The Effect of Surfactants on the Interfacial Tension of Frying Fat[1]

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ABSTRACT: Interfacial tension (IFT) between fat and water was measured as a means of evaluating fats used for frying. The Du Noüy ring method was used with a tensiometer to obtain IFT. The IFT of donut frying fats, which were diluted 1:1 with unused fat, decreased with increasing frying time from 21 mN/m in unused fat to 5 mN/m in fat at the point of discard. To determine which individual chemical components in donut frying fat are responsible for the decreased IFT, various surfactants were added. The addition of surfactants to the water phase (phosphatidylcholine, sodium oleate, and sodium chloride) or oil phase (monoacylglycerols, diacylglycerols, and fatty acids) had varying effects on the IFT of soybean oil against water at 25 ± 0.1°C. The IFT decreased with increasing concentration of monoacylglycerols, sodium oleate, phosphatidylcholine, and sodium chloride. Sodium oleate was the most effective agent in lowering IFT, reducing it almost to zero at a concentration of 0.1%. At a concentration of 0.2%, monoacylglycerols lowered IFT of fresh soybean oil by 14% (monolinolein), 22% (monoolein), and 26% (monostearin). Egg lecithin lowered the IFT by 42%. These surfactants changed the IFT of fresh soybean oil by their adsorption at the oil/water interface. Although sodium chloride is not a surfactant *per se*, it lowered IFT by salting out surfactants from the aqueous phase onto the interface. The addition of diacylglycerols or fatty acids had virtually no effect on IFT.

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KEY WORDS: Alkaline contaminant material, diacylglycerol, fatty acid, frying fat, interfacial tension, monoacylglycerol, phospholipid, soap, surfactant, tensiometer.

During frying, fat is exposed to high temperature, moisture, and oxygen for long periods of time. Complex chemical and physical changes occur under these conditions, causing fat deterioration that may reach a point where high-quality foods can no longer be prepared (1,2). Blumenthal (3) developed a surfactant theory, which states that control of surfactant formation is the key to maintaining the quality of fat and food during frying (reduced fat pickup, better control of color) because surfactants act as catalysts that enhance many of the breakdown reactions. He said that food materials leaching into the fat, breakdown of the fat itself, and oxygen absorption at the fat/air interface all affect heat transfer at the fat/food interface and reduce the initially high interfacial tension (IFT) between the two immiscible materials. However, he did not measure the change of the IFT of frying fat.

IFT, which measures the extent to which water and oil are able to mix together, was proposed by Fisher *et al.* (4) as a means of evaluating the purity of commercial vegetable oils. Gaonkar and Neuman (5) developed a method to determine the IFT between commercial vegetable oil and water and investigated the role of probable contaminants on the IFT of a purified soybean oil/water system. Gaonkar and co-workers further undertook extensive studies of the behavior of surfactants at the vegetable oil/water interface (6–9). Pinthus and Saguy (10,11) have developed an equation, based on contact angle, to estimate the IFT between a food product and the frying medium.

One commonly used method for the measurement of IFT is the Du Noüy ring method, whereby the IFT is calculated from the maximum upward force applied to a ring (12). Some researchers have stated that this method is inappropriate for the measurement of IFT because of lack of stable contact angles (4,6,13); however, Cram and Haynes (14) showed that the maximum pull was reduced by less than 3.5% for contact angles up to 30°, and by less than 1% for contact angles up to 10° when using the ring method. Also, they concluded that imperfect wetting of the ring, to an extent sufficiently small to escape visual observation, would not give rise to experimental errors. Therefore, the ring method was judged to be appropriate for this study.

The primary objective of this study was to develop appropriate experimental techniques for measuring IFT as a means of evaluating frying fat. A second objective was to show to what extent various surfactants, such as mono- and diacylglycerols, fatty acids, sodium oleate [one type of alkaline contaminant material (ACM)], NaCl and phospholipids, affect IFT and reduce the initially high IFT between oil and water.

MATERIALS AND METHODS

Liquid/liquid interfaces are sensitive to trace contaminants. To generate a clean interface, it is essential to purify all of the

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system components. Water used in this study was of high-performance liquid chromatography (HPLC) grade (Fisher Scientific, Pittsburgh, PA) and had a surface tension of 72 mN/m at 25°C. This value is in excellent agreement with that reported in the literature (15), thus indicating its high purity. Therefore, the water was used as received. Unused and used donut frying fats were partially hydrogenated soybean, supplied by Tasty Baking Company (Philadelphia, PA). Soybean oil was obtained from a local supermarket. Monostearin, monoolein, monolinolein, distearin, diolein, and dilinolein (all >99% pure) were obtained from Nu-Chek-Prep (Elysian, MN). L-α-Phosphatidylcholine, sodium oleate, and fatty acids were purchased from Sigma Chemical Company (St. Louis, MO).

Determination of IFT. The IFTs of frying fat/water and soybean oil/water were measured with a Krüss model K10ST tensiometer (Krüss USA, Charlotte, NC), which is based on the Du Noüy ring method. The Du Noüy ring was composed of 90% platinum and 10% iridium. Measurements were taken at 25 ± 0.1°C for soybean oil and at 40 ± 0.1°C for frying fat with a 10-min equilibration time, which is the time from mixing of the two liquid phases until measurement of IFT. All the associated glassware and ring were cleaned by soaking in concentrated H_2SO_4 that contained Nochromix (Godax Labr., Pawling, NY), rinsing with distilled water and finally with HPLC-grade water. The ring was heated above the reducing zone of a gas burner until it just began to glow red.

The effects of surfactants on the IFT between water and fresh soybean oil were measured at increasing concentrations. Mono- and diacylglycerols (oleate, linoleate, and stearate) and fatty acids (oleic and linoleic) were dissolved in the fat phase. Sodium oleate, phosphatidylcholine (PC), and sodium chloride were dissolved in the water phase.

RESULTS AND DISCUSSION

Change in IFT of frying fat with frying time. To determine the effect of frying time on the IFT, two series of samples were collected on five consecutive days of donut frying and analyzed (Table 1). Before the start of frying, the IFT of unused fat was high at 20.8 mN/m. After one day of frying, the IFT of frying fat was lowered to almost an unmeasurable value.

TABLE 1
Change in Interfacial Tension of Frying Fat Against Water During Deep-Fat Frying

Sample	Day of frying (day)	Interfacial tension (mN/m)	
		Series A	Series B
Unused fat	0	20.8	20.8
Donut frying fats[a]	1	8.4	8.2
	2	7.0	6.8
	3	6.2	6.5
	4	5.5	6.0
	5	4.8	5.4

[a] Donut frying fats were diluted with unused fat in a 1:1 ratio.

To obtain measurable IFT values throughout the five-day frying cycle, donut frying fat samples were diluted with unused fat at a 1:1 ratio. As the days of frying increased, the IFT values of the diluted fats decreased from 8 to 5 mN/m over five days in both series of samples.

At the start of donut frying, fresh frying fat is mixed with a portion (about 20%) of donut frying fat saved from the previous frying cycle. The used fat is needed to impart the desired color and flavor to the donuts. Because each frying cycle is unique, the addition of used fat can introduce many variables that potentially can affect fat degradation in a new frying cycle. However, IFT of donut frying fat on day 1 was not significantly different between the two series of samples (8.4 and 8.2 mN/m). Therefore, based on IFT, the two series of donut frying sequences started with similar frying fats. Because the donut frying fat samples were taken during production runs and production is determined by orders received, some differences between series will occur. These production differences probably account for the lower IFT on day 5 for series A compared to that for series B. As donut frying continued, IFT decreased due to formation of surfactants as a result of fat degradation. The lower IFT may be the cause of increased fat absorption by donuts as the frying cycle proceeds (16).

The effect of probable surfactants on the IFT of soybean oil was investigated by their addition to fresh soybean oil or frying fat.

Mono- and diacylglycerols. The results of monoacylglycerol (monooleate, monolinoleate, and monostearate) and diacylglycerol (dioleate, dilinoleate, and distearate) addition are shown in Figure 1. As the concentration of monoacylglycerols increased, the IFT decreased in the order of monoli-

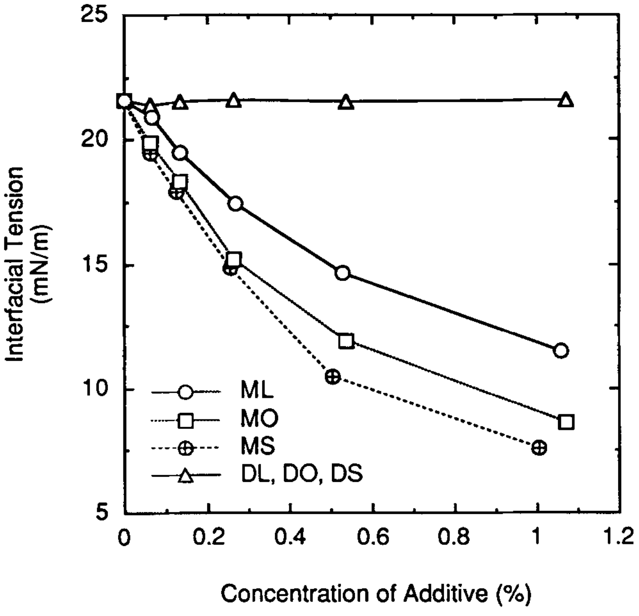

FIG. 1. The effect of monooleate (MO), monolinoleate (ML), monostearate (MS), dioleate (DO), dilinoleate (DL), and distearate (DS) on the interfacial tension of fresh soybean oil against water at 25 ± 0.1°C.

nolein, monoolein, and monostearin. All the monoacylglycerols have the same slope initially. IFT of fresh soybean oil decreased with a steep slope up to a monoacylglycerol concentration of 0.5%, and then decreased more slowly. Diacylglycerols did not change IFT, regardless of concentration or degree of unsaturation. These results are in good agreement with the report of Gaonkar (6), who showed that IFT decreased with an increase in the concentration of monolinoleate and that dilinoleate by itself was virtually inactive.

The differences of IFT-lowering effect among monoacylglycerols may be attributable to their degree of unsaturation. Because monostearin has no double bond, which causes a kink in the molecular structure, it can align at the interface more compactly than monoolein and monolinolein, which have one and two double bonds, respectively. These results agree with those of Krog (17), who found that monoacylglycerols containing unsaturated fatty acids decreased IFT less than those containing saturated ones. Smit *et al.* (18) reported that the effectiveness of surfactants in reducing IFT, regardless of their concentration, is proportional to the number of hydrophilic groups at the interface. Therefore, monostearin which packs closely is a more effective surfactant in lowering IFT than monoolein and monolinolein.

ACM. Soap and soap-like surfactants are known as ACM. ACM were not considered to be significant surfactants in frying fats until Blumenthal and Stockler (19) found them among the polar fraction of used frying fat and analyzed the ACM of restaurant fats with a quick-test kit (20). ACM form in the fat early in the chain of fat degradation reactions by the combination of fatty acids with metal ions. For example, sodium ions combine with oleic acid to form soap as sodium oleate.

The effect of ACM on IFT was investigated by increasing the concentration of sodium oleate added to the aqueous phase and measuring IFT against fresh soybean oil (Fig. 2). As little as 0.1% sodium oleate lowered IFT almost to zero. With 100 ppm (0.01%) of sodium oleate added, the IFT was lowered by 25%. One hundred ppm is reported as the ACM concentration of well-used frying fat by Blumenthal *et al.* (20). Two hundred ppm (0.02%) of sodium oleate lowered IFT by 50%.

Phospholipids. The effect of PC on the IFT is shown in Figure 3. Synthetic PC lowered IFT much less than that isolated from egg yolk (egg lecithin). Egg lecithin is less purified than synthetic PC, and the impurities present may be responsible for its greater IFT-lowering effect. At 0.2%, synthetic PC lowered IFT by 14%, while egg lecithin lowered IFT by 42%. Egg lecithin had a greater effect on the IFT in fresh soybean oil than monoacylglycerols at the same concentration. Monoacylglycerols lowered IFT of fresh soybean oil by 14% (monolinolein), 22% (monoolein), and 26% (monostearin) at 0.2% concentration (Fig. 1). Gaonkar and Borwankar (9) similarly showed that soy PC had higher surface activity than impurities they isolated from commercial oil and monoacylglycerols.

NaCl. The effect of NaCl on IFT behavior of unused and used donut frying fat against water at 40°C was investigated (Fig. 4). NaCl was dissolved in the water phase prior to forming the interface. NaCl addition led to a 8.7% reduction in the IFT of unused fat and a 54.9% reduction in the IFT of used donut frying fat. The more pronounced effect of NaCl on the IFT in used donut frying fat is probably due to its interaction with impurities in the used fat. It is likely that NaCl decreased IFT by salting out the impurities from the aqueous phase into the interface. Gaonkar (7) reported that oil impurities were salted out at high NaCl concentration.

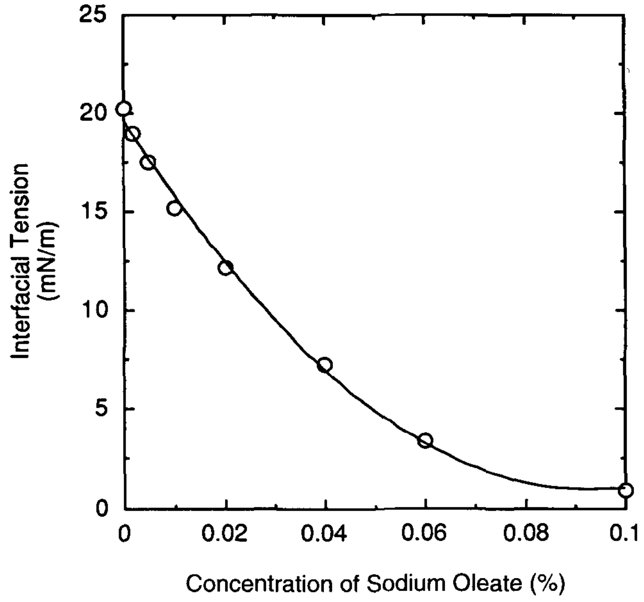

FIG. 2. The effect of sodium oleate on the interfacial tension of fresh soybean oil against water at 25 ± 0.1°C.

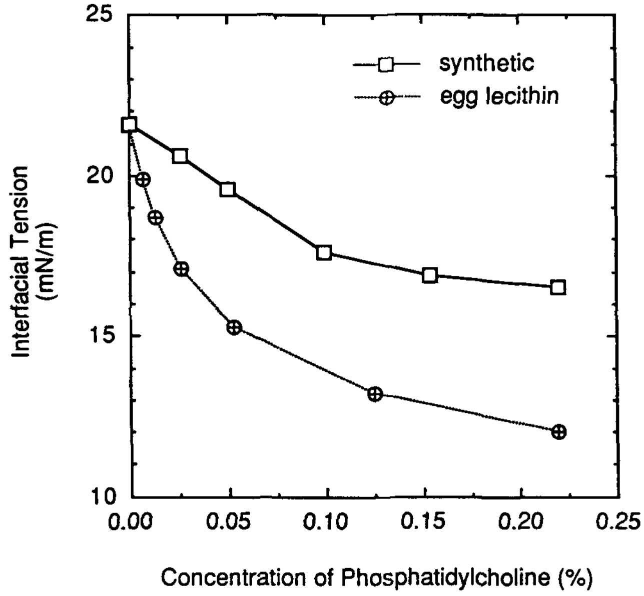

FIG. 3. The effect of phosphatidylcholine (synthetic and egg lecithin) on the interfacial tension of fresh soybean oil against water at 25 ± 0.1°C.

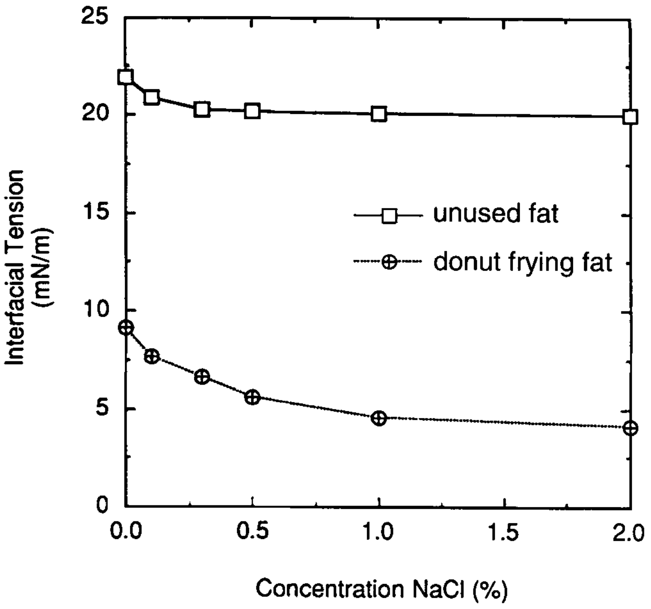

FIG. 4. Interfacial tensions of unused and donut frying fat against water as a function of concentration of NaCl at 40 ± 0.1°C.

Fatty acids. Most studies of used frying fats identify acid value, the degradation of triacylglycerols into fatty acids and other contributors to titratable acidity, as an indicator of the quality of fat. Figure 5 depicts the effects of fatty acids (oleic and linoleic) on the IFT of fresh soybean oil in the presence and absence of NaCl. Chemical analysis indicated that donut frying fat had 0.7 to 1.0% fatty acids. At this concentration of fatty acid, added to fresh oil in the absence of NaCl, IFT remained essentially constant. Fisher *et al.* (4) also reported that fatty acids did not lower the IFT of deacidified olive oil against water.

In the presence of 3% NaCl, fatty acids lowered the IFT of fresh soybean oil. Three percent NaCl was used because, above this concentration, NaCl did not affect IFT in used donut frying fat (Fig. 4). Although fatty acid addition in the presence of NaCl lowered IFT, the amount of reduction in IFT was not as great as when only NaCl was present (Fig. 4). In this model system, there is little chance of interaction between fatty acids and NaCl because fatty acids are soluble mainly in the oil phase and NaCl is soluble in the water phase; therefore, the reaction between sodium ions and fatty acids to yield ACM may occur only rarely in this situation. A greater interaction would be expected during frying due to the much greater interfacial surface area. The slight reduction of IFT shown in Figure 5 is caused by the impurities in fresh soybean oil through the salting out effect of 3% NaCl.

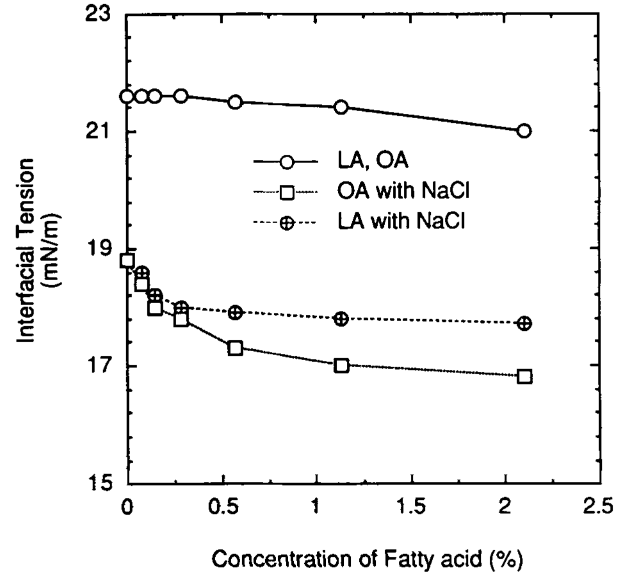

FIG. 5. The effects of oleic (OA) and linoleic (LA) acids on the interfacial tension of fresh soybean oil against water in the presence and absence of NaCl (3%) at 25 ± 0.1°C.

In the model systems studied, soaps had the greatest effect in reducing IFT. Phospholipids and monoacylglycerols also had a significant effect. Diacylglycerols and fatty acids had virtually no effect. NaCl did not have a large effect in the model system but did in used donut frying fat, where it can salt out surfactants into the interface. IFT decreases rapidly when a fat is used for frying and can be included among the many measures of frying fat quality. Because IFT measures the overall effect of many chemical species, it has advantages over chemical tests for specific compounds. IFT also measures surfactancy, which has been described by others to be a key element in frying performance.

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