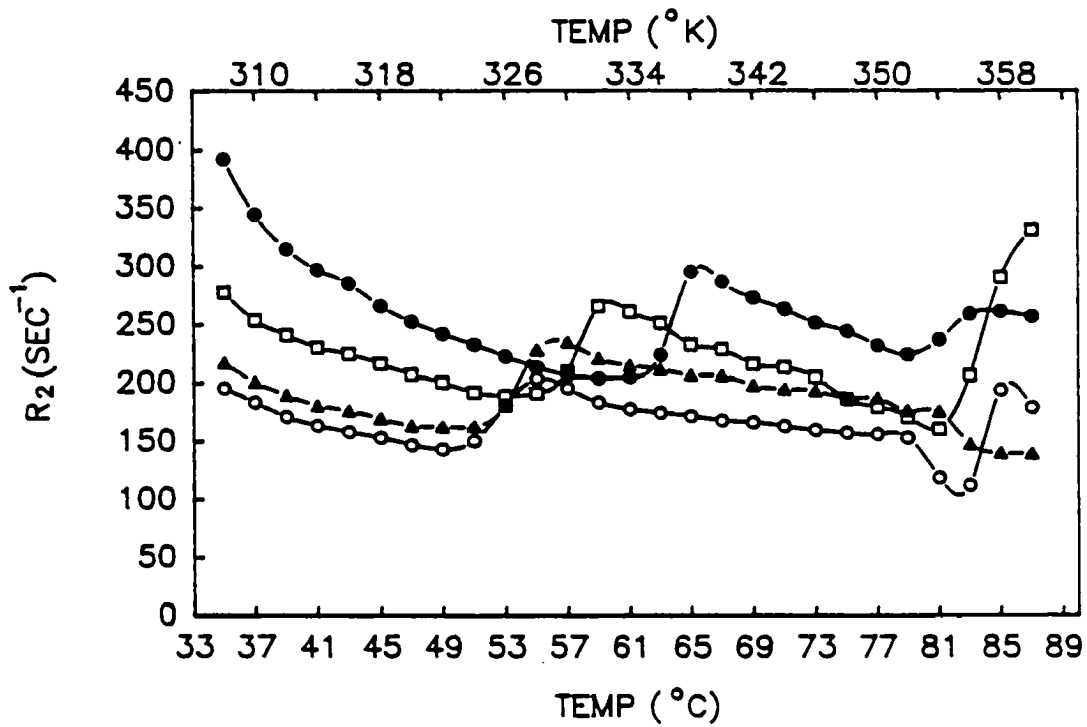
Fig. 3 - Transverse relaxation rates (R₂) of the 20% starch-maltose; O—O- 0.0 M, ▲—▲ - 0.5M, □—□ - 1.0M and ●—● -1.5M concentration-water dispersions as a function of increasing temperature.

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($C_{12}H_{22}O_{11}$; M.W. 342). However, structurally, maltose is composed of two molecules of glucose, whereas, sucrose has a glucose (pyranose ring) and a fructose (furanose ring) in the molecule. When sucrose reorients and associates with water, the pyranose ring of glucose interacts more favorably with water molecules (Allen and Wood, 1976; Sugget and Clark, 1976; Mathlouthi and Luu, 1980; Shallenberger, 1982). The furanose ring of fructose is known to participate in intramolecular hydrogen bonding for dimerization. This dimerization between glucose and fructose molecules increases the energy of vibration, which could decrease the mobility or increase the onset temperature of gelatinization (Mathlouthi and Luu, 1980; Mathlouthi et al., 1980). In addition, sucrose chains are possibly less flexible because of the two prime carbons that have CH_2OH groups in the fructose molecule (Shallenberger, 1982). Maltose interacts with the water readily because the two pyranose rings of glucose are mobile and flexible. These differences in structural features might explain the slight differences in water mobility patterns and onset temperatures of gelatinization between the two molecules having the same molecular weight.

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Maltotriose-starch-water dispersion

The changes of water mobility for 20% starch with
various concentrations of maltotriose (maltotriose
dispersions) shown in Fig. 4 were basically similar to the
sucrose dispersions (Fig. 1). Overall, the water mobility
changes and the R_1 maximum with maltotriose dispersions
(Fig. 4) were much greater than for the same concentrations
of sucrose dispersions (Fig. 1) at the same starch
concentrations. The 1.0M maltotriose dispersion had a
maximum R_1 of about 400 at 67C (340K) compared to about 270
at 61C (334K) for the 1.0M sucrose dispersion.
Interestingly, 1.5M maltotriose dispersions had a smaller R_1
maximum (about 350 at 81C) than the 1.0M maltotriose
dispersions (about 400 at 67C), even though, both are
greater than was noted for the 1.5M sucrose (about 320 at
67C). The 1.5M maltotriose dispersion was expected to have
a higher R_1 than the 1.0M maltotriose dispersion.
Maltotriose has a larger molecular weight (M.W. 504) and
longer chain length with three α-1,4 linked molecules of
glucose within the structure ($C_{18}H_{32}O_{16}$). The previous study
(Chap. 1) with sucrose showed that starch mainly increased
the R_1 and sucrose mainly increased the temperature at which
R_1 maximum occurred. Therefore, swelling of starch granules
that increase the R_1 was probably hindered by certain

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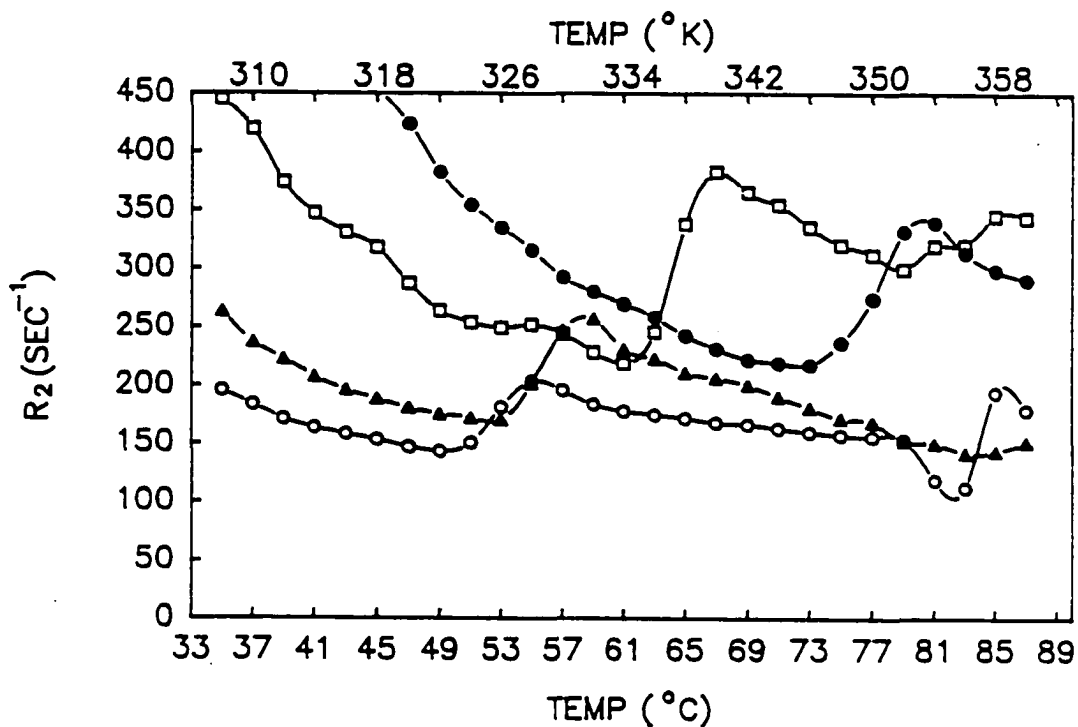
Fig. 4 - Transverse relaxation rates (R_2) of the 20%
starch-maltotriose; O—O - 0.0 M, ▲—▲ - 0.5M, □—□
- 1.0M and ●—● -1.5M concentration-water dispersions
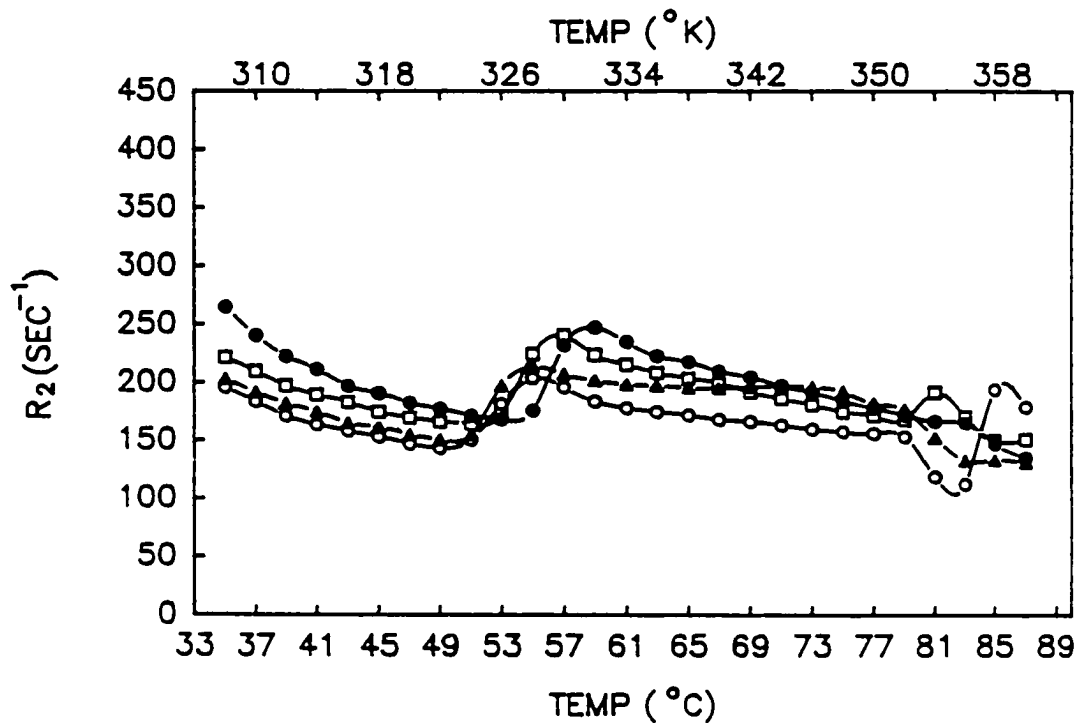as a function of increasing temperature.

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factor(s) with the 1.5M maltotriose dispersion.

Possibly, maltotriose, molecular weight of 504, is able to penetrate the starch granule as others have suggested (Brown and French, 1977; Spies and Hoseney, 1982; Hansen et al., 1989), but at the higher 1.5M concentration, less was needed to restrict starch swelling. The longer chain compared to sucrose or maltose could have resulted in more interactions with the starch chain for an equivalent concentration, which increased the temperature of starch gelatinization to a greater extent. However, because not as much maltotriose needed to penetrate the granule at the higher 1.5M concentration, more could have remained outside the granule to bind with the water, decreasing the available water outside the granule to bind with the starch, decreasing the water mobility so that it was lower than for the 1.0M system (Fig. 4). This result agrees with the thermal analysis results of DSC as shown in Table 1.

The onset temperatures of gelatinization of 0.5M, 1.0M and 1.5M maltotriose dispersions given in Table 1 were higher than those of the sucrose dispersions. This result contradicts previous studies (Spies and Hoseney, 1982; Slade and Levine, 1987) when maltotriose had lower gelatinizaton temperature than the sucrose using 1:1:1 starch:sugar:water ratio. However, the concentrations of sugar in the starch-sugar-water dispersions in this study were higher. For

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Table 1 - Comparison of mean* onset temperature, peak temperature and enthalpies (ΔH) for 0.5, 1.0, and 1.5M glucose, maltose, maltotriose and 20% starch dispersions

Dispersion	Onset temp($^\circ$C)	Peak temp ($^\circ$C)	ΔH (Cal/g)
Sucrose			
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
Glucose			
0.5M	58.1±0.93	62.1±0.36	0.2753±0.11
1.0M	59.9±0.36	64.1±0.14	0.2886±0.11
1.5M	62.3±0.58	66.3±0.58	0.3076±0.13
Maltose			
0.5M	59.9±0.21	64.5±0.00	0.2119±0.02
1.0M	66.8±1.04	70.8±0.44	0.2465±0.15
1.5M	75.3±0.42	79.2±0.69	0.2395±0.06
Maltotriose			
0.5M	62.3±0.00	67.2±0.28	0.2377±0.01
1.0M	74.2±0.59	78.2±1.78	0.2931±0.12
1.5M	86.8±1.72	91.9±0.96	0.2687±0.04

* Mean of least three measurements

example, 1.0M or 1.5M maltotriose dispersion had approximately 1:2:2 or 1:3:1 starch:maltotriose:water ratios, respectively. The difference in onset temperature of gelatinization between sucrose and maltotriose dispersions in Table 1 became increasingly larger with increasing sugar concentrations. These results, higher onset temperature of gelatinization with maltotriose than sucrose are reasonable and support the idea that it increases with increased molecular weight, at least up to a point.

An interesting relationship between concentration and number of saccharide units among the sugars is also noted in Table 1. For example, 1.0M glucose (1 saccharide unit) and 0.5M maltose (half the amount of 2 saccharide units) showed almost the same onset temperature of gelatinization (59.9C). Likewise, 1.5M glucose (one and half the amount of 1 saccharide unit) and 0.5M maltotriose (half the amount of 3 saccharide units), and 1.5M maltose (one and half the amount of 2 saccharide units) and 1.0M maltotriose (3 saccharide units) also had very close onset temperature of gelatinization, 62.3 and about 75C, respectively. These results indicate that the number of saccharide unit and the concentration of sugars are likely an influential factors increasing the onset temperature of starch gelatinization.

In conclusion, the changes of water mobility with

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different sugar dispersions exhibited similar patterns. The
increased temperatures at which the R_1 maximum occurred and
the magnitude of the R_1 maximum increased as molecular
weight and concentration of sugar dispersions were
increased. The water mobility changes occurred prior to
onset temperature of gelatinization with all sugar
dispersions studied. Structural differences also influenced
the rate of water mobility changes and onset temperature of
gelatinization at the same molecular weight. Limited starch
granule swelling seemed to occur with the 20% starch-1.5M
maltotriose-water dispersion and to influence the changes of
R_1 but not the temperature that water mobility increased.

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CHAPTER 3

DETERMINATION OF VARIED WATER STATES IN WHEAT
STARCH-SUCROSE-WATER DISPERSIONS USING ^{17}O NMR MEASUREMENTS

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ABSTRACT

Amount of water associated with the starch (P_{pol}), sucrose (P_{sol}), and free water was determined using ^{17}O NMR transverse relaxation rates (R_2) with increasing temperature (35-87C). Observed values of free water (P_f^{obs}) in wheat starch-sucrose-water dispersions were used for comparisons with calculated values of free water based on a theoretical model (P_f^{th}). The P_f^{th} and P_f^{obs} generally decreased as the amount of dispersed substrates were increased. The P_{pol} and P_{sol} increased as starch and sucrose concentrations were increased and, water gradually associated more with starch and less with sucrose. The sequence of changes seems to occur in the following order: component interactions, water mobility changes, and starch gelatinization.

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INTRODUCTION

Proton, deuteron or ^{17}O NMR measurements can be used to understand the states of water in polymer-solute-water systems. Water interacts in various ways with solutes or polymers in biological systems, and interactions can be important in determining macroscopic physical properties (Leung et al., 1983).

Current theories involving 'relaxation rates' determined by NMR studies are more likely to explain the behavior of water than the earlier studies measuring 'bound' and/or 'free' water in food systems (Maurice et al., 1985; Slade and Levin, 1987). This is because unstable thermodynamic states and/or non-equilibrium melting behavior exist in various food systems. However, the terms, 'bound' and/or 'free' water, remain inevitable. Generally, water associated with macromolecules ('bound' water) shows higher transverse relaxation rates (R_2) with a highly restricted motion as determined with NMR measurements than water less associated with the macromocules. Thus, NMR studies observing R_2 can be used to speculate changes of water associated with macromolecules (components).

Varied environmental states of water are characterized by different relaxation times. In previous pulsed NMR measurements, no single exponential behavior of the

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spin-echo decay curve of water was interpreted as the presence of different types of water molecules with different relaxation times corresponding to different molecular mobilities (Leung et al., 1976, 1979; Di Nola and Brosio, 1983). For example, in dry starch, free water was differentiated from water with varied degrees of 'boundness' (Tait et al., 1972; Lechert and Schwier, 1982). Polymer and solute waters had different NMR responses and both coexisted in a food as bound water (Lang and Steinberg, 1983). Types of bound water were distinguished as polymer or solute waters based on the different relaxation rates.

The amount of the different water states was determined by several researchers (Leung et al., 1976, 1979; Brosio et al., 1978; Deodhar and Luner, 1980; Di Nola and Brosio, 1983; Chinachoti and Steinberg, 1986). The T_1 value from pulsed NMR measurements was considered a measure of the strength of water binding by Leung et al. (1976). They reported that the amount of water in the bound fraction was consistent among six different macromolecules, while Brosio et al. (1983) reported inconsistent water binding values for powdered milk that increased as total water increased. Di Nola and Brosio (1983) reported that the amount of bound water determined by pulsed NMR, if the exchange process was considered, agreed with the amount of unfreezable water as determined by other techinques. They claimed that the

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disagreement between the amount of bound water determined by pulsed NMR and unfreezable water determined by wide-line NMR resulted if the exchange process was ignored (Leung et al., 1976, 1979).

Chinachoti and Steinberg (1986) tried to calculate the polymer and solute waters quantitatively in a starch-sucrose model system. Equations were developed for calculating solute water and polymer water from longitudinal relaxation rate (T_1) of a low field (10 MHz) pulsed H_1 NMR and a_w. They reported high correlation ($r^2 > 0.97$) between T_1 and a_w. The T_1 increased with increasing sucrose content and decreasing a_w.

Sobczynska et al. (1990) calculated the free, solute and polymer water in starch-sucrose-water model systems as temperature increased using ^{17}O NMR relaxation rates (R_1). The portion of free water observed was compared to a theoretical portion that was calculated. The equations for calculating solute and polymer waters assumed that the R_1 of a saturated solution of solute (sucrose) and polymer (starch) were equal to the intrinsic relaxation rate for solute water and polymer water, respectively. The R_1 of free water also was considered as the intrinsic relaxation rate for free water.

Water in heterogeneous systems, such as a polymer-solute-water system, is usually distributed between

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several environments as different states of water with different intrinsic relaxation rates and resonance frequencies such as polymer water, solute water and free water (Richardson et al., 1987a,c; Fanni et al., 1989). In case of a starch-sucrose-water dispersion, water associated with starch molecules (polymer water), water associated with sucrose (solute water), and bulk water, which also is referred to as free water, could be noted (Sobczynska et al., 1990).

This work extended the study of Sobczynska et al.(1990) by extending the temperature ranges to 87C (360K) and using additional starch concentrations. The objectives of this study were: 1) to determine the amount of water associated with the starch (polymer water), sucrose (solute water), and bulk water (free water); 2) to compare the amount of free water calculated by a theoretical model to the experimentally observed values obtained from measurements of transverse relaxation rates (R_2); 3) to check the validity of the Sobczynska et al. (1990) assumptions; and 4) to observe the changing trends of solute and polymer water mobility as temperature increases from 35 (308K) to 87C (360K) in the concentrations of wheat starch and sucrose dispersions as related to the polymer-solute-free water model system.

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Theoretical model for portion of free, solute, and polymer water (Data Analysis)

NMR measurements of polymer, solute, and free water were related to a calculated model of water in a polymer-solute-free water system at various concentrations of each component. Correlation times for the water molecules in wheat flour were calculated to be 16.7 picoseconds (ps) for a quadrupole coupling constant of I=6.67 MHz, or 45.8 ps for I=4.03 MHz (Richardson et al., 1986). Correlation times for the sucrose-water systems were calculated to range from 100 ps to 9.5 ps depending on the hydration number assumed (Richardson et al., 1987b). Correlation time for free water at 300K is 2.40 ps (Halle and Wennerstrom, 1981). In these states, the water molecules can exchange a few orders of magnitude faster than the intrinsic relaxation rates and inverse resonance frequency. Inverse resonance frequency was equal to 18.4 nanoseconds (ns); thus, it was slow enough to fulfill the extreme narrowing condition. Assuming that tnere are only three different states of water in starch-sucrose-water systems, the observed relaxation rates in extreme narrowing situations can be written as population weighted averages as was done by Sobczynska et al.(1990):

$$R_{stsu} = [P_{sol} * R_{sol}] + [P_{pol} * R_{pol}] + [P_f * R_f]$$

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where R=relaxation, st=starch, su=sucrose, sol=solute, pol=polymer, f=pure or free water in a specfic system, and P=proportion.

The intrinsic relaxation rate for the bulk water in a heterogeneous system is, by definition, equal to the measured rate for a sample containing only the aqueous medium. The intrinsic relaxation rates for solute water were determined from the rates measured for a saturated solution of a solute, such as a sucrose. The intrinsic relaxation rate for polymer water is equal to the rate measured for a saturated solution of a polymer such as starch.

To calculate the portion of theoretical (th) free water, P_f^{th}, in a starch-sucrose-water dispersion and to test their validity, the following assumptions had to be made:

1) The starch-sucrose interaction in a starch-sucrose-water dispersion was negligible in the temperature ranges studied, and

2) The amount of water associated with starch, P_{pol}, and water associated with sucrose, P_{sol}, were the same in a starch-sucrose-water dispersion as they were for starch-water and sucrose-water systems at the same temperature and concentration.

The proportion of free water was calculated from the equation,

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$$P_f^{th} = 1 - P_{pol} - P_{sol} \qquad [1]$$

This value was compared to the value calculated from observed experimental (obs) data using the same assumptions given above.

$$P_f^{obs} = (R_{stsu} - P_{sol} * R_{sol} - P_{pol} * R_{pol}) / R_f \qquad [2]$$

In both cases, the portion of polymer water, P_{pol}, and the portion of the solute water, P_{sol}, were calculated from the same data used for the separate systems of starch-water and sucrose-water, respectively.

$$P_{pol} = (R_{st} - R_f) / (R_{pol} - R_f) \qquad [3]$$

$$P_{sol} = (R_{su} - R_f) / (R_{sol} - R_f) \qquad [4]$$

MATERIALS AND METHODS

All materials and methods were the same as given in Chapter 1 unless otherwise specified. A saturated sucrose solution was prepared with 0.5% enriched ^{17}O water ($H_2^{17}O$) with 0.15% xanthan gum solution by adding sucrose until sucrose crystal seeds appeared at above 90C. A 60% starch

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concentration was considered as a saturated starch solution.

RESULTS AND DISCUSSION

Portion of theoretical and observed free water

Theoretical free water (P_f^{th}) calculated from equation (1), for 10%, 20%, and 30% starch with 0.5, 1.0, and 1.5M sucrose concentrations as temperature increases is shown in Fig. 1, 2, and 3, respectively. Fig. 4, 5, and 6 are the based upon experimentally observed free water (P_f^{obs}) (eq. 2), for the same systems. Results from temperatures greater than 79C (352K) were not considered in this study because they likely are artifacts of heating as was noted in Chap. 1. Results show that increased starch concentration caused decreased free water availability based on observed data or the theoretically calculated values. For example, the P_f^{th} decreased as starch concentration was increased from 10% to 30% (Fig. 1-3). Sucrose concentration increases at any one concentration of starch further decreased free water. For example, the overall portion of free water was in order of 1.5M < 1.0M < 0.5M sucrose concentration at each of starch concentrations (Fig. 1-6). Fig. 4 through 6 indicate that the magnitude of the change of P_f^{obs} increased as starch
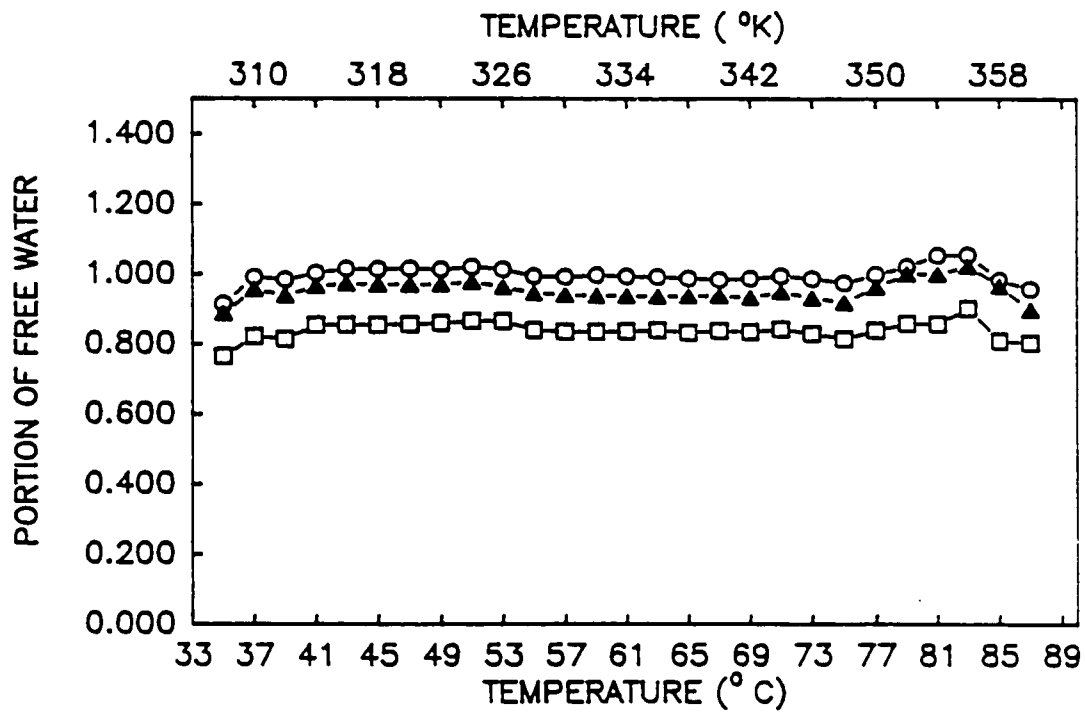
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Fig. 1 - Theoretical calculated portion of free water
(P_f^{th}) for 10% starch-sucrose; O—O - 0.5M, ▲—▲ - 1.0M,
and □—□-1.5M concentration-water dispersions as a
function of increasing temperature.

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TEMPERATURE (°K)

310   318   326   334   342   350   358
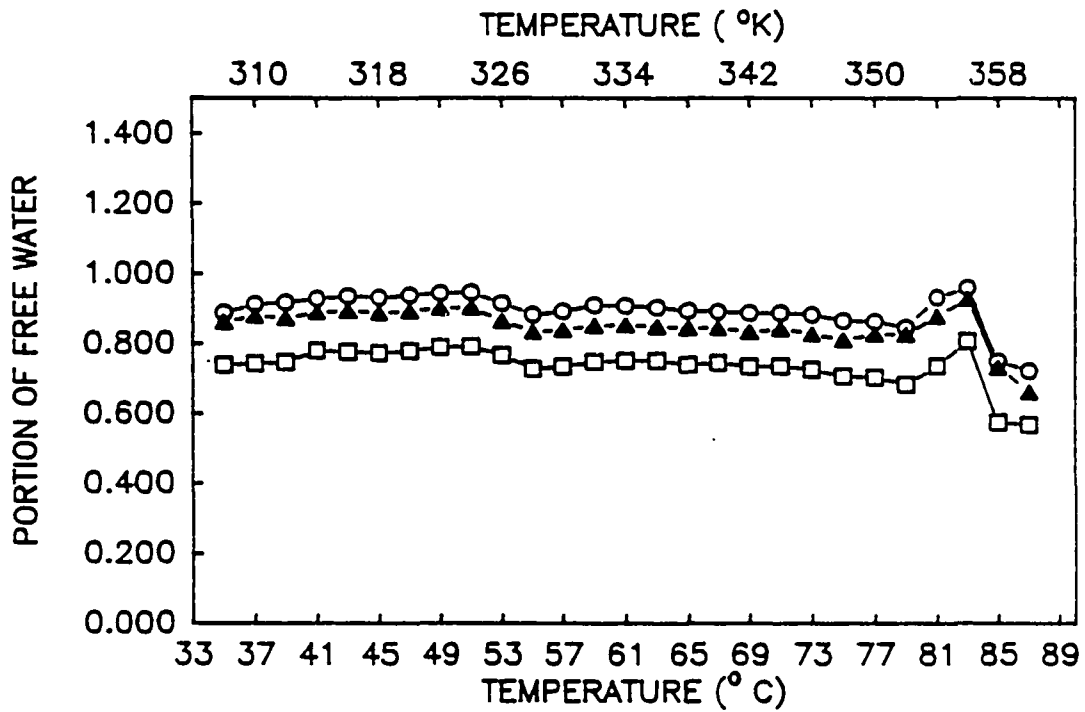
Fig. 2 - Theoretical calculated portion of free water
(P$_r^{th}$) for 20% starch-sucrose;O——O - 0.5M, ▲——▲ - 1.0M,
and □——□ -1.5M concentration-water dispersions as a
function of increasing temperature.

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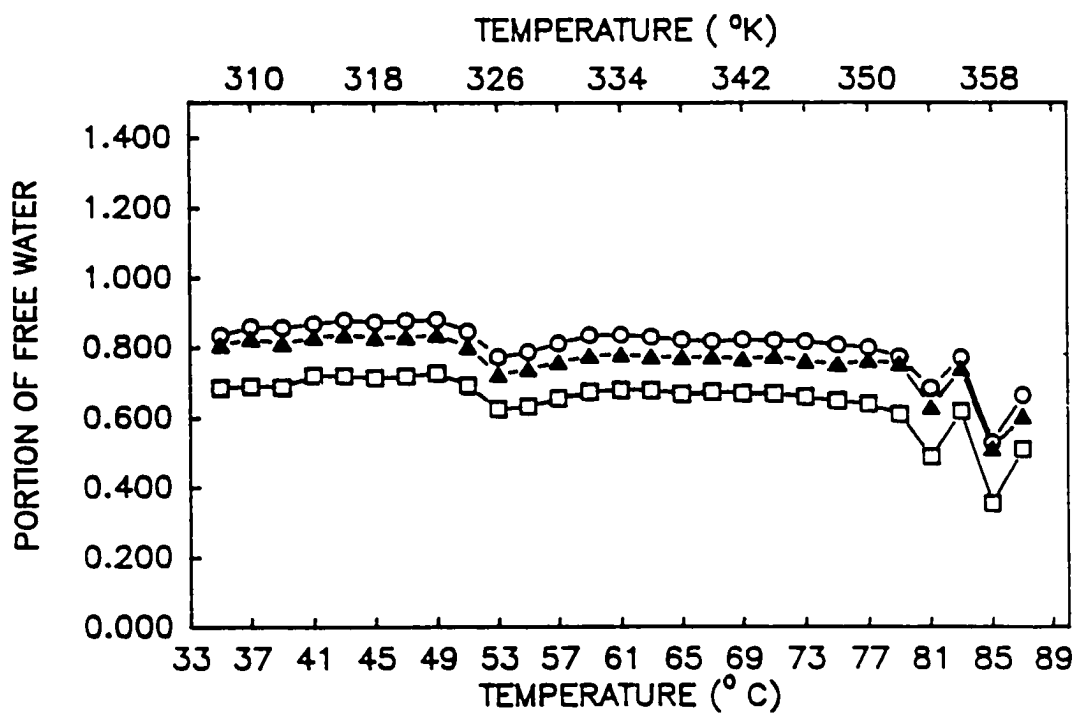
TEMPERATURE (°K)

Fig. 3 - Theoretical calculated portion of free water (P$_f^{th}$) for 30% starch-sucrose; O—O - 0.5M,▲—▲ - 1.0M, and□—□ -1.5M concentration-water dispersions as a function of increasing temperature.

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concentrations were increased with the different sucrose
concentrations from a minimum of approximately 0.5 to a
maximum value of 1.7 at 10% starch concentration (Fig. 4) to
-0.5 to 3.5 at a 30% starch concentration (Fig. 6). At the
same starch concentration, the P_t^{obs} also varied with sucrose
concentration over the temperature ranges studied. For
example, the 20% starch with 1.5M sucrose concentration
showed larger changes in the portion of P_t^{obs} than the 0.5M or
1.0M sucrose dispersions (Fig. 5). These results seem
reasonable because, at the same macromolecule concentration,
generally the higher solute concentration would restrict the
motion of water more than the lower solute concentration by
associating more tightly with macromolecules. Likewise, a
higher macromolecule concentration could associate more
tightly with solutes at the same solute concentration (Leung
et al., 1979).

The overall P_t^{th} for all dispersions was in order: 10%
starch:0.5M sucrose > 10% starch:1.0M sucrose > 20%
starch:0.5M sucrose > 10% starch:1.5M sucrose, 20%
starch:1.0M sucrose > 30% starch:0.5M sucrose > 30%
starch:1.0M sucrose > 20% starch:1.5M sucrose > 30%
starcn:1.5M sucrose. These results confirm generally the
results obtained by Sobczynska et al. (1990) that free water
decreases as the amount of dispersed substrates are
increased. However, the results with high sucrose

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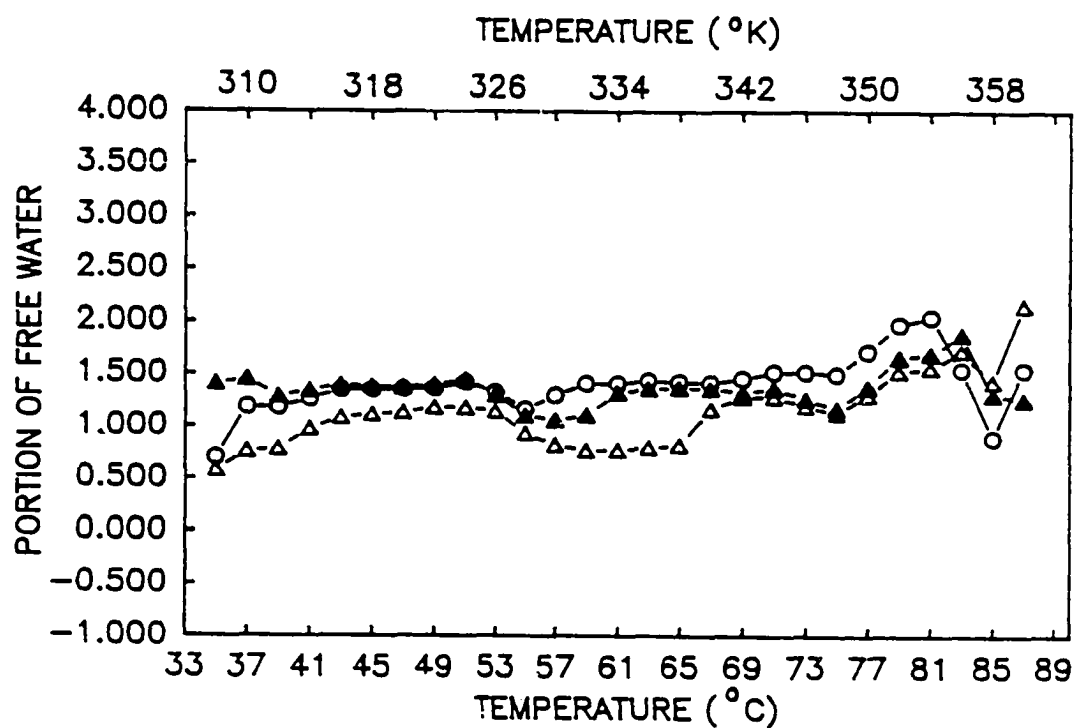
TEMPERATURE (°K)

Fig. 4 - Calculated portion of free water based on observations (P$_r^{\infty}$) for 10% starch-sucrose; O—O - 0.5M, ▲—▲ - 1.0M, and △—△ - 1.5M concentration-water dispersions as a function of increasing temperature.

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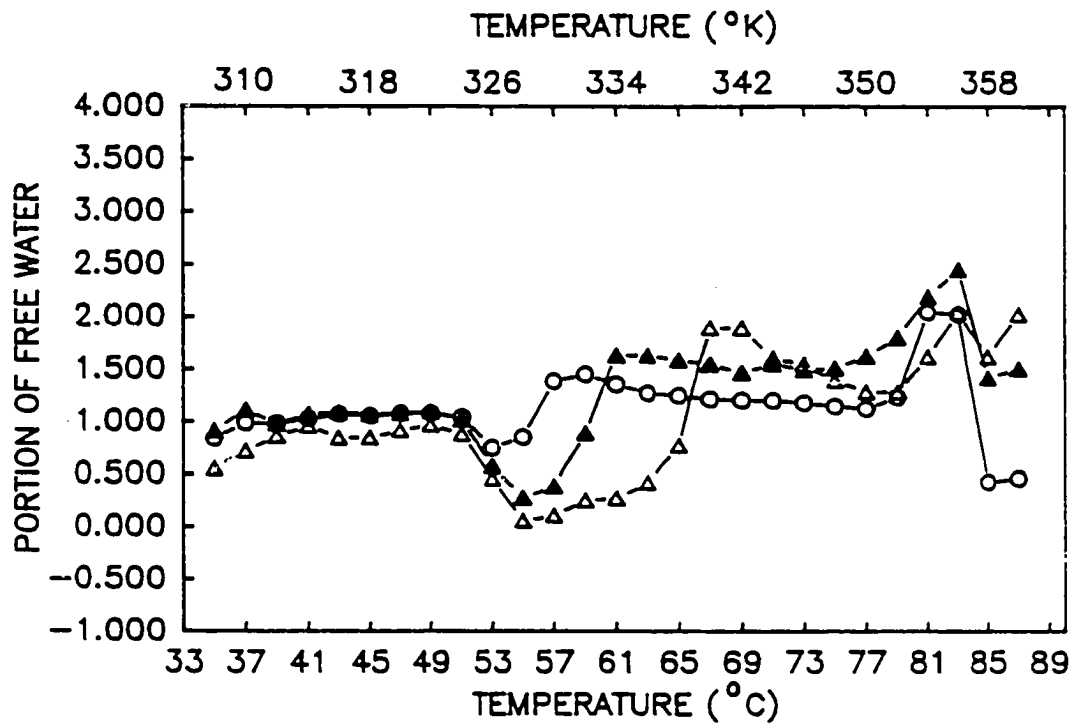
TEMPERATURE (°K)

Fig. 5 - Calculated portion of free water based on
observations (P_f^{obs}) for 20% starch-sucrose; O—O -
0.5M, ▲—▲ - 1.0M, and △—△ - 1.5M concentration-water
dispersions as a function of increasing temperature.

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TEMPERATURE (°K)

| 310 | 318 | 326 | 334 | 342 | 350 | 358 |
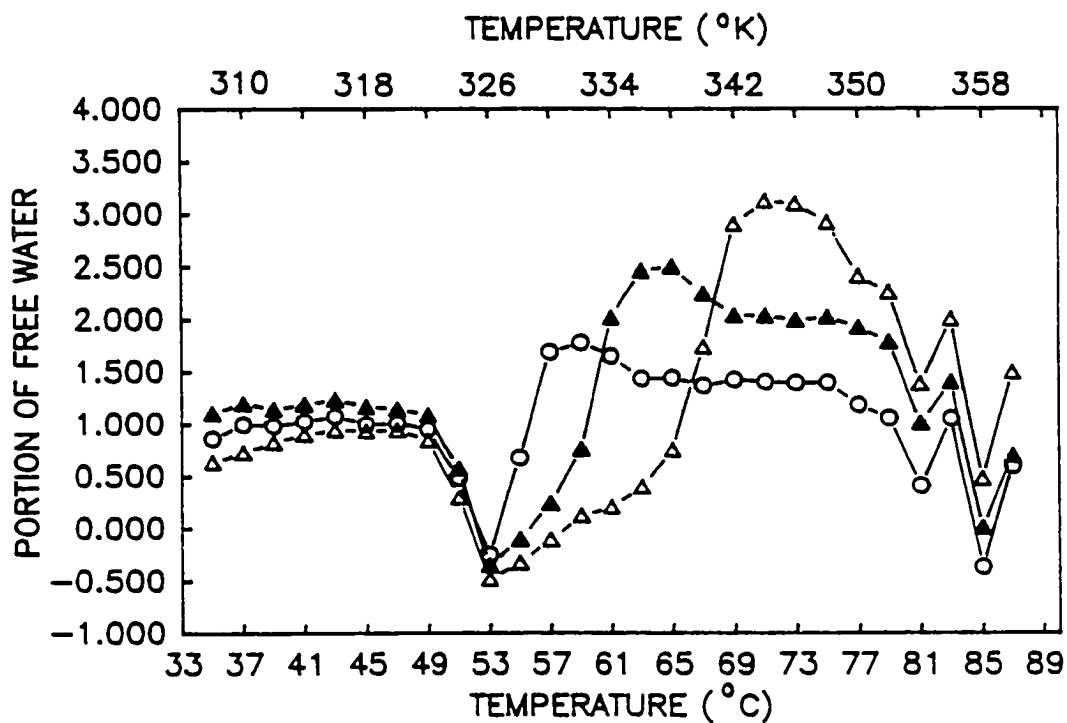
Fig. 6 - Calculated portion of free water based on observations (P_f^{obs}) for 30% starch-sucrose; O—O - 0.5M, ▲—▲ - 1.0M, and △—△ - 1.5M concentration-water dispersions as a function of increasing temperature.

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concentrations do not fit the pattern as neatly. For example, the amount of total dispersed substrates in the 10% starch:1.5M sucrose dispersion (40.6%) was lower than in the 20% starch:0.5M sucrose dispersion (41.6%); and, the 20% starch:1.5M sucrose dispersion (47.2%) was lower than the 30% starch:0.5M sucrose (48.9%) and 30% starch:1.0M sucrose dispersions (51.35%). Therefore, when sucrose concentration was high, the portion of free water did not always increase proportionally as dispersed substrates were increased. Also this was true for all sugars (glucose, maltose, and maltotriose) studied previously (Chap. 2) and, higher solute concentrations also increased the onset temperature of gelatinization with DSC measurements in this study.

The sucrose molecule ($C_{12}H_{22}O_{11}$) has eleven oxygen atoms, and each is a potential hydrogen bonding site for water molecules. At low sucrose concentrations, as Allen and Wood (1974) pointed out, each sucrose molecule is probably strongly associated with a number of water molecules, not exceeding eleven, and these molecules are in dynamic equilibrium with the remaining free water molecules. As the sucrose concentration increases, the number of free water molecules probably decreases according to these results. Allen and Wood (1974) reported that the solution consisted of a water structure strengthened by the presence of hydrated sucrose molecules at sucrose concentrations below

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30%. The amounts of substrates in the 1.0M and 1.5M sucrose systems with 0.15% xanthan gum were 30.5 and 34%, respectively. Futhermore, if starch is added to the sucrose solution, a competition will exist between sucrose and starch for the hydrogen bonding sites on the water molecules (Lelievre, 1976). As starch concentration increases, the number of free water molecules will decrease in the same mannner as for the sucrose solution. Thus, generally, less free water is present as the amount of dispersed substrates is increased. This held true at low concentrations of sucrose and/or starch however, at high concentrations it did not follow. The portion of free water seems to be influenced by other factors at high polymer or solute concentrations.

Changes of P_f^{th} and P_f^{obs} with increasing temperatures

Validation of assumption As in the previous study (Sobczynska et al., 1990), the overall change of P_f^{th} was relatively linear with small differences over the temperature ranges (Fig. 1-3) but, P_f^{obs} did not change linearly. Varied changes with increasing temperatures (Fig. 4-6) and the differences noted between P_f^{th} and P_f^{obs} for the same systems probably were a result of interactions. One of the assumptions of this study was that the

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interaction between starch and sucrose was negligible in a starch-water-sucrose dispersion. The calculation of P_f^{th} was done based on this assumption. The P_f^{th}, which was calculated using equation 1 (Fig. 1, 2, and 3) follows the assumption but P_f^{obs} which was calculated with equation 2 (Fig. 4, 5, and 6), does not. The observed data, R_{stsu} (eq. 2), which were determined experimentally, resulted in the differences between P_f^{obs} and P_f^{th}.

The polymer water (P_{pol}), solute water (P_{sol}), and free water of theoretical (P_f^{th}) and observed (P_f^{obs}) portions with 20% starch-sucrose-water dispersions were described in Fig. 7, 8, and 9. The only P_f^{obs} is noted dramatically different from P_f^{th}, P_{pol}, or P_{sol}. The P_{pol} and P_{sol} changed similarly with P_f^{th} over the temperature ranges studied. The P_{pol} (eq. 3) and P_{sol} (eq. 4) were obviously calculated without any interaction between starch and sucrose because they are only starch-water (P_{pol}) and sucrose-water (P_{sol}) systems, respectively. Equation 1 ($P_f^{th} = 1 - P_{pol} - P_{sol}$), assumes no interactions, thus P_f^{th} was similar to P_{pol} and P_{sol} in Fig. 7, 8, and 9. Therefore, these results suggest that the P_f^{obs} was altered by an interaction between starch and sucrose during the heating of the starch-sucrose-water dispersion over the temperature ranges studied confirming results noted by Hansen et al. (1989) in Chapter 1. However, the overall trends of P_f^{th} and P_f^{obs} as temperature increased were probably

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TEMPERATURE (°K)
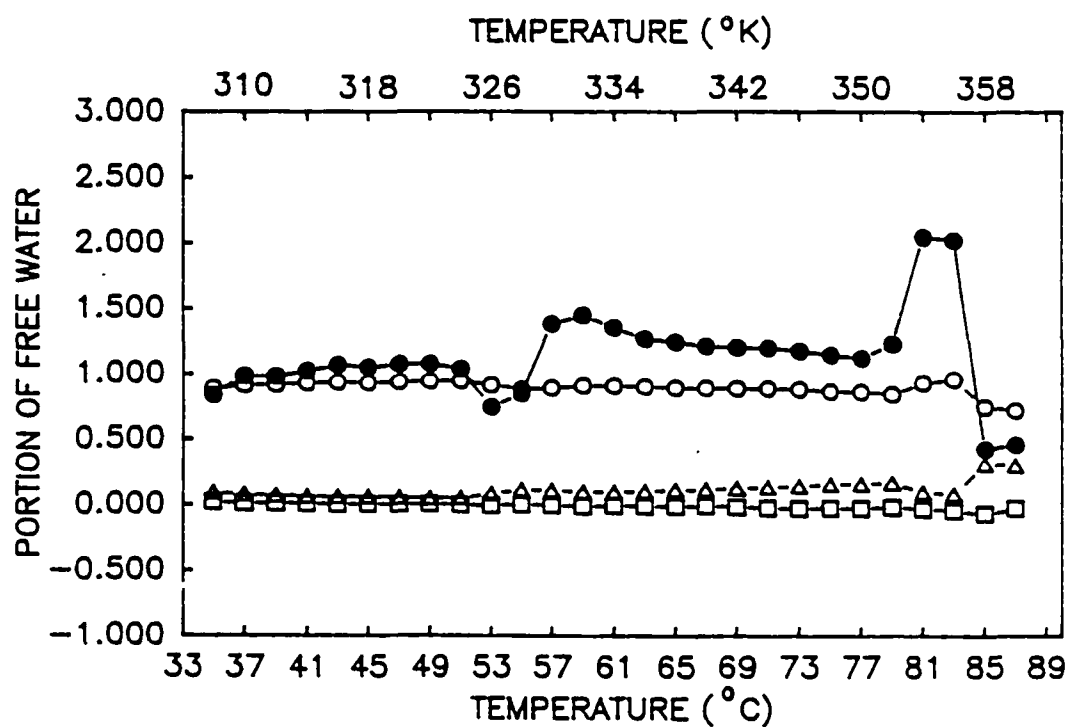
Fig. 7 - Comparison of portion of theoretical free water
(P_f^{th}; O——O), observed free water (P_f^{obs}; ●——●), polymer
water (P_{pol}; △——△), and solute water (P_{sol}; □——□) in
the 20% starch-0.5M sucrose-water dispersion.

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Fig. 8 - Comparison of portion of theoretical free water
(P_t^{th}; O——O), observed free water (P_t^{obs}; ●——●), polymer
water (P_{pol}; △——△), and solute water (P_{sol}; □——□) in the
20% starch-1.0M sucrose-water dispersion.

TEMPERATURE (°K)
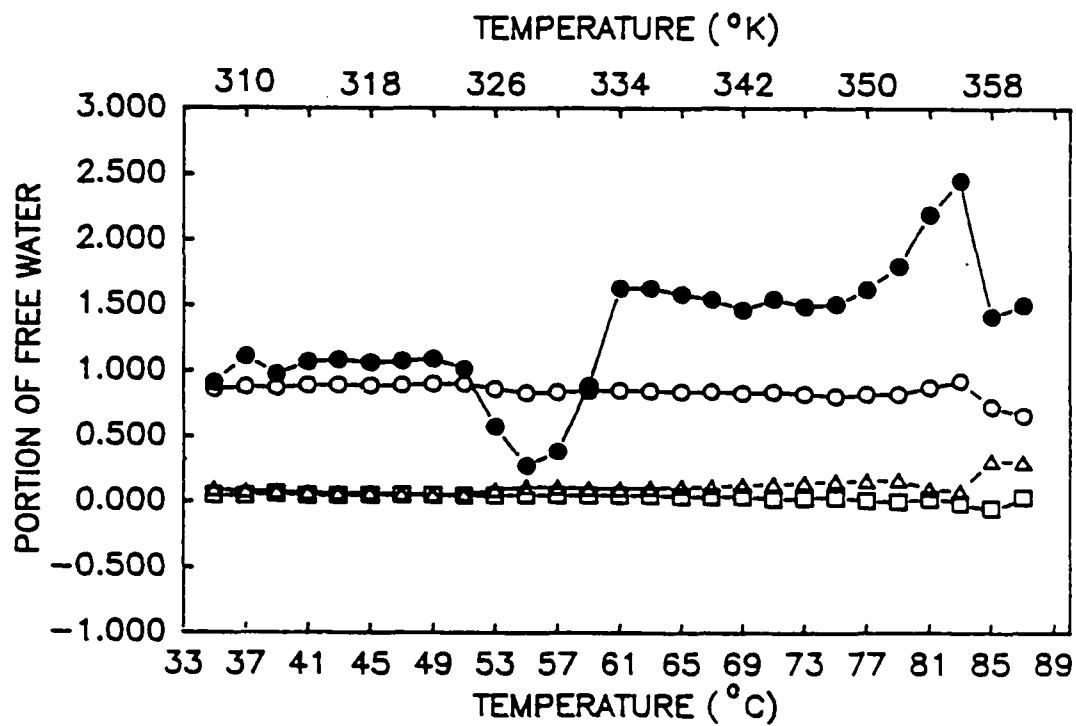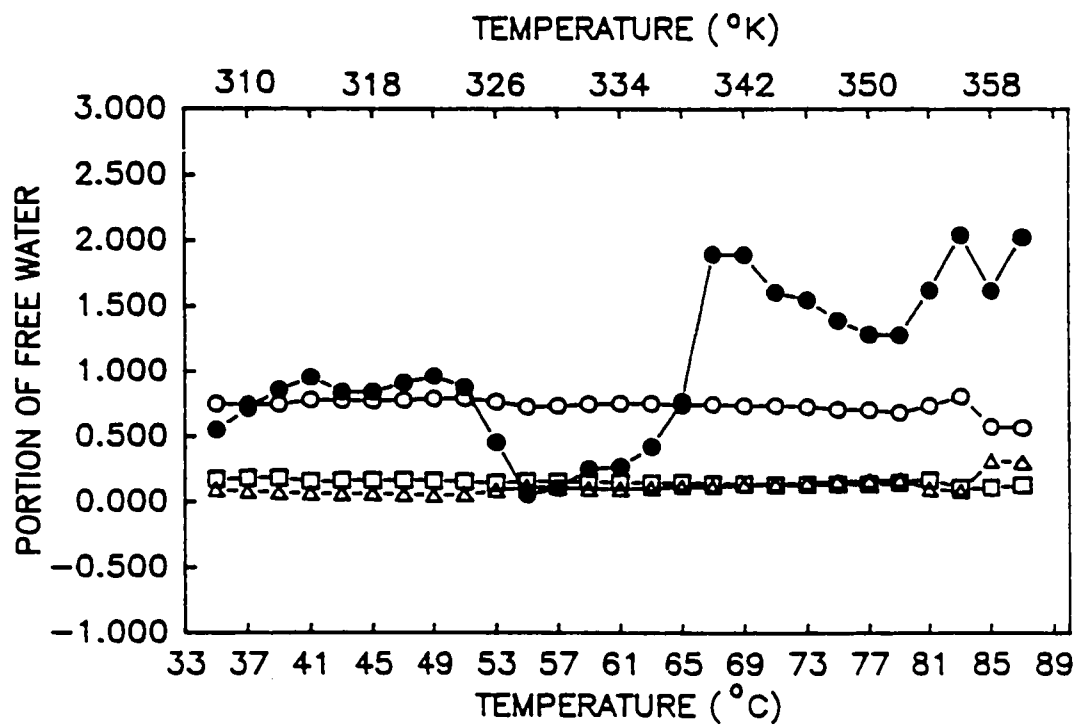

Fig. 9 - Comparison of portion of theoretical free water
(P$_f^{th}$; O——O), observed free water (P$_f^{obs}$; ●——●), polymer
water (P$_{pol}$; △——△), and solute water (P$_{sol}$; □——□) in the
30% starch-1.5M sucrose-water dispersion.

more meaningful than absolute values of P_t^{th} and P_t^{obs} for understanding changes of water's state with temperature. The P_{pol} and P_{sol} are not constant as temperature changes as shown in Fig. 7, 8, and 9.

In assumption 2 of this study, P_{pol} and P_{sol} were hypothesized to be the same in a starch-sucrose-water dispersion as they were for starch-water and sucrose-water systems, individually, at the same temperature and concentrations. The calculated P_{pol} and P_{sol} using equation 3 and 4 at different concentrations, respectively, over the temperature ranges studied are described in Table 1 and 2. The P_{pol} and P_{sol} increased as starch and sucrose concentrations increased, respectively. However, water gradually associated more with starch (Table 1) and less with sucrose (Table 2) as the temperature increased. Also, P_{pol} and P_{sol} increased as starch and sucrose concentrations were increased as shown in Table 1 and 2, respectively, even though the association ratio is not precisely proportional to the concentration. Allen and Wood (1974) explained that when more starch or sucrose is added to the system, the binding sites for water molecules are increased. Therefore P_{pol} and P_{sol} could be larger at the higher concentrations. The data given in Fig. 7 (8, 9) and Table 1 and 2 do not disprove assumption 2 at this point. Measurements were done at individual temperature points over the temperature ranges

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studied, thus, even though P_{pol} and P_{sol} were not constant with temperature changes. However, they could be the same at any one temperature or concentration.

Comparison of changing trend   The point at which mobility changes occurred for 0.5, 1.0, and 1.5M sucrose concentrations at the same starch concentration for P_t^{obs} was the same as for P_t^{th}. The P_t^{th} changes were not large (compare Fig. 1 and 4, Fig. 2 and 5, and Fig. 3 and 6). Therefore, observing only the changes of P_t^{obs} with temperature is probably enough. The P_t^{obs} began changing at 51C (324K) (Fig. 4), and the curves rapidly differed for 0.5, 1.0, and 1.5M sucrose concentrations from 55C (328K) with 10% starch-sucrose-water dispersions (Fig. 4). Likewise, the critical temperature at which free water changes occurred for the 20% starch-sucrose-water dispersions (Fig. 5) were 49C (322K) and 55C (328K) and they were 49 (322K) and 53C for the 30% starch-sucrose-water dispersions (Fig. 6). Interestingly, the temperatures when free water changed were identical to the minimum and maximum R_1 points of corresponding concentrations of starch-water system discussed in Chap. 1. The P_t^{obs} increased somewhat abruptly and reached the maximum P_t^{obs} point with increasing temperature with all sample systems. These maximum P_t^{obs} points (Fig. 6 for 30% starch system) were again identical with the maximum R_1 points

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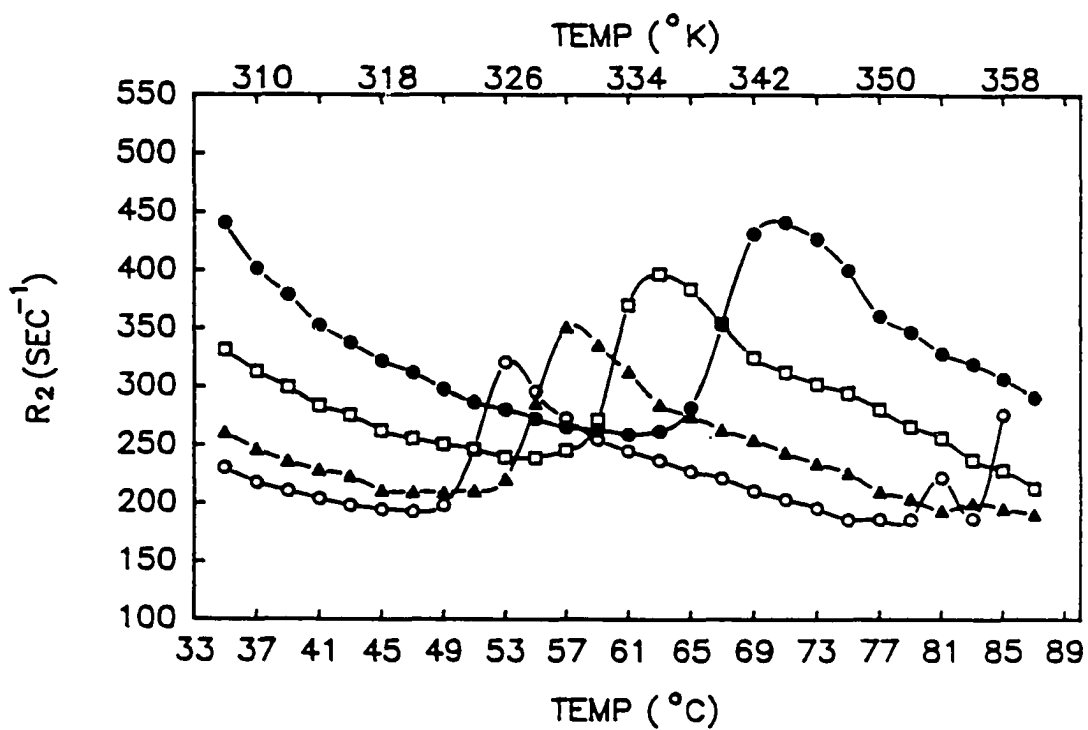
Fig. 10 - Changes of water mobility for 30% starch-sucrose; O—O - 0.0M, ▲——▲ - 0.5M, □——□ - 1.0M, and ●——● - 1.5M concentration-water dispersions as a function of increasing temperature.

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(Fig. 10 for 30% starch system) of the corresponding

concentrations of sample systems discussed in Chap. 1.

The minimum P_f^{obs} appeared, as would be logically expected, at

the minimum water mobility (maximum R_1) point of 30% starch-

water system. Using equation 3, the proportion of polymer

water (P_{pol}), was calculated by considering R_1 of the

corresponding concentration of starch-water alone system

with the observed starch-sucrose-water dispersions. If

these points are compared closely, P_f^{obs} in Fig. 6 resulted in

broader curves, requiring 2-4° longer, than was noted for

the water mobility curves (Fig. 10).

The higher values of P_f^{obs} at lower water mobility

(higher R_1) for the same system, is different to interpret.

The higher R_1 (or lower water mobility) might indicate a

greater solute-water interaction or polymer-water

interaction (Suggett et al., 1976; Richardson et al.,

1987a). Results shown in Table 1 and 2 indicate

associations of starch and/or sucrose with water were not

stable with temperature changes. If we assume no starch-

sucrose-water interaction, solute water was decreasing with

weaker sucrose-water interaction as temperature was

increased (Table 2) and, polymer water was increasing as

starch gelatinization proceeded (Table 1). Negative values

obtained for solute and polymer waters at some temperature

points, especially at low concentrations, probably indicate

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a net absorption of water by sucrose or starch with weak interactions. However, at the time of preparation of the starch-sucrose-water dispersion, most of the polymer and solute waters would be separate with only starch-water and sucrose-water interactions, respectively. As temperature increased, hydration of starch granule and polymer water (starch-water interaction) increased. Futher starch hydration or gelatinization would be expected to decrease the chemical potential of water inside of the granule and possibly solute water would be absorbed by starch. Meanwhile, the association between water and starch likely was becoming weaker and less stable. The sucrose could then easily interact with starch and the starch-sucrose-water interaction became stronger with formation of a gel network as temperature was increased. Sucrose has a lower molecular weight compared to the starch. The highly polar sucrose molecules, which are capable of forming strong hydrogen bonds, could have interacted with water molecules and with polar sites on the starch surfaces to which the water could bond by disrupting existing intermolecular associations between starch and water in a hydrated starch system (Duckworth, 1981). Greater solute-water or polymer-water interaction does not mean a greater amount of solute or polymer water but refers to the strength of those interactions (Leung et al.1983; Wynne-Jones and Blanshard,

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Table 1 — Portion of polymer waters for 10, 20, and
30% starch dispersions and their ratios at different
temperatures.

TEMP	STARCH CONCENTRATION			
°C (K)	10%	20%	30%	Ratio
35 (308)	.0652	.0909	.1452	1:1.4:2.2
37 (310)	-.0017	.0768	.1308	1:45.2:76.9
39 (312)	.0046	.0707	.1316	1:15.4:28.6
41 (314)	-.0096	.0644	.1248	1:6.7:13
43 (316)	-.0179	.0610	.1189	1:3.4:6.4
45 (318)	-.0179	.0634	.1236	1:3.5:6.9
47 (320)	-.0208	.0557	.1185	1:2.7:5.7
49 (322)	-.0195	.0487	.1136	1:2.5:5.8
51 (324)	-.0206	.0537	.1545	1:2.6:7.5
53 (326)	-.0103	.0870	.2295	1:8.5:22.3
55 (328)	.0039	.1148	.2103	1:29.4:53.9
57 (330)	.0108	.1101	.1910	1:10.2:17.7
59 (332)	.0135	.0992	.1746	1:7.4:12.9
61 (334)	.0143	.0982	.1708	1:6.9:11.9
63 (336)	.0170	.1050	.1783	1:6.2:10.5
65 (338)	.0216	.1146	.1864	1:5.3:8.6
67 (340)	.0240	.1162	.1884	1:4.8:7.9
69 (342)	.0271	.1269	.1923	1:4.7:7.1
71 (344)	.0278	.1353	.2021	1:4.9:7.3
73 (346)	.0396	.1436	.2091	1:3.7:5.3
75 (348)	.0490	.1576	.2155	1:3.2:4.4
77 (350)	.0247	.1606	.2241	1:6.5:9.1
79 (352)	-.0071	.1686	.2412	1:23.6:34
81 (354)	-.0237	.0976	.3466	1:6.4:27.1
83 (356)	-.0128	.0823	.2702	1:6.4:21.1
85 (358)	.0802	.3156	.5361	1:3.9:6.6
87 (360)	.0665	.3029	.3612	1:4.6:5.4

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TABLE 2 - Portion of solute waters for 0.5, 1.0, and 1.5M sucrose solution and their ratios at different temperatures.

TEMP	SUCROSE CONCENTRATION			
°C (K)	0.5M	1.0M	1.5M	Ratio
35 (308)	.0210	.0473	.1706	1:2.3:8.1
37 (310)	.0100	.0446	.1799	1:4.5:18
39 (312)	.0115	.0570	.1820	1:4.5:15.8
41 (314)	.0067	.0450	.1558	1:6.6:22.9
43 (316)	.0030	.0456	.1634	1:15.2:54.5
45 (318)	.0041	.0488	.1640	1:11.9:40
47 (320)	.0049	.0513	.1649	1:10.5:33.7
49 (322)	.0064	.0494	.1608	1:7.7:25.1
51 (324)	-.0003	.0436	.1546	1:145.3:515.3
53 (326)	-.0026	.0479	.1457	1:18.4:56
55 (328)	.0019	.0511	.1568	1:42.6:82.5
57 (330)	-.0033	.0496	.1545	1:15:46.8
59 (332)	-.0103	.0487	.1516	1:4.8:14.7
61 (334)	-.0073	.0479	.1500	1:6.6:20.6
63 (336)	-.0092	.0465	.1428	1:5.1:15.5
65 (338)	-.0099	.0405	.1458	1:4.1:14.6
67 (340)	-.0078	.0377	.1375	1:4.8:17.6
69 (342)	-.0150	.0395	.1382	1:2.3:9.1
71 (344)	-.0230	.0221	.1291	1:1:5.8
73 (346)	-.0268	.0286	.1307	1:1.1:4.9
75 (348)	-.0239	.0317	.1357	1:1.3:5.7
77 (350)	-.0250	.0118	.1355	1:0.5:5.4
79 (352)	-.0157	.0047	.1477	1:0.3:9.4
81 (354)	-.0311	.0220	.1656	1:0.7:5.3
83 (356)	-.0432	-.0116	.0198	1:0.3:2.5
85 (358)	-.0656	-.0480	.1099	1:0.7:1.7
87 (360)	-.0245	.0353	.1294	1:1.4:5.2

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1986). Therefore, more free water was available as more starch-sucrose-water interaction occurred, and the greater starch-sucrose-water interaction probably caused the lower water mobility with higher R_1 shown in Fig. 6 and 10.

In addition, in Table 2 one can see that, although the increasing rate is not precisely proportional to the concentrations, the ratio of solute water (0.5M:1.0M:1.5M sucrose) among three different sucrose concentrations changed dramatically from about 43C (316K) to 57C (330K), and the ratio was abruptly different at 51C (324K) (Table 2). The ratio of polymer water with three concentrations of starch (10%:20%:30% starch) was changed at approximately 53C (326K) (Table 1). This difference predicts the abrupt change of solute water (sucrose-water interaction) preceding the polymer water (starch-water interaction). Both polymer and solute water changes occurred earlier than the water mobility changes discussed in Chap. 1. These phenomena lend support to the supposition that the changes in the proportion of free water occurred before the water mobility changes. Therefore, the changes of P_{sol} with sucrose-water interactions could precede changes of water mobility with sucrose-starch-water interaction. In turn, the changes of water mobility might precede the onset temperature of gelatinization of sucrose-starch-water interactions.

Several sucrose concentrations with 10, 20, or 30%

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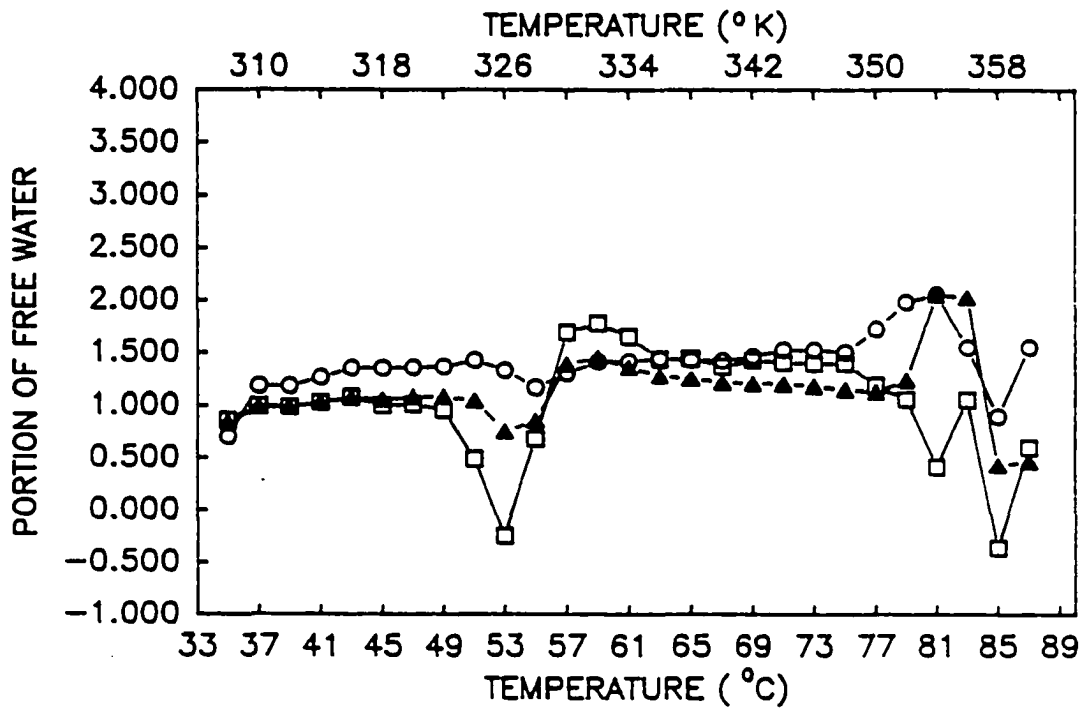
Fig. 11 - Calculated portion of free water based on
observations (P_f^{obs}) for starch; O—O - 10%, ▲—▲ - 20%,
and □——□ - 30% concentration-0.5M sucrose-water
dispersions as a function of increasing temperature.

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Fig. 12 - Calculated portion of free water based on observations (P_f^{obs}) for starch; O—O - 10%, ▲—▲- 20%, and □—□ - 30% concentration-1.0M sucrose-water dispersions as a function of increasing temperature.

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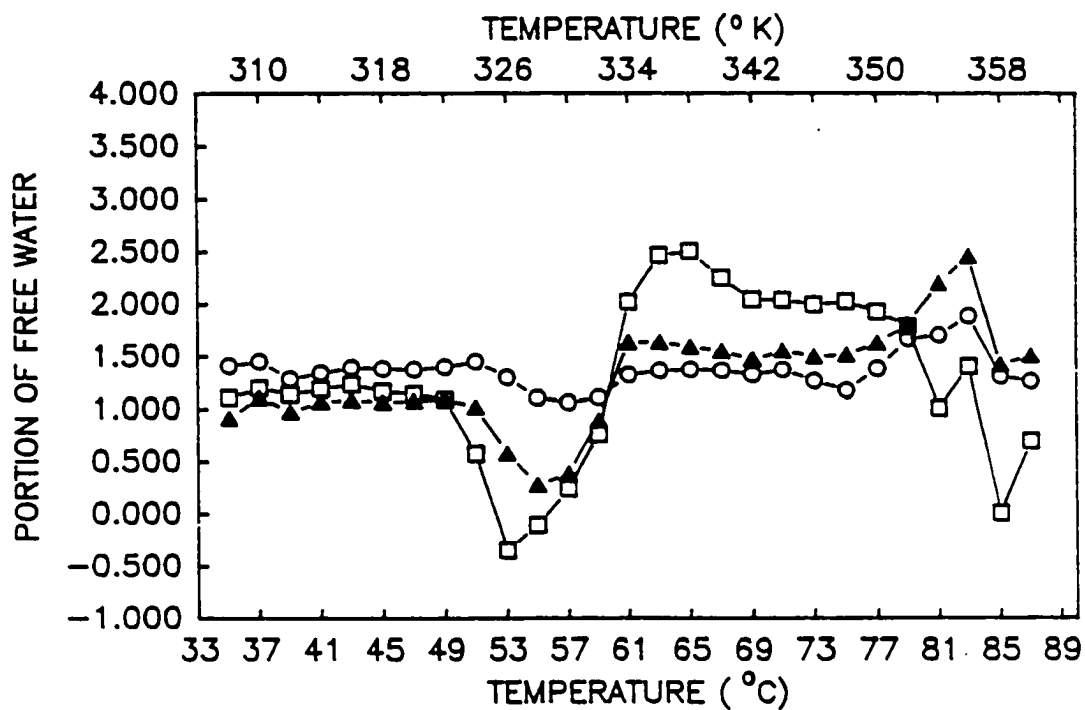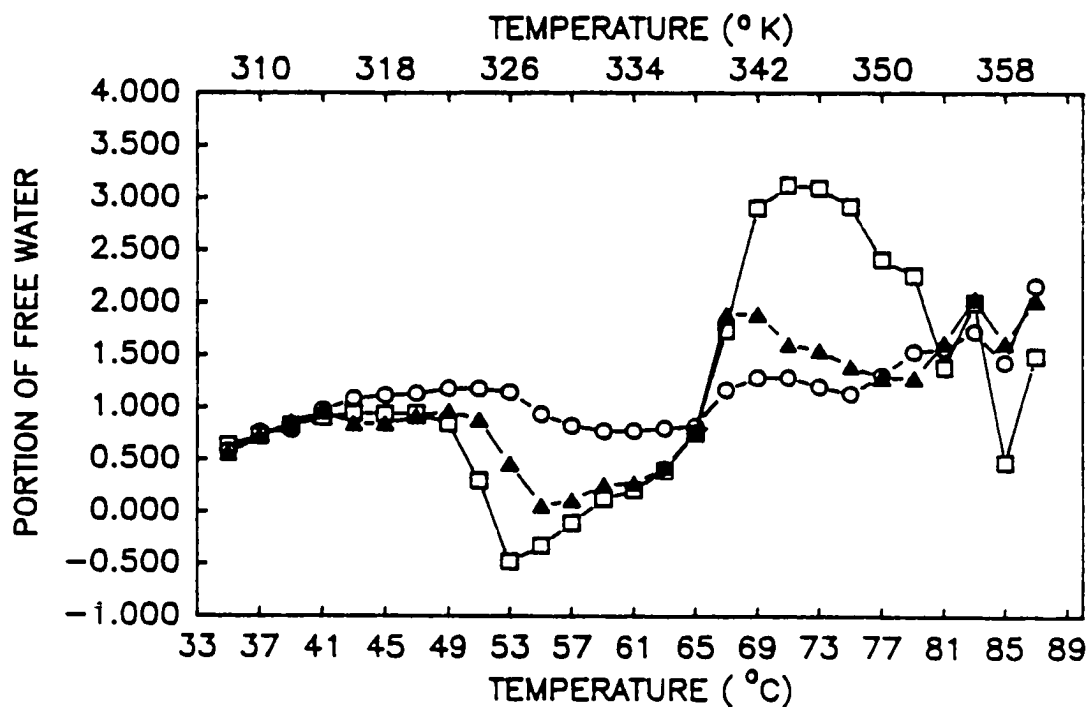
Fig. 13 - Calculated portion of free water based on observations (P_f^{obs}) for starch; O—O - 10%, ▲—▲ - 20%, and □——□ - 30% concentration-1.5M sucrose-water dispersions as a function of increasing temperature.

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starch (Fig. 11-13) depict clearly that the sucrose
concentrations resulted in the increased temperature
points for the free water portion (P_f^{obs}). For example, the
shifting temperature points are 55 (Fig. 11), 61 (Fig. 12),
and 65C (Fig. 13) for 0.5M, 1.0M, and 1.5M sucrose
concentrations, respectively, for each of three starch
concentrations. At the same sucrose concentration, the
points are similar for the three different starch
concentrations. Interestingly enough, these temperature
points are again identical with the increased temperature at
which R_1 occurs of the corresponding systems reported in
Chapter 1 (Fig. 5, 6, and 7 in Chap. 1). Therefore, these
results clearly support the idea that the major changes of
P_f^{obs} came from the starch concentrations and the increased
temperature that changes occurred depended on the sucrose
concentrations and clearly reflected the interaction between
starch and sucrose as did the R_1 discussed in Chap. 1.

CONCLUSIONS

1. The P_f^{th} and P_f^{obs} generally decreased as the amount of
   starch and/or sucrose were increased.
2. The test of assumption 1, the negligibility of
   interaction between starch and sucrose in a starch-

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sucrose-water dispersion over the temperature ranges studied, indicated the assumption 1 was not valid with P_f^{obs}. The P_f^{obs} reflected the interaction between starch and sucrose shown in earlier studies.

3. Test of assumption 2 was valid for this study but more data at individual temperature points are needed to prove this assumption.

4. The P_{pol} and P_{sol} increased as starch and sucrose concentrations were increased, respectively, and, water gradually associated more with starch and less with sucrose as temperature was increased.

5. Overall changes of the P_f^{th}, P_{pol}, and P_{sol} were similar to each other over the temperature ranges studied.

6. Changes of the P_f^{obs} and water mobility were comparable to each other.

   a. Major changes of P_f^{obs} depended on the starch concentration and the increased temperatures of changes depended on the sucrose concentration.

   b. The lowest P_f^{obs} was identical to the maximum R_1 of the corresponding starch-water system.

   c. The highest P_f^{obs} was identical to the maximum R_1 of the corresponding sample system and reflected the interaction between starch and sucrose.

   d. Changes in temperature by sucrose were identical to the peak increased temperature of R_1 with the

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corresponding sucrose concentration.

7. The sequence of changes seems to be in the following order: 1) component interactions, 2) water mobility changes, and 3) starch gelatinization.

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STUDIES OF WATER MOBILITY AND DETERMINATION OF POLYMER,
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DISPERSIONS BY USING ^{17}O NUCLEAR MAGNETIC RESONANCE
SPECTROSCOPY

by

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AN ABSTRACT OF A DISSERTATION

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requirements for the degree

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KANSAS STATE UNIVERSITY
Manhattan, Kansas

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ABSTRACT

Water mobility in wheat starch-sugar (sucrose, glucose, maltose, and maltotriose)-water dispersions was observed by measuring the transverse relaxation rate (R_2) from the ^{17}O nuclear magnetic resonance (NMR) spectra. Sugar-water, starch-water, and sugar-starch-water interactions were observed as the temperature of the systems increased from 35 to 87C (308-360K). The principal effect of sucrose was an increase in the temperature of the R_2 maximum, and the overall R_2 also increased slightly in its presence. Starch's primary effect was to decrease the mobility of water in the sample dispersions. As molecular weight and concentration of sugar were increased, the temperature at which the R_2 maximum occurred and the magnitude of the R_2 maximum both increased. Structural differences influenced the rate of water mobility changes and onset temperature of gelatinization at the same molecular weight. The principal water mobility changes with all sugar dispersions studied occurred prior to onset temperature of gelatinization as determined by using DSC.

Amount of water associated with the starch (P_{pol}) and sucrose (P_{sol}) considering the R_2 of saturated starch and sucrose solutions as the instrinsic R_2 of P_{pol} and P_{sol}, respectively, were determined for the hypothetical models. Observed values of free water (P_f^{obs}) in wheat starch-sucrose-

water dispersions with increasing temperature (35-87C) were used for comparisons with calculated values of free water based on a theoretical model (P_f^{th}). The P_f^{th} and P_f^{obs} generally decreased as the amount of dispersed substrates were increased. The P_{pol} and P_{sol} increased as starch and sucrose concentrations were increased and, water gradually associated more with starch and less with sucrose as temperature was increased. The changes of P_f^{th}, P_{pol}, and P_{sol} were similar to each other over the temperature ranges studied. A sequence of changes seems to be in the following order: 1) component interactions, 2) water mobility changes, and 3) starch gelatinization.