

BUBBLE MECHANICS IN THICK FOAMS AND THEIR EFFECTS ON CAKE QUALITY¹

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ABSTRACT

Characteristics of finished cakes are compared with those predicted by a theoretical treatment of properties of the batter which would affect the growth and movement of bubbles. Surface tensions, viscosities, and yield values were measured in several white and yellow cake batters, and the rates of bubble-to-bubble gas diffusion were observed in sequential photomicrographs of a single field of each batter. It was observed that, in batters prepared with unemulsified shortening, bubble-to-bubble diffusion was extremely slow, and leavening gas was evolved into only a small percentage of the bubbles. As predicted by the mathematics, when a given amount of gas is evolved into a small number of bubbles, a large proportion attain critical buoyancy and rise. These cakes had lower volumes, indicating that a significant proportion of the gas was lost, presumably by this mechanism. Where diffusion was more rapid and involved larger numbers of bubbles, volumes were higher. In a case where the yield and viscosity values were high, even the tendency to layer (larger cells to accumulate nearer the surface) was minimized.

It is generally accepted that the cells of a cake originate as bubbles in the batter. Pneumatic support provided by the bubbles maintains the structure of a cake until mechanical strength is developed in the nongaseous phases. Hence, the strength, texture, volume, shape, and grain of cakes are determined by size distribution, inflation, movement, film permeability, and stability of bubbles, along with mechanical properties developed in the setting of the batter.

Since the mathematics of bubble formation, growth, and movement have been developed fairly well, it was thought worth while to determine where they provide explanations for some of the observations made in practical cake-batter systems. Knowledge of this type should reduce the experimentation required in product development.

In this study, viscosities and yield values of cake batters have been measured; two types of interfacial tensions have been measured; accompanying bubble distribution and growth characteristics have been observed in the cold batter; and cakes resulting from these batters have been evaluated. Batters and cakes studied were all prepared with one base formulation. Whole egg, egg white, and egg white plus 0.1% lecithin (dry mix basis) were used with three different commercial shortenings, which varied primarily in type of emulsification. These formulation variations were chosen to provide a range in the

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measured and observed properties, so that trends could be recognized and compared with those predicted by theory.

Materials and Methods

Batter Preparation. Large batches of dry mix were prepared by commercial procedures with pilot-plant equipment, according to the formulation given in Table I. Each of three test shortenings was

TABLE I
FORMULATION OF DRY MIXES USED TO PREPARE EXPERIMENTAL BATTERS

INGREDIENT	TYPE	PERCENT OF DRY MIX
Flour	Commercial cake—9.3% moisture, 8.7% protein (14% moisture basis), 0.36% ash, AACC viscosity 37, pH 4.85	36.2
Sugar	Baker's Special fine granulated	45.3
Shortening	Varied; types described below	12.0
Milk	High-heat, spray-dried, nonfat dry	4.0
Salt	Reagent grade, unfilled	0.8
Sodium bicarbonate	Granular (about 5% retained on 100-mesh and about 5% through 270-mesh)	0.7
Sodium Acid Pyro-phosphate	Slow, ^a food grade	0.7
Monocalcium Phosphate Monohydrate	Food grade	0.3

^a Trademark RD-1.

used. Batters were prepared by the following three-step mixing procedure in a Hobart N-50 mixer with a 4-qt. stainless-steel bowl and paddle.

1. Dry mix, 1,000 g., was blended with 130 g. tapwater for 15 seconds at speed 1 and beaten 2 minutes at speed 2; bowl scraped down.
2. Water, 100 g., and half the egg were added and blended 15 seconds at speed 1 and beaten 1 minute at speed 2; bowl scraped down.
3. The remaining egg and 170 g. of water were added and blended 15 seconds at speed 1 and beaten 1 minute at speed 2.

Cakes. Cakes were baked from one-fourth of each batter in 8-in. aluminum cake pans at 350°F. for 35 minutes.

Formulation Variations. The three commercial shortenings used were: 1) a hydrogenated vegetable shortening (unemulsified), 2) a normal high-ratio shortening containing mono- and diglycerides and lechithin, and 3) a high-aerating shortening containing mono- and diglycerides and probably a lactylated monoglyceride emulsifier.

With each of these shortenings, three test batters were studied. These batters varied in that they contained, in addition to water,

1) 120 g. egg white; 2) 120 g. egg white and 72 g. egg yolk; or 3) 120 g. egg white and 1 g. lecithin.

The lecithin was added as a 20% hydrated slurry at the beginning of the first stage of mixing. The material was a commercial drug product obtained from soybeans. This design permits detection of effects and interactions of shortening emulsification, egg yolk, and lecithin, introduced into the aqueous phase.

Formulation Fractions for Interfacial Tension Measurement. Three aqueous systems were prepared for interfacial tension measurements against each of the shortenings. The components of these aqueous systems were present in the same proportions used in the complete batters. Systems prepared were 1) sugar, water, and egg white; 2) sugar, water, egg white, and egg yolk; 3) sugar, water, egg white, and lecithin.

Interfacial Tension Measurements. The air or gas-liquid interfacial tension acting on a single bubble in cake batter was calculated from the maximum pressure reached in blowing a bubble with a capillary of known inside diameter submerged in the batter at a known depth. After correcting for depth of submergence, γ can be calculated from equation 5. The radius of the capillary is the minimum radius of curvature which a bubble at the tip can attain, and, therefore, is the radius at maximum pressure. This radius was calculated from the maximum bubble pressure attained with water and literature value for the surface tension of water at its air interface. Measurements were made at room temperature with each experimental batter.

Interfacial tensions were measured between the shortenings and some components of the aqueous phase of the batters by a pendant drop technique (1) with measurements made on photomicrographs of the drop and capillary.

Viscosity Measurements. Apparent viscous coefficients at varying shear rates were determined for each batter with a MacMichael Viscometer. Results showed a significant increase in apparent viscosity as shear rate decreased.

Yield Value Measurements. Yield value was calculated from the residual force on a metal plate vertically suspended in a test batter after displacement of the plate and 5-minute relaxation of the batter.

Bubble Distribution and Growth. Carlin (3) photographed bubbles in cake batters to show effects of shortening emulsification. In the present study, however, sequential photomicrographs of a single field were taken over a period of 90 minutes with each test batter. Slides were prepared by gently pressing a small drop of batter between a slide and cover glass and then sealing the cover glass boundary with stopcock grease to reduce drying of the batter. Only transmitted light

was used, although it was observed that reflected light sharpened boundaries between aqueous and fat phases. Microscope magnification was $60\times$ and this was approximately tripled in the photographs.

Cake Volume and Conformation. Cakes were measured according to the method developed by the AACC committee on cake flour testing. The height of a center cross-section was measured at the center and 60 mm. in each direction from the center. Height measurements were reported in the following order: side, center, side.

The radius was also measured and the volume calculated from this and the average height. Specific volume was the calculated volume in cc. divided by the batter weight in g.

Finished Cake Photographs. Finished cake photographs provide an excellent record of many subjective characteristics of baked products, and a standardized method has been adopted in this laboratory and was used in this study. Cakes were photographed, one at a time, with half a layer standing on its cross-section and a thin section of the cross-section placed in front. This arrangement was adopted to show the most crust, shape, and texture characteristics.

The following precautions were taken to assure uniform photographic conditions: 1) The two lights and Crown Graphic camera were mounted in fixed positions with fixed settings, and the subject was positioned with a template; 2) the Panatomic-X sheet film was developed by a set, reproducible procedure, which limited variations due to developer age, development time, etc.

Negatives were sufficiently uniform to permit compositing for useful comparisons. Further, the procedure, once established, is sufficiently simple and rapid to be used routinely with baking studies.

Results and Discussion

Bubble Mechanics (1,2). For a single, submerged bubble in an ideal thick-walled foam:

$$F_1 = \pi r^2 p, \quad (1)$$

$$F_2 = 2\pi r \gamma, \quad (2)$$

$$F_3 = 4/3\pi r^3 g(\rho_2 - \rho_1), \text{ and} \quad (3)$$

$$F_4 = 6\pi r \eta \sigma. \quad (4)$$

In these expressions:

F_1 = force tending to expand the bubble;

F_2 = force tending to contract the bubble;

F_3 = bouyant force tending to make the bubble rise;

F_4 = frictional force exerted against a spherical body moving in a viscous fluid (Stokes' law);

r = radius of bubble;

- p = pressure of gas in bubble in excess of hydrostatic;
 γ = surface tension at the gas-liquid interface;
 g = gravitational constant;
 ρ_1 = density of gas in bubble;
 ρ_2 = density of liquid in foam;
 η = Newtonian viscosity;
 σ = rate at which the sphere moves in the fluid.

Equating the expressions for F_1 and F_2 and solving for p , it can be shown that, for a bubble in equilibrium (1),

$$p = 2\gamma/r \quad (5)$$

From equation 5, it is apparent that, as bubbles become extremely small, their internal pressures become exorbitantly large, so that spontaneous nucleation of bubbles in a continuous fluid is extremely unlikely. This difficulty is overcome in cake batters by mechanically entraining and subdividing bubbles of air and leavening gas during mixing. These bubbles then provide the majority of sites for collecting leavening gas and water vapor as they are evolved (3,4). If the number of nucleating sites is small, then individual cells will tend to be large and the cake to be open-grained. Conversely, with a large number of sites available to be inflated, the cells will be small and the grain fine or close. Since it has been shown² that bubble sizes in thick-walled foams follow a single log-normal distribution, average bubble size should be sufficient for predicting the proportion of bubbles which will become critical.

If the expressions for F_3 and F_4 are equated and the expression solved for σ , it is found that the terminal rising velocity of a bubble is

$$\sigma = 2gr^2(\rho_2 - \rho_1)/9\eta \quad (6)$$

Equation 6 shows that, in a liquid of given viscosity, the rate of rise of a bubble due to its buoyancy is proportional to the square of the bubble radius and is inversely proportional to the viscosity. These relationships show that a foam composed of small bubbles suspended in a viscous Newtonian fluid would be more stable with respect to buoyancy-induced segregation than a foam composed of larger bubbles or a foam in a less viscous Newtonian fluid.

In cakes, rapidly rising bubbles cause loss of volume and layering (a gradient in cake grain varying from tight at the bottom of the cake to open at the top). Fewer bubbles should reach sufficient size to rise out of the batter during baking when the number in which the leavening gas collects is large than in the case where only a few bubbles are available to serve as nuclei. This is assumed, because, if only a few

² Overbeek, J. th. G. Rijksuniversiteit Te Utrecht, Utrecht, Domplein 28, The Netherlands. Private communication.

sites receive all the gas, these sites must each attain relatively larger size. An increase in viscosity should also reduce volume loss by increasing the critical size which a bubble must attain to rise rapidly.

In the case of cake batters, which are neither homogeneous nor Newtonian, the relationship between gas-liquid surface tension and bubble pressure should hold. Our measurements show some bubble-to-bubble variation in surface tension within a cake batter, due apparently to the inhomogeneity of the system. The batter properties governing bubble movement act in a more complicated way, however. These studies show that cake batters are pseudoplastic (apparent viscosity decreases with increasing shear rate or rate of bubble movement), and that they have a small yield value. Equations 7 and 8, below, describe the effect of yield value, and equation 6 will also apply to cake batters if σ is made the proper function of η .

$$F_5 = Yf(r) \quad (7)$$

F_5 = force which must be exceeded for bubble movement;

Y = yield value;

$f(r)$ = an unspecified function of the bubble radius.

If the expressions for F_3 and F_5 are equated, the boundary condition for no bubble movement is given by the expression:

$$4/3\pi r^3 g(\rho_2 - \rho_1) = Yf(r) \quad (8)$$

If the bubbles which increase in size during the microscopic observation period are taken to be the available nucleating sites, it can be seen that the number increases from unemulsified to the mono- and diglyceride shortening and increases again from that shortening to the high-aerating shortening. Table II shows that average specific volumes obtained increase at the same time the number of nucleating sites increases. It can be argued that the specific volume differences between the cakes made with high-aerating shortening and those made with shortening containing mono- and diglycerides are due to the difference in amount of air incorporated during mixing, with this air serving to augment the gas generated by the leavening system. However, since batters prepared with the unemulsified shortening and those prepared with the mono- and diglyceride shortening had similar specific gravities (Table II), it must be concluded that more of the leavening gas escaped from the unemulsified-shortening batters, presumably by the mechanism described above.

The fact that leavening gas is evolved only into relatively low-pressure bubbles, when they are present, is adequately demonstrated by the photomicrographs in Fig. 1. Neither leavening system nor batter

TABLE II
PHYSICAL CHARACTERISTICS OF BATTERS AND FRACTIONS AND
EVALUATIONS OF CAKES PREPARED FROM THEM

VARIANT FORMULA (SHORTEN- ING)	VISCO- SITY ^a	YIELD VALUE	SURFACE TENSION OF AQUEOUS FLUID (BUBBLE WALL)	INTER- FACIAL TENSION (FAT VS. WATER)	BATTER SPEC. GRAVITY	CAKE		
						Spec. Vol.	Confor- mation	Texture and Grain
		<i>dynes/ cm²</i>						
Unemulsified								
Whole egg	37	10.5	55	5.6	0.93	2.7	34-34-35	Tight—sl. coarse
White	72	26	69	12.9	0.93	2.4	29-32-28	Tight—sl. coarse
Wh + lecithin	39	2	52	2.3	1.06	2.3	28-30-28	Tight—sl. coarse
Mono- and diglyceride								
Whole egg	70	39	46	0.7	0.92	3.1	39-40-39	Fairly open, med. fine
White	83	28	50	0.7	0.94	2.9	35-38-36	Fairly open, fine
Wh. + lecithin	56	10	45	0.6	0.94	2.8	33-36-33	Open—med. fine
High-Aerating								
Whole egg	67	32	45	0.5	0.77	3.2	41-41-41	Open—med. fine
White	160	75	55	0.8	0.75	2.7	35-27-35	Open—coarse
Wh. + lecithin	152	85	64	0.6	0.75	3.1	38-38-37	Open—fine
St. error of measurement	$s \leq 2$	$s \leq 4$	$s \leq 1.5$	$s \leq 10\%$	$s \leq 0.02$	$s \leq 0.03$		

^a Centipoise at a low rate of shear of 2 sec.⁻¹

temperature varied in the test, so it is safe to assume that about the same amount of leavening gas was evolved during the observation period of each series of photomicrographs. In spite of this, the small (high-pressure) bubbles in the emulsified shortening batters shrank. The growth of the larger bubbles had to be from leavening and diffusion of gas from the small bubbles. The tendency of leavening gas to seek the larger bubbles suggests that the release of shortening-entrained bubbles during baking (3) should provide few nuclei for new cells, since the newly released bubbles would be smaller and have higher internal pressure than those which had been growing longer in the aqueous phase. It is possible, however, that in batters with extremely few effective nuclei, all originally active bubbles will escape and nucleation of the final structure will come from entrained bubbles.

Interfacial Tension Effects. The emulsified shortenings yielded much lower fat vs. aqueous interfacial tensions (Table II), and this was accompanied by much less diffusion inhibition. Presumably, dispersibility was increased with the lower surface tensions resulting in smaller fat units, which did not present a sufficient barrier to block diffusion. Neither gas-liquid nor liquid-liquid interfacial tension seemed to affect significantly the amount of air incorporated in a batter during mixing, since the specific gravities of the unemulsified-shortening batters and those made with shortening containing mono- and diglycerides were approximately the same, whereas their liquid-liquid interfacial tensions were markedly different (Table II). The lack of correlation is also shown by the fact that the high-aerating shortening caused a great deal more air incorporation (lower batter specific gravities) than did the mono- and diglyceride shortening, even though their interfacial tension effects were similar. No correlation was observed between the gas-liquid interfacial tension and the amount of air incorporated into the batter during mixing.

Rheological Effects. From the discussion above, it should follow that higher volume and less layering should be obtained with the cakes having high yield values and viscosities. In the experimental cakes prepared in this study (Fig. 2 and Table II), no instance was observed in which an increase in specific volume could be attributed to a change in viscosity or yield value. In the case of C3, Fig. 2, layering was markedly reduced over that in any of the other high-volume cakes, B1, B2, or C1. Since C3 had a yield value more than double that of any of the other high-volume cakes, it is probable that a relationship existed. Apparently, to demonstrate definitely the influence of rheological characteristics, it would be necessary to produce much greater variations without seriously altering the other batter properties.

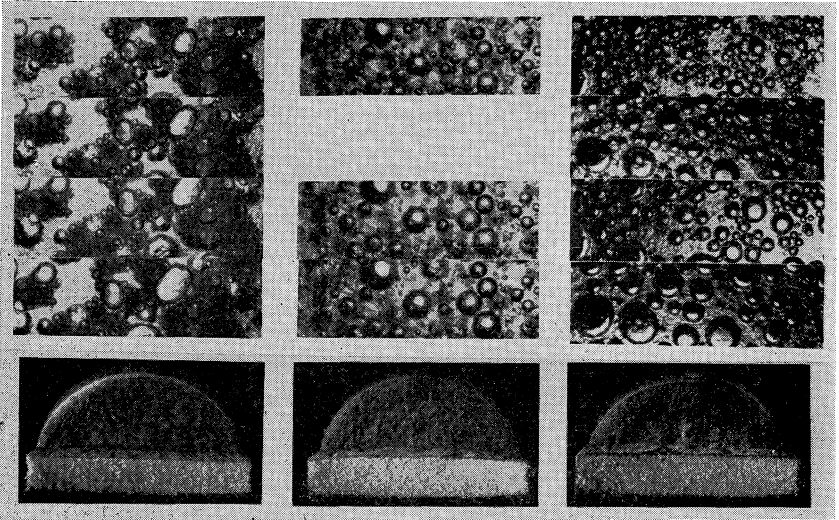


Fig. 1. Photomicrographs of batter distribution and bubble growth in whole-egg cake batters at 25°C; approx. 150 times actual size. Holding time, top to bottom strips: 0, 15, 45, and 90 minutes. Shortening, left to right: unemulsified; mono- and diglycerides and lecithin; high-aerating. The resulting cakes (respectively) are shown below.

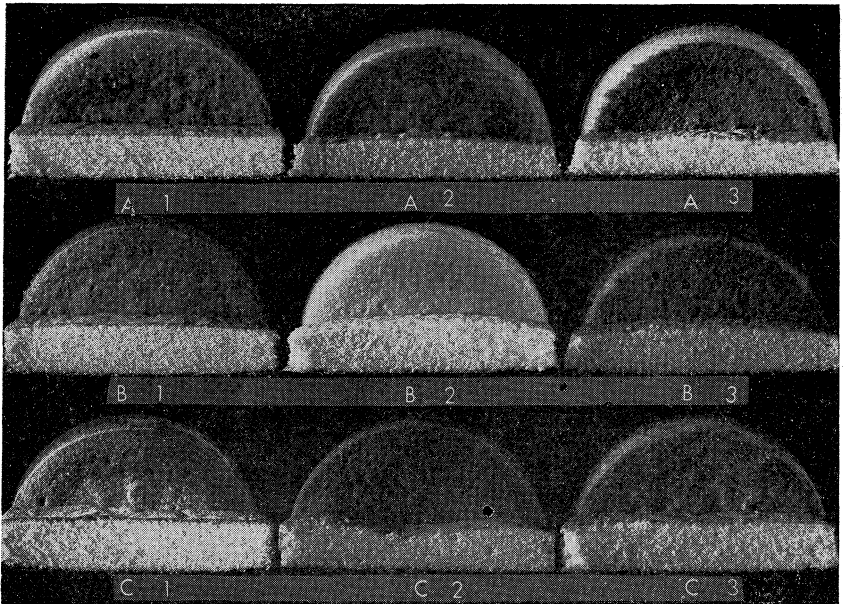


Fig. 2. Layer cakes from experimental batters. A1,2,3, unemulsified shortening; B1,2,3, shortening emulsified with mono- and diglycerides and lecithin; C1,2,3, high-aerating shortening. A1, B1, C1, whole-egg; A2, B2, C2, egg white only; A3, B3, C3, egg white plus lecithin.

If $f(r)$ in equation 7 were specified, equation 8 could be solved for the maximum size of stationary bubbles. However, to the authors' knowledge, this function has not been specified. Although yield values should have the same effect of stopping bubble movement as would very high viscosities, no case was observed in which restriction of bubble movement could be attributed to yield value.

On standing, the bubbles in cake batters appear to increase in size, even if no new leavening gas is evolved. The mechanics of this effect are described below, because they clarify some of the observations in this study. The following equations describe the interaction of two bubbles of radii r_1 and r_2 in a thick-walled foam.

$$dV/dt = -DA \, dC/dX \quad (9)$$

$$P = CK \quad (10)$$

$$dC/dX = (C_2 - C_1)/X \quad (11)$$

In these expressions:

V = ml. of gas;

t = time in seconds;

D = diffusion constant;

A = area normal to the concentration gradient;

C = concentration of the dissolved gas;

X = effective distance on the concentration gradient;

K = Henry's law constant.

If the expression for pressure in equation 5 is substituted in equation 10 (Henry's law, 5), and the resulting expression solved for C, it is found that

$$C = 2\gamma/rK \quad (12)$$

Substituting the expression for C given in equation 12 in the assumed concentration gradient, equation 11, the concentration gradient in terms of surface tension, bubble radii, and Henry's law constant becomes:

$$dC/dX = 2\gamma(r_1 - r_2)/r_1r_2XK \quad (13)$$

Using the description of the concentration gradient in equation 13 in the Fick equation 9 (5), it is found that the rate of diffusion at bubble 2,

$$dV/dt = 2\gamma D\pi r_2(r_2 - r_1)/KXr_1 \quad (14)$$

From equation 14, it is apparent that diffusion will take place toward the larger bubble (dV/dt is positive if r_2 is greater than r_1 and negative if r_1 is larger). The general tendency described more or less exactly by equation 14 is intuitively apparent from a consideration of the following. From equation 5, pressure is higher in smaller bubbles,

and, from equation 10, solubility increases with increasing pressure. The equilibrium concentration of the dissolved gas in the fluid around a small bubble, then, is higher than that surrounding a larger bubble in the same fluid. The dissolved gas, in moving from the region of high concentration to that of low concentration, raises the concentration around the large bubble above the level in equilibrium with the internal pressure of the bubble and comes out of solution into the bubble. This, in turn, makes F_1 exceed F_2 (equations 1 and 2), and that bubble expands to restore the balance, with the net result that the larger bubble's size is increased and pressure is further decreased. Meanwhile, the reduction in concentration around the small bubble causes more gas to be dissolved, further reducing its size and increasing its internal pressure. It can be seen that the driving force causing gas to move from the smaller to the larger bubble is the internal pressure difference or size difference and becomes increasingly large as the process proceeds. The rate at which this takes place is controlled by the constants, γ , D , K , and X in equation 14.

Equation 14 suggests that cakes prepared from batters which have stood (even if no leavening gas is evolved during standing) should have coarser texture and lower volume if no effects other than bubble-to-bubble diffusion are present. As large bubbles grow and small bubbles shrink and disappear, the number of active nucleating sites is reduced, and the mean size of cells must increase. Consequently, the proportion of bubbles attaining critical buoyancy increases. In this study no attempt was made to measure diffusion constants, but the rate of diffusion could be roughly observed in photomicrographs by following the shrinkage of small bubbles.

Diffusion Effects. The photomicrographs in Fig. 1 show size distributions and room-temperature growth patterns of bubbles in whole-egg cake batters made from the three test shortenings. Diffusion results with every test batter are not shown, because differences were shortening-oriented. The shrinkage of small bubbles and growth of large bubbles predicted by the diffusion equation (eq. 14) are quite evident in the cases of the two emulsified shortenings. In the case of the unemulsified shortening, the smaller bubbles, entrained in the fat, show little size change, while a few of the large bubbles show considerable growth. Apparently, very little bubble-to-bubble diffusion is taking place in this case, and the growth of the few large bubbles stems from the slight leavening activity going on during the period of observation. The fact that only a few of the bubbles change in size may mean that only these have sufficient contact with the aqueous phase to serve as nucleating sites, and the entrained bubbles are inert in this phase of structure

development. In any case, the limited number of nucleating sites in the unemulsified shortening must result in a larger proportion of the bubbles attaining critical buoyancy. This result is predicted by the foregoing discussion and is confirmed by the lower specific volumes obtained with the cakes prepared with the unemulsified shortening (Table II).

The dip in cake C2, Fig. 2, is not satisfactorily explained by the batter properties considered in this study.

Conclusion

Experimental results support the theoretical conclusion that by increasing the number of sites which can receive leavening gas one can reduce the average size of individual bubbles and minimize the numbers which reach a critically buoyant size and rise out of the system, carrying their leavening gas with them. Shortening emulsification can affect this situation by 1) permitting the incorporation of more air (bubbles), or 2) making the fat sufficiently dispersible to avoid screening a large portion of the bubbles and rendering them ineffective as nucleating sites.

There is insufficient variation in air-batter surface tension among the formulation variations examined to implicate this property as a major factor affecting bubble or batter characteristics. Fat-aqueous surface tensions, as measured in this study, do not account for the property of high aeration associated with some emulsifier systems, but they do seem to indicate whether a shortening will disperse sufficiently so as not to shroud bubbles and prevent their acting as nucleating sites.

It is clear that these relationships do not account for all variations in cake performance, but their ability to explain many of the examples cited in this study demands further work along these lines.

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