

Gelatinization of Wheat Starch in the Presence of Sucrose and Sodium Chloride: Correlation Between Gelatinization Temperature and Water Mobility as Determined by Oxygen-17 Nuclear Magnetic Resonance¹

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ABSTRACT

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The inhibitory effect of sucrose and NaCl on starch gelatinization was investigated by differential scanning calorimetry and nuclear magnetic resonance (NMR) spectroscopy. The increase in gelatinization temperature (T_p) resulting from added solutes was correlated to various physical properties, such as water activity, solute-solvent average molecular weight, and ¹⁷O NMR D₂O mobility. As the solute concentration increased, ¹⁷O relaxation time (T_2) decreased, indicating that D₂O mobility decreased. This reduced the plasticizing effect, leading to an increased T_p . However, the dependency of T_p on D₂O mobility was limited to only some solute concen-

trations. At a sucrose concentration above 20% (starch basis), T_p increased with solute content, but T_2 remained relatively constant, resulting in a negative correlation. A decrease in free volume by added solutes also played an important role. A balance between both of these factors was proposed to be responsible for the final T_p . The T_p - T_2 relationship for NaCl was complicated by ionic properties, which resulted in a much higher T_p at a given T_2 than for sucrose, regardless of its smaller molecular weight.

Studies have proposed that sugars increase the gelatinization temperature (T_p) of starches by various means, such as their ability to compete for water against starch and reduce the system water activity (a_w) (D'Appolonia 1972, Derby et al 1975, Labuza 1975), the sugar-starch interaction (Lelievre 1976; Spies and Hosney 1982; Hansen et al 1987, 1989), and the increase in free volume, resulting in less plasticizing effect of the sucrose-water solvent (Levine and Slade 1988, 1989). The effects of salt have also been studied and are reportedly quite different in mechanism, since salts may affect the physical property of the water (J. Jane, *personal communication*, 1990) and Donnan potential due to cation-starch interactions (Oosten 1982, 1983).

Nuclear magnetic resonance (NMR) spectroscopy is one of the best alternatives for determining the molecular dynamics of starch, as reviewed by Chinachoti et al (1991). NMR shows that water mobility, as measured by relaxation time (T_2), decreases drastically during starch gelatinization. In the presence of solutes, such as sugar and salt, T_2 for water was lowered and has been hypothesized to play an important role in the antiplasticizing effect on starch (Chinachoti et al 1991). As Levine and Slade (1988, 1989) pointed out, using the a_w concept to try to explain the phenomenon above is inappropriate, because a_w cannot provide direct information regarding the molecular dynamics and thus the plasticizing property of the water. Levine and Slade also mentioned that this plasticizing property was rather dependent on translational mobility, which could be approximated by rotational mobility of a solute-solvent system. Unfortunately, little has been reported to correlate the mobility of water to its ability to gelatinize starch.

Despite the increasing number of ¹⁷O NMR (O-NMR) experiments to determine water mobility, little has been reported on starch gelatinization at elevated temperatures. An earlier paper (Chinachoti et al 1991) showed the versatility of such techniques for understanding the dynamic molecular changes during gelatinization. Because of their common use in foods, sucrose and NaCl were selected for this work. Our objective was to use the measurement of O-NMR mobility to study the inhibitory effects of sucrose and NaCl on starch gelatinization and to relate these effects to changes in a_w , free volume, and mobility.

MATERIALS AND METHODS

Wheat starch (Manildra Milling Corp. Minneapolis, MN), deuterium oxide (99%, Wilmad Glass Co., Inc., Buena, NJ), sucrose, NaCl, glucose, and fructose (Fisher Scientific Co., Fairlawn, NJ), were used. All samples contained starch and free water (D₂O) (40:60). Sucrose, NaCl, fructose, or glucose was added to starch to make a given mixture of starch, solute, and D₂O. The sucrose content (starch basis) ranged from 0 to 41.3%, NaCl (starch basis) from 0 to 30%; glucose and fructose were both 10%. The samples were mixed mechanically and left resting overnight before the gelatinization experiment. D₂O instead of H₂O was used to avoid the proton exchange broadening of the ¹⁷O water peak (Richardson et al 1987).

Differential Scanning Calorimetry

A differential scanning calorimeter (DSC2, Perkin Elmer Corp., Norwalk, CT) was used to measure T_p . A 10-mg starch sample was weighed and sealed in a hermetically sealed pan and then heated under the DSC from 7 to 160°C at a rate of 10°C/min. An empty pan was used as the reference. The initial temperature (T_o) and peak temperature (T_p) were measured by thermal analysis data system (Lund 1983).

NMR

A starch sample was heated in the NMR probe from 25 to 45°C in a 10-mm NMR tube (Wilmad Glass Co., Inc., Buena, NJ). After reaching 45°C, an O-NMR spectrum was obtained. ¹⁷O in natural abundance (3.7 × 10⁻²%) was used. The spectra were obtained at 40.67 MHz with a Varian XL-300 instrument. Spectra width was 20,000 Hz; pulse width, 15 μsec; recycle delay, 15 msec; number of scans, 6,000. A set of duplicate samples was tested. The experimental error was within 5% (the average is used here). The transverse relaxation rate (R_2) was calculated from the line width ($\Delta\nu$) at half height of the Fourier transformed spectra as $R_2 = \pi\Delta\nu$.

RESULTS AND DISCUSSION

DSC Results

The DSC data for the water-mediated gelatinization process (the 60°C peak) are shown in Table I for starch-D₂O mixtures (40:60) with various solutes. As expected, where sucrose and NaCl were present, T_o and T_p increased as the solute content increased. The T_p of the wheat starch increased as more solutes were added (Fig. 1); the increase in T_p caused by NaCl was greater than the increase caused by sucrose of the same concentration. At the 10% sugar level, no significant differences were observed in T_p among the samples containing sucrose, glucose, and fructose.

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A number of explanations have been proposed for the antiplasticizing effect of these solutes. The classic explanation is competition for water among the solids, resulting in a lowered a_w ; thus less water is available for the gelatinization process

TABLE I
Results of Differential Scanning Calorimetry for the Endothermic Gelatinization of Wheat Starch in Free Water^a in the Presence of Sucrose, Sodium Chloride, Glucose, and Fructose

Additive		Temperature, °C	
Solute	Percent (starch basis)	Initial	Peak
None	...	60.93 ± 0.33	66.15 ± 0.38
Sucrose	10.0	63.01 ± 0.63	68.19 ± 0.73
	20.0	64.67 ± 0.09	69.85 ± 0.19
	30.0	65.67 ± 0.14	71.01 ± 0.06
	41.3	67.48 ± 0.14	72.88 ± 0.18
Glucose	10.0	62.69 ± 0.60	67.58 ± 0.18
Fructose	10.0	63.21 ± 0.09	67.89 ± 0.09
NaCl	0.5	62.29 ± 0.16	67.90 ± 0.60
	1.0	64.82 ± 0.21	70.45 ± 0.25
	1.5	66.14 ± 0.88	71.25 ± 0.65
	2.0	65.96 ± 0.03	71.73 ± 0.10
	2.5	67.39 ± 0.37	72.60 ± 0.20
	3.0	67.36 ± 0.29	72.08 ± 0.18
	10.0	70.08	74.73
	20.0	70.21	75.47
	30.0	68.77	76.33

^aRatio of wheat starch to free water = 40:60; scanning rate = 10°C/min.

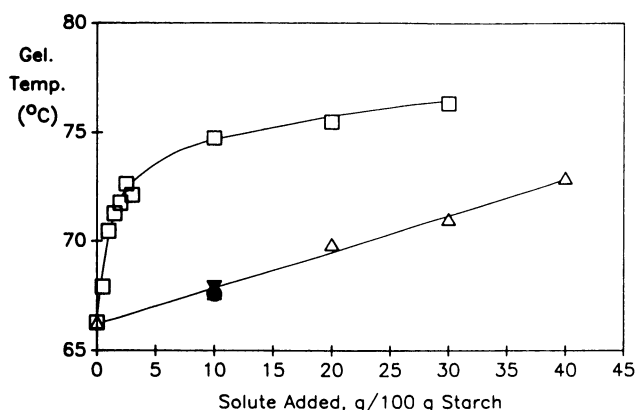


Fig. 1. Gelatinization temperature for wheat starch in the presence of free water (60:40), sucrose (Δ), and NaCl (\square) at various concentrations. Gelatinization temperature in the presence of 10% (starch basis) sucrose (\blacktriangle), fructose (\blacktriangledown), and glucose (\bullet).

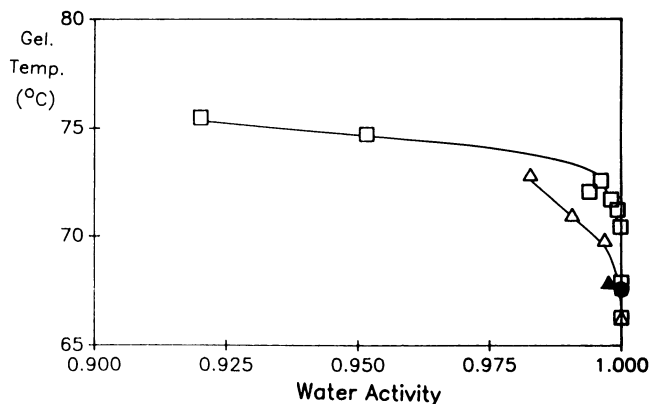


Fig. 2. Gelatinization temperature plotted against water activity, calculated from mixtures of starch and free water (40:60) with various levels and types of solutes. \square = NaCl, Δ , \blacktriangle = sucrose, \blacktriangledown = fructose, \bullet = glucose.

(D'Appolonia 1972, Derby et al 1975, Labuza 1975). To facilitate this argument, a_w for each sample (25°C) was calculated based on a mass balance (Chinachoti 1990) and plotted against T_p (Fig. 2). Although some correlation was observed between a_w and the plasticizing properties, a_w is not appropriate to describe the plasticizing properties of the water (Levine and Slade 1988, 1989). Levine and Slade (1989) suggested that the antiplasticizing properties of these sugars are rather related to the decreased free volume of the liquid fraction (sugar-water cosolvent), which can be represented by the increasing average molecular weight (mol wt) of the liquid fraction. As a result, the free volume of the amorphous fringes in the fringe micelle of starch granules has less ability to increase due to a decrease in chain mobility (Levine and Slade 1989). These authors also showed that a plot between T_p and the inverse of the mol wt was linearly correlated in sugars of 50% aqueous concentration.

Our results were plotted in a similar fashion (Fig. 3) but show a curvilinear relationship, which could be explained by the fact that our samples varied in the aqueous concentration of sugar, ranging from 0 to 27%. The type of solutes was important to this relationship; sucrose, glucose, and fructose were similar, whereas NaCl showed a much higher increase in T_p at a given average mol wt (Fig. 3). NaCl, added only at 0–3% (starch basis), increased sharply in T_p (Fig. 3, I). T_p then leveled off at 10–20% NaCl (Fig. 3, II). As indicated previously (Oosten 1982, 1983; Chungcharoen and Lund 1987; Chinachoti et al 1991), ionic inter-

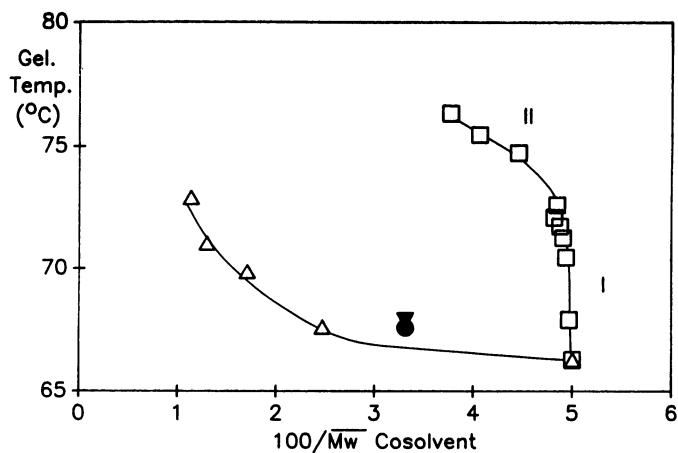


Fig. 3. Gelatinization temperature of wheat starch in free water (40:60) in the presence of sucrose (Δ) and NaCl (\square) as a function of the inverse of the average molecular weight (M_w) of the solute- D_2O cosolvent. Data in the presence of and fructose (\blacktriangledown) and glucose (\bullet).

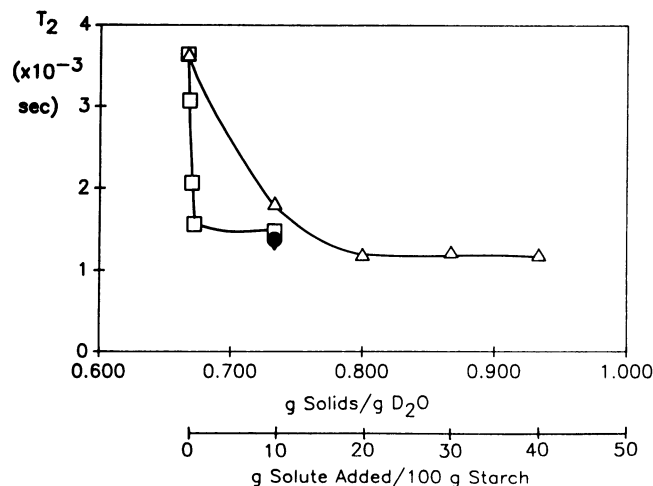


Fig. 4. Changes in ^{17}O NMR relaxation time (T_2) for free water in wheat starch (60:40), measured at 45°C in the presence of varying concentrations of sucrose (Δ), NaCl (\square), fructose (\blacktriangledown), and glucose (\bullet).

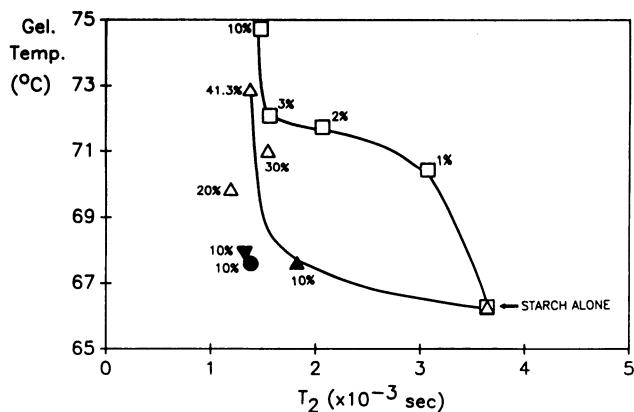


Fig. 5. Correlation between gelatinization temperature of wheat starch (starch to free water, 40:60) and the transverse relaxation time (T_2) for the ^{17}O NMR spectra obtained from the sample at 45°C . Samples containing sucrose (Δ, \blacktriangle) and NaCl (\square), glucose (\bullet), and fructose (\blacktriangledown) are labeled with the percent present (starch basis).

actions between cations (sodium, in this case) played an important role in the gelatinization process. It has been proposed that the resulting increased Donnan potential excludes the anions from the starch granules. This interaction is probably limited and dependent on the concentration and ionic strength of the solute.

NMR Results

The relationship between T_p and a_w and between T_p and the average mol wt of cosolvents has been demonstrated above. This section presents the relationship between T_p and D_2O mobility as determined by O-NMR. Figure 4 shows the O-NMR T_2 representing the D_2O mobility just before the gelatinization process. As plotted against solid content or the amount of added solutes (Fig. 4), T_2 decreased rapidly at the beginning and then leveled off. The decreased T_2 indicated a significant decrease in the D_2O mobility in the presence of sucrose and NaCl (at a given D_2O content). At some higher levels of sucrose and NaCl, T_2 decreased less drastically and appeared to approach some asymptotic levels. T_2 was much more sensitive to NaCl than to sucrose. This corresponds with the finding that T_p was also more sensitive to NaCl than to sucrose of the same concentration, which could be related to the decreased T_2 (i.e., decreased D_2O mobility).

When T_p was plotted against T_2 (Fig. 5) from the O-NMR scans, T_p increased in a curvilinear fashion as T_2 decreased (i.e., D_2O mobility decreased due to the added solute). For sucrose, T_p increased with the decreased T_2 only moderately at first; as the sucrose level increased beyond 10% (starch basis), T_p increased more abruptly, whereas T_2 remained relatively unchanged (Fig. 5, T_2 from 1.2 to 1.6×10^{-3} sec). At the same 10% concentration, adding glucose or fructose did not affect T_p any differently than did adding sucrose, though it decreased the D_2O mobility to a greater extent than did sucrose (Fig. 5). This indicates that D_2O mobility was not the only factor involved. Because glucose and fructose have a lower mol wt than does sucrose, they could have contributed to a greater degree of plasticization than sucrose of the same concentration. This is probably why T_p for such samples was quite low, considering that their D_2O mobility is lower than that of sucrose, and thus should result in a higher T_p .

For NaCl (Fig. 5), T_p drastically increased with decreasing T_2 on addition of a low level of NaCl (1–2%). As the NaCl concentration further increased, no significant change in T_p was found until the 10% level of NaCl, when T_p again rose sharply. This resulted in an S-shaped curve. For a given T_2 , T_p for a sample containing NaCl was always higher than that for a sample containing sucrose. Except for the first point (starch alone) on the NaCl curve in Fig. 5, the overall curve for the T_p - T_2 relationship was very similar to that of sucrose, i.e., the two curves were almost parallel. This could mean that the ionic interaction between NaCl and starch raised T_p to a higher level at a low (1–2%)

concentration; the T_p - T_2 relationship at NaCl levels higher than this fell in the same pattern as that for sucrose. Thus, the ionic property of NaCl played an important role. This contribution of the ionic interaction between sodium and the hydroxyl groups of starch polymers has been pointed out by various investigators (Oosten 1982, 1983; Chungcharoen and Lund 1987). Recent work on NMR (Chinachoti et al 1991) showed Na-starch interactions, as indicated by a line broadening of ^{23}Na spectra during starch gelatinization.

CONCLUSION

The present work presents different views of analysis and interpretation of the inhibitory effect of sucrose and NaCl on starch gelatinization. Although the increased solute concentration also resulted in a lower a_w , the increase in T_p is better explained in terms of other physical properties, i.e., the average mol wt of the cosolvent (Levine and Slade 1988) as well as the molecular mobility of the solvent. The O-NMR transverse T_2 increased with added solutes, indicating a decrease in D_2O mobility. For the base of sugars, replacing sucrose with glucose or fructose did not change the T_p despite the decreased T_2 . This was probably due to the reduced average mol wt of the cosolvent for glucose or fructose. The effect of NaCl showed that the T_p - T_2 relationship was complicated by some contribution of the ionic interaction in a 1–2% NaCl concentration, which resulted in a much higher T_p at a given T_2 than for sucrose. The T_p - T_2 relationship at higher NaCl concentrations paralleled that for sucrose. Solvent mobility was useful for expressing starch gelatinization.

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LITERATURE CITED

- CHINACHOTI, P. 1990. Isotherm equation for starch, sucrose and salt for calculation of high system water activities. *J. Food Sci.* 55:265.
- CHINACHOTI, P., WHITE, V. A., LO, L., and STENGLE, T. R. 1991. Application of high resolution carbon-13, oxygen-17, and sodium-23 nuclear magnetic resonance to study the influence of water, sucrose and NaCl on starch gelatinization. *Cereal Chem.* 68:238.
- CHUNGCHAROEN, A., and LUND, D. B. 1987. Influence of solutes and water on rice starch gelatinization. *Cereal Chem.* 64:240.
- D'APPOLONIA, B. L. 1972. Effect of bread ingredients on starch gelatinization properties as measured in the amylograph. *Cereal Chem.* 49:532.
- DERBY, R. I., MILLER, B. S., MILLER, B. F., and TRIMBO, H. B. 1975. Visual observations of wheat starch gelatinization in limited water systems. *Cereal Chem.* 52:702.
- HANSEN, L. M., PAUKSTELIS, J. V., and SETSER, C. S. 1987. ^{13}C Nuclear magnetic resonance spectroscopic methods for investigating sucrose-starch interactions with increasing temperature. *Cereal Chem.* 64:449.
- HANSEN, L. M., SETSER, C. S., and PAUKSTELIS, J. V. 1989. Investigations of sugar-starch interactions using carbon-13 nuclear magnetic resonance. I. Sucrose. *Cereal Chem.* 66:411.
- LABUZA, T. P. 1975. Interpretation of sorption data in relation to the state of constituent water. Pages 155-172 in: *Water Relations in Foods*. R. B. Duckworth, ed. Academic Press: New York.
- LELIEVRE, J. 1976. Theory of gelatinization in starch-water-solute systems. *Polymer* 17:854.
- LEVINE, H., and SLADE, L. 1988. Non-equilibrium behavior of small carbohydrate-water systems. *Pure Appl. Chem.* 60:1841.
- LEVINE, H., and SLADE, L. 1989. Influence of glassy and rubbery states on the thermal, mechanical, and structural properties of doughs and baked products. Pages 157-300 in: *Dough Rheology and Baked Product Texture: Theory and Practice*. H. Faridi and J. M. Faubion, eds. Van Nostrand Reinhold/AVI: New York.
- LUND, D. B. 1983. Applications of differential scanning calorimetry in foods. Pages 125-143 in: *Physical Properties of Foods*, M. Peleg and E. B. Bagley, eds. AVI Publishing Co., Inc.: Westport, CT.
- OOSTEN, B. J. 1982. Tentative hypothesis to explain how electrolytes affect the gelatinization temperature of starches in water. *Starch/*

Stärke 34:233.
OOSTEN, B. J. 1983. Explanations for phenomena arising from starch-electrolytes interactions. *Starch/Stärke* 35:166.
RICHARDSON, S. J., BAIANU, I. C., and STEINBERG, M. P. 1987.

Mobility of water in corn starch suspensions determined by nuclear magnetic resonance. *Starch/Stärke* 39:79.
SPIES, R. D., and HOSENEY, R. C. 1982. Effect of sugars on starch gelatinization. *Cereal Chem.* 59:128.

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