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# Water relations in high ratio white cake batters and cellulose substituted white cake batters

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WATER RELATIONS IN HIGH RATIO WHITE CAKE BATTERS AND  
CELLULOSE SUBSTITUTED WHITE CAKE BATTERS

*Iowa State University*

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Water relations in high ratio  
white cake batters and cellulose  
substituted white cake batters

by

Oleane Carden Zenoble

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## INTRODUCTION

The need for reduced calorie products which maintain food volume to aid in control of energy intake of obese individuals has been discussed (Lee et al., 1969; Brys and Zabik, 1976; Scala, 1978). Several baked products have been formulated and tested which reduce calories by removing flour and replacing it with a nondigestible bulking agent, microcrystalline cellulose (MCC). The acceptable levels for MCC in these products resulted in a reduction of calories by 10-12% (Lee et al., 1969; Brys and Zabik, 1976). Beach (1980) formulated a cake acceptable to a taste panel which replaced 70% of the sugar with MCC, resulting in a 26% reduction in calories. Since sucrose represents 38% of the calories in a high ratio white cake, it is reasonable to look to this fraction for further calorie reduction.

The properties of sucrose which an ideal bulking agent must possess have been reviewed by Beck (1978). As sugar is removed from the white cake and replaced, most of the remaining ingredients are affected. Many of the changes are related to the solubility of sugar in water, thus in the aqueous phase of the cake. There is a need to know more about the interaction of ingredients and processes occurring in products as sugar is removed from foods to produce products with decreased calories. This project was proposed to investigate the effect of the decrease in sucrose and corresponding increase in cellulose in high ratio white cakes, particularly the effect on the water binding characteristics of the batter emulsion.

Several researchers have studied the water binding characteristics of pure food constituents (Berlin et al., 1970, 1971; Shanbhag, 1970; Duckworth, 1971; Leung, 1975; Wooton and Bamunuarachchi, 1978). Others have studied model systems (Bone et al., 1975; Ross, 1978). There is little data available on actual complex food systems, although water in flour doughs has received much attention (Bushuk and Winkler, 1957, Daniels, 1975; Bushuk and Mehrotra, 1977a,b,c).

Since the interaction of ingredients in a cake system is important to the overall quality and acceptability of the finished product, this project was designed to study the water binding properties of the high ratio white cake batter. Through this study, more will be learned about the water binding characteristics of a cellulose substituted white cake. These findings will be compared to the noncellulose product.

The following objectives were formulated for the present research:

- 1) Study the water binding capacity (WBC) of high ratio cake batters by differential scanning calorimetry (DSC).
- 2) Investigate the water binding capacity of sucrose and MCC by DSC in an effort to relate to the WBC of the cake emulsion.
- 3) Determine the energy for the vaporization of water from the high ratio white cake batter relative to the substituted cake batters in an effort to better understand the water binding properties.
- 4) Investigate the effect of MCC on gelatinization temperature of the high ratio white cake batter by viscosity measurements with the Brabender Visco/amylograph.

- 5) Observe and evaluate how MCC is physically incorporated into a high ratio white cake batter utilizing light microscopic techniques.

## LITERATURE REVIEW

## Water

Molecular structure

A water molecule, which consists of a single oxygen bonded to two hydrogen atoms, is formed by covalent bonding. The equilibrium position for the hydrogen atoms relative to the oxygen atom results in a configuration with a bond angle of  $104.5^\circ$ . The resulting V-like form of a water molecule and the polarized nature of the O-H bond result in an unsymmetrical charge distribution. Because of this asymmetry, water molecules have a tendency to orient themselves in an electrical field, hydrogen toward the negative pole and the negatively charged oxygen toward the positive pole. This arrangement, known as the dipole moment, results in water having a large dielectric constant. This large dipole moment cannot explain the unusually high intermolecular attractive force of water. This force is thought to be due to the ability of water to engage in hydrogen bonding which joins water molecule to water molecule with remarkable force on a three dimensional basis. Hydrogen bonds are weak (less than 10 kcal/mole) when compared to covalent bonds (average bond energy of about 80 kcal/mole). Each water molecule is able to hydrogen bond with four others, forming a tetrahedral arrangement. This ability to engage in three dimensional hydrogen bonding explains the large magnitude of values for heat capacity, melting point, boiling point, surface tension, heat of fusion, heat of vaporization, and sublimation for water. These values are related to the extra energy necessary to break intermolecular hydrogen bonds (Fennema, 1976).



### Structure of water

In spite of the abundance of information available, the problem of the structure of water remains unsolved. Several mutually contradictory theories have been proposed. These theories generally attempt to explain only limited aspects of the behavior of water. Reviews of water structure theories have been presented (Frank, 1970; Franks, 1973).

In general, models of water structure can be divided into two categories, the continuum models and the mixture models. In the continuum models, the theory holds that intermolecular hydrogen bonds are distributed uniformly throughout the water, so that each water molecule has essentially the same environment. In the mixture models, liquid water is usually considered to be a mixture of a small number of distinctly different species, wherein intermolecular hydrogen bonds are concentrated, at any given moment, in localized multimolecular clumps or clusters of water molecules (Fennema, 1976).

The simplest mixture models are the two state models, in which a bulky species and a dense species are postulated. The bulky species is considered to be an ice-like cluster of hydrogen bonded molecules, short-lived and of undetermined structure(s) as yet. It is thought to exist in dynamic equilibrium with at least one species of a dense nature; this species is assumed to be more closely packed and to be of higher energy (Fennema, 1976; Franks, 1973).

The flickering cluster models postulated that the formation and breaking of hydrogen bonds are cooperative processes. The formation of one hydrogen bond promotes the formation of other hydrogen bonds in its vicinity. Conversely, the breaking of a hydrogen bond causes the whole cluster

to "dissolve." The short-lived ( $10^{-10}$ - $10^{-11}$  seconds) ice-like clusters of varying extent are mixing and exchanging with nonbonded molecules. The high rate of formation and breakdown of the clusters introduces the necessary fluidity into the model. The cluster size is believed to be less than one hundred molecules (Frank and Quist, 1961; Nemethy and Scheraga, 1962).

#### Bound water

The subject of bound water has aroused the interest of many scientists, yet a universally accepted definition does not exist. According to Fennema (1976), bound water is not a homogeneous, easily identifiable entity, and, because of this fact, description terminology is difficult and a concise definition is nearly impossible. Usually, discussions of free and bound water are preceded by that author's definition; most frequently, definitions are in terms of the method used for the determination of the free and bound water. For example, free water in wheat products has been defined and measured by Davies and Webb (1969) as that water which freezes when the material is cooled to  $-50^{\circ}\text{C}$ . This definition of free water depends on one property of bound water, unfreezability at low temperatures. Other well-known properties of bound water include unavailability to function as a solvent, high binding energy and low vapor pressure. The term bound water usually refers to the portion of water that is so closely associated with the host substance that it exhibits different physical properties, compared to pure or free water.

Kuprianoff (1958) summarized the methods for free water measurement. One of the oldest and still one of the best methods of bound water

determination is freezing; temperatures for this determination given by Kuprianoff range from  $-50^{\circ}\text{C}$  to  $-70^{\circ}\text{C}$ . Bound water is equal to the unfrozen water, the free or frozen out water is determined calorimetrically. This process involves measurement of the latent heat of fusion; the bound water is determined from the difference in enthalpy. Unfrozen water may also be determined by dilatometry, which measures the change in volume of the sample due to freezing out of the free water. Recent workers in the field have employed calorimetric methods (Biswas et al., 1975; Bushuk and Mehrotra, 1977b,c; Ross, 1978; Wooton and Bamunuarachchi, 1978).

Solvent methods may be used to determine bound water. After adding a known solute, the freezing point or vapor point depression can be measured; the temperature depression is proportional to the bound water present (Kuprianoff, 1958).

The third group of methods reviewed by Kuprianoff (1958) was chemical methods; cobalt chloride hexahydrate changes from pink to blue when the water of crystallization is lost. Hexahydrate is added to a sample of food in a dryer at  $25-30^{\circ}\text{C}$ , and when blue is observed, no free water is present. Bound water is then determined by weighing.

Sussman and Chin (1966) and Toledo et al. (1968) used nuclear magnetic resonance spectroscopy (NMR) to quantitate the amount of bound water in cod muscle and wheat flour. Their methods were based on the fact that ice does not contribute to the NMR signal because of its very broad resonance line width. The abrupt change in signal at the freezing temperature was used to determine the amount of liquid water that remained in the system. Duckworth (1972) used NMR techniques to investigate the solvent

properties of some food colloids. Using sucrose as a reference solute, he found that the bound water contents were 0.34, 0.27, 0.24, and 0.11 g/g dry matter for agar, gelatin, starch, and cellulose. These water contents corresponded to a water activity of approximately 0.82 for the polymers studied. In 1970, Shanbhag et al. developed a NMR technique for quantitative determination of both bound water in a material and the maximum isothermal bound water capacity. This technique was based on the finding that the free water signal is saturated at high radiofrequency power, and thus becomes negligible, while at the same power the bound water signal is significant. The weight of bound water per unit weight of dry matter increased linearly with increasing moisture content to a maximum, which was called the bound water capacity (BWC). BWC remained constant upon further dilution. The BWCs have been determined for wheat flour, corn starch, egg white, and some derivatives of corn starch (Shanbhag et al., 1970; Mousseri et al., 1974). Pulsed NMR was used to study both the amount and strength of water binding by several macromolecules: cellulose, casein, starch, pectin, and sodium alginate (Leung, 1975; Leung et al., 1976).

#### Water activity

A common method of studying water in food systems is to examine their isotherms. This relationship is a graph of the water activity ( $a_w$ , defined as  $p/p_0$ , where  $p$  is the partial pressure of water in a sample and  $p_0$  is the vapor pressure of pure water at the same temperature) as a function of the moisture content of the system at a constant temperature. The sorption isotherm phenomena in foods have been reviewed by Labuza (1968). For example, isotherms for wheat flour and wheat starch are similar, as are

the isotherms for most other natural, high molecular weight polymers. The wheat starch isotherm, as measured by Bushuk and Winkler (1957), is shown in Figure 1.

Isotherms generally can be divided into three regions corresponding to the state of water present. Region A corresponds to the absorption of a monomolecular film of water on the surface of the starch molecule; such water is tightly bound by hydrogen bonding and is not easily removed. The region of the monomolecular layer ranges from  $a_w$  0 to 0.25. It is characterized by a large heat of absorption and represents the tightly bound portion of water directly adsorbed to polar or ionic sites on starch surfaces. All of this water is unfreezable (Labuza, 1968; Wootton et al., 1974; Fennema, 1976).

Region B corresponds to the absorption of further amounts of water above the monolayer. Although fairly strongly bound, the water and starch molecules are not in direct contact and binding is weaker than in Region A. This multilayer region extends from an  $a_w$  of about 0.25 to 0.70. Most "dry" food products have a water content corresponding to  $a_w$ 's in this range. The major proportion of water in Region B is unfreezable. Included here is water in microcapillaries, water hydrogen bonded to solutes, and hydrogen bonded in multilayers to other water molecules adjacent to food surfaces.

Region C, beyond an  $a_w$  of 0.70 on the curve, corresponds to the area of so-called capillary condensation in which absorbed water is not bound by surface forces and can be considered as free water. Water vapor is adsorbed on the surface by capillary condensation and solutes begin to go into

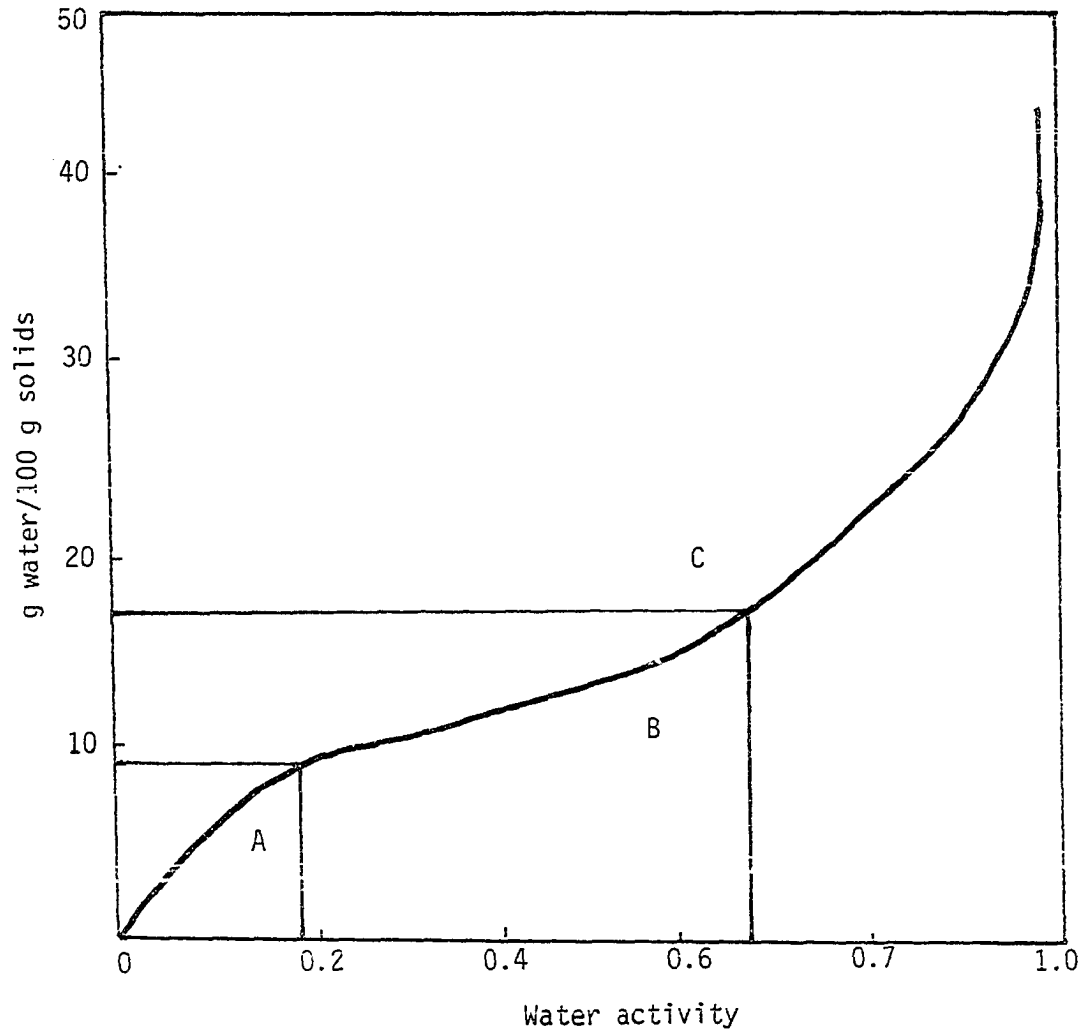


Figure 1. Relationship between water content and water activity of starch (Bushuk and Winkler, 1957)

solution in this region. This water is the first water removed in the dehydration process. Most of this water is available to support growth of microorganisms and to mobilize reactants in chemical reactions.

The isotherm is continuous and there exist no distinct boundaries between the different regions. The amount of bound water and its corresponding  $a_w$  in a food depends upon the method of measurement and may fall at different points on the isotherm. The phenomenon of water sorption is a dynamic rather than a static one. The water molecules are constantly in dynamic equilibrium with the atmosphere. Also, water molecules possessing different binding energies may exchange with each other on different sites. This exchange decreases as the degree of boundness increases. Water that is bound, however, should not be thought of as immobilized. Water that is bound to hydrophilic solutes is more structured than ordinary water, but its structure is different from that of ordinary ice (Labuza, 1968; Wootton et al., 1974; Fennema, 1976).

The manner in which a given water molecule is bound to other molecules can change as the total water content of the system is altered. At water levels in excess of the monolayer value, a given water molecule is believed to bind with only one site on a macromolecule, whereas at levels below the monolayer value this same molecule can apparently bind simultaneously with two adjacent sites on a macromolecule. Water levels in excess of the monolayer value occur in the high moisture portion of Region C (Figure 1), and represent the amount of water needed to provide one molecule of water for each binding site (Fuller and Brey, 1968).

The methodology for measurement of sorption properties has been reviewed by Gur-Arieh et al. (1965).

#### Moisture adsorption of wheat flours and cake baking performance

The air circulation method developed by Gur-Arieh et al. (1965) was used to investigate the effect of certain characteristics of a wheat flour on its moisture adsorption to determine whether this adsorption was related to cake baking performance (Gur-Arieh et al., 1967). Using the same method, the rates of moisture adsorption for four genetic variants of a hard wheat flour have been correlated to physical, chemical and baking characteristics of the flour (Udani et al., 1968).

Adsorption isotherms and desorption isotherms of several flours showed that particle size distribution does not affect moisture adsorption capacity of flours. The  $a_w$  of the flours ranged from 0.05 to 0.80 (Bushuk and Winkler, 1957; Gur-Arieh et al., 1967; Udani et al., 1968). Rates of moisture adsorption also were not affected by particle size distribution (Udani et al., 1968). The finding that the  $a_w$  of flour is not dependent on particle size seems to contradict the theory of adsorption. Adsorption is hypothesized to be a surface phenomenon and the amount of adsorbate adsorbed is dependent upon the specific surface of the adsorbent. Flour samples with smaller particle size and, therefore, larger surface area would be expected to have both a faster rate of adsorption and greater amount (Gur-Arieh et al., 1967; Udani et al., 1968). It was suggested by Gur-Arieh et al. (1967) that adsorption on the flour took place on specific sites of the adsorbate molecules, and that the number of these sites did not increase with a decrease in particle size.



To further emphasize differences in flour performance, a lean cake formula was used to relate baking performance of the flour to  $a_w$ . Cake volumes increased with a decrease in the particle size distribution of flour samples (Gur-Arieh et al., 1967; Udani et al., 1968). Cakes with different volumes exhibited different moisture adsorption isotherms; the moisture adsorption capacity decreased slightly with an increase in volume, especially at low  $a_w$  (Gur-Arieh et al., 1967). The adsorption rate of the flour was not related to cake volume or to baking performance of the flour (Udani et al., 1968).

### Calorimetric Measurements on Water in Foods

#### Calorimetry

Differential scanning calorimetry (DSC) has been defined by the International Confederation for Thermal Analysis (ICTA) Nomenclature Committee as:

... a technique for recording the energy necessary to establish a zero temperature difference between a substance and a reference material against either time or temperature, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate (MacKenzie, 1969).

The sample and references are placed in identical environments, metal pans on individual bases which each contain a platinum resistance thermometer and a heater. The DSC system measures the differential energy required to keep both sample and reference channels at the same temperature throughout the analysis. When an endothermic transition occurs, the energy absorbed by the sample is replenished by an increased energy input to the sample to maintain the temperature balance. Because this energy input is precisely equal in magnitude to the energy absorbed in the

transition, a recording of this balancing energy yields a direct calorimetric measurement of the energy of a phase transition. Thus, a fundamental difference in DSC and conventional thermal analyzers is that the conventional analyzers measure and record the temperature difference between the sample and reference channels, while the DSC measures the differential energy to maintain both at the same temperature (Watson et al., 1964).

Differential thermal analysis is a technique for recording the difference in temperature ( $\Delta T$ ) between a test substance and a reference as both are subjected to identical temperature regimes (Duckworth, 1971). Experimental data obtained are expressed in the form of a DTA curve; the temperature difference between the test and reference materials is measured and plotted on the ordinate; either time or temperature may be plotted on the abscissa. The area under the peak can be used as a quantitative measure of the amount of heat evolved or absorbed by the physical or chemical change which has occurred (Pope and Judd, 1977).

The ordinate of a DSC curve represents the rate of energy absorption by the test sample, relative to that of the reference sample; this rate naturally depends on the heat capacity of the sample (Pope and Judd, 1977). The amplitude of the pen from the baseline position is directly measured as the rate of the energy output or input (millicalories per second) and the area under a peak equals total phase transition energy (Watson et al., 1964). The DSC operates in the range  $-100^{\circ}\text{C}$  to  $500^{\circ}\text{C}$ . Cooling below ambient is accomplished by substituting an enclosure cover containing a liquid nitrogen well and Dewar jacket for the standard enclosure cover.

Samples in the range of 0.1 to 10 mg are placed in small aluminum pans and placed in the sample wells. An empty sealed pan is placed in the reference well (Watson et al., 1964).

Differential thermal analysis and DSC can both be used for 1) qualitative or semiquantitative evaluation of thermal events and the processes causing them, including the determination of phase transition temperatures, and 2) quantitative evaluation of the heats of reaction, specific heats, etc. DSC is best suited to accomplish the latter by its basic principle of operation (Daniels, 1973).

#### Measurement of freezable water

Differential thermal analysis and DSC have been used to determine the amount of unfreezable (bound) water in food systems. Bound water is defined as that portion of water in food which does not freeze. The water binding capacity (WBC) has been defined as the moisture content below which all water is unfreezable water (Ruegg et al., 1974). The water has been suggested to be held in an ice-like form due to strong hydrogen bond formation between the water and the parent compound or solute (Berlin et al., 1970).

Duckworth (1971) measured the thermal phase transitions occurring between  $-78^{\circ}\text{C}$  (or  $-70^{\circ}\text{C}$ ) and ambient temperature in 11 food products, using a DTA apparatus that he had designed and constructed. Curves for the moister samples for every food had an endothermic peak, produced as a result of the thawing of ice formed during the cooling process. There was a reduction in size of the peak for samples containing lesser amounts of freezable water. These curves were directly related to the quantity of

freezable water present in the sample. The WBC was determined for each food. This water content was determined by decreasing the moisture level in a step-wise manner until there was no peak for freezable water.

The amount of unfreezable water in cotton cellulose was between 13.1 and 14.7 g water/100 g dry solids. Moisture contents investigated were not given for all samples, but appear to range from about 13 to 46 g water/100 g dry solids.

Duckworth suggests

... that, for each of the materials examined, there exists a definite and fixed amount of water of hydration which is incapable of undergoing a normal freezing process. Additional water above this level freezes in a normal manner ....

Ruegg et al. (1974) used a Perkin Elmer DSC 1B to study the differences in water binding of two casein systems. The amount of unfreezable water was based on the peak areas of the heats of fusion. Three methods were used to estimate the amount of nonfreezable water. A procedure similar to that described above (Duckworth, 1971) gave a rough estimation of the amount of unfreezable water because of the electronic noise generated by the instrument. The second method was based on the assumption that the heat of fusion ( $\Delta H_f$ ) of freezable water was equal to the  $\Delta H_f$  of pure water (79.6 cal/g). The last method graphed the heats of fusion against the respective total water contents and extrapolated the curve to  $\Delta H_f = 0$  to obtain a value for the nonfreezable water fraction.

Casein samples with water contents ranging from 0.3 to 5.0 g water/g dry casein were cooled to  $-40^\circ\text{C}$ , then heated to  $10^\circ\text{C}$ . Unfreezable water values ranged from 0.429 to 0.442 g water/g solids depending on the casein water content.

Davies and Webb (1969) used a DSC cell on a differential thermal analyzer (duPont 900) to determine freezable water in doughs. Various levels of added water were used. The 0.5 mg samples were cooled to  $-50^{\circ}\text{C}$ , then heated at a rate of  $10^{\circ}\text{C}/\text{min}$  to  $50^{\circ}\text{C}$ . The resulting endothermic peaks were measured by a planimeter and a calibration factor was determined to relate the area of the endotherm peak to the weight of water involved in the phase transition. This factor included the latent heat of fusion of ice and a calibration coefficient for the machine for pure water at  $0^{\circ}\text{C}$ . The amount of bound water was determined by subtracting the amount of freezable water from the total water in that sample. These researchers did not state the method used for determining total water.

The results showed that, over the range of moisture levels examined, the freezable water was directly proportional to the total water. The authors suggested that, above 24.85% moisture, extra water was not sufficiently bound to prevent it from freezing at about  $0^{\circ}\text{C}$ . At this moisture level, a mean value of unfreezable water, 0.33 g/g dry flour, was determined.

Bushuk and Mehrotra (1977b) used the same procedure as Davies and Webb (1969), except that their duPont 990 thermal analyzer was equipped with the DTA cell. The bound water (BW) content of wheat flour doughs with moisture contents up to 50% were measured. The samples were cooled to  $-30^{\circ}\text{C}$ , then heated to  $30^{\circ}\text{C}$  at  $5^{\circ}\text{C}/\text{min}$ . Several factors were investigated, including the effect of mixing strength, mixing time, and water content.

When freezable water for their doughs was graphed as a function of moisture content, the curve intersected the X-axis (dough moisture mg/mg flour) at a value of about 0.3 mg/mg dry flour. Below this moisture level, all of the water was of the bound type. When the dough containing 24.7% moisture (0.33 mg/mg) was subjected to DTA, it did not show any melting peak. This indicated that there was no freezable water in this dough. This amount of bound water was considered to be bound, initially, to the available sites on the flour.

Davies and Webb (1969) reported all of the water in dough above their minimal value of 0.33 mg/mg dry matter as freezable water. Bushuk and Mehrotra (1977b) explained this difference by the two modes of thermal analysis used in the two studies.

Bushuk and Mehrotra (1977c) also used the melting mode of a DTA to measure and follow changes of bound water during storage of baked bread. There was a significant decrease in bound water during post baking storage, thought to be due to the transfer of moisture from the crumb to the crust region, since the total weight of the bread loaves did not change. There was a rapid decrease in free water in the crumb during the first 2-3 days after baking, then a leveling off, with no change during 4-7 days after baking. Bound water showed little change during the initial 4 days storage; beyond this time there was a marked decrease in bound water. The moisture loss from bread crumb to crust was initially free water. Later, when free water reached a low level, bound water contributed to the total moisture loss. Apparently free water must reach a critical low value before bound water is lost from the crumb. This loss was temperature dependent; less loss was observed at  $-20^{\circ}\text{C}$ . Fat added to the dough resulted

in a slower rate of bound water loss. It was postulated that crumb staling and a decrease in bound water content are related to the same physical changes in crumb constituents. If this fact were true, the bound water content of bread could be used as an index of bread staling.

Wooton et al. (1974) used the DSC 1B to study the water binding capacity of wheat starch and to examine the effect of salt and sugar on the level of bound water. A standard curve was established using known weights of pure water. The amount of frozen water in a sample was determined using this standard. Bound water was determined by plotting the free water vs. total water in a sample and extrapolating this line to zero free water. At the X-axis intercept, all the water in the sample was considered bound. This procedure has been described previously (Davies and Webb, 1969; Ruegg et al., 1973; Bushuk and Mehrotra, 1977b).

The starch-water mixtures with moisture contents of 29-45% were equilibrated 24 hrs at room temperature. A 4% salt or 23% sucrose solution was used in place of water to investigate these effects. Moisture content was determined by tabulating the amount of original water and the amount of water added, as well as by air oven drying at 130°C to constant weight. There was excellent agreement between the two methods.

Extrapolation of a plot of their data to 0 g free water gave a level of 0.38 g bound water/g dry starch; water in excess of this value was considered freezable and free. This value was higher than the value Davies and Webb (1969) had found in wheat doughs. The lower water binding capacity of the protein in the wheat flour was suggested as the reason for this difference.

As in the study by Davies and Webb (1969), salt had no effect on water binding capacity. Salt was felt to be part of the bound water in the system. Above 18% sucrose, as the level of sucrose increased, the bound water increased; 18% was considered the level of no effect for sucrose on the WBC. The higher water binding capacity of sucrose compared with starch explained the effect of sugar.

Starch gelatinization caused an increase in bound water to 0.41 g/g dry matter. Gelatinization causes granules to swell and disrupts weakened bonds in the amorphous regions of the granule which allows greater hydration of the molecules in these regions, and, thus, an increase in the water binding capacity of the starch.

The water binding capacities of five cereal and three tuberous starches, as well as 14 modified wheat starches, were determined with a DSC 1B (Wooton and Bamunuarachchi, 1978). An integrating chart recorder was used to measure the area of the endothermic peak representing the melting of freezable water in a sample. This was converted to a weight of freezable water by reference to a calibration plot of integrator response against known weights of water frozen and thawed under the conditions used for the starch water systems. Freezable water and total water (calculated from initial moisture content of starch plus added water) were determined for each sample and used to obtain a linear regression equation for that starch. The level of bound water was calculated from this equation at 0 g freezable water and expressed as g water per g dry starch.

Tuberous starches had higher moisture binding capacities than cereal starches; of the cereal starches, wheat starch had the highest moisture



binding capacity, 0.33 g water/g dry starch. Gelatinization also increased the WBC of starches in their study.

The effect of a number of mono-, di-, tri-, and polysaccharides on the average molar enthalpy for the fusion of water was determined using a DSC 1B (Biswas et al., 1975). The average molar enthalpy of fusion ( $\Delta H_f$ ) was calculated for the total water content of each solution; marked effects on  $\Delta H_f$  were observed at low concentrations.

These authors concluded that the amount of water bound to the solute was dependent on the water activity of the solutions. They postulated that an equilibrium existed in the solutions between bound and free water and that additional water shifted the equilibrium so that more water became bound to the solutes.

Nonfreezable (bound) water as a function of  $a_w$  was determined in several model systems using a DSC cell on a duPont 990 thermal analyzer (Ross, 1978). Since the amount of bound water is dependent on the nature of the components, he stated that correlations between bound water and  $a_w$  are meaningful only for specific systems. In every food system, bound water, as g water/g solids, decreased with decreasing  $a_w$ , along a bound water isotherm. He concluded that, for a specific system in which at least one component does bind water, the extent of binding is dependent on  $a_w$ . As  $a_w$  decreased, the amount of bound water per gram of macromolecule decreased concomitantly. The relationship between bound water and  $a_w$  was not linear. Ross states that the data were not sufficient to assign any simple functional form to the relationship. He advised caution when attempting to interpret bound water measurements. The macromolecular

concentration and the  $a_w$  of the system must be specified in order to compare results from various systems and laboratories.

### Heat of vaporization

Water binding in dough was studied using the boiling mode of the DTA (duPont Model 990) (Bushuk and Mehrotra, 1977a). This analysis is based on the fact that, owing to the boiling-off of the dough moisture, the area of the endotherm peak at about 100°C is directly proportional to the amount of energy absorbed in the vaporization of water, an endothermic process. At constant moisture, dough samples that gave a larger peak area required more energy to boil-off the same quantity of water. These authors assumed that the endothermic process at 100°C removed both bound and free water, since there were no other endothermic transitions up to 160°C.

An increase in endotherm peak area was observed with an increase in moisture content over the range investigated (35-52%). Bushuk and Mehrotra explained this by the assumption that water in dough uncovers binding sites that might not be accessible at a lower moisture content. The peak area decreased with increases in protein content of flour and increased linearly with increasing starch damage. These results imply flour proteins bind water less strongly than damaged starch. Addition of sodium chloride also decreased the energy of water binding measured in this manner. Earlier studies using the melting mode of the DTA found that salt had no effect on the bound water content (Davies and Webb, 1969; Wooton et al., 1974).

Berlin et al. (1970) used a DSC 1B to measure the integral heat of vaporization (average  $\Delta H_v$ /hydrogen bond,  $\Delta H_v$ ) of the water in four proteins hydrated to varying degrees. At lower to intermediate quantities of sorbed

water, the values for  $\Delta H_V$  were close to values for pure water. At higher moisture levels, when the sorbed water exceeded 0.18 g water per gram protein, the  $\Delta H_V$  values were 80-125 cal/g higher than pure water. At very low moisture levels, 0.05 g water sorbed per g protein, a higher value of  $\Delta H_V$  per g water was observed.

The authors explain the results in terms of a mechanism of water sorption by dry protein. At low humidities, water is bound to specific hydrophilic sites through hydrogen bonding; as more water is sorbed, the binding is weaker and the heat of adsorption decreases. The adsorption of water vapor by a protein leads to swelling of the solid, resulting in increased sites. They further suggested that, once a critical amount of water is sorbed, the sorbed water may form a quasi solid, "icelike" structure. The  $\Delta H_V$  of this "icelike" water resembles the heat of sublimation of ice rather than the  $\Delta H_V$  of liquid water.

A later study by the same researchers measured the heat of vaporization of water from whey, skim milk and whole milk powders (Berlin et al., 1971). The results of the earlier study were confirmed. When the protein powders sorbed a sufficient amount of water, the heat of vaporization of that water increased by 80 to 136 cal/g.

Muffett and Synder (1980) used a DSC 1B to investigate the  $\Delta H_V$  of water soy mixtures at various water contents to determine information on unfrozen water. When  $\Delta H_V$  was graphed as a function of water, a well-defined peak was observed before the critical moisture content was reached. There was a 200-230 cal/g difference between the  $\Delta H_V$  minimum and  $\Delta H_V$  peak for each mixture.

## Cake Technology

### Functions of ingredients

Fat, sugar, eggs, and flour are the principal raw materials used in making a cake. Water or liquid must be added to these ingredients. Each ingredient plays an important functional role in the structure and eating quality of the cake.

In the cake batter system, water is the continuous phase, containing the dissolved sugar and suspended flour particles. The fat is held in this phase in a fat in water emulsion. The air bubbles are initially held in the fat phase, and at a temperature of 40°C are transferred to the aqueous phase. At the intermediate stage of baking, air is held in the aqueous phase foam and the batter expands as the air cells expand. In the final stages, the cake structure is set as the proteins coagulate and the wheat starch partially gelatinizes. The finished cake is a heat set foam; it should have a light, aerated structure with regular and even air cell distribution (Shepard and Yoell, 1975).

Sugar In the American Association of Cereal Chemists (AACC) high-ratio white cake formula, sugar represents 140% of the flour in the formula (American Association of Cereal Chemists, 1976). Rules for the classification of cakes by Matz (1972) state that cakes in which the weight of the sugar is 110 to 160% of the weight of the flour are considered high ratio cakes.

Sucrose represents not only a large physical portion of the cake batter, but it also has many important functional properties as well. In addition to contributing sweetness to the product, sucrose acts as a

tenderizing agent. This effect is exerted during mixing through its competition with flour gluten proteins for water. Sucrose also competes with starch for water (Miller and Trimbo, 1965). Sucrose further functions to tenderize the final product by increasing the coagulation temperature of the egg proteins and the gelatinization temperature of the wheat starch, thus allowing greater expansion of the cake batter before the final setting stage. Sugar is important to the shelf life of the baked cake in that sucrose retains moisture in the crumb and, thereby, retards staling. This effect varies directly with its concentration (Matz, 1972; Shepard and Yoell, 1975).

The high osmotic pressure of the sucrose in solution in baked goods decreases the equilibrium relative humidity, or  $a_w$ . This condition suppresses microbial growth (Matz, 1972; Shepard and Yoell, 1975).

Sucrose does not contribute to crust color through the Maillard reaction (carbonyl-amine browning) as in yeast dough. However, it does contribute to caramelization browning (Campbell, 1972).

Flour Cake flour is mainly made up of lipids (about 2%), protein (about 9%), moisture (about 14%), and starch (Shepard and Yoell, 1975). On a dry weight basis, starch represents 75-80% of cake flour (Campbell, 1972). Donovan (1977) likened cake structure to a brick and mortar composite. The starch granules of flour form the bricks and the egg and flour proteins the mortar. The proteins and starch form the cake structure by being denatured and gelatinized in the same temperature range (near 95°C). The physical structural unit of starch is the granule. Studies have shown starch removed from granules did not make satisfactory cakes (Howard et al., 1968).

The water absorption properties of the starch and the degree of gelatinization in baking are important properties in cake flours (Shepard and Yoell, 1975). Starch and protein compete with sucrose for the water. Direct interaction of sucrose with protein and starch is unlikely, but interaction with protein, starch, and water is likely (Donovan, 1977).

Addition of sucrose has a greater effect on starch denaturation than on protein denaturation; when water is limited, some starch remains undenatured (Donovan, 1977).

Fat Cake properties such as appearance, volume, texture, tenderness, and flavor are affected by shortening in the batter preparation.

The crumb tenderizing effect is important. Shortening agents have this ability due to their hydrophobicity, and they can, thus, spread through a flour mixture interfering with the cohesiveness of the structure (Campbell, 1972). Shortening agents entrap air during mixing. These air bubbles contribute directly to the leavening effect, but they also help to control grain size by serving as foci for gas evolution (Matz, 1972).

Carlin (1944) used the squash technique to study the basic structure of cake batters by microscopy. Fat and flour were stained to depict the location of each. He noted the fat appeared in dark irregular clumps or lakes of fat in a continuous field of the aqueous phase which contains dissolved sugar, salt, and baking powder, and suspended flour and eggs. Air bubbles were present only in the lakes of fat. These observations demonstrate the importance of the creaming function of shortening, regardless of whether or not the fat is creamed in a separate stage (Matz, 1972).

Dispersion of shortening and air cells aid in development of proper grain, a tender and moist crumb and a large volume cake with a well-rounded top. Emulsifiers assist in this dispersion and function to incorporate air and distribute shortening to give the maximum number of air cells (Painter, 1981).

Eggs Flours used in cakes characteristically have a weak gluten structure; egg protein, thus, becomes important to the structure of the cake. In combination with gluten, proteins of the egg form the vesicle wall and permit the entrapment of air during mixing. Because of the thinness of the films formed with egg white proteins, they alone do not have sufficient strength to withstand oven expansion or handling after baking. Therefore, they do not contribute substantially to expected texture of cakes. Structural attributes must be obtained from the flour (Matz, 1972). Egg white fractions important in cake making are: globulins to produce a good foam, ovomucin to stabilize the foam, and the heat setting proteins, ovalbumin and conalbumin (Shepard and Yoell, 1975).

Egg yolks contribute emulsifying and tenderizing effects (Matz, 1972). Yolks also contribute color.

Liquid Sufficient liquid is necessary to dissolve the sugar and provide adequate moisture for starch gelatinization. The amount necessary depends on the flour absorption and the specific formula used in the cake (Wilson and Donelson, 1963). The total weight of the liquid, including the water in the eggs and milk should exceed the amount of sugar by 25-35% (Matz, 1972). Additional water is usually not added when the

formula contains dry milk, but if the formula water is not sufficient to equal reconstitution water for the milk, one percent of water for each additional percentage of milk solids should be added (Matz, 1972). Nonfat dry milk is commonly used in research formulas (American Association of Cereal Chemists, 1976). Milk solids contribute to carbonyl-amine browning and milk also contributes to flavor (Campbell, 1972).

Wilson and Donelson (1963) tested seven liquid levels (79-115%) at 6% intervals. As the amount of water added to the formula was increased, the contour of the cake went from a sunken contour to a well-rounded one and then to a peaked contour. At low water levels, the crumb was dry and coarse with a broad distribution of thick open, irregular cells. Intermediate water levels produced tight, uniform, small, thin-walled cells, and the highest levels resulted in a cake with a compact, very moist texture. The volume of the product increased rapidly with an increase in liquid to a maximum point followed by a decrease in volume. These researchers used two cake formulations, a lean cake formula with no milk or eggs, and a full formula. There was a similar pattern of response for both formulas; however, the lean formula showed a more exaggerated response and was more sensitive to changes in the liquid. It was determined that the egg and milk proteins tempered the effects of the liquid alterations. The full formula cake had about 20% higher liquid absorption. The higher liquid requirement of the full formula was attributed to additional water binding capacity supplied by the milk solids and egg albumin.



These authors concluded that the moisture requirement must be met if a successful cake is to be obtained. Sufficient water must be supplied for sorption by flour and association with sugar. Also, hydration of milk solids and egg proteins must be complete if the formula is to be in balance. Too little water to satisfy hydration requirements of the milk and egg proteins resulted in a sunken contour. Convex layers occurred even when sufficient water was present for the flour and sugar. Crumb formation requires a degree of starch gelatinization; however, starch is in an unfavorable position when competing against strongly hydrophilic sugar and proteins for the water. Excess water, however, means enough for hydrophilic ingredients and an amount left over for extensive gelatinization. In the study by Wilson and Donelson (1963), cakes formulated with high water contents assumed a gel-like character. The correct liquid balance resulted in a satisfactory cake with sufficient, but not excessive, gelatinization. Insufficient water resulted in a dry, coarse, granular crumb.

#### Lean cake formula

Criticism has been directed at traditional layer cake baking tests for being unable to differentiate among flours, because the other ingredients tend to obscure the real differences (Shellenberger et al., 1942). A simplified lean white layer cake method was developed by L. T. Kissell (1959) for the evaluation of soft wheat varieties. The sensitivity of the cake test was increased by the omission of egg whites and milk solids. This formula emphasized the structure producing ability of the test flour. The cake test manipulation was simple enough to permit mixing at a rate of

one sample for every 8 min, and also was able to provide information on other cake characteristics in addition to volume and internal appearance scores.

This lean formula was modified by Wilson and Donelson (1963) and used to determine the effects of water level on characteristics of the white layer cake. The lean formula was determined to be a minimal formula in the sense that omission of any remaining ingredients precluded formation of crumb with typical cellular appearances and texture. Comparison of a balanced complete formula with a balanced simplified formula on the basis of equal amounts of the common ingredients was not possible; balancing rules required changes in the amounts of sugar, leavening, and shortening. However, baking comparisons indicated that the simplified lean formula yielded a product with the typical characteristics of the white layer cake and had the advantage of greater sensitivity to added liquid (Kissell and Marshall, 1962).

#### Cake baking

The mechanism of layer cake baking has been summarized in three important steps: 1) initial aeration of the batter; 2) thermal stability of the fluid batter; and 3) thermal setting of the batter to form a rigid and porous expanded structure at the end of the baking cycle. The initial aeration stage depends on the entrapment of air by the fat during mixing; emulsifiers also play a part in this stage (Howard et al., 1968).

In the early stage of baking, as temperature increases, batter volume is increased by expansion of bubbles. Further increases in temperature cause starch swelling (Mizukoshi et al., 1980). The granular starch is

considered important during this early heating of the fluid batter in the oven, contributing to the thermal stability of the batter at this stage. The rate of swelling of the starch, which is accompanied by some water absorption, increases the viscosity of the fluid batter and, therefore, increases emulsion stability (Howard et al., 1968; Gordon et al., 1979). At this time, the starch is almost gelatinized and protein coagulation is accelerated. At the same time, the sol of the cake batter begins to change to the gel-like structure of the cake (Mizukoshi et al., 1980).

During the thermal setting stage, the batter changes from a fluid aerated emulsion to a solid porous structure which will not shrink appreciably or collapse on removal from the oven. For this change to occur, there has to be absorption of "free" water present in the system. At the point of thermal setting, the water absorption properties of the starch granule control the final properties of the baked cake (Howard et al., 1968). Expansion of the cake batter is stopped. Continued heating causes further coagulation of the egg and flour proteins, and the strengthening of the cake structure continues until the end of the baking period (Mizukoshi et al., 1980).

#### Starch gelatinization

Starch, the major component of flour, has been shown to be the principal ingredient determining the crumb structure of baked products (Lineback and Wongsrikasem, 1980; Bean and Yamazaki, 1978). In a cake batter, the starch exerts its greatest influence on cake characteristics through the phenomenon of gelatinization, and the timing, rate, and extent of starch swelling can be expected to influence batter and finished cake properties

significantly (Tipples, 1980). It has been shown that layer cakes can be produced with starch as the only flour component if certain ingredients were present to stabilize the batter emulsion during baking (Howard et al., 1968).

Factors which affect the gelatinization properties of wheat starch were reviewed by Olkku and Rha (1978). Changes that affected the gelatinization temperature of starch have been shown to alter the consistency of white cake batters and the quality of the baked cake (Miller and Trimbo, 1965). Studies have shown that initial gelatinization occurs at progressively higher temperatures as sucrose is increased (Jacobsberg and Daniels, 1974; D'Appolonia, 1972). Photomicrographic techniques, amylograph viscosity curves, and studies of cakes baked with a lean research formula have been used to determine the effect of sugars on cake performance (Bean and Yamazaki, 1978; Bean et al., 1978). The delaying effect of sugars on starch gelatinization appeared to be a major factor in determining layer cake volume and contour. Satisfactory cakes were obtained if the sugar/water ratio in the batter allowed the onset of gelatinization between 87 and 92°C (Bean et al., 1978).

Sandstedt and Abbott (1964) compared methods for studying the cause of starch gelatinization. Included were: light transmission measurement using a spectrophotometer; water-absorption and solubles measurement by centrifugation and drying; the amylograph; and the amylograph technique modified by use of carboxymethyl cellulose. More recent methods for studying gelatinization of starch in baked products include susceptibility of starch to beta-amylases (Watson and Johnson, 1965), light microscopy

(Derby et al., 1975), and scanning electron microscopy (Hoseney et al., 1978; Lineback and Wongsrikasem, 1980).

The most commonly used instrument is the Brabender Visco/amylograph or amylograph. This instrument records the retarding force induced by a slurry on a five spindle transducer. The slurry is heated in a cylindrical bowl with several spindles at a rate of 1.5°C per minute. The capacity of the bowl is about 500 ml. The force is recorded against a spring loaded cartridge. An increase in viscosity is represented by a greater deflection of the pen from zero (Oikku and Rha, 1978). Yasunga et al. (1968) used an amylograph to determine the various degrees of starch gelatinization that could be obtained during the baking of bread. A farinograph equipped with a 300-g stainless steel bowl was used to study the consistency development of complete cake batters at temperatures ranging from 30° to 96°C (Miller and Trimbo, 1965).

Mizukoshi et al. (1979) reported continuous starch gelatinization and protein coagulation during the baking of model systems. Light transmission was plotted against temperature and showed an increase in light transmission during starch gelatinization and a subsequent decrease in light transmission during protein coagulation. The effects of sugar on light transmission, batter volume, and gas release were also determined (Mizukoshi et al., 1980). Gas release, protein coagulation, and cessation of both batter expansion and starch gelatinization took place at the same temperature, which was raised by the addition of sugar to the formula.

### Cellulose substituted cakes

To reduce calories, while maintaining diet volume and increasing dietary fiber, cellulose has been tested for use in cake formulas. Micro-crystalline cellulose (MCC) was used to replace 0, 20, 40, and 60% of the flour, volume for volume, in a lean formula yellow cake (Brys and Zabik, 1976). Cakes were evaluated for color, tenderness, texture, moisture, flavor, and general acceptability by a trained taste panel. Cakes with 60% MCC, which were described as being too moist and gummy, scored significantly lower than the others. Cakes with 20% MCC received the highest ratings for all characteristics except color. Volume decreased as MCC increased. Cake contour and uniformity were not affected by MCC replacement. A good quality cake was attained with replacement of up to 40% of the flour, representing a 12% reduction in calories. The AACC white layer cake formula was used to determine acceptability of cakes with 30% of the flour substituted with various cellulose types and products (Zabik et al., 1977). All of the layer cakes with various types of cellulose or carboxymethyl cellulose coated cellulose were deemed high quality and feasible carriers of dietary fibers. Cakes with pectin coated cellulose were poor quality.

Beach (1980) attempted to ascertain if a white cake formulated by substitution of MCC for sucrose would produce a good quality, calorically reduced product. Three levels of three independent variables were investigated. The variables were substitution of MCC for sucrose, variation in the formula water, and the fructose/sucrose ratio. These combinations gave a total of 15 formulations.

Physical parameters measured by the Universal Testing instrument employing the texture profile method of Bourne (1968) showed the control to be softer than substituted cakes. Hardness values were the least for the substituted cake with the lowest MCC, intermediate water content, and high fructose levels. Considering only the intermediate level of MCC substituted cakes, as the fructose content increased, the hardness values increased. Springiness values decreased as MCC and fructose increased; this variability seemed related to water availability. Adhesiveness measures decreased with an increase in MCC. An increase in MCC also increased chewiness values.

Specific gravity was lowest for the control (no MCC). The control also lost the smallest amount of mass during baking. Baking loss measures increased dramatically at the highest water level. It was suggested that the water level was above that level for maximum binding. Cakes with the highest formula water also had the lowest volume. Volume measures for the substituted product were not different from the control for the cakes at the two higher levels of fructose and for the cakes formulated with MCC and water at the intermediate amount of fructose. These formulations also produced cakes with contours similar to the control as measured by the AACC template.

Moisture content increased with an increase in MCC; the higher water formulations also had higher moisture content.

Quantitative descriptive analysis by a trained taste panel was used to measure springiness, hardness, adhesiveness, and moistness. The panel found the control more springy. Hardness scores appeared to be influenced

by fructose content. Increases in fructose resulted in higher scores for hardness. These results were contrary to the objective measurements. Adhesiveness values increased with an increase in fructose at low and intermediate levels of MCC. At high levels of MCC, adhesiveness measures decreased with an increase in fructose. One formulation was determined to be like the control for adhesiveness and moistness scores (intermediate level of MCC, high water, intermediate fructose). The low MCC, low water and low fructose formulation was like the control for adhesiveness measures, and the formulation with intermediate levels of MCC and water and the highest level of fructose was like the control for moistness scores.

Considering only the substitution of MCC, the objective measurements of hardness, adhesiveness, chewiness, specific gravity, moisture content, symmetry, and volume for the 30% MCC substitution for sucrose produced cakes of quality similar to the control. Sensory evaluation showed that at 70% MCC the sensory parameters of hardness, adhesiveness, cohesiveness, graininess, and moistness were similar to the control. A 70% reduction of sugar in the control cake formula and replacement with MCC resulted in a 26.4% caloric reduction over the control formula. This caloric reduction was achieved without a corresponding loss in the product volume.

#### Microcrystalline Cellulose

Cellulose is a polysaccharide composed exclusively of glucose units. Partial hydrolysis of cellulose and x-ray evidence have shown the sugar units to consist of D-glucopyranose rings, with a beta linkage joining the #4 carbon of one glucose to the #6 carbon of the next. Cellulose is a



polymer of high molecular weight. The molecule is threadlike, several thousand times as long as it is broad, and studded with hydroxyl groups. Long linear polymers tend to align themselves to form bundles; the hydrogen bonds between adjacent molecules effectively "zipper" them together. Such bundles of molecules are called fibrils (Ward, 1969).

The inertness of digestive enzymes to the cellulose in foods is thought to be related to both chemical and physical structure, but particularly to the latter. The high degree of order in native cellulose is associated with the level of hydrogen-bonding. It is so prevalent that even water does not penetrate the crystal lattice. The accessibility of the lattice to larger molecules, like enzymes, is simply too low for action to proceed without some means for swelling of the structure. If cellulose is heated with moderately strong acid, it loses its cohesiveness and becomes a friable mass, which is shown to consist of bundles of very tiny needles. Chemically, it is still cellulose, but the molecules have shorter lengths (Ward, 1969). Hydrolysis of purified cellulose for 15 minutes in 2.5 N HCl at 105°C yields level-off degree of polymerization ( $\overline{DP}$ ) in cellulose. Microcrystalline cellulose is a mechanically disintegrated  $\overline{DP}$  cellulose. By using appropriate mechanical disintegration procedures, particle size and size distribution can be controlled (Battista and Smith, 1962). Unlike natural cellulose, MCC is nonfibrous; thus, it does not impart a graininess to foods. It consists of particles of colloidal dimensions with a narrow particle-size range. The average size of the MCC particle is 10.5  $\mu$ , the molecular weight is 30,000 to 50,000 (Trauberman, 1961).

Microcrystalline cellulose has generally recognized as safe status (Food and Drug Administration, 1972). Human clinical investigations (as cited by Battista and Smith, 1962) found no adverse effects. It is not digested by humans (Tusing et al., 1964) and has been recommended for use as a nonnutritive additive to foods where too many calories are to be avoided (Trauberman, 1961). It has been used as part of the control diet in studies on the effect of gums on the nutritive value of the diet of laboratory animals, an indication of its safe status (Rhee et al., 1981).

## MATERIALS AND METHODS

## Cake Preparation

Two cake formulas were used to evaluate the effect of substituting MCC for sucrose on the physical properties of cakes. The 10-90 white cake formula of the American Association of Cereal Chemists (AACC) (American Association of Cereal Chemists, 1976), and a lean formula based on the work of Kissell (1959) as modified by Wilson and Donelson (1963), were used. The lean formula omits the proteins from milk and eggs, thus simplifying assessment of the interactions.

The basic formulas are given in Table 1. The amount of water used in the full formula batter was as determined by Beach (1980). During her study, she determined that a dough conditioner had beneficial effects on hardness measures, grain, volume, and mitigated against the tunneling phenomena in MCC cakes. Vanall<sup>1</sup> dough conditioner was, therefore, incorporated into the basic cake formula (8 g or 4.0% on a flour basis). Microcrystalline cellulose<sup>2</sup> was substituted by volume (0.33 g MCC per g sucrose removed) for sucrose in amounts from 0 to 80%.

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<sup>1</sup>Sorbitan monostearate, mono and diglycerides, polysorbate-60, propylene glycol, lactic acid, and sodium propionate, Patco Products, Kansas City, Missouri.

<sup>2</sup>Avicel microcrystalline cellulose type PH-102, FMC, Montana, Pennsylvania.

Table 1. Layer cake formulas

| Ingredient                    | Lean formula |         | AACC 10-90 |         |
|-------------------------------|--------------|---------|------------|---------|
|                               | grams        | % flour | grams      | % flour |
| Flour <sup>a</sup>            | 150.0        | 100.0   | 200.0      | 100.0   |
| Sugar <sup>b</sup>            | 180.0        | 130.0   | 280.0      | 140.0   |
| Shortening <sup>b</sup>       | 41.8         | 27.9    | 100.0      | 50.0    |
| Nonfat dry milk <sup>b</sup>  |              |         | 24.0       | 12.0    |
| Dried egg whites <sup>c</sup> |              |         | 18.0       | 9.0     |
| Salt <sup>b</sup>             |              |         | 6.0        | 3.0     |
| Baking powder <sup>d</sup>    | 7.1          | 4.7     | 9.5        | 4.8     |
| Distilled water               | 154.5        |         | 310.0      |         |

<sup>a</sup>Softasilk bakers high ratio cake flour, General Mills, Minneapolis, Minnesota.

<sup>b</sup>Common retail lots.

<sup>c</sup>Henningsen spray dried egg white solids type P-11, Henningsen Foods, White Plains, New York.

<sup>d</sup>SAS-phosphate baking powder purchased locally.

### Calorimetric Measurements

#### Calibration

The Differential Scanning Calorimeter (DSC) 1B was calibrated according to the instructions of the manufacturer (Perkin-Elmer Corp., 1968). The standards used were naphthalene, benzene and doubly distilled water. Benzene was the calibration standard used to determine average temperature when heats of fusion were determined, and naphthalene was the standard for determination of the heats of vaporization. These two standards have melting points in the ranges of interest (5.5°C and 80.2°C, respectively).

Calibration of the instrument was accomplished by setting the differential temperature of the two sample pans to zero. This was checked and adjusted daily. Doubly distilled water was used to establish the area of the heat of fusion for 1 mg of water. This value represented the water calibration factor for this instrument.

#### Freezable water

Each sample was sealed in a Perkin Elmer volatile sample pan, weighed, and placed in the right-hand sample holder. An empty volatile sample pan was placed in the left-hand (reference) sample holder. Dry nitrogen was used as a purge to prevent condensation of moisture in the sample environment.

The low temperature cover was placed over the sample holder assembly and filled with liquid nitrogen to cool the sample to  $-50^{\circ}\text{C}$ . The sample was heated at a rate of  $20^{\circ}\text{C}/\text{min}$  to at least  $5^{\circ}\text{C}$  to obtain an endothermic peak representative of the heat of fusion.

A typical peak with the baseline drawn in is shown in Figure 2. The area of this peak was determined with a programmable Varian<sup>1</sup> integrator and divided by the water area factor to determine the amount of freezable water in the sample. The amount of bound water was determined by subtracting the freezable water from the total moisture content of the batter sample. This procedure, as described by Davies and Webb (1969), is based on the fact that bound water is that fraction of the total water in the sample that does not freeze at very low temperatures.

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<sup>1</sup>Varian Associates, Palo Alto, California.

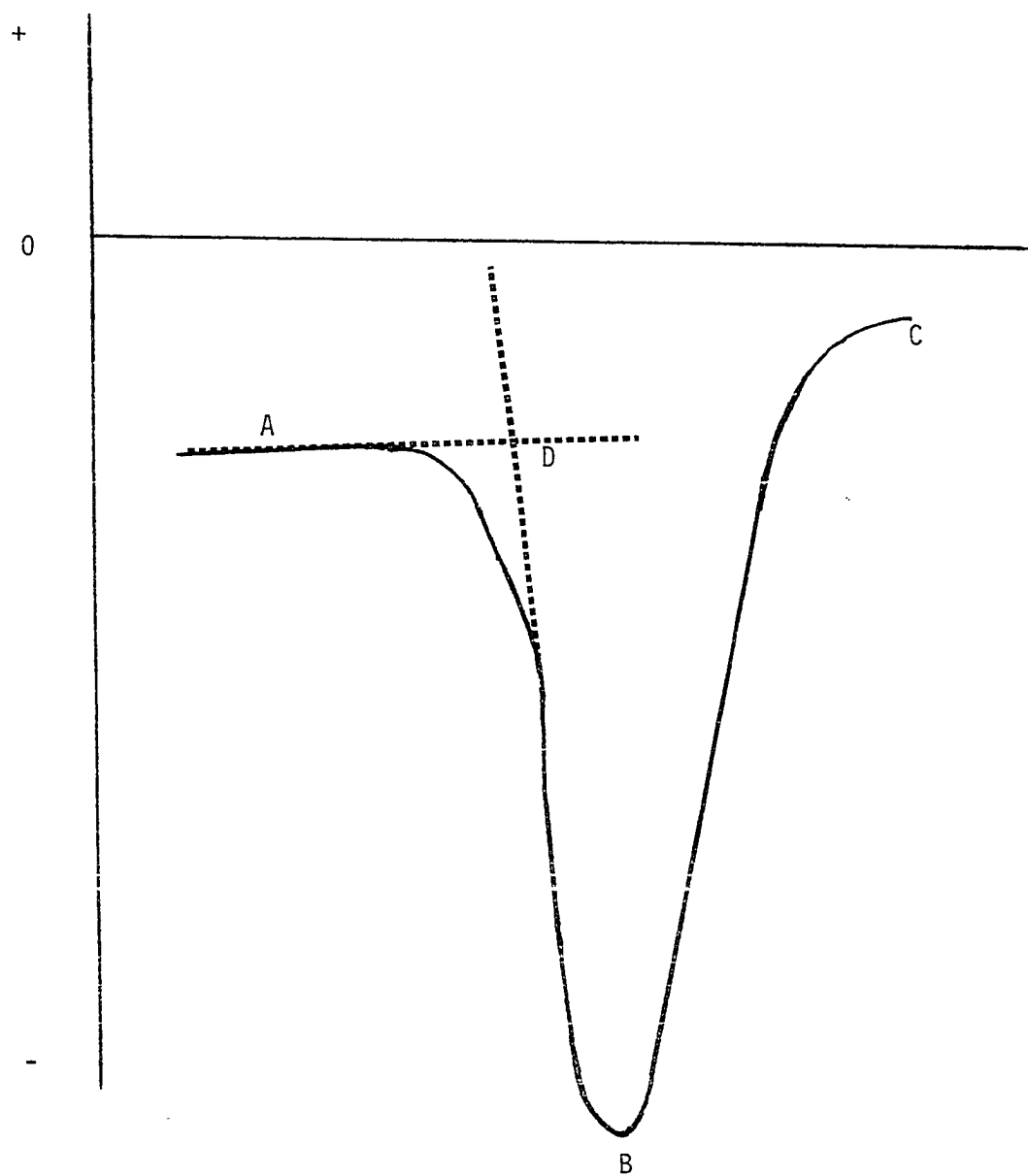


Figure 2. Example of an endothermic peak obtained by heating a frozen sample containing free water. The extrapolated onset temperature, D, is given by the intersection of the tangent drawn at the point of greatest slope on the leading edge of the peak, AB, with the extrapolated baseline AD (Pope and Judd, 1977)

### Moisture content

To determine the total water content of a sample for calculation of bound water content, the lid of the sample pan was punctured, and the sample dried to a constant weight using the DSC to heat the sample. This method was compared with standard methods of moisture determination in the preliminary work and was determined to give the same results.

### Phase transition temperatures

The heat of fusion phase transition temperatures were determined by the method described by Pope and Judd (1977). The baseline established with this method is shown in Figure 2.

### Heat of vaporization

Each sample was sealed in a sample pan for volatiles and weighed. Two to 10 mg samples were used. The sample holder was cooled to 20°C, using the cooling cover filled with liquid nitrogen or dry ice and acetone, and held at this temperature for 3 min. The sample was then placed in the holder, brought to 30°C with the cooling cover on and held for an additional minute before it was punctured to volatilize the water.

The sample was then heated at a rate of 20°C/min to 170°C. All samples produced an endothermic peak because of the heat required to vaporize the water present. The area of this peak was measured with a programmable Varian integrator. This area was divided by the g water present to determine the peak area per g of total water present in the batter. The heat of vaporization is the total energy required to remove all the water in the sample.

Each sample was weighed immediately after the scan. The difference between the weights before and after the scan was the total water weight, since further heating produced no weight change.

#### Sample preparation

Twenty-four percent of the formulas discussed above were used in DSC studies. Four levels of MCC (0, 30, 60, and 70%) were used at two levels of water (100 and 120%) to investigate the effect of MCC and the interaction with water. Water was varied (7 levels, 70-150%) to determine the bound water capacity for the control (0 MCC) and the 70% substituted formulas. Samples were mixed according to a modified two-stage method. The dry ingredients were sifted together, and the shortening and distilled water added. The batter was then mixed 0.5 min, sides scraped, mixed an additional 2.0 min, sides scraped, and mixed an additional 0.5 min. Samples were transferred to DSC pans and sealed within 30 min after mixing.

Sucrose solutions were mixed on a weight/weight (w/w) basis. When necessary, they were heated in a water bath at 90°C to create a solution. Microcrystalline cellulose suspensions were mixed according to procedures used in mixing the cake formulas.

#### Weights

A Cahn 25 Automatic Electrobalance<sup>1</sup> was used for all DSC sample weighings. Samples were weighed to the nearest microgram.

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<sup>1</sup>Cahn Instruments, Paramount, CA.



### Statistical analyses

Analysis of variance was used to determine the effect of the treatment variables on bound water and the heat of vaporization peak areas. Student's t-test was used to test significance of mean differences. Linear regression was used to determine the equations describing the intercept at which g free water equaled zero for each system. Linear regression also determined the fit and slopes of the lines drawn representing each system. The significance of the difference in slopes was investigated using general linear regression (Snedecor and Cochran, 1980). The Statistical Analysis System package (version 79.5) was used in the statistical analyses. (Statistical Analysis System, 1979).

### Viscosity Measurements

#### Batter measurements

A Brabender Visco/amylograph<sup>1</sup> (Model VA-VE) with a 700 cm-gm cartridge and a rotational speed of 75 RPM was used to determine the increase in viscosity of the batters on heating, after the method of Hsu et al. (1980). Batters were started at 30°C and heated for 50 min. The temperature necessary to reach a viscosity of 10 Brabender Units (BU) was recorded as the temperatures for initial viscosity increase.

The amount of the ingredients in Table 1 determined to give the maximum range on the recording scale of the amylograph was 24% of the lean formula and 12.4% of the full formula. Microcrystalline cellulose was substituted by volume for sucrose at six levels (0, 30, 60, 70, 75 and 80%) in the full formula and four levels in the lean formula (0, 30, 60, 70%). The

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<sup>1</sup>Brabender Industries, Hackensack, NJ.

mixing method described earlier was used with a final addition of 200 g water followed by mixing 0.5 min. The mixing bowl was rinsed with an additional 170 g water for the lean formula and 120 g for the full formula. This water was also transferred to the amylograph bowl.

#### Slurry measurements

Viscosity measurements were determined in sucrose concentrations equivalent to the high ratio white and substituted cake systems to determine the effect of MCC substitution on the increase in viscosity in the presence of the actual sucrose concentrations in the cake batters. Sucrose concentrations are expressed as percent by weight of total solution (sucrose and water); MCC was substituted by volume for the sucrose removed. Slurries were made up of 75 g cake flour dispersed in 450 ml of water, sucrose solution, or sucrose and MCC suspensions. Slurries were heated until the viscosity of the suspensions caused the recorder to go off scale. The initial increase in viscosity was recorded as the temperature at which an increase in viscosity of 10 BUs above baseline was reached.

Curves were determined for solutions of decreased sucrose content and for the same solutions with MCC present. Compensation for the decrease in sucrose content was accomplished by addition of MCC.

#### Statistical analyses

Linear regression was used to determine if MCC had a significant effect on the  $T_{10}$  and the maximum Brabender Units reached. Statistical analyses by orthogonal contrasts were used to determine whether the temperature

at each sucrose concentration was the same with and without MCC present (Snedecor and Cochran, 1980). The Statistical Analysis Systems package (version 79.5) was used in statistical analyses (Statistical Analysis Systems, 1979).

#### Batter Microscopy

The physical incorporation of MCC into the cake batters was studied by light microscopy as described by Beach (1980). In this technique, the cake batter is frozen, dehydrated, fixed, and embedded in Paraplast<sup>1</sup>. Using a rotary microtome, 8  $\mu\text{m}$  sections were cut from the embedded batter, mounted, stained, and examined under a phase contrast light microscope.

The physical structure of the batters was also studied using the smear technique. A drop of batter was placed on a microscope slide and compressed with a cover glass. Relationships between the microscopic structure of batters and quality of the resulting baked product have been established using this method (Carlin, 1944). Batters were mixed using Sudan IV stained fat. Shulzes' differential solution (Bradbury, 1973) was used to stain carbohydrates and proteins in the batters and on the slides.

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<sup>1</sup> Brunswick Company, St. Louis, Missouri.

## RESULTS AND DISCUSSION

## Freezable Water

Effect of MCC and water

Substitution of the solute, sucrose, with a macromolecule, MCC, should result in altered water binding capacity. More water was required to mix the substituted cakes, yet these cakes had a lower moisture content in the final product, indicating that the water is much more readily given up (Beach, 1980).

The first study compared batters mixed with MCC at two levels (70% and 80%), water added at two levels (100 and 120%), and the control. The 70% MCC level was determined by Beach (1980) to be acceptable; 80% substitution for sucrose would result in a greater calorie savings. A higher water level was investigated, since it produced a better product with the MCC substitutions. The results for total water are shown in Table 2 (g water/g sample). The control was significantly ( $p < 0.05$ ) different from the substitutions. This relationship was true for all parameters measured.

When the water in the sample was divided into freezable (free) and nonfreezable (bound) water (Table 3), the amount of water added to the batter significantly ( $p < 0.01$ ) affected the percent bound water in the sample at the 80% level. Within the 70% substitution, the amount of water added did not significantly affect the bound water percentage. At the higher water level, as MCC increased the bound water percentage decreased.

The overall trends seen in Tables 2 and 3 indicate that, as the moisture content of the batter increased, a greater amount of the water was added as free water. This relationship is in agreement with several

Table 2. Percent total water present in control and substituted cake batters

| % MCC             | % Water added           |            | $\bar{X}$  |
|-------------------|-------------------------|------------|------------|
|                   | 100                     | 120        |            |
| 0<br>(AACC 10-90) | 35.3 ± 0.2 <sup>a</sup> |            |            |
| 70                | 41.2 ± 0.2              | 45.2 ± 0.2 | 43.2 ± 0.2 |
| 80                | 42.1 ± 0.1              | 46.2 ± 0.1 | 44.2 ± 0.1 |
| $\bar{X}^b$       | 41.7 ± 0.3              | 45.7 ± 0.2 |            |

<sup>a</sup>Mean of 6 observations ± standard error.

<sup>b</sup>Control not included.

Table 3. Percent total water as bound and free water

| % MCC          | % Water added |                         |
|----------------|---------------|-------------------------|
|                | 100           | 120                     |
| 0 (AACC 10-90) |               |                         |
|                | % bound water | 65.5 ± 1.0 <sup>a</sup> |
|                | % free water  | 35.3 ± 0.6              |
| 70             |               |                         |
|                | % bound water | 44.4 ± 1.5              |
|                | % free water  | 55.6 ± 1.5              |
| 80             |               |                         |
|                | % bound water | 43.7 ± 2.2              |
|                | % free water  | 56.3 ± 2.2              |

<sup>a</sup>Mean of 6 observations ± standard error.

researchers who have concluded that all water added in a food system above a critical point is free water (Berlin et al., 1970, 1971; Davies and Webb, 1969; Duckworth, 1971; Ruegg et al., 1974). Most researchers using the NMR technique to measure bound water have concluded that the amount of bound water is independent of total water content (Leung et al., 1979; Toledo et al., 1968; Shanbhag et al., 1970). When the bound water in the batters was expressed on a solids basis, g bound water/g solids (Table 4), with the exception of the 80% MCC, 120% water batter the g bound water/g solids increased with total moisture content increase. The phase transition temperatures, indicating the beginning of the heat of fusion peak, decreased as the bound water fraction of the total water increased (Table 5). This would be expected, since the free water present acts more nearly like pure water and, thus, would have a phase transition heat of fusion temperature closer to zero. As the free water fraction of the total water increased, the transition temperature moved closer to zero.

Table 4. Grams bound water per g solids in control and substituted cake batters

| % MCC                  | % Water added            |             | $\bar{X}$   |
|------------------------|--------------------------|-------------|-------------|
|                        | 100                      | 120         |             |
| 0<br>(AACC 10-90)      | 0.36 ± 0.01 <sup>a</sup> |             | $\bar{X}$   |
| 70                     | 0.31 ± 0.01              | 0.34 ± 0.01 | 0.32 ± 0.01 |
| 80                     | 0.32 ± 0.02              | 0.30 ± 0.02 | 0.31 ± 0.02 |
| $\bar{X}$ <sup>b</sup> | 0.33 ± 0.01              | 0.32 ± 0.02 |             |

<sup>a</sup>Mean of 6 ± standard error.

<sup>b</sup>Control not included.

Table 5. Phase transition temperatures of cake batter

| % MCC             | % water added               |             |
|-------------------|-----------------------------|-------------|
|                   | 100                         | 120         |
| 0<br>(AACC 10-90) | - 22.6 ± 0.2 <sup>a,*</sup> |             |
| 70                | - 10.8 ± 0.4                | - 9.4 ± 0.4 |
| 80                | - 8.8 ± 0.5                 | - 8.6 ± 0.7 |

<sup>a</sup>Mean of 6 ± standard error.

\*Different from all others,  $p < 0.01$ .

This experiment illustrated the fact that the substituted batters have different bound water contents from the control, but the effect of increasing MCC was unclear. The second series of experiments was designed to determine the water binding capacity (WBC) of the control and the 70% substituted cake batters. The substitution of MCC results in a decrease in sucrose and is compensated for by an increase in MCC; therefore, the WBC of these two ingredients was also determined in an attempt to better explain the interactions.

#### Water binding capacity

The WBC has been defined as the moisture content which has no free water present in the food (Ruegg et al., 1974; Duckworth, 1971). Methods for the determination of this moisture content were reviewed (page 18).

AACC 10-90, control The data obtained for the AACC 10-90 control by varying the amount of water added are shown in Table 6. The bound water at different moisture contents is shown in Table 6. The bound water is graphed as a function of total water content in Figure 3. From this

Table 6. Data from AACC 10-90 cake batter with varying levels of water, means and standard errors

| % water added    | g water total | g free water | g bound water | g free water      | g bound water | g free water | g bound water | g total water |
|------------------|---------------|--------------|---------------|-------------------|---------------|--------------|---------------|---------------|
|                  | per g sample  |              |               | per g total water |               | per g solids |               |               |
| 60 <sup>a</sup>  | 0.236         | 0.01         | 0.22          | 0.04              | 0.96          | 0.01         | 0.30          | 0.31          |
| 70 <sup>b</sup>  | 0.27±.01      | 0.12±.00     | 0.26±.01      | 0.05±.00          | 0.95±.00      | 0.02±.00     | 0.35±.00      | 0.37±.02      |
| 80 <sup>c</sup>  | 0.31±.00      | 0.05±.03     | 0.26±.03      | 0.16±.11          | 0.84±.11      | 0.07±.05     | 0.37±.05      | 0.44±.00      |
| 100 <sup>d</sup> | 0.35±.00      | 0.12±.00     | 0.23±.00      | 0.35±.01          | 0.65±.01      | 0.19±.00     | 0.36±.00      | 0.55±.00      |
| 120 <sup>e</sup> | 0.40±.00      | 0.18±.02     | 0.21±.02      | 0.46±.05          | 0.54±.05      | 0.30±.03     | 0.36±.03      | 0.66±.01      |
| 140 <sup>f</sup> | 0.41±.00      | 0.20±.00     | 0.22±.00      | 0.47±.02          | 0.53±.02      | 0.33±.01     | 0.38±.01      | 0.71±.01      |
| 150 <sup>g</sup> | 0.42±.01      | 0.21±.02     | 0.21±.02      | 0.51±.03          | 0.49±.03      | 0.35±.02     | 0.39±.02      | 0.76±.02      |

<sup>a</sup>N=1.  
<sup>b</sup>N=2.  
<sup>c</sup>N=2.  
<sup>d</sup>N=8.  
<sup>e</sup>N=4.  
<sup>f</sup>N=2.  
<sup>g</sup>N=2.



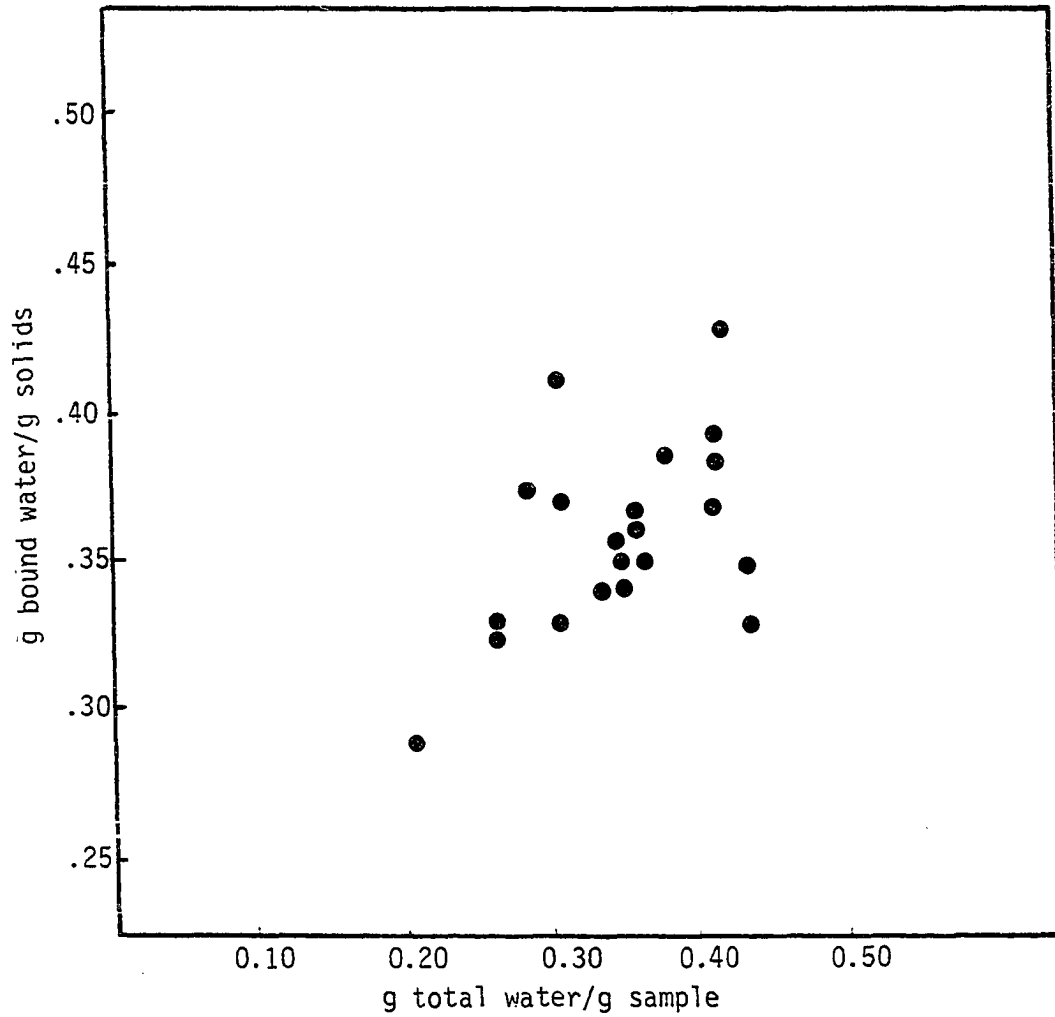


Figure 3. Bound water content of the AACC 10-90 white cake as a function of total water

graph, it appears that water content has little effect on the bound water of the batter. The critical moisture point for this system seems to fall between the lowest moisture content, 23.6% and the next higher one, 26.9%. All of the water above this critical point appears to add as free water with the amount of bound water remaining stable. As discussed, many researchers feel that this principle governs water binding in other food systems. Yet, when the results were plotted as freezable water versus total moisture (Figure 4), after the method of Davies and Webb (1969), it appears that, with an increase in the amount of water in the batter, there is no freezable water until the batter reaches a water content of about 0.335 g total water/g solids. This water content was obtained from a linear regression equation after the method of Wooton and Bamunuarachchi, 1978):

$$W_f = aW_t + b$$

where:  $W_f$  = freezable water,  $W_t$  = total water,  $a$  is the slope of the line, and  $b$  the y-intercept ( $W_f$ ). The level of bound water was calculated from this equation at zero freezable water, and expressed as g water/g solids. This water content is defined as the water binding capacity of this system. That is, the moisture level where all the water in the system is bound; thus, no measurable freezable water exists (shown by the arrow in Figure 4). The lowest moisture content used was 23.6% moisture (0.309 g total water/g solids) which corresponded to 0.014 g free water/g solids. This data point is lower than the extrapolated value for freezable water to exist. The data for this moisture content were

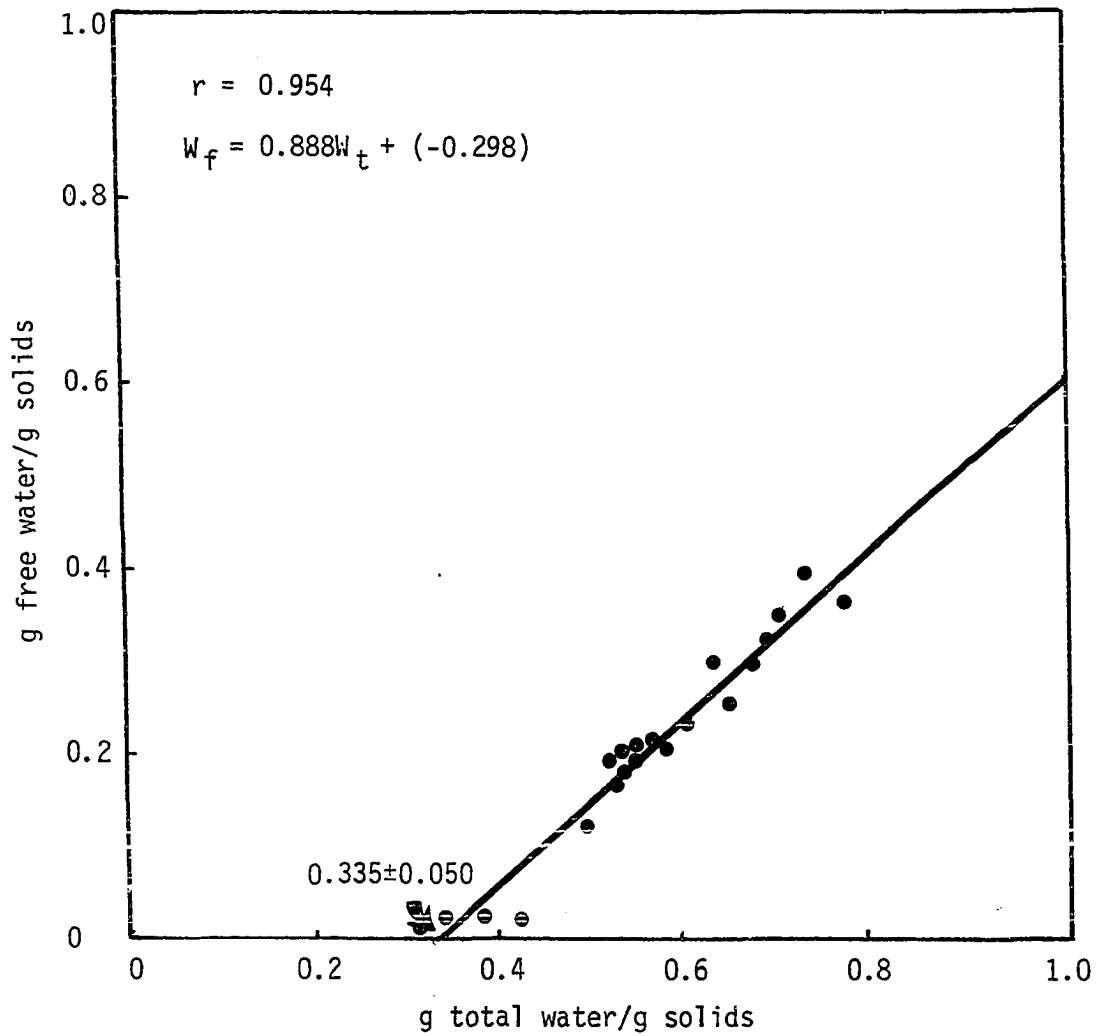


Figure 4. Amount of free water found at various levels of total water in AACC 10-90 cake formula

very difficult to obtain. The DSC 1B had to be set to the most sensitive setting which resulted in a high background noise. A large sample was also required. There was 4% less moisture in this sample than in the sample with 70% of the water added, yet the amount of freezable water was the same for both batters. It was felt that this was due to the limits of the instrument being challenged by the very small amount or nonexistent amounts of freezable water present. This data point is a single point because repeated attempts to determine freezable water at this moisture level were unsuccessful. Thus, this 60% added water batter was considered to have no free water according to the linear regression equation. This batter also appeared to have undissolved sugar crystals.

If all the moisture in the batter above the extrapolated value for zero free water, 0.335 g total water/g solids, were free water, as concluded by Duckworth (1971) and Davies and Webb (1969) and others, then the slope of the line in Figure 4 would be equal to one, indicating every g of water added is free. However, the slope was  $0.888 \pm 0.065$  meaning nearly 11% of the water added to the sample was bound. Bushuk and Mehrota (1977b) found that, above the dough WBC value of 0.3 mg freezable water/mg dry flour, only two-thirds of water added was of the free type, and the rest was bound. They felt that this increase in bound water with additional moisture suggested that the additional water uncovers new sites for water binding that are not accessible initially.

The WBC of doughs was expressed as mg freezable water/mg dry flour. The WBC in this study was expressed as g freezable water/g solids. The major ingredient in doughs to bind water is flour. In the cake batter, flour, sucrose and the egg and milk proteins all contribute to the WBC.

For these reasons, the data are calculated as g freezable water/g solids. If these data were expressed as g freezable water/g flour, the value would be higher (1.061 g/g). This higher WBC value over that of doughs is felt to be due to the presence of the additional ingredients.

Substituted batter The data for the high ratio cake batter with 70% of the sucrose removed and substituted with MCC by volume are shown in Table 7. Bound water as a function of total water is shown in Figure 5. There appears to be no relationship between total water in the sample and bound water. When total water content was expressed as g water/g solids, rather than as g water/g sample (wet weight), graphs of the data for the control (Figure 4) and the 70% MCC substituted cake (Figure 6) suggested a linear relationship between the freezable water content and the total water content. Expressing both freezable and total water content as g/g solids makes possible a direct comparison between the two values, a comparison which should reflect the actual physical system of the hydrated carbohydrates in the batters. This method was determined to be satisfactory for the estimation of freezable water in wheat flour doughs by Davies and Webb (1969), and has been used in wheat starch and wheat flour systems (Bushuk and Mehrotra, 1977a, b, c; Wooton et al., 1974; Wooton and Bamunuarachchi, 1978). The linear regression equation for this system gave a WBC of the MCC batter as 0.299 g total water/g solids, the minimum level for free water in this system. The slope of this line was  $0.976 \pm 0.046$ , indicating that for practical purposes all of the water added above the minimum level was added as free water. Thus, the WBC of the substituted system is less than the control and, as water is added above this level,

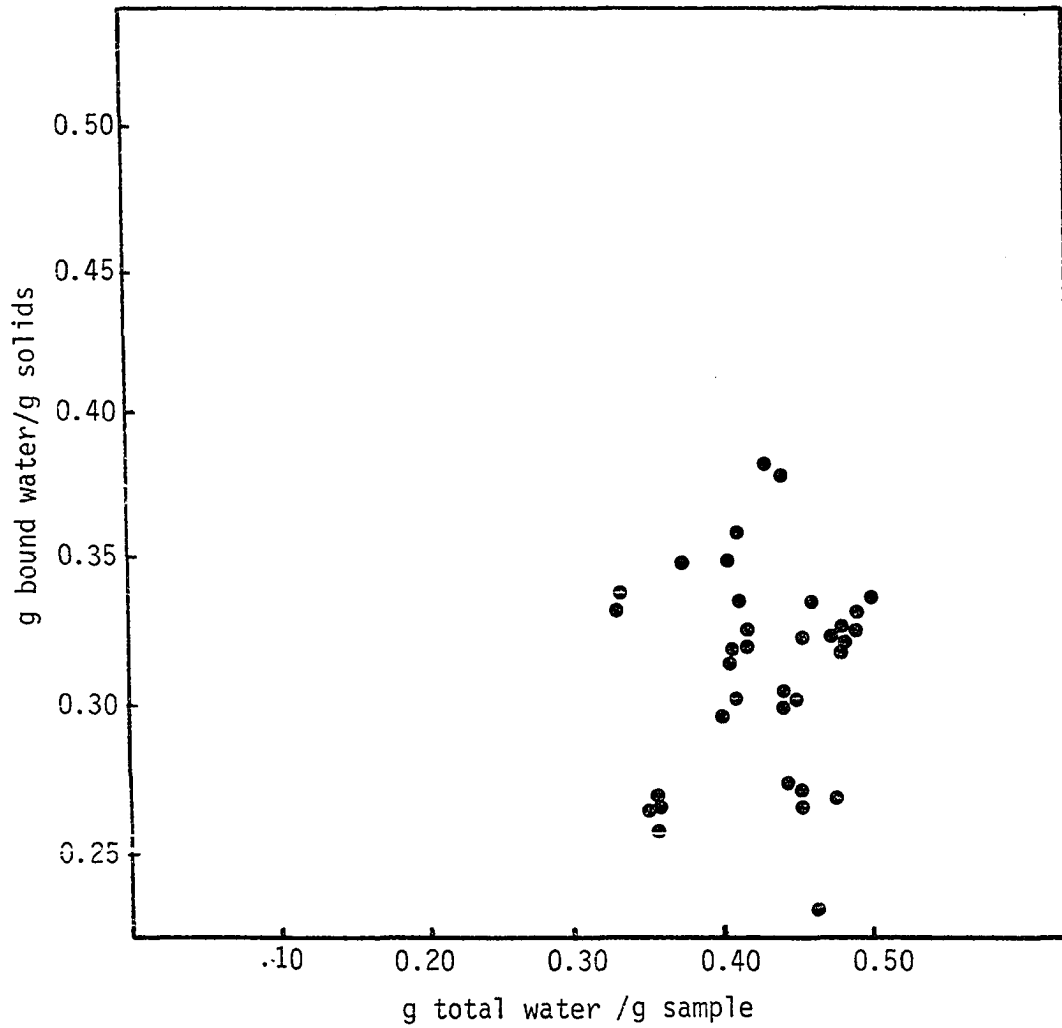


Figure 5. Bound water content of the 70% MCC substituted white cake batter as a function of the total water

Table 7. Data from 70% MCC substituted cake batter with varying levels of water, means and standard errors

| % water added    | g total water | g free water | g bound water | g free water      | g bound water | g free water | g bound water | g free water |
|------------------|---------------|--------------|---------------|-------------------|---------------|--------------|---------------|--------------|
|                  | per g sample  |              |               | per g total water |               | per g solids |               |              |
| 70 <sup>a</sup>  | 0.34±.003     | 0.11±.001    | 0.22±.002     | 0.34±.000         | 0.66±.000     | 0.17±.002    | 0.34±.002     | 0.51±.007    |
| 80 <sup>b</sup>  | 0.36±.002     | 0.19±.001    | 0.17±.001     | 0.53±.001         | 0.47±.001     | 0.30±.003    | 0.26±.003     | 0.56±.004    |
| 100 <sup>c</sup> | 0.41±.004     | 0.22±.008    | 0.19±.006     | 0.53±.017         | 0.47±.017     | 0.37±.016    | 0.32±.016     | 0.69±.011    |
| 120 <sup>d</sup> | 0.46±.002     | 0.28±.006    | 0.17±.006     | 0.62±.013         | 0.38±.013     | 0.52±.012    | 0.32±.012     | 0.84±.008    |
| 130 <sup>e</sup> | 0.47±.002     | 0.33±.010    | 0.14±.012     | 0.70±.024         | 0.30±.024     | 0.62±.018    | 0.27±.018     | 0.89±.008    |
| 140 <sup>f</sup> | 0.49±.001     | 0.32±.001    | 0.17±.001     | 0.66±.002         | 0.34±.002     | 0.64±.003    | 0.33±.003     | 0.97±.006    |

<sup>a</sup>N= 2.

<sup>b</sup>N= 4.

<sup>c</sup>N=10.

<sup>d</sup>N=11.

<sup>e</sup>N= 4.

<sup>f</sup>N= 4.

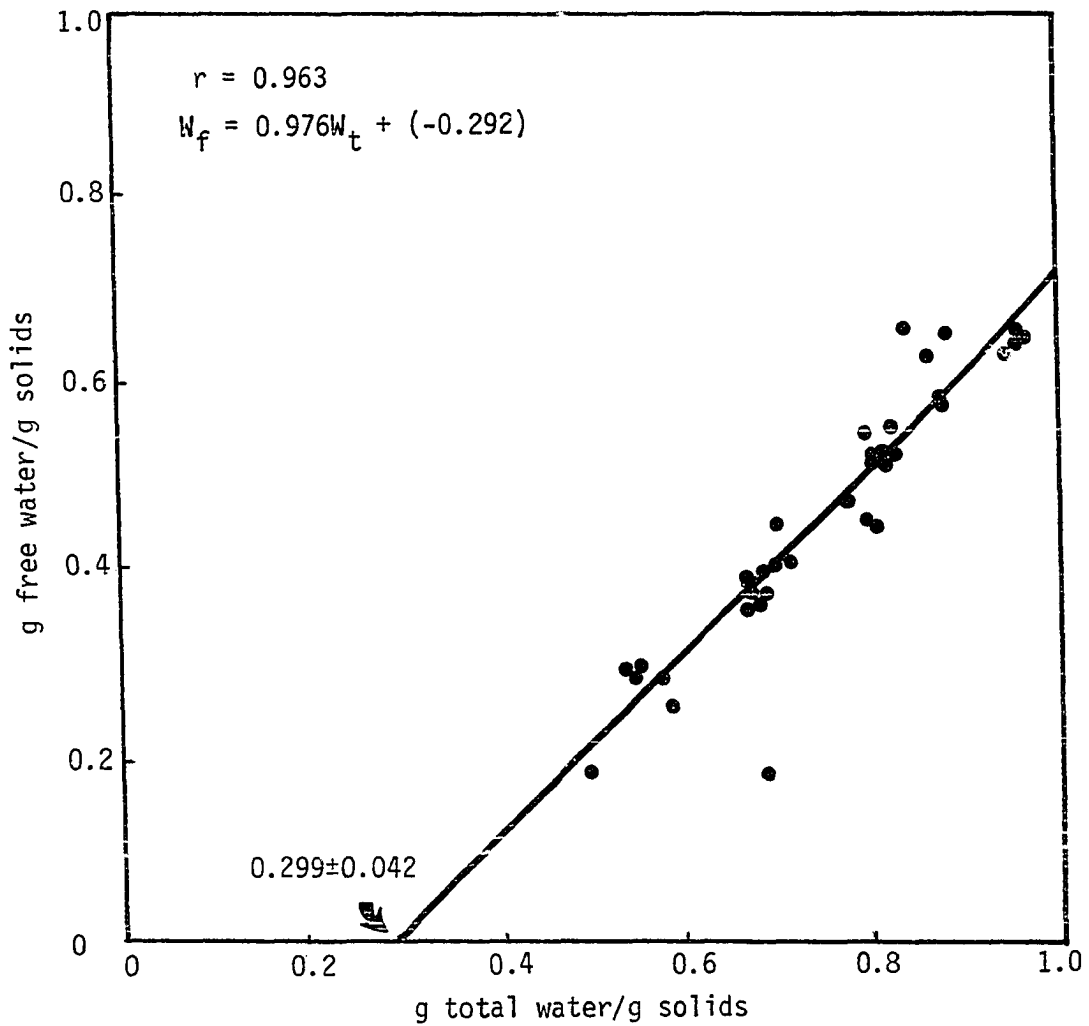


Figure 6. Amount of free water found at various levels of total water in 70% MCC batter



all of the water in the substituted system is added as free water, whereas the sucrose system has some ability to continue to bind water above the minimum level.

The WBC value of the control cake batter was closer to the value for starch water systems 0.38 and 0.33 g bound water/g dry starch than the substituted system (Wooton et al., 1974; Wooton and Bamunuarachchi, 1978). Toledo et al. (1968) applied the freezing technique with wide-line NMR to measure liquid water in samples of wheat flour and dough. The bound water content, defined as that which remained liquid at  $-18^{\circ}\text{C}$ , was 0.29 g water/g dry solid in wheat flour doughs. This value was independent of the total moisture content for doughs with moisture contents greater than 24.6% and was the same for wheat flours or wheat doughs. Shanbhag et al. (1970) suggested that water binding may be temperature dependent and, thus, used a wide line NMR at different temperatures to measure the signal at 0 rf decibels (db). They determined the bound water capacity of wheat cake flour to be 33.0% moisture, wet basis. Above this moisture content, the bound water signal was essentially constant, indicating all added water above this level was added as free water. The WBC of dough was determined by DSC to be 0.33 g/g dry flour (Davies and Webb, 1969; Bushuk and Mehrotra, 1977b). It would appear that the WBC of the cake system should be much higher because of the presence of sucrose as reflected by the lower WBC when sucrose is removed in the substituted cakes. Wooton et al. (1974) determined the level of bound water in three starch-sugar-water mixtures. They found that an increase in sucrose level resulted in an increase of

bound water levels in the starch-water system from 0.38 to 0.42 g bound water/g dry starch. The sucrose concentrations studied were 18.4-19.7% sucrose (w/w), much lower than the 45-50% sucrose concentrations present in the AACC 10-90 cake. They are close to the value in the 70% substituted cake.

Comparison of control and substituted batters When the two systems are placed on the same graph (Figure 7), water binding differences are readily seen. This is felt to be due to the decreased sucrose content of the substituted batter. A literature search revealed that several researchers had determined the WBC for sucrose-water systems, but no values were found for MCC. Pulsed NMR was used to determine the water binding ability of several macromolecules, including cellulose (Leung et al., 1976, 1979). The relaxation value for cellulose samples was three times as high as those for other materials in the high moisture range (corn starch, casein, pectin and sodium alginate), which suggested that cellulose was a weak water binder.

Water absorption studies showed that cellulose absorbs little water even at high relative humidity (Leung, 1975). Duckworth (1971) and Leung (1975) determined the WBC of cellulose, but not of MCC. As discussed in the review, MCC is acid hydrolyzed  $\overline{DP}$  cellulose with amorphous and crystalline regions. The high level of hydrogen bonding in native cellulose does not allow water to penetrate the crystal lattice. Some modified celluloses have gel forming abilities, forming a three-dimensional network by a mechanism classified as micelle junctions; methylcellulose and hydroxycellulose are examples. The gels form on heating a cold solution and the

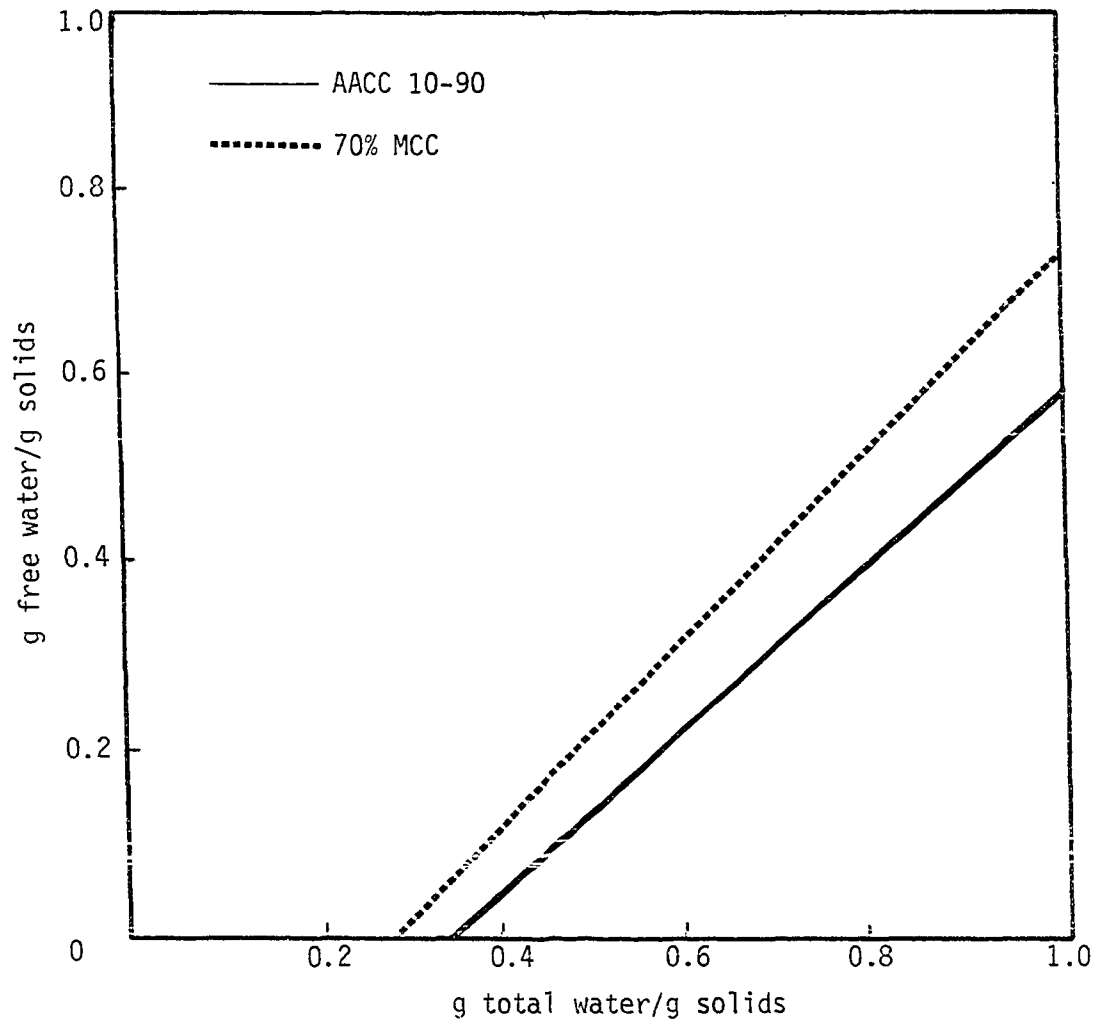


Figure 7. Amount of free water found at various levels of total water in the AACC 10-90 and the 70% MCC cake batters

mechanism is envisaged as involving the hydrophobic interaction of the most densely substituted region of the cellulose chains, leaving relatively unsubstituted (and hydrophilic) parts of the chains free in solution (Ward, 1969).

Methylcelluloses contribute to cell structure and reduce crumbling in baked products, while allowing more water to be carried in a dough permitting more complete gelatinization of the starch (Greminger and Savage, 1959). Cellulose gums (sodium carboxymethylcellulose) have wide use in baked goods to increase volume and prolong freshness. Cellulose gums bind water, preventing syneresis in food products and preventing undesirable ice crystal growth in frozen confections (Batdorf, 1959).

Since the substituted cakes require more water to mix, as the amount of MCC was increased, it was questioned if this water was required for water of hydration or merely a requirement due to the large physical size of the MCC molecule as compared to sucrose.

Sucrose and MCC The WBCs of sucrose and MCC were determined by the DSC 1B and are shown in Figures 8 and 9. Total water was determined by calculation of the known moisture content of the product plus added water at each level. The linear regression equation indicated the g total water/g solids level for all the water to be present as freezable water was 0.415 for sucrose and 0.270 for MCC. This calculation confirms the much greater WBC of sugar over MCC.

MCC:water At water levels below 29.1% (point a, Figure 8), there was no freezable water determined by measurements on the DSC 1B. The lowest moisture level represented 0.410 g total water/g solids. This level is above the maximum level of 0.270 g total water/g solids determined

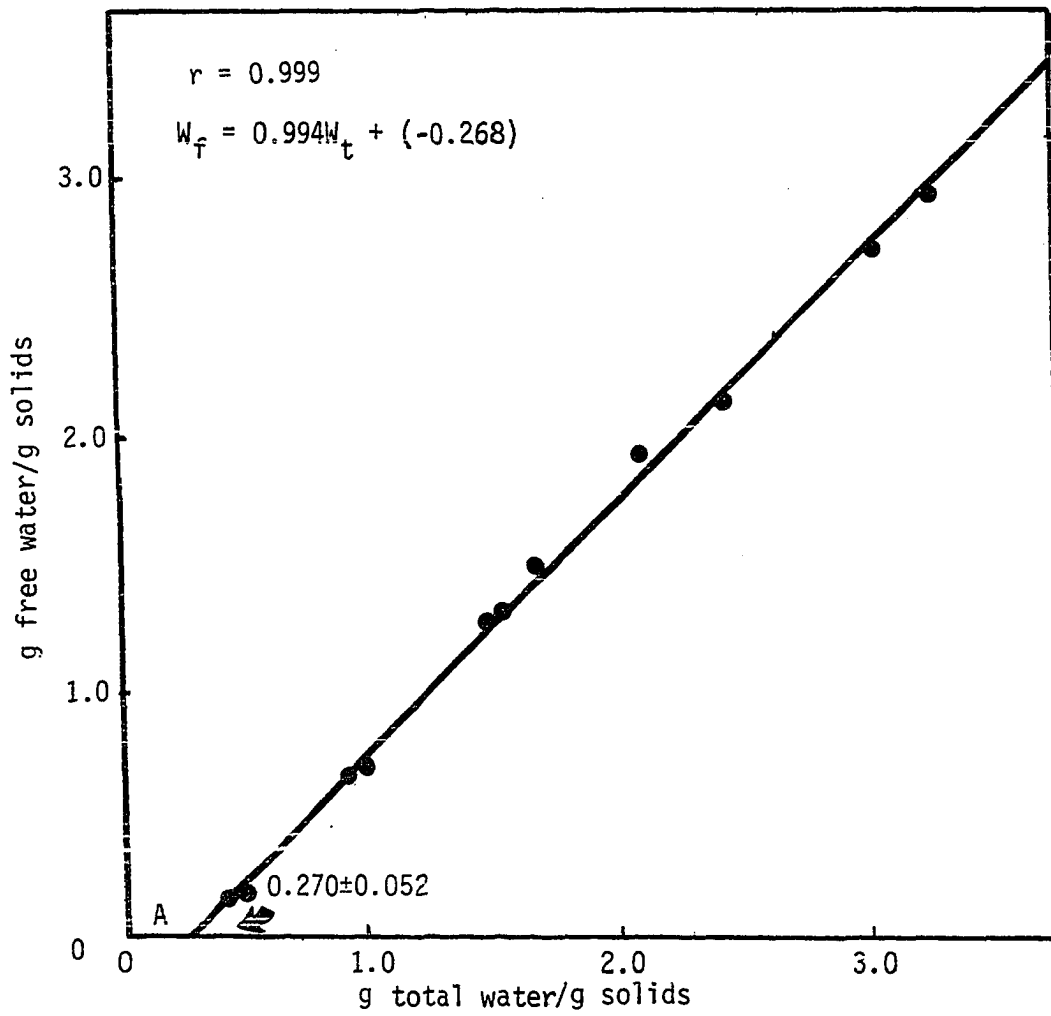


Figure 8. Amount of free water found at various levels of total water in MCC:water suspensions

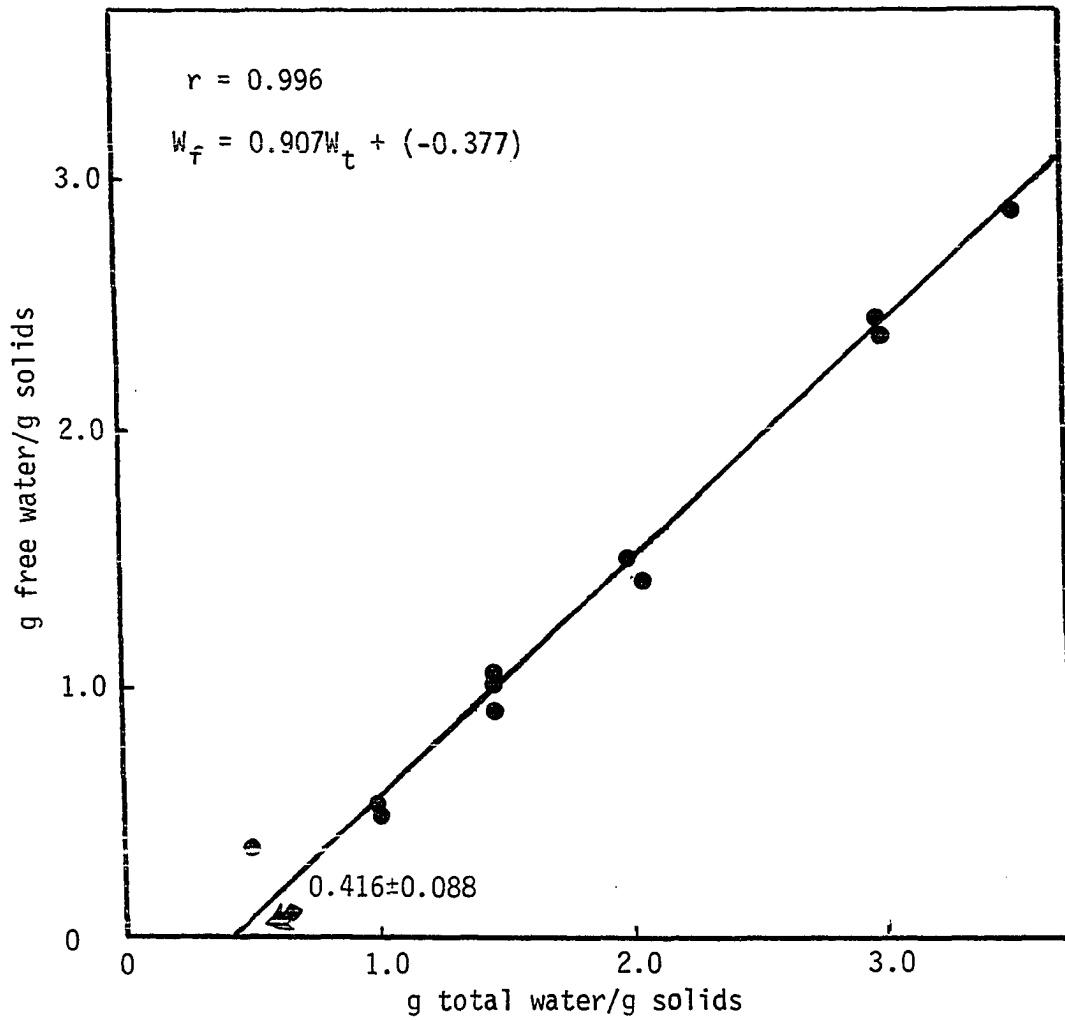


Figure 9. Amount of free water found at various levels of water in sucrose:water solutions

to be the point below which no freezable water exists. Above this point, freezable water should exist, yet, even at this level, there was difficulty in determining the freezable water present. Unsuccessful attempts were made to record freezable water below this moisture level. The correlation of the line in Figure 8 was 0.999, indicating an excellent fit.

Leung (1975) determined cellulose to contain 0.124 g unfreezable water /g dry matter. This value compared closely to Duckworth's (1972) value of 0.11 g bound water/g dry matter. The value determined for MCC, 0.270 g unfreezable water/g dry matter, was much higher, indicating that this type of cellulose has greater water binding capabilities than the cellulose investigated by those workers. The manufacture of MCC yields a porous product with a large surface area having many terminal hydroxyl groups capable of binding water.

The slope of the line in Figure 8 was  $0.994 \pm 0.017$ , indicating that all water added above the WBC was added as free water. Leung (1975) and Duckworth (1971) also concluded this to be true in their studies concerning cellulose.

Sucrose:water Sucrose has a much smaller molecular weight than MCC, and it is water soluble; so, different water binding properties were expected. The line in Figure 9 had a slope of  $0.907 \pm 0.028$  indicating the ability of sucrose to bind water above the WBC. The WBC of sucrose was 0.416 g total water/g solids. The lowest moisture content at which freezable water was present was 33.3% moisture; below this value the DSC 1B did not detect a peak for the freezing of water. This moisture content represents 0.499 g total water/g solids; therefore, the extrapolated value of 0.416 g total water/g solids seems reasonable. This extrapolated value

agrees well with the value determined by Leung (1975) using NMR, which was 32.7% moisture for the bound water capacity of sucrose. Shanbhag (1970) obtained a different WBC for sucrose using wide line NMR, 20.45%. This difference could be due to incomplete solubilization of the sucrose. Water was added to solid sucrose, whereas, Leung (1975) started with a saturated solution to which sucrose or water was added. In the present study, we started with a solid and solubilized the sucrose. In a low radiofrequency field (28 db) NMR study, the NMR signal increased linearly with percent moisture content to what was termed a "critical point," 34.0% moisture content for sucrose which coincided with the solubility limit of sucrose at 25°C. At this point, the increase was linear with a much smaller slope. This response was similar for fructose and glucose. The explanation for this shift in the slope seemed to be related to the solubility limit; the addition of water tended to dissolve the sugar and mobilize the sugar molecules (Leung, 1975). The NMR signal was coming from both the liquid water and the mobilized sugar molecules. As the moisture content increased, more sugar became mobilized and more water was present. Therefore, the signal increased rapidly with addition of water. After the solubility limit was reached, all the sugar had become dissolved and mobilized, and the increase in signal was due to the addition of water alone, resulting in a lower slope.

The signal at radiofrequency, 0 db, was used to determine the WBC. This signal was graphed as a function of moisture content. The resulting graph resembled a teepee, extrapolation to the x-axis from the apex was defined as the bound water capacity, the moisture content at which all the water is bound. In most cases, this plot ascended linearly with increasing



signal to a peak (WBC), then descended linearly. However, the sucrose plots gave an ascending linear line, but the descending line was linear for only the first third of the descent, then curvilinear at higher moisture contents. This occurrence was explained on the basis that dissolved sucrose cannot bind water. This curvilinear relation results from the fact that sucrose is a soluble solid. The ascending part of the curve indicated that all the water added to sugar up to the WBC is bound and does not dissolve any sucrose. Then, as the WBC is exceeded so that free water is present, the free water dissolved some sucrose; if saturated, 1 g of water would dissolve 2 g of sucrose. The sucrose that is dissolved can no longer bind water because only a solid can bind water as measured by NMR. This change in state sets free the water that had been bound by the sugar that had just been solubilized (Shanbhag, 1970).

This process cannot continue to complete solution of the sucrose, because the process is limited by the solubility of sugar in water. However, Shanbhag stated that this does explain the concave nature of the descending curve; at any given moisture content, there is less crystalline solid present than the total solids content, and, therefore, less bound water than expected.

Discussion It should be noted that the water binding mechanisms of sugar and most food macromolecules are different. For water-insoluble macromolecules, such as MCC, water is adsorbed at various binding sites on the surface by hydrogen bonding, van der Waals forces, and capillary condensation. The interactions between sugar and water are typical of those interactions of solute and solvent; whereas, addition of sugar to water tends to reduce its effective concentration and its activity. In

general, Raoult's law can be used to calculate the water activity of a solution by knowing the concentration of the solute (Bone, 1969; Bone et al., 1975).

Biswas et al. (1975) attributed the solute/solvent interactions in disaccharides to the presence of polar groups in the carbohydrate which can form hydrogen bonds with the solvent. For macromolecules, multilayer hydration of the solute molecule has been proposed (Hoover and Mellon, 1950).

When solute:solvent concentration is decreased, a limiting value is reached at which no water in the solution is frozen. The same is true for macromolecules and for aqueous suspensions, as observed in the sucrose:water solution, and the MCC:water suspension. The solute sucrose had greater WBC than MCC; the heat of fusion ( $\Delta H_f$ ) was higher for MCC, indicating more free water was present at a given moisture content. Biswas et al. (1975) determined the  $\Delta H_f$  of water for sucrose at varying concentrations. Extrapolation to  $\Delta H_f = 0$  gave a solution of approximately 70% w/w, in good agreement with the concentration at which no freezable water was present in the current study. Both methods used a DSC 1B, but a slightly different interpretation technique. The sucrose:water  $\Delta H_f$  decreased initially, then showed a leveling off effect as the concentration increased. But, as the concentration increased still further, the  $\Delta H_f$  continued to decrease (Biswas et al., 1975). This leveling off was not observed in the present study.

The amount of bound water is due to the presence of polar solute groups which can form hydrogen bonds with the water molecules (Biswas et

al, 1975). However, in this study, as in others, the amount of bound water (as % total water) increased with decreasing solute concentration; that is, the bound water is not independent of the total water in the sucrose:water solutions. Multilayer arrangement of water molecules around the sucrose molecule has been proposed as one possibility at low concentrations (Biswas et al., 1975).

In the MCC:water suspensions, the bound water content was a constant value above the WBC, indicating no additional water was bound. The MCC also did not depress the freezing point of water as does sucrose, indicating little interference by the MCC with the freezing of the water present.

It is felt that the water initially bound to the MCC molecule is held by hydrogen bonding to the surfaces of the amorphous and crystalline regions; by capillary condensation in a polymer network in the amorphous regions and by van der Waals forces. The effect is mainly a surface phenomenon, since the amorphous regions are limited due to the manufacturing process. Many of the amorphous regions are hydrolyzed, leaving a predominantly crystalline product (Battista and Smith, 1962).

#### Effect of varying MCC on unfreezable water

A third study was designed in which the water added was held constant at 120% of normal and five levels of MCC were investigated. The levels of MCC used and results are shown in Table 8. As MCC increased, the percentage of total water in the sample increased by 7% in the 80% substituted cake over the control. The percent of this water that was free increased. When expressed as g free water/g solids (Table 8), the amount of free water more than doubled, while g total water/g solids increased by about

Table 8. Parameters for 120% water added batter with 5 levels of MCC, means<sup>a</sup> and standard errors

| % MCC           | g total water | g free water | g bound water | g free water | g bound water             | g free water | g bound water | g total water |
|-----------------|---------------|--------------|---------------|--------------|---------------------------|--------------|---------------|---------------|
|                 | per g sample  |              |               | per g water  |                           | per g solids |               |               |
| 0 <sup>b</sup>  | 0.40 ± 0.00   | 0.18 ± 0.02  | 0.22 ± 0.02   | 0.46 ± 0.05  | 0.54 ± 0.05 <sup>a</sup>  | 0.31 ± 0.03  | 0.36 ± 0.04   | 0.66 ± 0.01   |
| 30 <sup>c</sup> | 0.43 ± 0.01   | 0.24 ± 0.00  | 0.19 ± 0.00   | 0.56 ± 0.00  | 0.44 ± 0.00 <sup>b</sup>  | 0.92 ± 0.01  | 0.33 ± 0.01   | 0.75 ± 0.02   |
| 60 <sup>d</sup> | 0.44 ± 0.01   | 0.25 ± 0.02  | 0.18 ± 0.02   | 0.57 ± 0.05  | 0.43 ± 0.05 <sup>bc</sup> | 0.44 ± 0.02  | 0.34 ± 0.05   | 0.72 ± 0.02   |
| 70 <sup>e</sup> | 0.46 ± 0.00   | 0.28 ± 0.01  | 0.18 ± 0.01   | 0.62 ± 0.01  | 0.38 ± 0.01 <sup>cd</sup> | 0.52 ± 0.01  | 0.32 ± 0.02   | 0.84 ± 0.01   |
| 80 <sup>f</sup> | 0.47 ± 0.00   | 0.30 ± 0.01  | 0.17 ± 0.01   | 0.65 ± 0.02  | 0.35 ± 0.02 <sup>d</sup>  | 0.57 ± 0.02  | 0.31 ± 0.02   | 0.89 ± 0.02   |

<sup>a</sup>Means with different superscripts are different (p<0.01).

<sup>b</sup>N=4.

<sup>c</sup>N=2.

<sup>d</sup>N=2.

<sup>e</sup>N=11.

<sup>f</sup>N=8.

one-third. MCC had an effect on the percent water in the sample, because MCC was substituted on a volume basis. In the control with 120% water, water added comprised 36.6% of the weight of the batter ingredients; for the 30, 60, 70, and 80% substituted batters, the values were 38.7, 39.5, 42.0, and 42.9%, respectively. The increase in the amount of total water/g sample was expected, although the increase is slightly greater than the increase in the percent of added water. Since the g total water/g sample was unavoidably varied in this part of the study, the bound water as a percent of the total water was the parameter tested. As MCC was increased, the bound water expressed per g water (Figure 10) decreased significantly ( $p < 0.01$ ). The control had more bound water than the substituted batters (Table 8). The 30 and 60% MCC batters were similar, as were the 70 and 80% batters. These data confirm the trends seen in the experiments with 2 levels of MCC. As MCC was added, the batter exhibited a decreased water binding capacity compared to formulas with higher sucrose content.

### Heat of Vaporization

#### Effect of varying water

Analysis of water binding from peak areas assumes that the endotherm peak is proportional to the amount of heat energy absorbed in the vaporization of the water. This assumption was valid since the vaporization of water is an endothermic process. At a constant moisture content, batter samples which gave a larger peak area required more energy to remove the same quantity of water. As with Bushuk and Mehrotra (1977a), it was assumed that the peak area represented energy necessary for removal

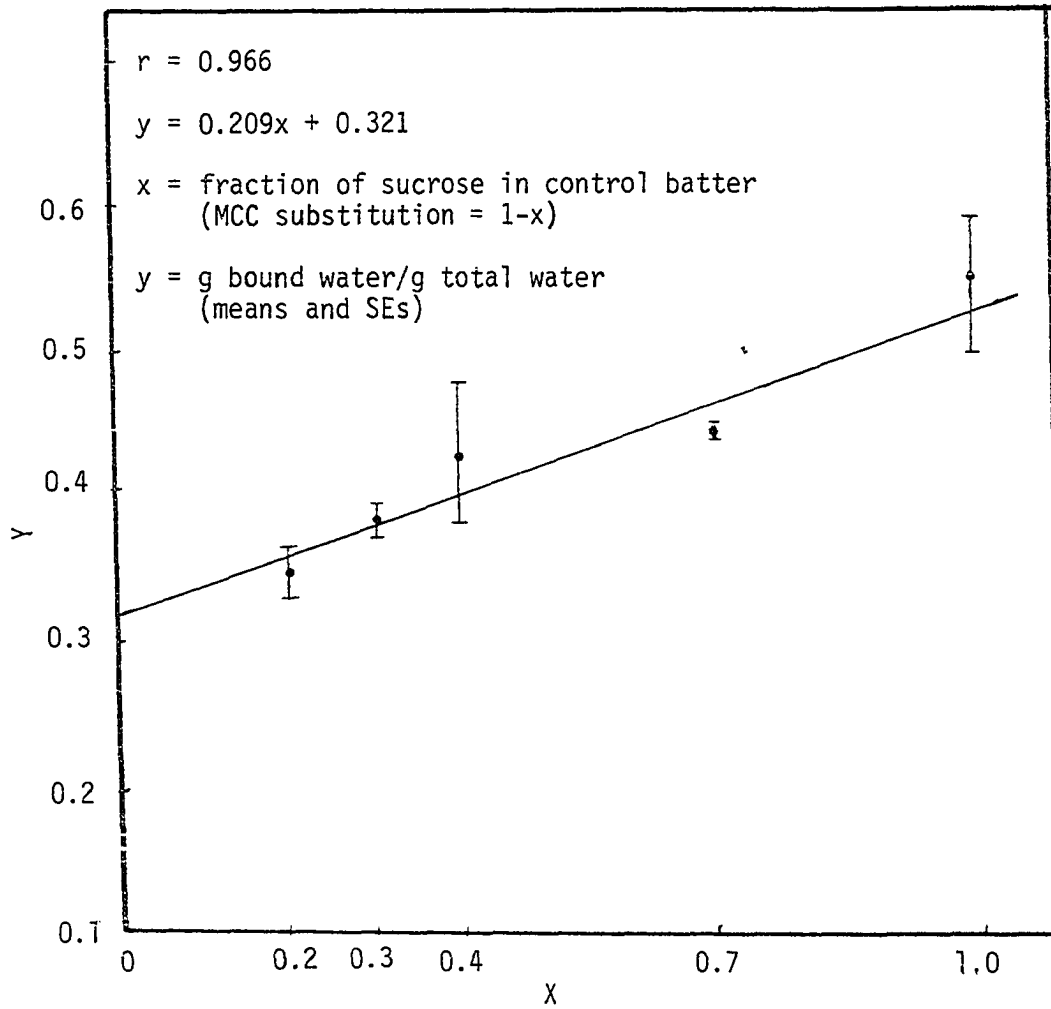


Figure 10. Bound water percentage of total water in cake batters with 120% added water as a function of MCC substitution

of both bound and free water, since no other endothermic transitions were observed up to 170°C. Samples were routinely heated to 170°C, since the endothermic event was over at this temperature. These data gave comparative results in terms of water binding. This method cannot be used to determine the amount of free or bound water in the batter.

The peak area, expressed on a solids basis, increased as the batter moisture content increased in the AACC 10-90 control and in the 70% substituted batter (Table 9). These data are shown graphically in Figure 11. The effect of water added on the peak area/g solids was significant at the  $p < 0.01$  level. The effect of MCC was significant at this level, also. The 70% MCC batters required more energy to drive off the moisture at the same level of added water. However, the 70% substituted batter had higher moisture content at the same level of water added than the control. Peak area/g solids is graphed as a function of actual batter moisture in Figure 11. The 70% and AACC 10-90 cake batters at similar moisture contents appear to require the same amount of energy to drive off the water present. More of the water in the substituted batters was free at a given moisture content than in the AACC 10-90 batter, as determined by the amount of freezable water present.

The peak area/g solids increased as percent moisture content increased. This was true in wheat doughs also. Those authors (Bushuk and Mehrotra, 1977a) felt that the additional water uncovered binding sites that might not be accessible at a lower moisture content. A more likely explanation may be that the presence of more water in the batter required more energy to drive off this additional moisture. This also explains the

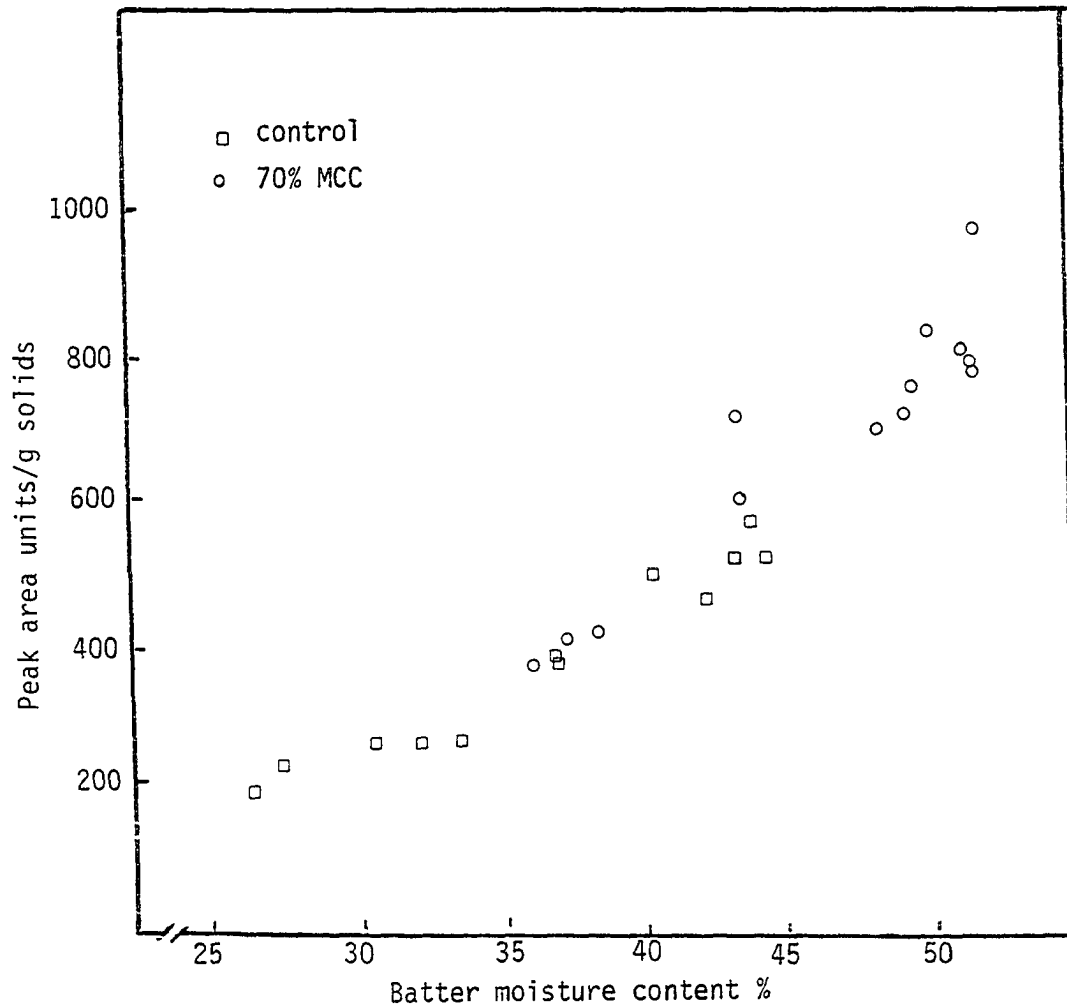


Figure 11. Heat of vaporization of AACC 10-90 control and 70% MCC substituted cake batters as a function of batter moisture



higher peak area/g solids of the 70% substituted over the control batter, but does not explain the differences in slopes.

To adjust for the increase in percent moisture content of a sample, the peak area was expressed on the basis of total water in the batter. These data are shown in Table 9 and Figure 12. When expressed as the energy required to drive off 1 g of water in the batter, there was little difference between the 70% substituted batter and the control.

The freezable water data show more water bound in the control batter. These data do not show that any more energy was required to drive off that bound water compared to the water in the 70% substituted batter, which had a greater percentage of free water.

Table 9. Heat of vaporization peak area for the AACC 10-90 and 70% MCC substituted cake batters at varying water levels, means<sup>a</sup> and standard errors

| Batter                      | Water added        |                    |                     |                      |                     |                     |
|-----------------------------|--------------------|--------------------|---------------------|----------------------|---------------------|---------------------|
|                             | 70                 | 80                 | 100                 | 120                  | 140                 | 150                 |
| AACC 10-90                  |                    |                    |                     |                      |                     |                     |
| Peak area per g solids      | 235±8 <sup>a</sup> | 263±3 <sup>a</sup> | 390±4 <sup>b</sup>  | 505±33 <sup>c</sup>  | 535±30 <sup>c</sup> | --                  |
| Peak area per g total water | 641±64             | 593±11             | 705±8               | 724±60               | 801±81              | --                  |
| 70% MCC                     |                    |                    |                     |                      |                     |                     |
| Peak area per g solids      | 382±4 <sup>a</sup> | 412±7 <sup>a</sup> | 659±51 <sup>b</sup> | 721±21 <sup>bc</sup> | 792±2 <sup>c</sup>  | 965±20 <sup>d</sup> |
| Peak area per g total water | 735±4              | 734±2              | 840±55              | 830±36               | 855±8               | 813±31              |

<sup>a</sup>Means with different superscripts in the same row are different ( $p < 0.05$ ).

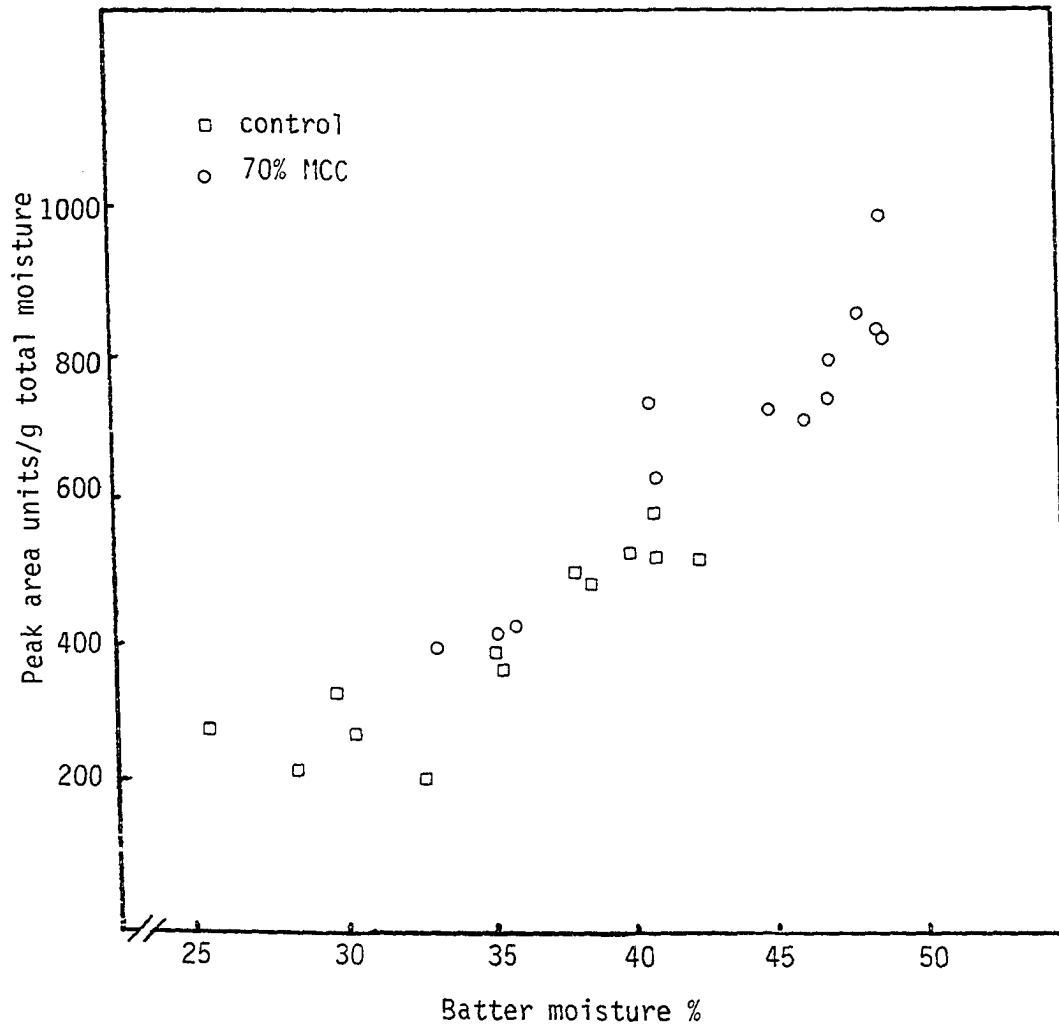


Figure 12. Heat of vaporization, peak area units/g total water of AACC 10-90 and 70% substituted cake batters as a function of batter moisture

MCC varied, water added constant

The peak area/g solids over varying MCC levels at a constant water added level are shown in Table 10. These data imply that MCC binds water to a greater degree, requiring more energy to drive the water from the sample. The percent moisture content of the batters are shown and the peak area/g total water in the sample for comparison. As discussed earlier, the percent moisture content of the batter increases with increases in MCC substitution level (Table 10). When expressed as peak area units/g total water, MCC had no effect on the area of the vaporization peak.

Table 10. Parameters for the 120% water added batter at varying MCC levels, means<sup>a</sup> and standard errors

|                        | % MCC substituted for sucrose |                     |                      |                      |                      |
|------------------------|-------------------------------|---------------------|----------------------|----------------------|----------------------|
|                        | 0                             | 30                  | 60                   | 70                   | 80                   |
| Peak area/<br>g solids | 505 ±33 <sup>a</sup>          | 622 ±8 <sup>b</sup> | 632 ±17 <sup>b</sup> | 721 ±21 <sup>c</sup> | 792 ±12 <sup>c</sup> |
| Peak area/<br>g sample | 762 ±47                       | 830 ±12             | 812 ±2               | 836 ±30              | 817 ±18              |
| g Water/<br>g sample   | .398 ±.005                    | .428 ±.006          | .438 ±.008           | .455 ±.002           | .469 ±.005           |

<sup>a</sup>Means with different superscripts in the same row are different ( $p < 0.05$ ).

### Viscosity Measurements

The importance of starch gelatinization to proper cake structure has been discussed in the literature review. Starch has been shown to be the principal constituent determining the crumb structure of baked products (Bean and Yamazaki, 1978). Sucrose concentration dramatically affects the gelatinization temperatures in cake batters as shown by Mizukoshi et al. (1979, 1980). An increase in the content of fructose and glucose also increased the temperature at which gelatinization was initiated. The greatest gelatinization temperature increase occurred in systems using sucrose (Bean et al., 1978).

In substituting MCC for sucrose in the high ratio white cake batter, the effective concentration of sucrose in the batter has been decreased from 47.54% sucrose concentration (w/w) in the AACC 10-90 formula to 18.75% sucrose in the 70% substituted batter. Such a decrease in sucrose alone would be expected to result in a corresponding decrease in gelatinization temperature of the starch; however, since the decrease in sucrose in this study was compensated by an increase in the macromolecule content through substitution by volume for the sucrose, the effect was not as predictable. The reasons for the effect of sucrose on gelatinization are not clear; water availability to the starch is the most widely accepted theory. The WBC studies in this research project indicate that sucrose has the ability to bind more water per g than does MCC. Initially, this water becomes unavailable to starch for gelatinization. However, the volume that the sugar occupies in a solution has been considered as a reason for the decrease in gelatinization temperature. Olkku and Rha (1978) considered

water vapor pressures of sucrose solutions as a determining factor in the temperature of gelatinization of starch. Flory (1953) developed an equation to predict starch gelatinization temperature which agreed quite well with actual observations. This equation considered interactions of the sugar, water, and starch, as well as, the space in the solution that the sugar occupied. Thus, space and water availability may both be important in understanding sugar effects on starch gelatinization. Microcrystalline cellulose has the ability to bind about half as much water as sucrose, plus it has the additional effect of occupying the same amount of volume in the cake formula as sucrose. Therefore, MCC should have some effect on the gelatinization temperature of starch in the cake batter. The extent of this effect remains unpredictable until the modes of action of sucrose on starch gelatinization are better known.

#### Batter studies

This study substituted MCC for sucrose at varying levels to determine if the onset temperature of gelatinization, as measured by an increase in viscosity by the Brabender amylograph, is related to the decrease in sucrose even if replaced by MCC. A lean formula (Kissell, 1959) batter and the AACC 10-90 high ratio white cake formula (American Association of Cereal Chemists, 1976) were used. In the lean formula, flour is the only source of protein; therefore, the interactions with other components are simpler. Protein denaturation in the cake batter has been shown to occur in the same temperature range as starch gelatinization (Mizukoshi et al., 1980). The gelatinization temperature in this study was taken as the temperature at which an initial increase of 10 Brabender Units (BU) was

reached ( $T_{10}$ ) (Biliaderis et al., 1980). The maximum viscosity attained on heating each suspension was also recorded (BU max). Microcrystalline cellulose was substituted by volume for sucrose at six levels (0, 30, 60, 70, 75, and 80%) in the AACC 10-90 formula. As sucrose was decreased in the AACC 10-90 cake batters and MCC substituted, the  $T_{10}$  value decreased. This is shown in Table 11. The decrease was significant at 30% substitution, and remained stable from 30 to 60%. There was a significant drop from 60 to 75%, but the  $T_{10}$  remained stable after this substitution. While statistically significantly different, these temperatures were grouped over a very narrow range and may not be practically different. Results for the lean formula (Table 12) were similar in that the  $T_{10}$  for the higher concentrations of MCC (least sucrose) were different from the control. The  $T_{10}$  for the 30% MCC substitution was the same as the control.

The BU max remained the same over the decreasing sucrose concentrations in the lean formula, but increased significantly with the increase in MCC in the full formula. An increase in the maximum viscosity would be expected in light of the addition of the macromolecule, MCC. At lower concentrations of sucrose (<25-30%) as sucrose increased the maximum viscosity increased (Hester et al., 1956; Bean and Osman, 1959; Miller and Trimbo, 1965). Above this concentration, the maximum viscosity decreased. A small amount of sucrose delayed fragmentation of the most rapidly swelling starch granules without preventing swelling of the other granules, resulting in an increase in BU max at lower sucrose concentrations.

The sucrose concentrations in the diluted batters range from 2-10%. The differences in the BU max between the lean formula and the full formula

Table 11. Means<sup>a</sup> and standard error of 12 observations of T<sub>10</sub> and BU max determined by the amylograph on the AACC 10-90 cake formula and MCC substituted cake formula

|                 | % Sucrose substituted with MCC |                       |                       |                        |                       |                       |
|-----------------|--------------------------------|-----------------------|-----------------------|------------------------|-----------------------|-----------------------|
|                 | 0                              | 30                    | 60                    | 70                     | 75                    | 80                    |
| T <sub>10</sub> | 80.1±0.1 <sup>a</sup>          | 79.5±0.1 <sup>b</sup> | 79.6±0.2 <sup>b</sup> | 79.3±0.2 <sup>bc</sup> | 79.1±0.2 <sup>c</sup> | 79.1±0.1 <sup>c</sup> |
| BU max          | 348±2 <sup>a</sup>             | 368±5 <sup>b</sup>    | 364±6 <sup>b</sup>    | 392±6 <sup>c</sup>     | 394±3 <sup>cd</sup>   | 404±2 <sup>d</sup>    |

<sup>a</sup>Means with different superscripts in the same row are different (p < 0.05).

Table 12. Means<sup>a</sup> and standard errors of 4 observations of T<sub>10</sub> and BU max determined by the amylograph on the lean formula and MCC substituted lean formula cake batters

|                 | % Sucrose substituted with MCC |                        |                        |                       |
|-----------------|--------------------------------|------------------------|------------------------|-----------------------|
|                 | 0                              | 30                     | 60                     | 70                    |
| T <sub>10</sub> | 84.4±0.4 <sup>a</sup>          | 84.4±0.3 <sup>ab</sup> | 83.2±0.3 <sup>bc</sup> | 82.5±0.7 <sup>c</sup> |
| BU max          | 191±2 <sup>a</sup>             | 192±1 <sup>a</sup>     | 186±4 <sup>a</sup>     | 186±3 <sup>a</sup>    |

<sup>a</sup>Means with different superscripts in the same row are different (p < 0.05).

are probably a result of the more complex full formula having proteins present. Proteins and starches interact to form complexes during the gelatinization process which may affect viscosity (Oikku and Rha, 1978).

Sucrose has been shown to raise the initial gelatinization temperature of wheat starch substantially. One theory is that the sugar in the formula competes with the starch for water, thus limiting water available for binding to the starch.

Using the cake formulations diluted to an extent to allow the amylograph to measure the increase in viscosity did not give conclusive results related to the effect of substituting MCC for sucrose. It was unclear as to whether the effects seen were attributable to an increase in MCC or merely a decrease in sucrose. Also, the environment of wheat starch in the dilute slurry used in this amylograph procedure is not at all like that of a starch in a cake batter where the sugar concentration is higher and water concentration lower. Miller and Trimbo (1965) attributed the amount of swelling of starch in a cake batter to be equivalent to that observed in the amylograph after 20 min and stated that the starch never fully gelatinizes in a cake batter. Lineback and Wongsrikasem (1980) used an enzymatic method to measure extent of starch gelatinization. They determined starch isolated from angel food cakes was about 97% gelatinized.

#### Model systems

To separate the effects of decreasing sucrose from those achieved by increasing MCC and to duplicate more nearly actual cake formulation, a second study using the amylograph was done. Procedures followed were those described under Materials and Methods; the results are shown in Table 13.



Table 13. Temperatures ( $^{\circ}\text{C}$ ) to reach 10 BU of sucrose solutions corresponding to correlations in substituted cakes with and without MCC replacing sucrose

|                | Representing % sucrose removed |                 |                 |                 |
|----------------|--------------------------------|-----------------|-----------------|-----------------|
|                | 0 <sup>a</sup>                 | 30 <sup>a</sup> | 60 <sup>a</sup> | 70 <sup>a</sup> |
| No MCC         | 80 <sup>b**</sup>              | 74              | 66              | 64*             |
| MCC present    |                                | 73              | 65              | 62              |
| F <sup>c</sup> | 489                            | 3               | 1               | 12              |

<sup>a</sup>Error mean square 0.6.

<sup>b\*\*</sup> $p < 0.01$ , \* $p < 0.05$ .

<sup>c</sup>F value.

A sucrose solution of 47.5% (w/w) is representative of the sucrose level in the control formula; this amount of sucrose increased the  $T_{10}$  by  $21^{\circ}\text{C}$  over the  $T_{10}$  of a flour and water suspension. This increase is similar to the increase in initial temperature of gelatinization found by Bean et al. (1978) under similar conditions.

The  $T_{10}$  and BU max determinations were made on a flour and water slurry, as well as a flour, water, MCC slurry to compare these data with sucrose solutions. The amount of MCC added was the same as in a 60% substitution for sucrose. A 100% MCC addition resulted in a slurry too viscous to operate in the amylograph (even with a counterweight of 1000 g).

If MCC can substitute for sucrose in delaying the gelation temperature, then the sucrose solutions with MCC should have  $T_{10}$ s similar to the control. The results from Table 13 are shown graphically in Figure 13. The MCC substituted line is essentially the same as the line for decreasing

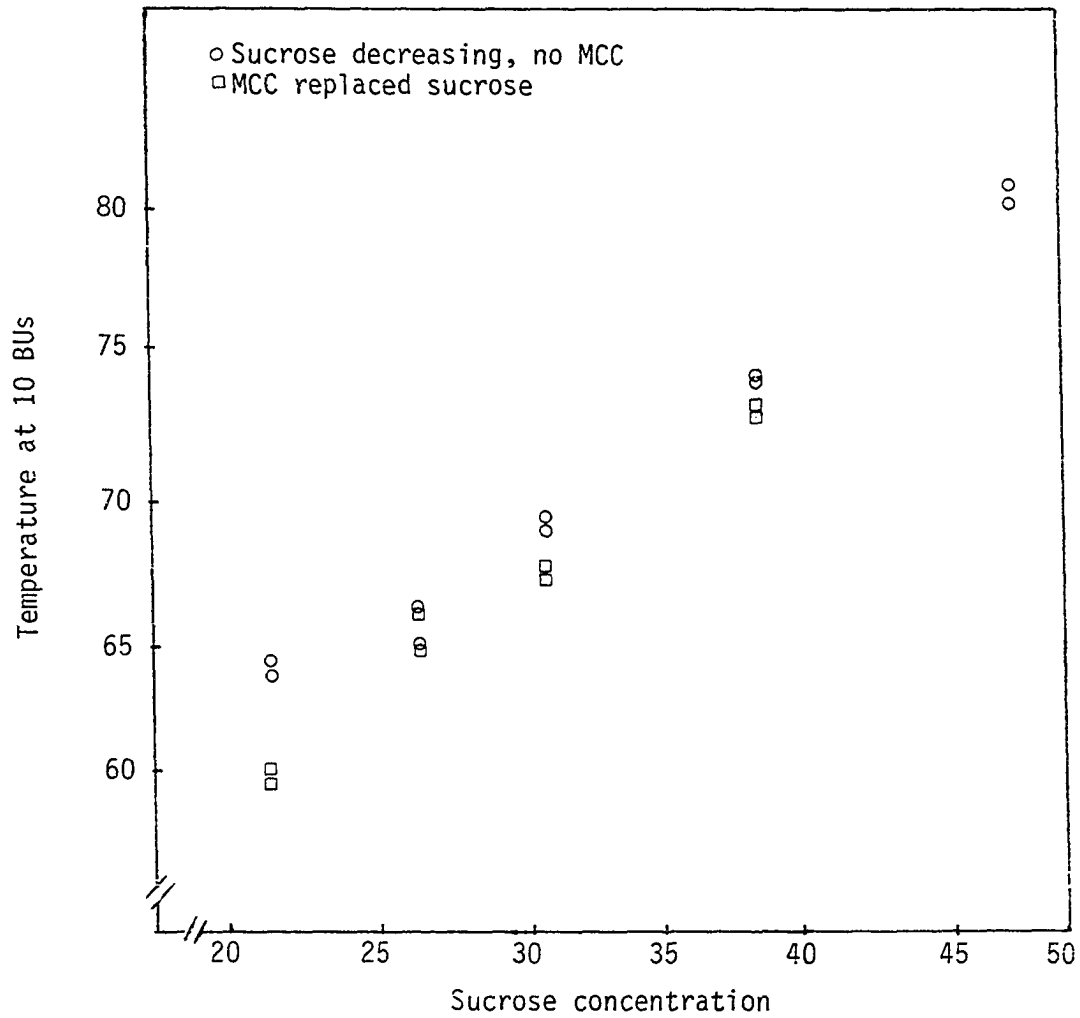


Figure 13. Temperature at which a viscosity of 10 BUs was reached for decreasing sucrose solutions with and without added MCC

sucrose concentration. Only the highest substitution level of MCC had  $T_{10}$ s different from the corresponding sucrose solutions ( $p < 0.05$ ). At this level of MCC, the physical displacement of sucrose in the 450 ml of suspension used to mix the slurry resulted in less sucrose present in the amylograph bowl. Even though the sucrose concentration and volume of liquid (450 ml) was the same for each formulation (sucrose and water or sucrose, MCC and water), there would be physically less sucrose present in the MCC substituted systems. This substitution resulted in slightly lower  $T_{10}$ s for the MCC slurries and the effect was significant at the highest level of MCC. The flour-MCC-water slurry had a  $T_{10}$  of  $57^{\circ}\text{C}$ , similar to the flour-water slurry ( $59^{\circ}\text{C}$ ). These results indicate that MCC does not compete with starch in flour for water at any level. The increase in viscosity of the MCC suspensions on mixing is viewed as the result of the physical presence of the molecules, and is not due to any uptake of water by the MCC. The MCC is insoluble in water (Battista and Smith, 1962). Any effects in MCC systems on  $T_{10}$  in the cake formulations are rather the effects of removing sucrose.

#### Gelatinization studies

Differential scanning calorimetry has been used to determine the heating rate, moisture level and effect of sucrose and sodium chloride on the endothermic changes associated with starch gelatinization (Wooton and Bamunuarachchi, 1979a,b, 1980). The temperature at which endotherms began ( $T_0$ ), reached their peak ( $T_p$ ) and concluded ( $T_c$ ) were measured. The  $T_0$  and  $T_c$  were not affected by sucrose concentrations of 15, 30, and 45%, while  $T_p$  was increased. From the lack of change in  $T_0$  and  $T_p$ , these workers

concluded that, while the peak temperature of the gelatinization endotherm rises with increased sucrose concentration, the temperature range over which the process extends was not affected by the concentrations of sucrose in that study. The extent of gelatinization of the wheat starch was measured by  $-\Delta H_{\text{Gelatinization}} (\Delta H_G)$ ; sucrose had a restrictive effect. This observation agrees with the current study. This effect of sucrose has been explained by various reasons as already discussed: competition between starch and sucrose for available water (Derby et al., 1975), decreases in available water due to moisture binding by sucrose (Hoseney et al., 1978), and inhibition of granular hydration (D'Appolonia, 1972).

If a change in the level of available water due to moisture binding by sucrose was the only effect operating, Wooton and Bamunuarachchi (1980) suggest a linear relationship between  $-\Delta H_G$  and sucrose level in the aqueous phase would be expected. They did not find this relationship. In the current study, there was a linear relationship ( $r = 0.98$ ) between sucrose concentration and  $T_{10}$ . The substitution of MCC for sucrose had no effect on the increase in viscosity, suggesting that the sucrose lowered the water available for gelatinization, while the MCC did not. This effect could be due to the ability of sucrose to go into solution, while MCC does not. Earlier results in this research indicate that MCC does have water binding ability; no effect of this ability was seen in the viscosity studies.

MCC functions in the substituted batter to increase the viscosity while baking. The air cells do not escape during the initial heating and expansion of the batter, and thus, should contribute to cake volume.

At the same time, MCC (or rather absence of sucrose) decreases the temperature at which the batter sets, and thereby, should lower the volume of the finished product by not allowing the sol to expand fully before becoming a rigid gel. The physical presence of MCC did not compensate for the decrease in sucrose.

#### Physical Incorporation of Microcrystalline Cellulose

Microcrystalline cellulose is not soluble in water, but has many functional characteristics typical of hydrophilic materials. The many fissures and holes in the surface area make it extremely absorbent, particularly for fatty materials. The attraction for fat substances has been used to convert such products as shortening and peanut butter to free flowing powders (Glicksman, 1963; Trauberman, 1961). Since the affinity for fat and lack of solubility of MCC in water was known, the influence of the physical presence of MCC in the batter was of interest. Some information on the WBC could be gained by determining if the MCC was associated with the liquid or fat phase of the batter. Also, the effect of the presence of MCC on the structure of the batter was of interest. The lean and AACC 10-90 batters were studied by the two microscopic analytical techniques described earlier.

#### Squash technique, lean cake

The starch granules were readily seen in the aqueous phase of the lean control cake. Air cells were noted in association with or surrounded by a thin film of fat in agreement with other researchers (Carlin, 1944; Bell et al., 1975). The substituted batters were more dense with smaller

air cells which were more finely dispersed. The MCC was readily seen associated with the aqueous phase. The size of the MCC crystals varied from about the size of the larger starch granules to a length as much as 50 times the diameter of the spherical starch granules. Most MCC crystals were observed as long rectangles. The change in the physical structure of the batter most noted was an increase in denseness.

Cakes prepared from the substituted batters were more compact with a finer texture, indicating more air cells. The increased number of air cells in the 30% substituted batter was originally felt to be due to the ability of the MCC crystals to entrap more air. However, cakes prepared from the 80% substituted batter were much more compact and dense. They were unacceptable to a taste panel (Beach, 1980). At the 80% level, and perhaps at the lower levels, it appears that MCC acts more to subdivide the air cells present in the batter. It may still function to entrap air, but the major effect appears to be decreasing the air cell size. An increase in air cell number and a decrease in size could result in a lighter more velvety cake if the cells were allowed to expand.

#### Embedded sections

The squash technique has been criticized for its failure to immobilize ingredients as they exist in the actual batter. A dehydration, embedding technique was used to further investigate the physical presence of MCC in the lean and AACC 10-90 cake batters. This technique was also used by Beach (1980) for the same purpose.

The embedding technique resulted in an 8  $\mu\text{m}$  thick slice of frozen, dehydrated fixed cake batter. After mounting the section on a glass slide, the embedding material is removed by immersion in xylene. Since xylene is a fat solvent, it was felt that most of the shortening in the cake was also removed in this process. Air cells have been shown to exist in the fat phase. The remaining protein matrix and starch granules outline the aqueous phase. A stain was used to differentiate protein and carbohydrate. Fat was also stained. Very little remained. Empty spaces were viewed as the localization of the fat phase which, hypothetically, was removed by xylene. This interpretation differs from that of Beach (1980) and results from refinement in the differential histo-microscopic analytical procedure.

The protein matrix (egg whites and flour proteins) was readily observed with the starch granules suspended in this matrix as described by Donovan (1977). The MCC crystals were observed in the starch-protein matrix representing the aqueous phase. Parts of some larger MCC crystals extended into the clear area and were hypothesized to have been associated with the fat phase. This occurrence could have been due to the physical size of the MCC crystals.

The light microscopy studies confirmed the MCC is in suspension in the cake batter much in the same manner as the starch granules. Since sucrose is soluble in the aqueous phase, it was not observed in the slide preparations. These results are similar to the interpretation of Beach (1980).

## SUMMARY AND CONCLUSIONS

The water relations in high ratio white cake batters and cellulose substituted white cake batters were investigated using three techniques. A calorimetric technique using a differential scanning calorimeter, viscosity on heating was measured using the Brabender Visco/amylograph and the physical incorporation of MCC in the high ratio white cake batter was investigated using phase contrast light microscopy.

The major investigation utilized differential scanning calorimetry (DSC) to determine the amount of free and bound water present in the AACC 10-90 high ratio white cake batter. The bound water was defined as that water which remained unfrozen at  $-50^{\circ}\text{C}$ . Free water was determined by measuring the peak area for the heat of fusion of freezable water in the sample. This value was subtracted from the total water in the sample to determine unfreezable water. Bound water was determined by the same method in cellulose substituted white cakes. Micro-crystalline cellulose was substituted for sucrose on a volume basis at varying percentages to determine the effect of cellulose substitution on the water binding capacity (WBC) of the white cake batter. The WBC was determined for the high ratio white cake batter, the cellulose substituted cake batter, MCC, and sucrose. The DSC was also used to determine the effect of MCC and water level on the heat of vaporization of the control and cellulose substituted batters.

The first study using DSC compared batters mixed at two water levels (100 and 120% of normal) and two MCC levels (70% and 80% substitutions for sucrose) with the control AACC 10-90 cake batter. As MCC



was increased the percent total water increased, and bound water as a percent of total water decreased. The control was significantly different from all batters. The decrease in bound water from 70 to 80% MCC was significant at the higher water level.

The phase transitions temperatures indicating the beginning of the heat of fusion peak for freezable water in the samples increased inversely with bound water percent in the sample.

The WBC of the control batter was determined by decreasing the amount of water added in the control and determining the amount of free water at each level of water added. A linear regression equation was determined to express the freezable water (g water/g solids) as a function of total water (g water/g solids) in the sample. This equation was used to obtain the water content at which no freezable water existed, all the water present was of the bound type. This water content was defined as the WBC of the control batter. The same technique was used to determine the WBC for the 70% substituted batter, MCC, and sucrose.

The WBC for the control batter was 0.335 g total water/g solids, the WBC of the substituted batter was 0.299 g total water/g solids, indicating the substituted batter had less ability to bind water than the control with 100% sucrose present. The slope (g free water/g total water) of the lines drawn using the linear regression equations also gave an indication of the water binding ability of the two systems. If the slope was one, all the water added above the WBC would have been added as free water. The slope for the control was 0.888, significantly different from the substituted batter slope, 0.976. The control had a continued ability to

bind the water added above the WBC (about 11%). The substituted batter slope indicated no ability to bind water above the WBC. The WBC of sucrose was 0.416 g total water/g solids, for MCC 0.270 g total water/g solids, verifying that the WBC difference for the cake batters was due to the sucrose removal and substitution by MCC. The slope of the sucrose line was 0.907 compared to 0.994 for the MCC, indicating the greater ability of sucrose to bind water above the WBC. These slopes were significantly different.

The third study using DSC varied the amount of MCC in 120% added water batters. As MCC was increased, the bound water percent of total water decreased significantly.

The heat of vaporization peaks were measured by DSC for the control and substituted batters. The AACC 10-90 control and the 70% substituted batters required the same amount of energy to drive off the water present at similar levels of added water. The peak area/g solids increased as percent moisture content of the batter increased, greater energy was required to drive off more moisture. When peak area was expressed per g of water in the batter, there was no difference between the 70% substituted batter and the control. The earlier study showed that more water was bound in the control batter. Heat of vaporization data did not indicate greater energy was required to drive off one g of water in the control compared to one g in the 70% substituted batter. MCC was substituted for the sucrose at five levels, peak area/g total water did not change as the MCC content increased.

The initial gelatinization temperature of starch in the batters was

measured by determining the time for viscosity to increase to 10 BUs in the control and substituted batters.

Sucrose increased the gelatinization temperature of cake batters, which is thought to be due to a decrease in water available to the starch in the flour. Therefore, the effect of MCC on the gelatinization temperature of starch as compared to sucrose was of interest to further determine if MCC acted to replace sucrose in this function. If sucrose exerts its effect on starch gelatinization temperature through initially binding water present, more information on WBC of MCC should be obtained. MCC was substituted by volume for sucrose at four levels in a diluted lean batter and at six levels in a diluted AACC 10-90 control cake batter. As MCC increased, the  $T_{10}$  decreased significantly over a very narrow range for both formulas.

The temperature for 10 BUs increase in viscosity was determined for flour-sucrose-water slurries having the same sucrose concentration as the actual cake formulas and MCC substituted formulas. The  $T_{10}$  for the very same sucrose concentrations were then determined, but MCC was added to one set as sucrose was decreased in hopes that the data should reflect the effect of replacing sucrose with MCC.

The flour-sucrose-MCC-water slurry gave the same line when graphed as  $T_{10}$  vs sucrose concentration as the flour-sucrose-water slurry. The  $T_{10}$  decreased as sucrose decreased. No effect on temperature was seen with MCC replacement.

Microcrystalline cellulose was observed in the aqueous phase of the cake batter using phase contrast light microscopic techniques. Macro-

molecules have been shown to create a greater degree of order in aqueous emulsions. The major effect of MCC observed was a thicker batter with more numerous and smaller air cells.

The cake baked with MCC substitution was generally denser and more compact with a finer texture as MCC increased. This texture resulted from the reduced WBC of the MCC in the cake batter. MCC competed less successfully for the water than sucrose. Thus, starch imbibed more water, giving an effect similar to adding too much moisture to the batter. In high water level cakes the cake assumed a gel-like character (Wilson & Donelson, 1963). A similar effect is seen in the high MCC substituted cakes.

Cellulose substituted cakes were more compact with less volume due to the lower gelation temperature of the MCC batters. During baking the water turns to steam and air cells expand. The cake continues to expand until the proteins are denatured and the starch is gelatinized, usually around 80-92°C. The decrease in sucrose in the MCC substituted cakes reduced the temperature of gelatinization and thus the length of time for the cake to expand.

The increased water necessary to mix the higher MCC substituted batters is due to the large physical size of the MCC molecule. MCC is not capable of binding as much water as sucrose, thus MCC can act as a bulking agent in the cake, but it does not replace sucrose as a water binding agent. Further, modification of MCC or use of a more hydrophilic product could solve this problem. However, the insolubility of MCC aids in maintaining the grain of the cake. Gums which bind a great amount of water may result in cakes with even greater gel-like qualities.

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