The Role of Emulsifiers in the Incorporation of Air into Layer Cake Batter Systems[1]

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ABSTRACT

Surface-active lipids, which in the bulk state are alpha-tending in crystalline form, have been found to act as enhancers of air incorporation in cake batters when used as shortening emulsifiers. The ability to enhance air incorporation is related to the unique interfacial behavior of these lipids at oil-water boundaries. If the concentration at the interface exceeds the solubility limit, these lipids crystallize in an alpha-tending form. The interfacial film so formed possesses the waxlike properties of the alpha-crystalline phase and, it is suggested, in effect encapsulates the dispersed oil (shortening) droplets within a protective coating. In this way it is possible that the lipids normally detrimental to the foaming properties of soluble proteins are prevented from migrating into the aqueous phase and interfering with air incorporation. The results of this work show that surface-active additives or additive mixtures which are stable in the alpha-crystalline form are valuable as enhancers of air incorporation. Examples of lipids which show this alpha-tendency include the fatty esters of aliphatic diols, mixed acid diglycerides, and hydroxy acid esters of mono- and diglycerides.

The role of shortening in the cake-baking process has been described by Carlin (1), who considered the aeration of batters to be due to incorporation of air into the plastic shortening phase during batter-mixing. Photographs of batters showed the air cells to be associated with fat; the stability of these cells during mixing and in the early stages of baking was therefore associated with certain characteristics of the shortening.

Shortenings which have been used generally in the making of cakes for a long period of time have contained only mono- and diglycerides as additives, and these have been termed emulsifiers and "high-ratio" agents. Such shortenings are effective only when the batter is mixed in a multistage method; they cannot be used successfully in layer cake batters mixed in a single stage.

In recent years, shortening additives have become available which show marked improvement in emulsification and air incorporation in batters and in volume and grain in cakes (2) over that obtained with mono-diglycerides. Additives of this type also make it possible to prepare well-aerated batters in a single stage without the necessity of an initial creaming step. A common example of these "aerating shortenings" (3) has contained emulsifiers composed of lactoylated glycerides. Actually, although such emulsifiers are rather complex and contain a mixture of molecular species, the predominant components are monolactoyl monoglyceride, monolactoyl diglyceride, and dilactoyl monoglyceride (4). A more recent additive mixture used in liquid shortenings for enhancement of air incorporation is propylene glycol monostearate (PGMS) and stearic acid (5).

A study was undertaken to determine the mechanism by which these

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additives enhance air incorporation in cake batter systems containing liquid shortenings.

MATERIALS AND METHODS

Surface-Active Lipids

Diol monoesters. Various sources of fatty acid esters of aliphatic diols were employed. Commercial preparations of propylene glycol monostearate (PGMS), which were really 50-50 mixtures of the mono- and di- fatty acid esters of 1,2-propanediol, were used where noted. Chemically pure PGMS and other diol esters were prepared by reaction of stearic acid (97–98% pure) with the diol in xylene under reflux and with *p*-toluene sulfonic acid as a catalyst (6).

Mixed acid diglycerides. The preparation and properties of these compounds are described by Martin and Lutton.[2]

Lactoylated glycerides. Various commercial preparations produced either by esterification of lactic acid with partial glycerides or by reaction of fatty acid, glycerol, and lactic acid were examined. One preparation (2) was fractionated by silicic acid chromatography, according to Quinlin and Weiser (7), to yield fractions rich in monolactoyl-diglyceride and mono-lactoyl-monoglyceride. The latter was separated from monoglyceride by fractional precipitation from petroleum ether.

The terminology for solid-state polymorphism used in this paper is based on the definitions of Lutton (8). The sub-alpha designation is used to describe a phase which is reversibly interconvertible to the alpha phase in the solid state. The terms "β'-like" and "β-like" are used instead of β' and β because the latter descriptions have not, as yet, been generally accepted for compounds other than those based on glycerol.

Interfacial Tension Determinations

The interfacial tension of the cottonseed oil-water interface was measured with the DuNuöy tensiometer. In the presence of some of the materials under discussion, the formation of a plastic film greatly increased the force (F) necessary to pull the platinum ring through the interface. Such a measurement is, of course, not a measurement of interfacial tension, but rather of the coherence of the film.

Preparation of Shortenings

Samples of a plastic shortening from vegetable oil hydrogenated to an Iodine Value of about 75 (A), the same plastic shortening containing 4.5% mono-/diglycerides (B), unhydrogenated cottonseed oil (C), and the same cottonseed oil containing 4.5% mono-/diglycerides (D) were used where noted.

Oil shortenings containing additive mixtures were prepared by dissolving the additive in oil C at elevated temperatures. In some cases the solubility limits at room temperature were exceeded. Such shortenings were heated to dissolve the precipitate and then cooled before use.

Plastic shortenings containing additives were made by plasticizing the additive into melted triglyceride shortening A.

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[2] Martin, J. B., and Lutton, E. S. The preparation and phase behavior of acetyl monoglycerides. (Manuscript in preparation.)

Batter Preparation

The high-ratio white cake batter system had the following composition and preparation procedure:

	g.		g.
Cake flour	95	Baking powder (double-acting)	5.7
Sugar	133	Mix 30 sec., setting 1 (100 r.p.m.)	
Shortening	50	Milk	40
Salt	1.5	Egg whites	60
Milk	80	Vanilla extract	2.5 (ml.)
Mix 2 min., Mixmaster setting 5 (500 r.p.m.)		Mix 2 min., setting 5	

Bake 400 g. batter in 8-in. pan for 25–30 min. at 365°F.

This multistage mixing procedure was required where shortening A, B, C, or D was employed. However, it was found that single-stage mixing was possible with shortenings containing certain of the additives to be described. All data for alpha-tending additives, except where otherwise noted, were obtained with batters prepared by mixing together all ingredients except leavening for 4 min. (single-stage mixing) at Mixmaster setting No. 5, and finally blending in baking powder for 30 sec.

A yellow mix formulation containing plastic shortenings was employed for some experiments (see formula).

Yellow Mix Formula

Dry mix

	%
Cake flour	89.8
Nonfat dry milk	4.5
Salt	1.7
Soda	1.7
Monocalcium phosphate	1.5
Sodium acid pyrophosphate	0.8
	100.0

Cream mix

	%
Hydrogenated shortening	22.0
Sugar	78.0
	100.0

Complete mix

	%
Dry mix	45.3
Cream mix	54.7
	100.0

Batter composition

	g.
Complete mix	540
Water	280
Whole egg	96

Mix 3 min. at 500 r.p.m.; scale 8-in. pans with 400 g. batter; bake at 350°F. for 28–30 min.

RESULTS

Microscopic Appearance of White Cake Batters

The effects of four different shortenings on the microscopic appearance of the high-ratio white cake batters produced by multistage mixing are shown in Fig. 1. Plastic shortenings A and B give batters in which the light aqueous phase and the dark fat phase containing dispersed air bubbles can be clearly differentiated. The gaseous phase, or actually incorporated air, appears to be closely associated with the fat phase as pointed out by Carlin (1), but the rather poor emulsification—that is, the dispersion of fat in water—is also apparent. Liquid shortenings C and D produce batters in which it is difficult to recognize the shortening phase and in which very little air (the dark circles) is associated with that phase.
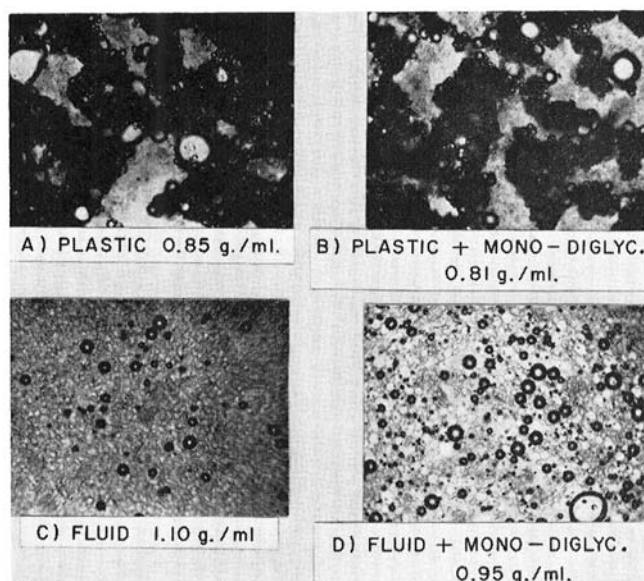
Fig. 1. Microscopic appearance (about $50\times$) of high-ratio white cake batters made by a three-stage method of mixing (75°). A, plastic shortening without emulsifier; B, plastic shortening with 4.5% mono-diglycerides; C, fluid cottonseed oil (CSO) shortening; D, fluid CSO shortening with 4.5% mono-diglycerides.

Behavior of Alpha-Tending and Alpha-Stable Shortening Additives at Oil-Water Interfaces

The unique interfacial property of alpha-tending surface-active lipids is described as the ability to form thick "plastic-like" interfacial membranes upon adsorption at oil-water interfaces. Figure 2 illustrates the microscopic appearance of such a membrane or interfacial film formed by 1-acetyl-3-monostearin. This was made by forming a drop of water on the tip of a microsyringe in oil containing 4% 1-acetyl-3-monostearin at 70°F. The formation of this interfacial film, which depends on the concentration of the particular additive and the temperature of the system, gives rise to an apparent increase in the interfacial tension as measured by the DuNuöy tensiometer. A typical plot, in this case for 1-acetyl-3-monostearin at three temperatures, is shown in Fig. 3[3].

Effect of Alpha-Additives on Air Incorporation in Batter Systems

It has been found that the detrimental action of fatty materials on the foaming properties of protein solutions is overcome in large part if alpha-tending additives are incorporated into the system. In addition, this allows a single-stage mixing procedure to be used. A valid demonstration of this in a cake batter system would be a positive effect of such additives on air incorporation in batters which normally do not incorporate much air, such as with shortening C of Fig. 1.

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[3]The value of 21–23 dynes/cm. for the interfacial tension of cottonseed oil reported in this paper is for a sample of cottonseed oil commonly described as refined and winterized. Passage of this oil through silica gel removes compounds which exist in very small amount in the original oil. The interfacial tension of this purified oil is 29–30 dynes/cm. The removal of this material has no significant effect on the behavior of the surface-active lipids in the concentration range leading to film formation.
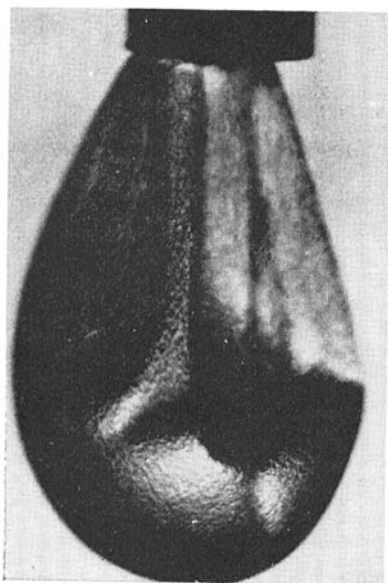
Fig. 2 (left). Microscopic appearance of interfacial film of 1-acetyl-3-monostearin at the oil-water interface at 70°F. (Some water was withdrawn from drop to emphasize apparent thickness and rigidity for photographic purposes.) CSO contained 4% 1-acetyl-3-monostearin (70°F.).
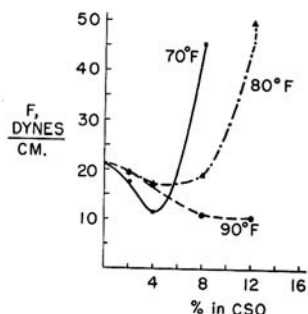
Fig. 3 (right). Effect of concentration of 1-acetyl-3-monostearin on the interfacial strength at the oil-water interfaces. Additive dissolved at stated concentrations in CSO.

Various alpha-additives as well as "nonaerating" emulsifiers were used in cottonseed oil and in plastic shortenings to prepare a variety of cake batter systems. Figures 4 and 5 give batter-density results which clearly indicate
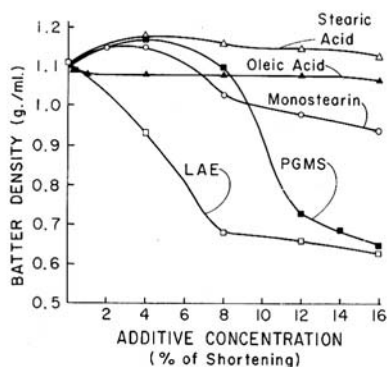

Fig. 4 (left). Effect of various emulsifiers on air incorporation in high-ratio white cake batters containing oil shortenings, CSO, and mixed in a single-stage procedure. LAE (lactoylated glyceride) and PGMS (propylene glycol monostearate) represent alpha-tending emulsifiers.
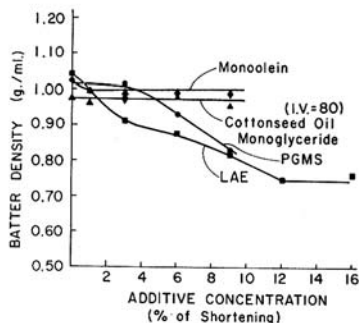
Fig. 5 (right). Effect of various emulsifiers on air incorporation in a yellow cake. Additives plasticized at stated concentrations in a plastic shortening (A).
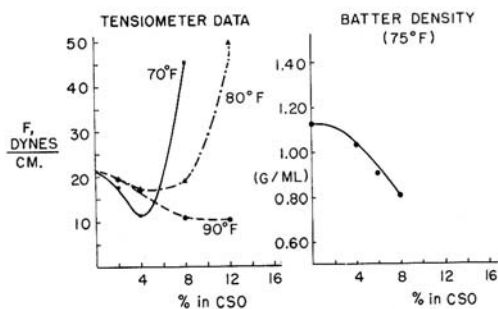
Fig. 6. Effect of concentration of 1-acetyl-3-monostearin on interfacial strength at CSO-water boundaries at 70°, 80°, and 90°F. and on air incorporation in high-ratio white cakes containing CSO shortening at 75°F.

the major differences between the alpha-additives and the other types in a high-ratio white cake batter and a yellow cake formulation. The fact that the concentration at which the alpha-additives form the thick interfacial films is related to the concentration required to enhance air incorporation is shown in Fig. 6 for a typical alpha-tending additive, 1-acetyl-3-monostearin. Similar results are obtained with other alpha-tending additives or alpha-tending mixtures. The ability of alpha-additives to enhance air incorporation
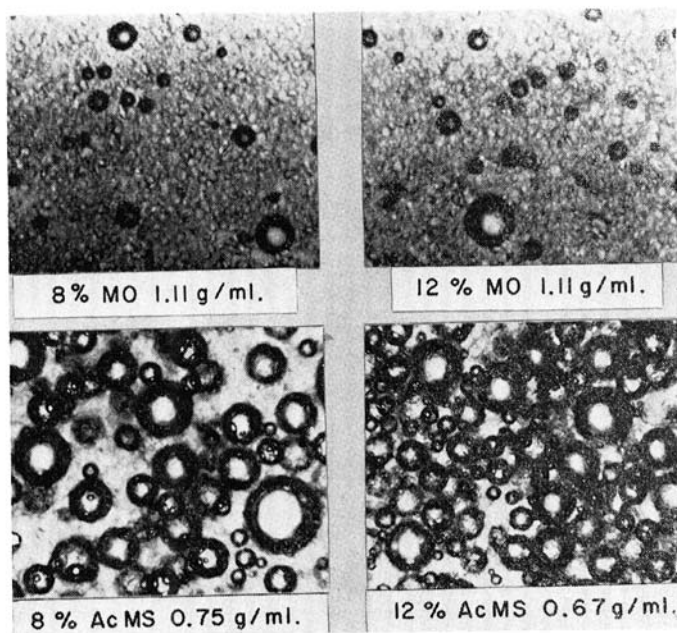

Fig. 7. Microscopic appearance (about 50×) of high-ratio white cake batters prepared with CSO shortening containing 1-monoolein and 1-acetyl-3-monostearin at concentrations of 8 and 12% of shortening weight. Single-stage mixing, 75°F. Batter densities are shown under each photograph.

in the Kissell lean formula (9) is shown below. In these examples, the Kissell lean formula was modified to use a single-stage method of mixing. Shortenings A–D are those used in the experiment of Fig. 1.

Shortening	Batter Density g./ml.
A	1.13
B	1.10
C (oil shortening)	1.11
D (oil shortening)	1.18
7% Lactoylated glyceride (alpha-additive) in hydrogenated shortening.	0.68
14% Propylene glycol monostearate (alpha-additive) in cottonseed oil.	0.79

The microscopic appearance of batters prepared with a non-alpha-tending additive, 1-monoolein, and an alpha-tending additive, 1-acetyl-3-monostearin, as a function of the concentration of the additive in cottonseed oil, is contrasted in Fig. 7. There is a marked increase in the amount of air incorporation (the dark circles) in the presence of the alpha-tending additive. This air does not appear to be associated with the lipid phase, as it is in the case of plastic shortenings (Fig. 1), but rather, it has the appearance of an aqueous foam. The importance of this observation will be emphasized further in connection with the role of soluble protein in cake made with a liquid shortening.

Behavior of Alpha-Tending Binary Mixtures of Lipids

Polymorphic studies have indicated that the stability in the alpha-polymorphic form of certain surface-active lipids can be markedly enhanced by admixture in binary systems with other fatty materials. For example, although pure propylene glycol monostearate exists in sub-alpha form at room temperature (the alpha form exists only above 35°C.), mixtures with stearic acid in amounts of 10 to 35% of the weight of the ester are stable in the alpha form at room temperature. Similarly, pure 1-acetyl-3-monostearin is alpha-tending at room temperature, whereas mixtures with 10 to 35% stearic acid have markedly increased alpha-stability.
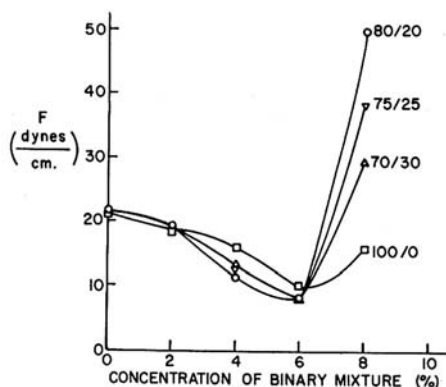

Fig. 8. Tensiometer data: Effect of admixture of stearic acid with propylene glycol monostearate on interfacial strength at the CSO-water boundaries. Ratios are propylene glycol monostearate:stearic acid (w./w.) measured at 70°F.
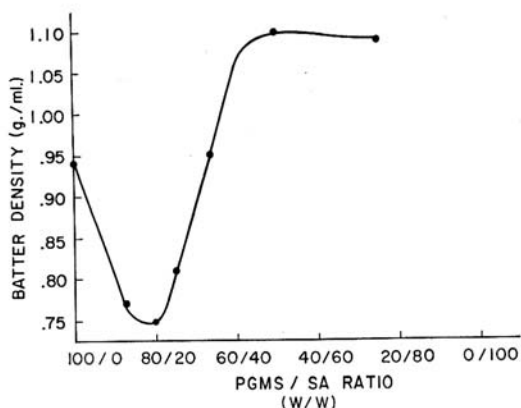
Fig. 9. Effect of admixture of stearic acid with propylene glycol monostearate on air incorporation in high-ratio white cake batters containing as shortening CSO with 6% total additive in the oil. Ratios are propylene glycol monostearate:stearic acid (w./w.) measured at 75°F.

This enhanced alpha-stability also correlates with the increased force, F, necessary to pull the tensiometer ring through the cottonseed oil-water interface in the presence of the binary mixtures. Figure 8 shows the dependence of this force at 70°F. on the concentration of the binary mixture in the cottonseed oil, and also on the ratio of propylene glycol monostearate to stearic acid (w./w.). Much higher readings are obtained from the binary mixtures (which are alpha-stable) as evidence of thicker and/or stronger film formation.

In Fig. 9 the effect on cake batter density of increasing the alpha-

TABLE I

EFFECT OF ALIPHATIC DIOL CHAIN LENGTH IN MIXTURES OF DIOL MONOESTERS AND STEARIC ACID ON POLYMORPHIC PHASE BEHAVIOR AND CAKE BATTER DENSITIES[a]

| DIOL MONOESTER | MIXTURE COMPOSITION | | POLYMORPHIC FORM[b] | BATTER DENSITY | ADDI- TIVE[d] |
	Diol Monoester	Stearic Acid			
	%	%		g./ml.	%
	....	100	β'-like[c]	1.15	2[d]
1,2-Propanediol monostearate[e]	100	....	sub-α-α	0.75	8
	80	20	α	0.71	10
1,3-Propanediol monostearate	100	....	β'-like	0.95	8
	80	20	α	0.63	10
1,4-Butanediol monostearate	100	....	β'-like	1.15	8
	80	20	α	0.68	10
1,5-Pentanediol monostearate	100	....	β'-like	1.15	8
	80	20	β'-like	1.09	10
1,6-Hexanediol monostearate	100	....	β-like	1.15	8
	80	20	β'-like	1.11	10

[a] High-ratio white cake batters, mixed in a single stage.
[b] From X-ray pattern of melted and chilled sample of bulk material.
[c] "β'-, β-like" terminology is used because these classifications have not as yet been extended over to compounds other than those which are based on a glyceride structure.
[d] Additive or additive mixture in cottonseed oil.
[e] Propylene glycol monostearate.

TABLE II
ALPHA-TENDENCY OF BINARY MIXTURES OF 1,4-BUTANEDIOL MONOSTEARATE (BDMS) AND PROPYLENE GLYCOL DISTEARATE (PGDS)

COMPOSITION OF MIXTURE		POLYMORPHIC FORM	BATTER DENSITY	ADDITIVE CONCEN- TRATION IN OIL SHORTENING
1,4-BDMS	PGDS			
%	%		g./ml.	%
100	....	β'-like	1.17	6
....	100	β'-like	1.15	6
80	20	α	0.70	6
80	20	α	0.70	8
70	30	α	0.69	8

tendency of the liquid shortening additive is clearly shown. Addition to the propylene glycol monostearate of stearic acid gives progressively lower batter densities (more air incorporation) until the optimum ratio of 80/20 is reached. More stearic acid results in a reversal of this trend and higher batter densities. A comparison of Figs. 8 and 9 leads to the generalization that air incorporation is directly proportional to the strength of the film formed at the oil-water interface.

The addition of stearic acid also increases the alpha-tendency of other aliphatic diol monoesters. Table I shows the effect on batter density of increasing alpha-tendency of the shortening additive by this means. The change in the polymorphic phase as the isomeric form or diol chain length (or both) is varied in mixtures with stearic acid is reflected in the batter densities. A dramatic lowering of batter densities was observed with those mixtures showing alpha-tendency.

Similarly, data in Table II reveal that freshly prepared binary mixtures of 1,4-butanediol monostearate and propylene glycol distearate (80/20 and 70/30) are alpha-stable in polymorphic form, in contrast to either material alone, and that the binary mixture enhances air incorporation in high-ratio cake batters prepared with oil shortenings.

Role of Soluble Protein in Air Incorporation

In batter systems containing hydrogenated triglycerides as shortenings (plastic shortenings), it is possible to incorporate some air in the absence of protein in the batter. This is possible probably because of the high viscosity of the shortening phase and physical entrapment of air during

TABLE III
AIR INCORPORATION IN OIL-WATER EMULSIONS
(6:1 Aqueous phase[a]:oil phase)

OIL PHASE	EMULSION DENSITY		EMULSION STABILITY (75°F.)
	No Protein	With Protein	
	g./ml.	g./ml.	
Cottonseed oil (CSO)	0.96	0.78	Very unstable
14% PGMS (50% monoester: 50% diester) in CSO	0.98	0.68	Very stable
6% Lactoylated glyceride[b] in CSO	0.98	0.72	Very stable

[a] Water or 5% egg white protein in water.
[b] For composition see ref. 4.

mechanical mixing. However, in batter systems containing fluid shortenings, soluble protein is directly involved in air incorporation. Table III shows the densities of oil-water emulsions as affected by the presence of soluble protein, 5% egg-white solids in water in this case. These results indicate that these shortening additives enhance air incorporation in an indirect way and that soluble protein is essential for optimum air incorporation.

DISCUSSION

The results of this study lend support to the idea of the foam nature of a single-stage cake batter system made with a fluid shortening. This emulsion consists essentially of a dispersion of air in liquid where the air is incorporated throughout the aqueous phase of the batter by means of the well-recognized foaming ability of dissolved protein. This idea was also described quite clearly recently by Handleman et al. (3) in a study of the bubble mechanics in thick foams. Some of the differences now recognized in microscopic appearance between batters are also apparent in the results of these workers.

It is also well known that the foaming ability of protein solutions can be inhibited very effectively by fatty materials. It appears possible that in single-stage batters such as some of those described in the present study, where liquid triglyceride shortenings and non-alpha-tending additives are employed, the total fatty phase of the batter inhibits air incorporation into the aqueous phase. (An exact description of antifoaming action is not available, nor is it known which of the many lipids present are actually involved in this effect on the protein solution.) However, the antifoaming activity of liquid triglycerides, alone or with other surface-active lipids present in the triglycerides, can be overcome in large part by addition of alpha-tending surface-active lipids to the oil phase.

This study points out that the peculiar interfacial properties of surface-active lipids which are stable in or tend toward the alpha-polymorphic crystalline form are directly related to the ability of these lipids to enhance air incorporation in cake batter systems. This beneficial effect is seen only under conditions where the alpha-additive mixtures form the strong interfacial films which can be seen microscopically and their strength can be estimated with the DuNuöy tensiometer.

It is suggested that, under such conditions, impermeable interfacial membranes form at the oil-water interface and in this way reduce the contact of those detrimental lipid components with the protein-stabilized foam of the batter system. These films which form at the oil-water boundary are generally stable up to temperatures somewhat above room temperature, the actual melting point varying with the particular additive mixture employed and its concentration in the oil.

The "interfacial strength" of these membranes can be estimated with the DuNuöy tensiometer and can be related to air incorporation into single-stage cake batters made with fluid shortenings. As the strength of the interfacial film increases, the amount of air incorporated into the batter increases.

Two facts support the proposition that these alpha-additives effect air incorporation through an indirect mechanism: 1) soluble protein is required for air incorporation in batters containing oil shortening, and 2) alpha-additive mixtures in oil shortenings alone will not incorporate air.

The hypothesis presented as a result of this work is that: a surface-active lipid which is alpha-tending in the bulk state and soluble in liquid oil of the shortening used in a cake batter 1) concentrates at the interface of the shortening and aqueous phases; 2) reaches a concentration at the interface which exceeds some value, as yet undefined, which is a function of the physicochemical forces involved in the interface; and 3) crystallizes to form a thick interfacial film of alpha-polymorphic form. This film, in effect, encapsulates the dispersed shortening particles or droplets in a protective membrane and prevents the lipid from inhibiting the foaming properties of the dissolved protein. The beneficial effects of alpha-tending additives in plastic shortenings (3) may be of this same nature, since in like fashion they would prevent the 70–80% of the liquid shortening present from destabilizing the protein foam formed during the mixing of the cake batter.

Three particular classes of alpha-tending lipids have been described: (a) hydroxycarboxylic acid esters of mono- and diglycerides (lactoylated glycerides), (b) mixed acid diglycerides (acetylated monoglycerides), and (c) fatty esters of aliphatic diols (propylene glycol monostearate). Although not all members of these classes are alpha-tending, admixture of these with many other lipid materials such as fatty acids, diglycerides, and solid triglycerides has been found to produce alpha-tendency.

The hypothesis regarding the mechanism of action of these shortening additives provides some answers to the questions regarding the value of liquid shortening in cake batter systems and adds another consideration to the role of emulsifiers in the mechanism of baking.

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