

# Enthalpy Changes in Model Cake Systems Containing Emulsifiers<sup>1</sup>

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## ABSTRACT

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Differential scanning calorimetry was used to measure enthalpies associated with starch transformations and with saturated monoglyceride (SMG) and unsaturated monoglyceride (USMG) phase transitions in a lean cake batter over the range of 40–120°C. Detectable thermograms were found only for the starch and SMG moieties. Small differences in the onset temperatures and total enthalpies were found under the component-dispersion conditions of the lean formula test system. Furthermore, SMG enthalpy values were lower after SMG was cooled and reheated, but the

temperature of onset of the phase transition was very close to that for the initial heating sequence. This was true whether SMG was present alone or in the presence of other batter components. These results suggest that the starch molecular conformational changes that occur in the batter in the early stages of baking, as detected by differential scanning calorimetry, are not affected by the presence of SMG or USMG. Therefore, some of these emulsifiers may serve a greater role in later stages of batter development than in the initial phase transitions.

Differential scanning calorimetry (DSC) has been used to study the thermal properties of several wheat flour-based model systems. These studies have focused on wheat flour, wheat starch, amylose, amylopectin, gluten and, to a lesser extent, on lipid components (Allen 1977; Donovan 1977, 1979; Eliasson 1980; Eliasson and Hegg 1980; Eliasson et al 1981; Jacobsberg and Daniels 1974; Kugimiya and Donovan 1981; Kugimiya et al 1980; Stevens and Elton 1971; Wootton and Bamunuarachchi 1979a, 1979b, 1980).

The thermal properties measured by DSC are the result of molecular phase transitions and give information on the heat requirements of these transitions. Definition of these heat requirements also helps to explain properties such as heat and mass transfer mechanisms in the system (Cloke 1981, Gordon et al 1979, Hsu et al 1980) and temperature-dependent physical and chemical changes observed at the ultrastructural level (Cloke et al 1982, Hsieh et al 1981).

The lean cake formulation of Kissell (1959) contains only wheat flour, water, sucrose, baking powder, and lipid, and is a convenient basic model system to which additional ingredients can be added to study ingredient interactions. To better explain crumb development and crumb staling characteristics when different emulsifiers were added to this model system, the heat requirements over the range 40–120°C for specific phase changes of the batter components were determined by DSC. The reheating characteristics of fresh and stored cake crumb were also determined by DSC.

## MATERIALS AND METHODS

### Test Formula

The lean cake formulation (Kissell 1959) is shown in Table I. A saturated monoglyceride (SMG) or an unsaturated monoglyceride (USMG) preparation replaced 5 and 10% of the shortening weight. No emulsifier was added to control batters. The composition and method of dispersion of the emulsifiers are also given in Table I. The method of dispersion for each emulsifier was that which gave optimum overall cake quality at the 5% level of each preparation (Cloke et al 1981). A modified two-stage mixing method was used for batter preparation (Cloke 1981). The flour and baking powder were sifted together, and then the corn oil, sucrose solution, and emulsifier solution were added. To maintain comparable volumes during mixing, 19.5 g of distilled water was added to the unemulsified and USMG batters. All batters were mixed for 3.5 min on a Hobart Kitchen Aid (model K 45) mixer with a cake beater. The remaining distilled water was added, and the batter mixed for 3 more min.

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### Enthalpy Measurements

Enthalpy measurements were calculated from thermograms of differential heat input vs temperature obtained by DSC on a Perkin-Elmer DSC II coupled to a Perkin-Elmer model 56 chart recorder. A Perkin-Elmer thermogravimetric system (TGS II) coupled to the chart recorder was used to determine sample weights. Approximately 10 mg total sample weight (4–16 mg) was sealed in volatile-sample pans, except when emulsifier was used alone (approximately 1 mg of emulsifier). Aluminum foil (10 mg) was used as the reference material. Experimental data were obtained between 40 and 120°C at a heating rate of 5°C/min and 1 mcal/sec. The chart recorder was set at 5 mV and 20 mm/min for the starch thermogram peak and at 50 mV and 20 mm/min for the systems in which emulsifier transitions could be studied. Peak areas were measured with a Hewlett Packard Digitizer (model 9107A). Calculations of enthalpy were based on the equation:  $\Delta H = A C/W$ , where  $\Delta H$  is the enthalpy in cal/g,  $A$  is the area under the thermogram peak,  $W$  is the sample weight, and  $C$  is the machine constant using indium as a standard, which has a heat of melting of 6.80 cal/g.

### Model Systems Studied

The following systems were studied by DSC: 42% sucrose solution, corn oil, baking powder in 42% sucrose solution, USMG, SMG, wheat starch, 1 mg of SMG or USMG in 10 mg oil, and 1 mg SMG or USMG in 10 mg 42% sucrose solution (emulsifiers were weighed into their dispersing media in the volatile-sample pans).

TABLE I  
Test Formula

Ingredient	Quantity (g)	Percent	Percent (flour basis)
Cake flour <sup>a</sup>	150.0	25.3	100
Baking powder <sup>b</sup> (sodium aluminum sulfate-phosphate)	7.1	1	5
Shortening (corn oil and monoglyceride <sup>d,e</sup> )	41.8	7.1	27.9
Sucrose solution			
Sucrose	167.4	28.2	111.6
Distilled water	107.0	38.2	151.0
Additional distilled water	19.5 + 100.0		

<sup>a</sup>Softasilk, General Mills.

<sup>b</sup>Calumet, General Foods Corporation.

<sup>c</sup>Mazola, Best Foods.

<sup>d</sup>Dimodan PV, Grinstead Products: 85–90% glycerol monostearate and 10–15% glycerol monopalmitate (referred to as SMG). When SMG was used, it was heated to 60°C in 19.5 g of water and allowed to cool to room temperature before being incorporated into the batter.

<sup>e</sup>Dimodan O, Grinstead Products: 70% glycerol monooleate (USMG). When USMG was used, it was heated to 60°C in 19.5 g of oil and allowed to cool to room temperature before being incorporated into the batter.

before DSC runs). If an endothermic peak was obtained, the sample was cooled and reheated.

### Test Formula Batters Studied

Batters were prepared as previously outlined, and a single drop of well-mixed batter was pipetted into the weighed DSC volatile-sample pan, and the pan was reweighed after sealing. Because some variability was caused by the problems in sampling such macroemulsive premixed systems (Cloke 1981), a minimum of six replicate determinations was made for each batter formulation as a basis for calculation of enthalpies. Approximately 12% variability must be tolerated in these premixed batter systems. The following batter combinations were studied: unemulsified batters, unemulsified batters with 150 g of wheat starch replacing 150 g of flour, batters containing 5 or 10% SMG, and batters containing 5 or 10% USMG. Unemulsified batters were prepared on three separate days to determine repeatability.

Completely baked cake batters were evaluated by DSC immediately after baking and after storage for four days at 4°C in a closed plastic container. These cakes had been baked at 191°C for 25 min. The final centerline temperatures of these cakes ranged from 107 to 121°C (Cloke 1981).

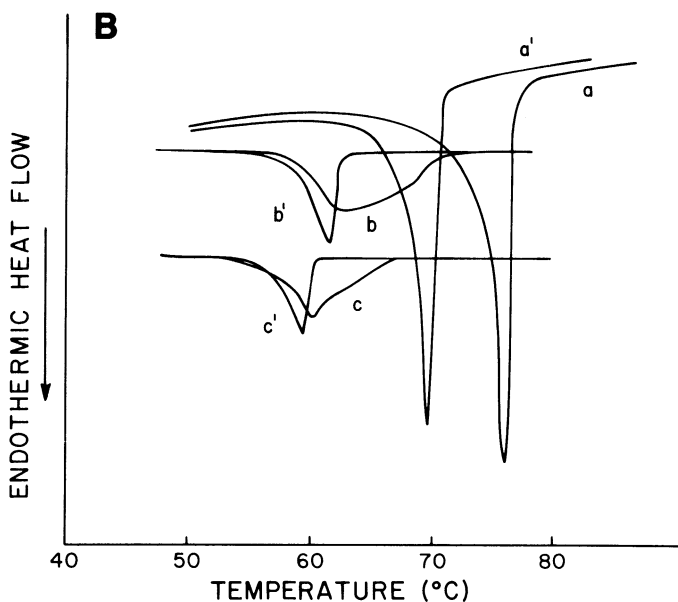
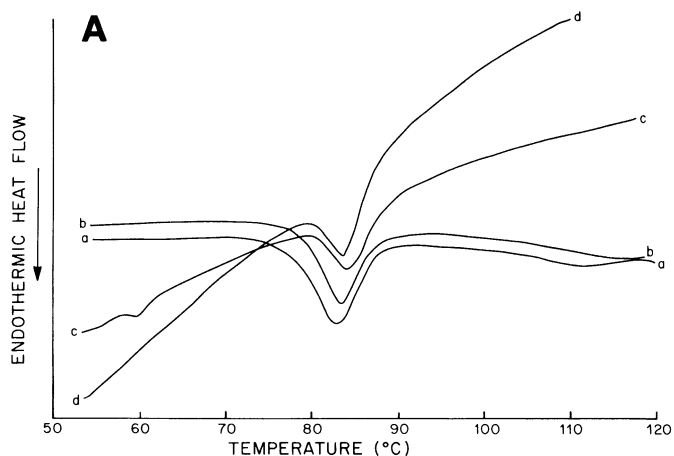


Fig. 1A. Representative DSC thermograms for: a, wheat starch in 42% sucrose; b, unemulsified batter; c, batter with 10% SMG; and d, batter with 10% USMG. B, Representative DSC thermograms for: a, SMG; a', a reheated; b, SMG in 42% sucrose; b', b reheated; c, SMG in water; and c', c reheated.

## RESULTS AND DISCUSSION

The data obtained for the model systems and batter formulations are summarized in Table II. Selected thermograms are shown in Fig. 1A and B to show the nature of the curves for each system studied. Enthalpies were calculated from the thermograms obtained, as described previously. Temperature ranges over which the endotherm peak areas were computed before calculation of enthalpy are also reported in Table II.

The temperature of maximum deflection and the shape of the curve for differential heat input data are affected by sample weight and proportion, and by the type of dispersing medium. Therefore, the temperature at which the onset of a particular phase transition occurs is the more reliable temperature to report under such conditions and is the temperature used here for comparisons between systems. Some discussion of differences in the qualitative features of these curves is made where appropriate. Enthalpies, however, are not affected by sample weight differences. The variability in enthalpies is mainly due to the inherent variability arising from sampling the inhomogeneous systems and cannot be easily overcome. Based on calculation of enthalpy for replicate determinations, a 10–12% variability in enthalpy values among replicates can be expected. Galletti et al (1980) found similar variability for potato starch.

Two major thermal phase transitions occur in these model systems and formulations between 40 and 120°C, which is the centerline temperature range found during the baking of these cakes (Table II; Fig. 1A and B). One is the starch phase transition (Fig. 1A), and the other is the SMG phase transition (Fig. 1B). Sucrose solution, corn oil, and USMG do not show transitions in this temperature range. Also, dry wheat starch and wheat starch in oil do not undergo phase transitions within the sensitivity limits of the calorimeter. Baking powder has many nonreproducible, spurious peaks that are attributed to the leavening mixture and corn starch filler, which react simultaneously to produce CO<sub>2</sub> and gelatinized the starch filler. Wheat starch in sucrose solution had an endotherm between 72 and 92°C (Table II; Fig. 1A). This observation agrees with previous DSC studies in which increased sugar content increased the temperature at which the starch phase transition began to occur (Wootton and Bamunuarachchi 1980).

TABLE II  
Thermal Transitions and Enthalpies of Batter Components  
Between 40 and 120°C

System Studied	Thermal Transition Temperature Range for Calculated Enthalpy (%)	Enthalpy (cal/g SMG)
Wheat starch (dry)	none	
Wheat starch in 42% sucrose	72–92	2.6 <sup>a</sup>
Wheat starch in corn oil	none	
Sucrose (42%)	none	
Corn oil	none	
Baking powder in 42% sucrose	many nonreproducible spurious peaks	
USMG <sup>b</sup>	none	
SMG <sup>c</sup> dry;	57–78	38.0
(cooled, reheated)	63–75	26.0
SMG dispersed in H <sub>2</sub> O	52–69	32.0
(cooled, reheated)	52–67	18.0
SMG dispersed in oil	58–72	37.0
(cooled, reheated)	52–62	15.0
SMG dispersed in 42% sucrose	57–73	38.0
(cooled, reheated)	55–63	18.0
SMG, wheat starch and oil	59–72	36.0
(cooled, reheated)	52–62	15.0
Wheat starch batter <sup>d</sup>	74–101	2.6 <sup>a</sup>
Wheat flour batter <sup>d</sup>	74–96	2.5 <sup>a</sup>

<sup>a</sup>Starch rather than SMG.

<sup>b</sup>Unsaturated monoglyceride (Dimodan PV).

<sup>c</sup>Saturated monoglyceride (Dimodan O).

<sup>d</sup>Wheat starch thermal transitions did not have a second thermal transition upon cooling and reheating.

Water is required for this particular starch transformation, since dry starch or starch in oil does not produce the characteristic endothermic peak (Table II). The presence of other ingredients such as oil, emulsifier, and baking powder does not affect the thermal requirements of the starch transformation that occurs in this temperature range, as long as 42% sucrose solution is also present.

Because wheat proteins in cake flour undergo thermal phase transitions at these temperatures (Eliasson and Hegg 1980), enthalpies for starch transformations in batters containing flour were compared with enthalpies for batters in which wheat starch was substituted for flour. The comparisons of the data from these batters were made on a starch dry weight basis. Enthalpy of the transition in wheat starch batter was 2.6 cal/g, and in cake flour batter was 2.5 cal/g of dry starch. These values are very similar to the 2.6 cal/g starch found in the model system containing starch in sucrose solution. Therefore, this endotherm can be more confidently attributed to early starch transformations, with minimal contributions being made by the protein phase transitions. The enthalpy associated with the transformation is similar to the 2.4–2.9 cal/g reported by Stevens and Elton (1971), 3.0 cal/g by Gough and Pybus (1971), and 2.2–2.4 cal/g by Lelievre (1975). These values are for wheat starch in the absence of sucrose. Wootton and Bamunuarachchi (1980), on the other hand, also reported a value of 2.3 cal/g for starch in 45% sucrose, which is lower than 4.7 cal/g, which they reported for starch in the absence of sucrose at a starch–water ratio of 1:2. Comparisons of enthalpy values among research groups are sometimes difficult because the rate of heating is now believed to affect enthalpy values as well as the temperature at which a transition begins to occur. Additionally, preparing samples of macrocolloidal dispersions by slurry and pipetting vs weighing components directly into DSC pans gives differing enthalpy values. In work recently done in our laboratory, using the procedures outlined, a starch–water ratio of 1:2 gave enthalpy values close to enthalpy values found using 42% sucrose solution and similar ratios of starch–water.

Reheating the starch systems after cooling did not show any reversible, residual, or different endothermic activity in this temperature region.

#### Emulsifier Phase Transitions

Systems containing SMG showed thermally induced phase transitions starting between 52 and 58°C, depending on the dispersing medium (Fig. 1B). The shapes of the curves, however, varied depending on the dispersing medium. The corresponding enthalpies associated with these transitions ranged between 32 and 38 cal/g SMG on the initial heating period. SMG is mainly glycerol monostearate. The melting points associated with glycerol monostearate are 47.5, 74, 79, and 81.5°C, depending on the crystal form (Bailey 1950). An alpha-form melt at 73–74°C, a beta-prime form melt at 78°C, and a beta-melt at about 81°C were reported by Lutton (1971). Because Lutton (1971) found the enthalpy of the alpha-melt for glycerol monostearate to be 34 cal/g, and because the enthalpy was calculated in this test as 36 cal/g, this form must predominate initially in the SMG. When SMG was heated in water, sucrose solution, or corn oil, similar phase transitions were observed. The small differences in the temperatures at which the phase transitions started may be due to differences in heat transfer in oil and sucrose solution, or possibly to the formation of mesophases in water as described by Krog and Lauridsen (1976). The thermograms (Fig. 1B) appear more complex upon initial heating as well as upon reheating for SMG heated alone, vs SMG in water, in 42% sucrose solution, or in oil. This indicates at least some interaction between the emulsifier and the dispersing medium.

The USMG (70% glycerol monooleate) emulsifier did not have a thermal transition above 40°C. This is not surprising, as this monoglyceride melts below 35°C (Bailey 1950).

Reheating the systems containing SMG showed a thermal transition that starts at a temperature close to the temperature of the original transition, but much less energy is associated with the transition upon reheating. The enthalpies of the transitions for the reheated samples (15–18 cal/g) are similar to the values of 17 cal/g

for the sub alpha<sub>2</sub> to alpha transition reported by Lutton (1971). The temperatures for the onset of the transition were 63°C for the dry SMG and 52–55°C for SMG dispersed in water, oil, or 42% sucrose solution. These temperatures are somewhat higher than the 47–52.5°C temperatures for the sub alpha<sub>1</sub> to alpha transition reported by Lutton. Therefore, not all of the emulsifier may have been converted to the original form, or conversions to other crystal forms or mesophases may have occurred. The fact that these reheated samples have different enthalpies, depending on the type of dispersing medium, implies that their roles can be different in batters and in doughs or in different batter formulations.

#### Complete Batter Combinations

The results of the study of complete batters are given in Table III and Fig. 1A. The temperatures at the onset of the starch endothermic peak were similar for batters containing SMG and USMG. The onset temperature for the starch endotherm for 5% SMG batters was slightly higher than temperatures for the other batters. The enthalpies did not differ within the experimental error of the system and encompassed those found for model studies (Table II).

The onset temperature of the endotherm and the calculated enthalpies varied more than did comparable DSC data for nonbatter systems, since the individual components could not be weighed directly into the sample holder but had to be dropped, premixed, into the sample pan. Even when starch–water premixed slurries were examined by Allen (1977), large sample variance occurred. In fact, Biliaderis et al (1980) examined a variety of starches and found that the  $\Delta H$  values had an average deviation of  $\pm 0.25$  cal/g for repeated analysis ( $n = 5-10$ ) of the sample. This is comparable to the deviation of  $\pm 0.3$  cal/g of starch obtained from unemulsified batters in this study.

Thermograms for crumb taken from the fresh and stored cakes were also obtained from DSC data. No endotherms were observed between 40 and 120°C, except for very small nonmeasurable perturbations at the SMG endotherm temperature range between 55 and 60°C (Fig. 1A). This was similar to the small endotherm, as seen in the DSC curve for the 10% SMG batter.

The molecular starch transformation, as measured by DSC between 40 and 120°C and within the variability of the sampling method, seems to be only slightly affected by the presence of SMG and not affected by the presence of USMG under the component dispersion conditions of the lean formula test system.

Molecular phase changes were also demonstrated for SMG (Fig. 1B; Table II). Furthermore, after cooling and reheating SMG, the enthalpy values were different, but the temperatures of the onset of the observable transitions were the same as those for the initial heating sequence. This suggests that the SMG changed phase after heating and cooling, either entirely or in part. On the other hand, stored cake crumb did not show any different or residual endotherm activity, which suggests that crystallization did not occur during storage.

Measurable complexing of emulsifier with starch was not detected in the temperature ranges that Kugimiya and Donovan

TABLE III  
Temperature Ranges of the Observed Thermal Transition  
for Batters in Calculating Enthalpies<sup>a</sup>

Batter	Onset Temperature (°C)	Final Temperature (°C)
Unemulsified	74–81	91–96
5% Saturated <sup>b</sup>	77–79	91
10% Saturated <sup>b</sup>	72–77	92–96
5% Unsaturated	74–78	92–94
10% Unsaturated	75–78	89–92

<sup>a</sup>Enthalpies ranged between 2.2 and 2.7 cal/g dry starch with standard deviation of  $\pm 0.3$  cal/g.

<sup>b</sup>Saturated monoglyceride emulsifier transitions are evident at 57°C. However, the quantity in the total batter is very small and difficult to measure.

(1981) reported for complex formation and melt. The starch-sucrose-water ratio in the model cake batters may delay the initial starch phase transition, such that starch-emulsifier complexing and melt occurred at temperatures higher than those found by Kugimiya and Donovan. This suggests that one effect of sugar in such a system is to delay formation of amylose-emulsifier complexes with subsequent complex "melts," as described by Kugimiya and Donovan (1981) when emulsifier levels are optimized in their roles as component-dispersing agents.

Emulsifiers were found to have relatively small effects on batter component molecular phase transitions, particularly those of starch; however, this does not preclude an influence on other aspects of batter structure and transformations during baking such as water migration, oil dispersion, and air cell size. They may indirectly influence starch granule swelling or granule coalescence. The roles of emulsifiers in water migration, oil dispersion, and air cell size have been investigated by transmission electron microscopy, employing freeze-etch techniques (Clove et al 1982), and by monitoring overall rates of water loss and temperature profiles during baking. The results of these studies will be reported in later papers.

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