

Interfacial Tension of Oil-Water Systems Containing Technical Mono- and Diglycerides¹

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TECHNICAL mono- and diglycerides find wide industrial use in the manufacture of products such as oil-modified alkyd resins, superglycerinated shortenings, and margarine. Probably the major uses of mono- and diglyceride preparations depend upon the ability of these substances to act as oil-soluble emulsifying agents.

It is generally recognized that monoglycerides are more active as surface-modifying agents than are the diglycerides; at present however, it is very difficult, if not impossible, to prepare, by a commercial process, a product consisting substantially of monoglycerides. Commercially available products are composed of a mixture of mono-, di-, and triglycerides. Acceptance of products intended for use as emulsifiers is generally dependent on the interfacial tension of fatty solutions of the products against water.

The literature contains little data on the interfacial tension of systems containing monoglycerides or mixtures of mono- and diglycerides. The scarcity of such data probably results from the fact that until recently no reliable method was available for determining the proportions of mono-, di-, and triglycerides in mixtures of these compounds.

The interfacial tension measurements reported here are intended to supply some quantitative data relative to the effectiveness of technical monoglycerides and diglycerides in lowering the interfacial tension of water against vegetable oils.

Experimental

The technical mono- and diglycerides used in these experiments were prepared from the same materials and by the same method described by Feuge and Bailey (3). Briefly the method is as follows: refined and bleached cottonseed oil, hydrogenated to an iodine value of 0.7, was reacted with varying percentages of U.S.P. glycerol while being stirred in a stainless steel-glass apparatus and maintained under hydrogen at one atmosphere pressure. Sodium hydroxide equal to 0.1% of the weight of fat was used as catalyst, and the reaction was continued for 5 hours at 200° C. (unless otherwise noted). The mean molecular weight of the fatty acids obtainable by saponification of the interesterified products was 279.4, calculated from the neutralization value of the acids.

The free glycerol and the soaps present in the reaction mixtures were removed. Free glycerol was eliminated by washing with 20% sodium sulfate solution. Removal of all traces of soap necessitated acidifying the mixtures. Under the conditions employed dilute mineral acids could not be used to destroy soap because these acids tended to decompose the monoglycer-

ides. Repeated washing with a 20% sodium sulfate solution containing monobasic sodium orthophosphate and dibasic sodium orthophosphate in a molar concentration of 0.1 and 0.025, respectively, was found to decompose the soaps without affecting the monoglycerides. Decomposition of the soaps was followed by several washings with 20% sodium sulfate solution after which the products were dried and filtered.

The purified products were analyzed for total combined glycerol by the bichromate method of the American Oil Chemists' Society (1), after alcoholic saponification and removal of the alcohol by the procedure of Smith and Matthews (6). They were also analyzed for monoglyceride content by the periodic acid oxidation method of Pohle, Mehlenbacher, and Cook (5). From the combined glycerol, monoglyceride, and free fatty acid contents, and the mean molecular weight of the fatty acids, the compositions of the different products were calculated in terms of mono-, di-, and triglycerides. The results of the calculations of the glyceride distribution are given in Table 1.

TABLE 1
Composition of Monoglyceride-Diglyceride Products

Product	Composition, ^a weight percent		
	Mono-glyceride	Di-glyceride	Tri-glyceride
1.....	1.40	17.57	80.38
2.....	10.25	41.06	48.04
3.....	17.92	45.49	35.94
4.....	27.01	48.32	24.02
5.....	38.00	44.13	17.22
6.....	44.24	34.07	21.04
7 ^b	58.84	40.51	0

^a The free fatty acid content resulting from the decomposed soaps was assumed to be 0.65% in each case which is sufficiently accurate for all practical purposes.

^b Product 7 was interesterified at 250° C. Previous work (3) has shown that use of such a high temperature produces some polymerization compounds.

The peanut oil, which was used in most of the interfacial tension measurements, was prepared in the laboratory from a good grade of crude oil. The oil was heavily alkali-refined and bleached. The last traces of soap were destroyed by washing with 1% hydrochloric acid solution, and the oil was then water-washed until the wash water was neutral to methyl orange. Dispersed water was removed from the oil by deodorizing for 45 minutes at 204° C. (400° F.) under 1 mm. pressure, using the apparatus described by Bailey and Feuge (2). The soybean oil and cottonseed oil were refined, bleached, and purified by exactly the same procedure as was used in the case of the peanut oil.

The interfacial tension measurements were made by the ring method using a Cenco-du Noüy interfacial tensiometer and a platinum-iridium ring of 5.98-cm. mean circumference. The ratio of the mean radius of the ring to the radius of the wire of the ring (R/r) was 53.7. Because some of the solutions would not remain completely liquid at temperatures of 50-60° C.,

¹ Presented at the 20th Annual Fall Meeting of the American Oil Chemists' Society, Chicago, Illinois, Oct. 30-Nov. 1, 1946.

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the entire series of tests was conducted at 70° C. To ensure a constant temperature during the period of measurement, beakers containing the oil system were immersed in a constant temperature bath. In every determination reported here the temperature at the distilled water-oil interface was $70 \pm 1^\circ$ C.

The correction factors determined by Harkins and Jordan (4) have been applied to all reported interfacial tension values. The density of each oil phase at 70° C. was assumed to be equal to the density of the pure oil at the same temperature. Errors introduced in the corrected values by this assumption are well within the accuracy of the ring method. For measurements made with peanut oil the correction factors for experimentally determined values of 2, 5, 10, 15, 20, and 25 dynes per centimeter are 0.852, 0.913, 0.963, 1.002, 1.035, and 1.066, respectively. Correction factors for measurements made with soybean and cottonseed oils are similar.

Results

Each monoglyceride-diglyceride product was added in varying amounts to the peanut oil, and the interfacial tension of distilled water against these various compositions was determined. The data obtained were plotted as concentration in weight percent of product against interfacial tension in dynes per centimeter. The curves for the 7 monoglyceride-diglyceride products are reproduced in Figure 1.

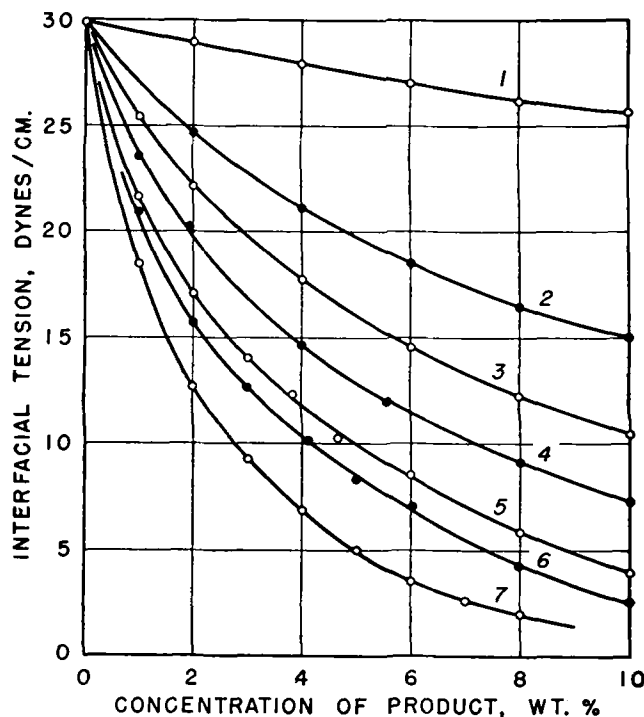


FIG. 1. Effect of the addition of different monoglyceride-diglyceride products on the interfacial tension at the peanut oil-water interface.

From this group of carefully plotted curves, the percentage of a product necessary to produce interfacial tensions of 25, 20, 15, 10, and 5 dynes per cm. was determined. These data together with those given in Table 1 were used to compile Table 2.

In view of the fact that 7 different and independently prepared products were used in these determinations the results given in Table 2 are quite interesting. Omitting preparation No. 7 in the group which is

TABLE 2
Percentage of Monoglycerides and Diglycerides in the Peanut Oil Phase for Given Interfacial Tensions at the Oil-Water Interface

Interfacial tension	Product No.	Composition of oil phase			
		Product, wt. %	Mono-, wt. %	Di-, wt. %	
25 dynes/cm. level	1	12.65	0.18	2.22	
	2	1.86	0.19	0.76	
	3	1.13	0.20	0.51	
	4	0.76	0.20	0.37	
	5	0.48	0.18	0.21	
	6	0.42	0.19	0.14	
	7*	0.33	0.19	0.13	
20 dynes/cm. level	2	4.82	0.49	1.98	
	3	2.91	0.52	1.32	
	4	1.92	0.52	0.93	
	5	1.31	0.50	0.58	
	6	1.10	0.49	0.38	
	7	0.82	0.48	0.33	
	15 dynes/cm. level	2	10.05	1.03	4.13
3		5.71	1.02	2.60	
4		3.83	1.03	1.85	
5		2.66	1.01	1.17	
6		2.20	0.97	0.75	
7		1.53	0.90	0.62	
10 dynes/cm. level		3	10.59	1.90	4.82
	4	7.20	1.94	3.48	
	5	4.98	1.89	2.20	
	6	4.16	1.84	1.42	
	7	2.75	1.62	1.11	
	5 dynes/cm. level	5	8.85	3.36	3.91
		6	7.40	3.27	2.52
7		4.95	2.91	2.01	

* This product is abnormal owing to the fact that it was interesterified at 250° C. and contains polymerized compounds.

abnormal for previously mentioned reasons (cf. Table 1), it is seen, for example, that to lower the value of the interfacial tension of the distilled water-peanut oil system to 20 dynes per cm. the amount of monoglyceride-diglyceride product required in the oil phase varies from product to product by as much as 440% on a product basis; and on a diglyceride basis the amount varies by as much as 530%; whereas on a monoglyceride basis the variation is only about 4% from an average value. On a product-plus-peanut oil basis the variation in monoglyceride content at the 20 dynes per cm. level is never more than 0.02% from the average value. The same is true at the 15 dyne per cm. level, and it would no doubt be the same for the 10 and 5 dyne levels if the same number of products had been compared. At the 25 dyne per cm. level these trends are even more noticeable; here the amount of product which must be present varies by 3,000% on the product basis, and the amount of diglyceride present varies by 1,500% on a diglyceride basis whereas on a monoglyceride basis the variation in monoglyceride content is only a few percent. The variation in monoglyceride content on a product-plus-peanut oil basis is within approximately 0.01% of the average value for the 25 dyne level. It must be concluded, therefore, that the diglycerides are less than 1% as effective as monoglycerides in lowering interfacial tension at peanut oil-water interfaces. Thus the interfacial tension is substantially a function of the monoglyceride content.

It seems safe to assume that these relative surface activities of monoglycerides and diglycerides should not be peculiar to peanut oil mixtures but should apply generally to most of the common oils and fats. Furthermore, it is reasonable to assume that for the common oils and fats, or at least for those containing principally C_{16} and C_{18} fatty acids, the interfacial tensions would be substantially equal for equal additions of a given monoglyceride preparation. To check these assumptions the interfacial tension of a mixture of each oil with monoglyceride-diglyceride product

No. 2 and with product No. 6 was determined against water in the usual manner. The results, which are recorded in Table 3, confirm these assumptions.

TABLE 3

Interfacial Tensions of Pure Peanut, Cottonseed, and Soybean Oils and of Mixtures of Each Oil With Monoglyceride-Diglyceride Products

Oil	Pure oil	Interfacial tension, ^a dynes/cm.			
		Product No. 2, 4% ^b	Product No. 2, 8%	Product No. 6, 4%	Product No. 6, 8%
Peanut.....	29.92	21.15	16.47	10.32	4.30
Cottonseed.....	29.76	21.62	16.89	10.84	4.58
Soybean.....	30.58	21.76	17.14	10.66	4.48

^a Interfacial tensions are against water at 70° C.

^b Concentrations are in weight-percent of product on a product-plus-pure oil basis.

If the data from Table 2 are used in plotting on log log coordinates the change in interfacial tension against average monoglyceride content (Product 7 excluded) of the system, a slightly curved line is obtained which may be used for interpolative and extrapolative purposes with considerable accuracy. From a plot of this type the data for Figure 2 were obtained. Figure 2 can be considered as portraying the relationships existing whenever monoglycerides from cottonseed oil stearine are added to common oils and fats containing principally C₁₆ and C₁₈ fatty acids.

A plot on log log coordinates of the percentage change in interfacial tension against monoglyceride content, in moles per 100 g., probably could be used in special cases for analyzing oil solutions for monoglyceride content. It is quite likely that monoglycerides of the different C₁₆ and C₁₈ acids have practically the same surface activities on a molar basis, and that the percentage change in interfacial tension for a given monoglyceride concentration is substantially the same regardless of the type of oil used as substrate.

Factors Affecting the Measurements

As a check on the reliability of the interfacial tension data, several special tests were made. For ex-

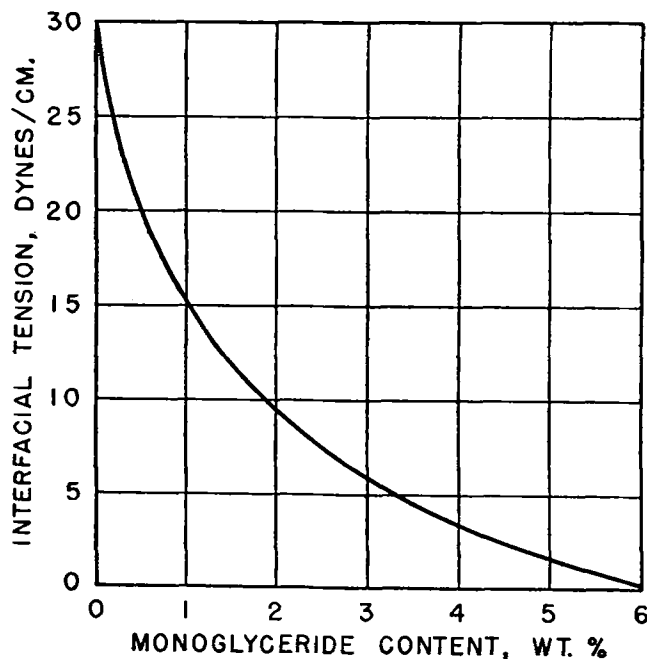


Fig. 2. Effect of monoglycerides on the interfacial tension at the peanut oil-water interface.

ample, a number of the purified monoglyceride-diglyceride products were water-washed and the washings tested with acidified barium chloride solution for traces of sodium sulfate. The results indicated that in no case were interfacial tension measurements made on solutions containing more than about 8 mg. of sodium sulfate per liter of oil; that is, the amount of sodium sulfate present was negligible.

Trillat and Nardin (7, 8) investigated the effects of time on the value of the interfacial tension between layers of pure castor oil and water at various temperatures and concluded that the interfacial tension, 2 minutes after formation of the interface, is practically independent of the temperature and that above 45° C. there are no time effects because thermal agitation prevents orientation of the molecules. Unfortunately, this does not hold for solutions of monoglycerides. A definite time effect was found to exist with the latter substances; however, with the instrument used, it was not detectable during the approximately first 3 minutes after the interfaces were formed. All values reported here were obtained within approximately 1 to 2 minutes after formation of the interface.

The interfacial tension changed with temperature, but relatively slowly. A 5° C. change in temperature in the region of 70° C. was scarcely detectable with the du Noüy tensiometer.

The most careful alkali-refining, bleaching, and deodorization still leaves minute traces of free fatty acids in a fat or oil, and the peanut oil used in these experiments contained approximately 0.01% free fatty acids. Also the monoglyceride-diglyceride products contained approximately 0.6-0.7% free fatty acids. Since fatty acids are surface active agents, their effect on interfacial tension was determined. Fatty acids from the interesterified products were used to prepare peanut oil solutions containing exactly 1, 2, 4, and 6% free fatty acids. These products were found to possess interfacial tensions against distilled water of 28.29, 26.99, 25.60, and 24.11 dynes per cm., respectively. The interfacial tension of distilled water against pure peanut oil was 29.92 dynes per cm. If in the interesterified product-peanut oil solutions the surface activities of the monoglycerides and free acids were additive, the free acids would have lowered the interfacial tension values by about 0.1 dyne per cm. at the maximum concentrations of interesterified product which were employed. In all probability the actual effect was less. In either case this effect can be disregarded.

Summary

1. Technical mono- and diglyceride products have been prepared from cottonseed oil stearine, and the effectiveness of these products in lowering the interfacial tension at vegetable oil-water interfaces has been investigated.

2. When both monoglycerides and diglycerides are present in the oil phase, the surface activity of the diglycerides is less than 1/100th that of the monoglycerides on a weight for weight basis; hence the interfacial tension is substantially a function of the monoglyceride content.

3. The interfacial tensions against water of such oils as peanut, cottonseed, and soybean are practically the same, and their interfacial tensions are lowered by practically equal amounts for equal additions of a given monoglyceride preparation.

4. A concentration of 1% of monoglycerides in the oil phase will lower the interfacial tension at the oil-water interface to approximately one-half that which is observed when no monoglycerides are present. A concentration of 6% of monoglycerides in the oil phase will lower the interfacial tension approximately to zero.

REFERENCES

1. American Oil Chemists' Society, *Official and Tentative Methods*, Revised 1943.
2. Bailey, A. E., and Feuge, R. O., *Ind. Eng. Chem., Anal. Ed.*, **15**, 280-281 (1943).
3. Feuge, R. O., and Bailey, A. E., *Oil & Soap*, **23**, 259-264 (1946).
4. Harkins, W. D., and Jordan, H. F., *J. Am. Chem. Soc.*, **52**, 1751-1772 (1930).
5. Pohle, W. D., Mehlenbacher, V. C., and Cook, J. H., *Oil & Soap*, **22**, 115-119 (1945).
6. Smith, L. B., and Matthews, H., *Oil & Soap*, **17**, 58-67 (1940).
7. Trillat, J. J., and Nardin, Pierre, *Compt. rend.* **207**, 291-293 (1938).
8. Trillat, J. J., and Nardin, Pierre, *Pub. sci. tech. ministere (France)* No. 152, 35 pp. (1939).

Oil From Calabash Seed, *Crescentia cujete* L.

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DURING the period of extreme scarcity and heavy demand of fats and oils engendered by dislocations in the supply and distribution of these products during World War II the Bureau of Agricultural and Industrial Chemistry was requested to examine a number of oils and oilseeds of Latin American origin with respect to their possible industrial utility. Among the products examined was a sample of seeds and oil obtained from *Crescentia cujete* L. grown in Honduras.

Crescentia cujete L., commonly referred to as calabash or gourd tree, is a native of tropical America and grows wild in Mexico, various Central and South American countries and the West Indies. It is known by a variety of local names, as for example, "tapara" or "totuma" in Venezuela, "jicara" in Cuba and Salvador, "cuia" in Brazil, "calabacero" in Costa Rica, and "guira" in Colombia. It is also known by such names as "calabacillo," "guira de Yucatan," "guira cimarrona," "guacal," "tecomate," and "cutuco."²

Crescentia cujete L. is described as a tree of medium to large size bearing globular or ellipsoidal fruit approximately the size of a cucumber, the shell of which upon drying becomes as hard as wood. Another description of the plant refers to it as a tree, 5 to 8 feet in height with a tap root one-third to one-half the height of the tree. Although the tree appears to grow wild in great profusion in all of the above-mentioned countries it can be propagated by cuttings which reach fruiting age in four years and from seeds in six years.

Although references to some of the constituents of the calabash fruit or gourd can be found in the literature (1), there appears to be no published information concerning the characteristics of the seed-oil.

The products submitted to the Bureau of Agricultural and Industrial Chemistry for examination consisted of seeds and screw-pressed oil. The seeds were flat and heart-shaped having thin brown hulls. The hulls represented 28% and the kernels 72% of the total weight of the seeds. The seeds ranged from 6 to 10 mm. in length, 5 to 8 mm. in width and 1 to 2 mm. in thickness. One hundred seeds weighed 3.93 grams. The endosperm was very light in color, ap-

pearing almost white with a slight greenish cast. The screw-pressed oil, which is referred to as gucha-nut oil by the producers³ had a greenish color resembling that of olive oil. Oil subsequently obtained in the laboratory by extraction of the seeds with petroleum naphtha (Skellysolve F) was light yellow, resembling refined cottonseed oil.

The characteristics and composition of the screw-pressed oil were determined and compared with those of oil extracted from seed imported from Honduras. Agreement in the characteristics of the screw-pressed and solvent-extracted oils served to establish the authenticity of the former.

Experimental

Composition and Characteristics of Calabash Seed and Crude Oil. The proximate composition of calabash seed is shown in Table I and the characteristics of the crude oil obtained from the seed are shown in Table II. The constants on the oil were determined by the methods of the American Oil Chemists' Society (2), with the exception of the unsaponifiable matter (3), saturated acids (4), tetrabromide value (5), hexabromide value (6), hydroxyl value (7), and peroxide value (8), which were determined by the methods described in the references cited.

Calculation of the composition of the oil on the basis of its iodine and thiocyanogen values, and equations applicable to cottonseed and peanut oils (9) gave results for the content of saturated acids which were not in accord with the experimentally determined values. A determination of the linoleic acid content by a tetrabromide method was made as a

³ Name coined by Meerbott Associates from whom the original sample of oil was obtained.

TABLE I.
Analysis of Calabash Seed,¹ *Crescentia cujete* L.

Constituent	As received ²	Moisture-free
	Per cent	Per cent
Moisture.....	7.80
Nitrogen.....	4.84	5.25
Protein (N × 6.25).....	30.25	32.80
Ash.....	3.34	3.62
Potassium.....	0.44	0.48
Phosphorus.....	0.69	0.75
Calcium.....	0.09	0.10
Crude fiber.....	12.98	14.07
Total sugar as invert sugar.....	2.43	2.64
Oil (Skellysolve F extract).....	34.10	36.98

¹ One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

² Private communication of the Mexican Secretaria de Agricultura y Fomento.

³ Data supplied by the Analytical Section of the Analytical, Physical Chemical, and Physics Division of this Laboratory.

⁴ All values reported are averages of closely agreeing duplicate determinations.