

# Comparisons of Water Mobility Using $^{17}\text{O}$ Nuclear Magnetic Resonance for Four Sugars: Glucose, Maltose, Maltotriose, and Sucrose<sup>1</sup>

H. LIM, C. S. SETSER, and J. V. PAUKSTELIS<sup>2</sup>

## ABSTRACT

Cereal Chem. 69(4):387-390

Water mobility in wheat starch-sugar (glucose, maltose, maltotriose, and sucrose)-water dispersions was observed as temperature was increased from 35 to 87°C by measuring the transverse relaxation rate ( $R_2$ ) from the  $^{17}\text{O}$  nuclear magnetic resonance spectra. The changes of water mobility with different sugar dispersions exhibited similar patterns. The temperatures at which the  $R_2$  maximum occurred and the magnitude of the  $R_2$

maximum both increased as molecular weights of sugars and concentrations of 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 influenced the changes of  $R_2$ .

Previous work indicated that water's ability to act as a plasticizing agent during starch gelatinization generally decreases as the molecular weight of the sugar and the concentration of the solution are increased (Chungcharoen and Lund 1987, Slade and Levine 1987). Sugars with molecular weights of about 800 (Brown and French 1977) can bridge a larger space and induce more bonding with starch chains than sugars with low molecular weights. The flexibility of the starch chains diminishes and the gelatinization temperature increases, thus requiring more energy to pull the crystallites apart (Spies and Hosney 1982).

Solutions of monosaccharides, such as glucose and fructose, increased gelatinization temperature of starch but to a lesser extent than solutions of disaccharides, such as sucrose or maltose (Osman 1975, Bean and Yamazaki 1978, Bean et al 1978, Hansen et al 1989). However, Spies and Hosney (1982) reported that sucrose raised the 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 differential scanning calorimetry (DSC). They reported an increasing gelatinization temperature with various sugars in the following order: water alone < galactose < xylose < fructose < mannose < glucose < maltose < lactose < 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 Hosney 1982, Hansen et al 1989). Brown and French (1977) reported that oligosaccharides with molecular weights of less than 800 were able to penetrate the starch granules along with water. In addition, the ability of sugar 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).

Water mobility of a starch-sucrose-water dispersion was found to be closely related to interactions among the components (Lim et al 1992). The major changes in water mobility indicated by nuclear magnetic resonance (NMR) measurements occurred before the onset temperature of gelatinization, as observed by DSC measurements in similar starch-sucrose-water dispersions. Lower molecular weights and smaller molecules, in general, have lower mobilization points (Leung et al 1976, 1979; Duckworth 1981). The molecular weights, structures, and chain lengths of glucose, maltose, maltotriose, and sucrose are different. In this study, glucose-, maltose-, and maltotriose-starch-water dispersions were compared with the sucrose system by  $^{17}\text{O}$  NMR. The objectives were 1) to observe whether glucose, maltose, and malto-

triose have effects on water mobility similar to those of sucrose; and 2) to determine, by comparing glucose, maltose, and maltotriose, whether any factor can be isolated that causes changes of water mobility in wheat starch-sugar-water model systems as temperature is increased from 35 (308 K) to 87°C (360 K).

## MATERIALS AND METHODS

All materials and methods were the same as given in Lim et al (1992) with the following additions. The D-glucose (dextrose) and maltose were purchased from Fisher Scientific Co. (Fair Lawn, NJ), and maltotriose was purchased from Sigma Chemical Co. (St. Louis, MO). 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 alone or with 0.5, 1.0, and 1.5M glucose concentrations (glucose dispersions) with increasing temperature are shown in Figure 1. Glucose dispersions showed similar changes when compared with sucrose-starch-water dispersions (sucrose dispersions) (Fig. 2). The transverse relaxation rate ( $R_2$ ) and  $R_2$  maximum temperature increased with increasing glucose concentrations but to a lesser extent than with increasing sucrose concentrations (Figs. 1 and 2). For example, the maximum  $R_2$  of the 1.5M glucose dispersion was about 250 at 59°C (332 K), whereas this value was about 320 at 67°C (340 K) for the 1.5M sucrose dispersion. These results agree with the supposition that a lower molecular weight results in a lower water mobility (Leung et al 1976, 1979). Glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) has six hydrogen bonding sites for water molecules; sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) has 11. Fewer hydrogen bonding sites probably resulted in more free water and less restricted water mobility in the glucose dispersions, as reflected by the lower overall  $R_2$  changes and increased temperatures of the  $R_2$  maxima.

The DSC measurements for each system are given in Table I and support the NMR results. The water mobility changed before the onset temperature of gelatinization for glucose, maltose, and maltotriose as it did for the sucrose dispersions, and the onset temperatures of 0.5, 1.0, and 1.5M glucose dispersions were lower than those for the same concentrations of sucrose dispersions. For example, onset gelatinization temperatures were about 62°C (335 K) for the 1.5M glucose system and about 76°C (349 K) for the 1.5M sucrose dispersion. The pattern of the overall  $R_2$  changes in glucose dispersions was similar to that of the changes in sucrose dispersions, but all changes were to a lesser degree.

### Maltose-Starch-Water Dispersion

Changes of water mobility for 20% starch alone or with 0.5, 1.0, and 1.5M maltose concentrations (maltose dispersions) with increasing temperature are given in Figure 3. The changes and overall patterns again were similar to those of the sucrose disper-

<sup>1</sup>Contribution 91-509-J from the Kansas Agricultural Experiment Station.

<sup>2</sup>Departments of Foods and Nutrition and Chemistry, Kansas State University, Manhattan 66506.

sion. The overall  $R_2$  values and the temperatures at which the  $R_2$  maximum occurred were slightly lower than those of the sucrose dispersions (Fig. 2). The  $R_2$  maxima were about 200 at 65°C (338 K) for the 1.5M maltose dispersion and about 220 at 67°C (340 K) for sucrose. The DSC results (Table I) were similar. Onset temperature of gelatinization was slightly lower for maltose than for sucrose at each concentration, an effect that was less noticeable at the highest concentration.

The molecular weight and the number of hydrogen bonding sites are the same ( $C_{12}H_{22}O_{11}$ ; molecular weight 342) for maltose and sucrose. However, structurally, maltose is composed of two molecules of glucose, whereas sucrose has a glucose (pyranose ring) and a fructose (furanose ring) molecule. When sucrose reorients and associates with water, the pyranose ring of glucose interacts more favorably with water molecules (Allen and Wood 1976, Suggett and Clark 1976, Mathlouthi and Luu 1980, Shallenberger 1982) than the furanose ring of fructose. 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 and the viscosity, 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 with  $CH_2OH$  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 of the same molecular weight.

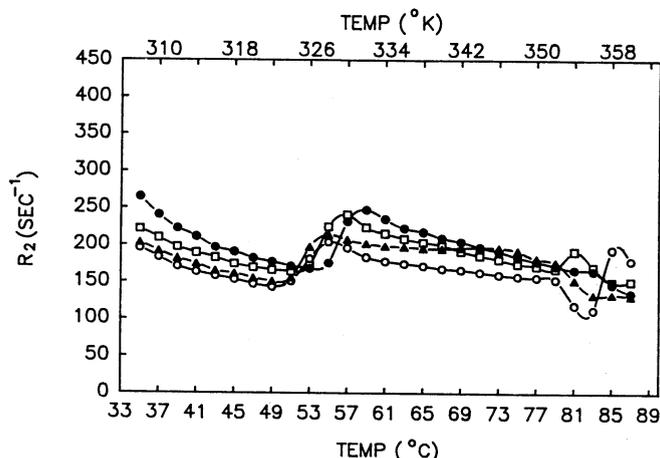


Fig. 1. Transverse relaxation rates ( $R_2$ ) of the 20% starch-glucose-water dispersions as a function of increasing temperature.  $\circ$  = No glucose.  $\blacktriangle$ ,  $\square$ ,  $\bullet$  = 0.5, 1.0, and 1.5M glucose concentrations, respectively.

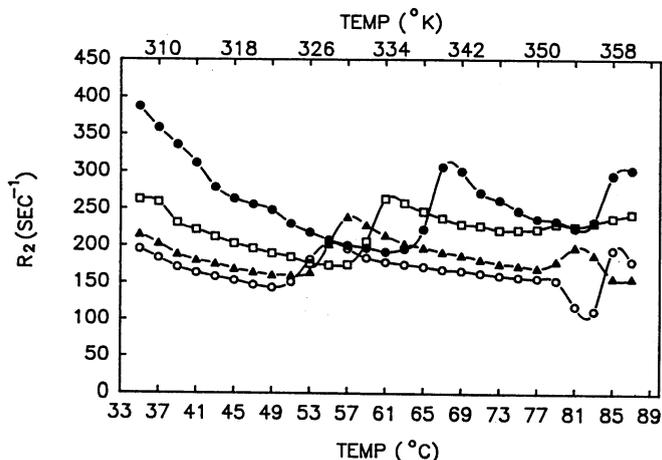


Fig. 2. Transverse relaxation rates ( $R_2$ ) of the 20% starch-sucrose-water dispersions as a function of increasing temperature.  $\circ$  = No sucrose.  $\blacktriangle$ ,  $\square$ ,  $\bullet$  = 0.5, 1.0, and 1.5M sucrose concentrations, respectively.

### Maltotriose-Starch-Water Dispersion

The changes of water mobility for 20% starch with various concentrations of maltotriose (maltotriose dispersions) shown in Figure 4 were basically similar to those of the sucrose dispersions (Fig. 2). Overall, the water mobility changes and the  $R_2$  maxima

TABLE I  
Comparison of Mean<sup>a</sup> Onset Temperature, Peak Temperature, and Enthalpies ( $\Delta H$ ) for Dispersions of Glucose, Maltose, Maltotriose, and Sucrose with 20% Starch

Dispersion	Onset Temperature (°C)	Peak Temperature (°C)	$\Delta H$ (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

<sup>a</sup>Mean of least three measurements.

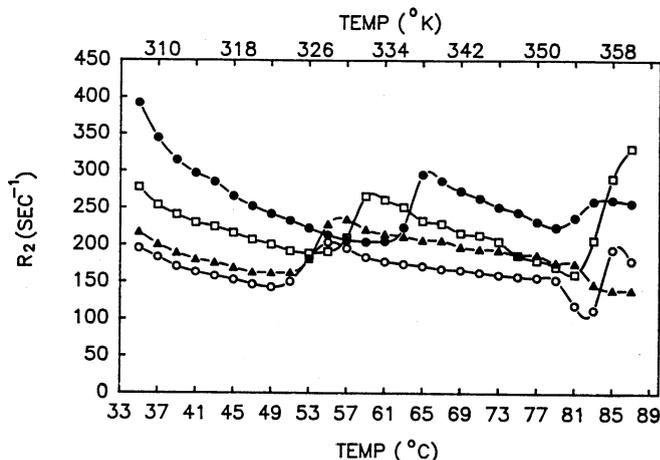


Fig. 3. Transverse relaxation rates ( $R_2$ ) of the 20% starch-maltose-water dispersions as a function of increasing temperature.  $\circ$  = No maltotriose.  $\blacktriangle$ ,  $\square$ ,  $\bullet$  = 0.5, 1.0, and 1.5M maltotriose concentrations, respectively.

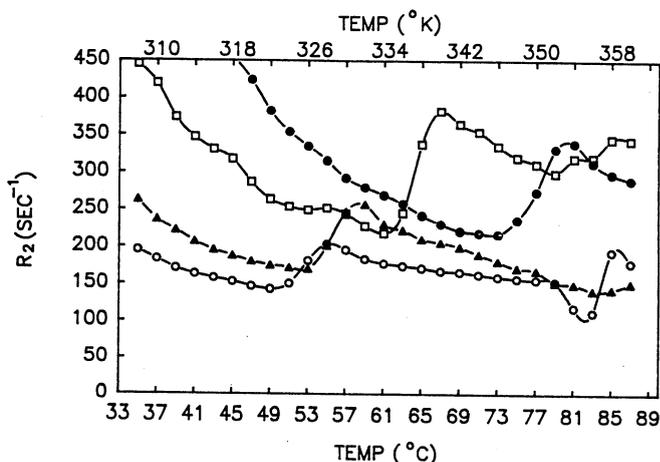


Fig. 4. Transverse relaxation rates ( $R_2$ ) of the 20% starch-maltotriose-water dispersions as a function of increasing temperature.  $\circ$  = No maltotriose.  $\blacktriangle$ ,  $\square$ ,  $\bullet$  = 0.5, 1.0, and 1.5M maltotriose concentrations, respectively.

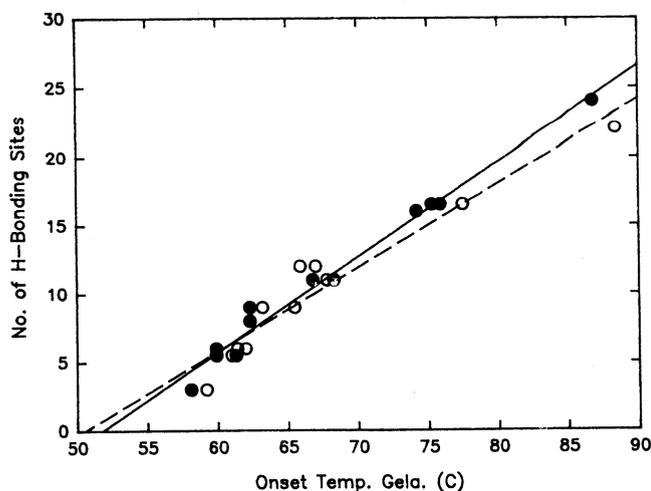


Fig. 5. Relationship between onset temperature of wheat starch gelatinization and number of hydrogen bonding sites times the molar concentrations of sugars from this study and from Hansen (1987). O: Calculated with concentrations used in this study, 0.5, 1.0, and 1.5M each of glucose, sucrose, maltose, and maltotriose;  $r = 0.99$ ;  $n = 12$ ;  $y = 1.41x + 52.07$ . ●: Calculated with 0.5, 1.0, 1.5, and 2.0M each of glucose and sucrose and 1.0, 1.5, and 2.0M fructose (Hansen 1987);  $r = 0.96$ ;  $n = 11$ ;  $y = 1.52x + 51.72$ .

were much greater for maltotriose dispersions than for the same concentrations of sucrose dispersions. The 1.0M maltotriose dispersion had a maximum  $R_2$  of about 400 at 67°C (340 K) compared with about 270 at 61°C (334 K) for the 1.0M sucrose dispersion. Interestingly, 1.5M maltotriose dispersions had a smaller  $R_2$  maximum (about 350 at 81°C) than that of the 1.0M maltotriose dispersions (about 400 at 67°C). However, both were greater than the maximum for the 1.5M sucrose dispersion (about 320 at 67°C). The 1.5M maltotriose dispersion was expected to have a higher  $R_2$  than that of the 1.0M maltotriose dispersion. Maltotriose has a larger molecular weight (504) and longer chain length with three  $\alpha$ -1,4 linked molecules of glucose within the structure ( $C_{18}H_{32}O_{16}$ ). The previous study (Lim et al 1992) with sucrose showed that starch increased the  $R_2$  value and sucrose increased both the  $R_2$  and the temperature at which  $R_2$  maximum occurred. Therefore, the swelling of starch granules that increases the  $R_2$  was probably hindered by certain factor(s) in the 1.5M maltotriose dispersion.

Possibly maltotriose is able to penetrate the starch granule, as others have suggested (Brown and French 1977, Spies and Hosney 1982, Hansen et al 1989), but at the higher 1.5M concentration, less was needed to restrict starch swelling. The longer chain, compared with those of sucrose or maltose, would have more interaction sites for an equivalent concentration to react with the starch. This would increase the temperature of starch gelatinization for maltotriose more than the reactions of starch with maltose or sucrose at lower concentrations. Because not as much maltotriose was needed to penetrate the granule at the higher 1.5M concentration, more could have remained outside the granule to bind with the water. This would decrease the water available outside the granule to bind with the starch by a type of steric exclusion (Walstra 1973) and decrease the water mobility to a lower level than that of the 1.0M system (Fig. 4). This result agrees with the thermal analysis results of DSC (Table I).

The onset temperatures of gelatinization of 0.5, 1.0, and 1.5M maltotriose dispersions (Table I) were higher than those of the sucrose dispersions. This result contradicts previous studies (Spies and Hosney 1982, Slade and Levine 1987), in which maltotriose had lower gelatinization temperature than sucrose using a 1:1:1 starch-sugar-water ratio. However, the concentrations of sugar in the starch-sugar-water dispersions used in this study were higher. For example, the 1.0 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 became increasingly

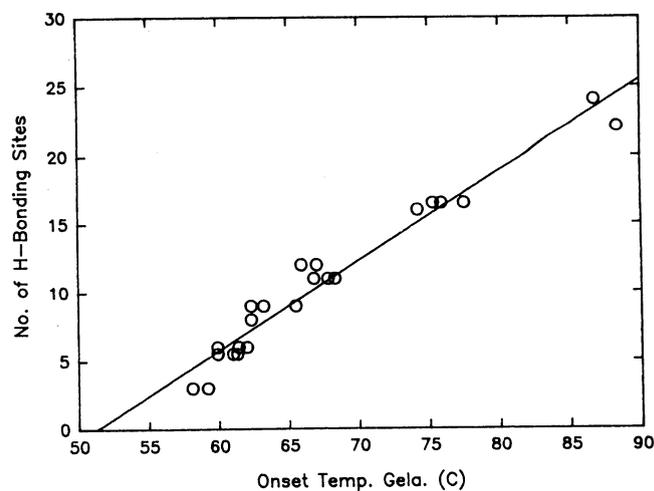


Fig. 6. Relationship between onset temperature of wheat starch gelatinization and number of hydrogen bonding sites times the molar concentrations of sugars from this study combined with data from Hansen (1987).  $r = 0.98$ ,  $n = 23$ , and  $y = 1.451x + 51.999$ .

larger with increasing sugar concentrations. This higher onset temperature of gelatinization with maltotriose is reasonable and supports the idea that onset temperature increases with increased molecular weight, at least up to a point.

An interesting relationship between concentration and number of saccharide units of the sugars was noted (Table I). For example, 1.0M glucose (1 saccharide unit) and 0.5M maltose (1 saccharide unit) showed almost the same onset temperature of gelatinization (59.9°C). Likewise, 1.5M glucose and 0.5M maltotriose, each 1.5 saccharide unit, and 1.5M maltose and 1.0M maltotriose, each 3 saccharide units, had very close onset temperatures of gelatinization—62.3 and about 75°C, respectively. The number of hydrogen bonding units times the concentration of the sugars was found to be related highly ( $r = 0.991$ ) to the onset temperature of gelatinization (Fig. 5). The data from previous work on glucose, sucrose, and fructose at 0.5, 1.0, 1.5, and 2.0M concentrations (Hansen 1987) were reevaluated accordingly, and the relationship (Fig. 5) of that data also was high ( $r = 0.964$ ). If data from both studies are combined (Fig. 6) ( $r = 0.977$ ), the results indicate that the total number of hydrogen bonding sites available for interactions with starch and water is an influential factor in increasing the onset temperature of starch gelatinization. Lim et al (1992) noted that water mobility was reduced with increases in viscosity as sucrose-water interactions increased. Viscosity increases as a result of hydrogen bonding; whether this is a cause or an effect of the decreased water mobility as measured by  $^{17}O$  NMR and the increased  $T_g$  measured by DSC remains unclear. Further studies are needed to clarify these relationships.

## CONCLUSIONS

The changes of water mobility with different sugar dispersions exhibited similar patterns. The temperatures at which the  $R_2$  maximum occurred and the magnitude of the  $R_2$  maximum both increased as molecular weights of sugars and concentrations of dispersions were increased. The water mobility changes occurred before onset temperature of gelatinization with all sugar dispersions studied. Structural differences also influenced the rate of water mobility changes and the 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 influenced the changes of  $R_2$  but not the temperature that water mobility increased.

## LITERATURE CITED

- ALLEN, A. T., and WOOD, R. W. 1974. Molecular association in the sucrose-water system. *Sugar Technol. Rev.* 2:165.

- BEAN, M. M., and YAMAZAKI, W. T. 1978. Wheat starch gelatinization in sugar solution. I. Sucrose: Microscopy and viscosity effects. *Cereal Chem.* 55:936.
- BEAN, M. M., YAMAZAKI, W. T., and DONELSON, D. H. 1978. Wheat starch gelatinization in sugar solution. II. Fructose, glucose, and sucrose: Cake performance. *Cereal Chem.* 55:945.
- BROWN, A., and FRENCH, D. 1977. Specific adsorption of starch oligosaccharide in the gel phase of starch granules. *Carbohydr. Res.* 59:203.
- CHUNGCHAROEN, A., and LUND, D. B. 1987. Influence of solutes and water on rice starch gelatinization. *Cereal Chem.* 64:240.
- DUCKWORTH, R. B. 1981. Solute mobility in relation to water content and water activity. Page 295 in: *Water Activity: Influences on Food Quality*. L. B. Rockland and G. F. Stewart, eds. Academic Press: New York.
- HANSEN, L. M. 1987. Thermal transitions of wheat starch as modified by other carbohydrate components: C-13 nuclear magnetic resonance spectroscopy and differential scanning calorimetric studies. Ph.D. dissertation. Kansas State University: Manhattan.
- 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.
- LEUNG, H. K., MAGNUSON, J. A., and BRUINSMA, B. L. 1979. Pulsed nuclear magnetic resonance study of water mobility in flour doughs. *J. Food Sci.* 44:1408.
- LEUNG, H. K., STEINBERG, M. P., WEI, L. S., and NELSON, A. I. 1976. Water binding of macromolecules determined by pulsed NMR. *J. Food Sci.* 41:297.
- LIM, H., SETSER, C. S., PAUKSTELIS, J. V., and SOBCZYNSKA, D. 1992.  $^{17}\text{O}$  nuclear magnetic resonance studies on wheat starch-sucrose-water interactions with increasing temperature. *Cereal Chem.* 69:382-386.
- MATHLOUTHI, M., and LUU, D. V. 1980. Laser-Raman spectra of D-glucose and sucrose in aqueous solution. *Carbohydr. Res.* 81:203.
- MATHLOUTHI, M., LUU, C., MEFFROY-BIGET, A. M., and LUU, D. V. 1980. Laser-Raman study of solute-solvent interactions in aqueous solutions of D-fructose, D-glucose, and sucrose. *Carbohydr. Res.* 81:213.
- OSMAN, E. M. 1975. Interaction of starch with other components of food systems. *Food Technol.* 29(4):30.
- RICHARDSON, S. J., BAIANU, I. C., and STEINBERG, M. P. 1987. Mobility of water in starch-sucrose systems determined by deuterium and oxygen-17 NMR. *Starch/Staerke* 39:302.
- SHALLENBERGER, R. S., ed. 1982. *Advanced Sugar Chemistry*. AVI Publishing Co.: Westport, CT.
- SLADE, L., and LEVINE, H. 1987. Recent advances in starch retrogradation. Page 387 in: *Industrial Polysaccharides: The Impact of Biotechnology and Advanced Methodologies*. S. S. Stivola, V. Crescenzi, and I. K. M. Dea, eds. Gordon and Breach Science Publishers: New York.
- SOBCZYNSKA, D., SETSER, C., LIM, H., HANSEN, L. M., and PAUKSTELIS, J. V. 1990. Use of  $^{13}\text{C}$  and  $^{17}\text{O}$  NMR to study wheat starch-water-sugar interactions with increasing temperature. Pages 461-480 in: *NMR Applications in Biopolymers*. J. W. Finley, S. J. Schmidt, and A. S. Serianni, eds. Plenum Press: New York.
- SPIES, R. D., and HOSENEY, R. C. 1982. Effect of sugars on starch gelatinization. *Cereal Chem.* 59:128.
- SUGGETT, A., and CLARK, A. H. 1976. Molecular motion and interactions in aqueous carbohydrate solutions. I. Dielectric-relaxation studies. *J. Solution Chem.* 5:1.
- WALSTRA, P. 1973. Non-solvent water and steric exclusion of solute. *Kolloid Z. Z. Polym.* 251:603.

[Received June 6, 1991. Revision received January 8, 1992. Accepted January 22, 1992.]