

Modification of Vegetable Oils. X. Effect of Monoglycerides on the Interfacial Tension of Oil-Water Systems¹

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MONOGLYCERIDES are employed widely as surface active agents in the preparation of oil-water emulsions. One of the early uses of these compounds for such a purpose was in the manufacture of "superglycerinated" or "high ratio" shortenings, and today this application is still considered to be the most important. However monoglycerides are used in substantial quantities in other types of emulsions, especially in the manufacture of cosmetic and pharmaceutical preparations. Cold creams, for example, may consist almost entirely of technical grade monostearin, mineral oils, and water.

Despite the widespread use of monoglycerides as emulsifiers few quantitative data have been published concerning their performance in this field. In a previous article (2) the effectiveness of technical grade monoglycerides (prepared from cottonseed oil stearine) in lowering the interfacial tension at vegetable oil-water interfaces was reported. Subsequently Kuhrt *et al.* (5) reported data on the interfacial tension of a number of monoglyceride-vegetable oil-water systems.

The present investigation was undertaken to obtain additional data on the behavior of monoglycerides in oil-water mixtures, particularly the monoglycerides monopalmitin, monostearin, mono-olein, and monolinolein. The monoglycerides of caprylic, capric, lauric, and myristic acids also were prepared and tested for comparative purposes.

Materials and Methods

Monoglycerides. The fatty acids employed in the preparation of monostearin and monopalmitin were prepared from commercial products (90% purity) by repeated fractional crystallization from acetone. The other saturated acids used in this investigation were obtained in relatively pure form from a chemical supply house. Each product contained 98% or more of the desired acid. Mono-olein was prepared from methyl oleate (approximately 97%) isolated from the mixed methyl esters of pecan oil fatty acids by repeated fractional crystallization from acetone. Monolinolein was prepared from methyl linoleate (approximately 95%) obtained from the mixed methyl esters of cottonseed oil by a similar fractionation procedure.

The fatty acids and methyl esters were converted to the corresponding monoglycerides by allowing them to react with U.S.P. glycerol for 3 hours at 200°C. in the presence of 0.1% of sodium hydroxide (on a fatty acid or ester basis) as catalyst.

In all cases the reaction was carried out under hydrogen, and the maximum amount of glycerol judged to be reactable and miscible with the fatty phase under these conditions was used in each case. Soap and unreacted glycerol were removed from the reaction products by acidifying with a 1% solution of acetic acid and washing with distilled water. In the case of the monoglycerides of the unsaturated acids a small amount of ethyl acetate also was added to facilitate washing. The products then were dried by melting them under vacuum and stripping with hydrogen.

The monoglycerides of the saturated fatty acids and mono-olein were concentrated by fractional crystallization from solvents. A solution containing 70% isopropanol was used for crystallizing monostearin and monopalmitin, and commercial hexane was used for the others. Residual solvent was removed from the concentrated products by melting under vacuum and stripping with hydrogen.

The products were analyzed for monoglyceride content by the periodic acid oxidation method as modified by Handshumacher and Linteris (3). The following values were obtained: monocaprylin, 92.8%; monocaprin, 96.2%; monolaurin, 86.9%; monomyristin, 78.6%; monopalmitin, 74.8%; monostearin, 86.2%; mono-olein, 88.6%; and monolinolein, 53.9%.

The products could have been further crystallized to increase their purity, but the procedures are time-

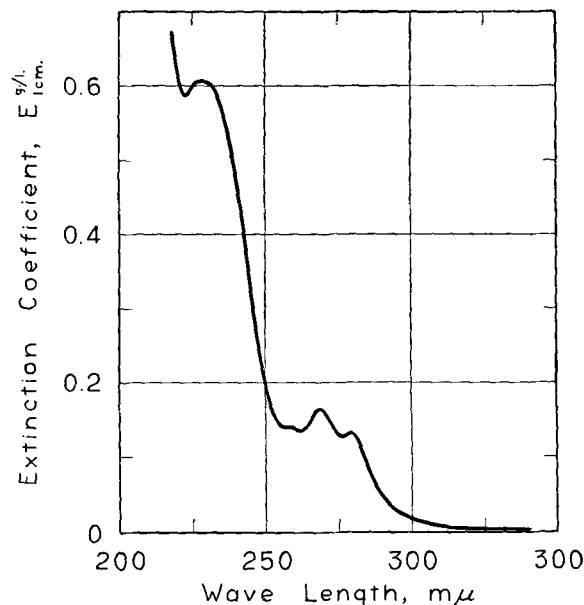


Fig. 1. Ultraviolet absorption spectrum of monolinolein

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consuming and lead to markedly lower yields. Previous work (2) has shown that the di- and triglycerides which constitute the impurities removed by fractional crystallization are practically devoid of surface activity.

Since the linoleic acid chain can be isomerized by heat in the presence of alkali and since isomerization may precede polymerization, the monolinolein was examined spectrophotometrically to determine if the small amount of sodium hydroxide used in its preparation had any undesirable effects. The spectral absorption curve is shown in Figure 1. On calculating the content of conjugated constituents in terms of conjugated C_{18} fatty acids, using the tentative method of the American Oil Chemists' Society (1), the percentage of diene and triene constituents was found to be 0.50 and 0.04, respectively. These percentages of conjugation are insignificant.

Nonaqueous Phase. Cottonseed oil, mineral oil, or amyl acetate was employed as the nonaqueous phase in each of the oil-water systems investigated. A re-refined and bleached commercial cottonseed oil was further purified by washing, first with a solution of 1% acetic acid and then with distilled water. The last traces of moisture were removed by warming under vacuum and stripping with hydrogen. The mineral oil employed was a light U.S.P. grade. It was acidified with acetic acid, washed, and dried prior to use. The amyl acetate was a C. P. grade and was used without further purification.

Interfacial Tension Measurements. A Cenco-du Nouÿ interfacial tensiometer and a platinum-iridium ring of 5.98-cm. mean circumference was used in all of the measurements. The ratio of the mean radius of the ring to the wire of the ring (R/r) was 53.7. Measurements were made in 250-ml. beakers contained in a constant temperature bath. For each measurement a beaker was almost filled with distilled water of the proper temperature, the ring was immersed just below the surface of the water, and the selected monoglyceride-oil solution, heated to the

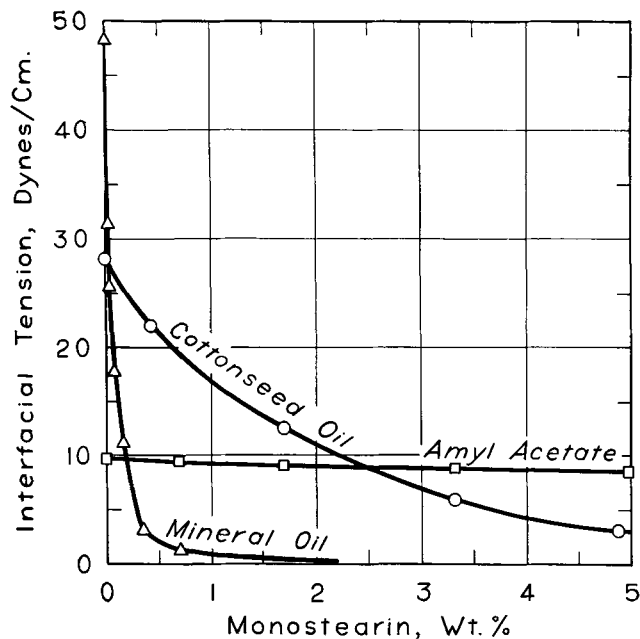


Fig. 2. Effect of type of nonaqueous phase on the surface activity of monostearin in oil-water systems at 70°C.

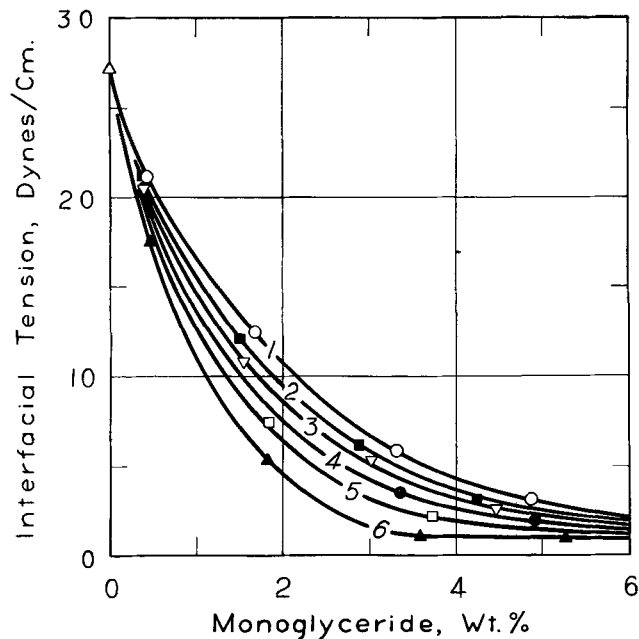


Fig. 3. Effect of saturated monoglycerides on the interfacial tension of cottonseed oil-water systems at 70°C. (1) Monostearin, (2) monopalmitin, (3) monomyristin, (4) monolaurin, (5) monocaprin, (6) monocaprylin.

proper temperature, was carefully poured onto the water surface. The temperature at the interface was maintained within 0.5° of the desired value.

The correction factors determined by Harkins and Jordan (6) were applied to all reported interfacial tension values. The density of each oil phase was assumed to be equal to the density of the pure oil at the same temperature. Any errors which may have been introduced in the corrected values by this assumption are well within the accuracy of the ring method.

Results

Influence of Type of Nonaqueous Medium. It is logical to expect that the effect of adding a given monoglyceride to the oil phase of an oil-water system will be conditioned by the type of oil used. Although an almost endless number of measurements could be conducted by merely changing the nature of the oily phase, it was considered sufficient to use an example of each of three types of oily compounds; i.e., triglycerides, petroleum hydrocarbons, and monoesters all of which are presently utilized with technical grade monoglycerides.

Figure 2 shows the effect on interfacial tension when various amounts of monostearin are dissolved in the oily phase of cottonseed oil-water, mineral oil-water, and amyl acetate-water systems maintained at 70°C. The mineral oil-water system was most sensitive to addition of monostearin while the amyl acetate-water system was only slightly affected. The curves show that on the addition of 0.5% of monostearin, the pre-existing interfacial tension decreased 96% for mineral oil, 24% for cottonseed oil, and 1% for amyl acetate. It was found that amyl acetate can be used to break emulsions formed with the aid of monoglycerides. No interfacial tension measurements were made with methyl acetate and the methyl esters of the fatty acids, but it was observed that they behaved qualitatively like amyl acetate.

Cottonseed Oil-Water Systems. Figure 3 compares the effect of monostearin, monopalmitin, monomyristin, monolaurin, monocaprin, and monocaprylin on the interfacial tension between cottonseed oil and water at 70°C. Each curve shows how the interfacial tension between cottonseed oil and water decreases as the concentration of the indicated monoglyceride increases in the cottonseed oil. In each case the concentration was calculated as percentage of monoglyceride on a monoglyceride-plus-cottonseed oil basis. No difference could be detected when soybean oil or peanut oil was substituted for cottonseed oil (2).

Apparently, as the chain lengths of saturated fatty acids decrease, the corresponding monoglycerides progressively become better surface active agents for vegetable oil-water mixtures when compared on a weight-for-weight basis. Since monoglycerides and vegetable oils are chemically alike in many respects, the surface activity of the monoglycerides of the saturated acids should be a linear function of the number of surface active groups per unit weight of monoglyceride; that is, the various saturated monoglycerides should be equally active in vegetable oil-water mixtures when compared on a mole basis. This probability was suggested by one of the authors in a report of an earlier investigation (2), and it has since been tested to a limited extent by Kuhrt *et al.* (5).

The data used to obtain each of the curves in Figure 3 were recalculated to express monoglyceride concentration in terms of moles in 100 grams of oily phase. The recalculated data are plotted in Figure 4. The symbol used to represent a given monoglyc-

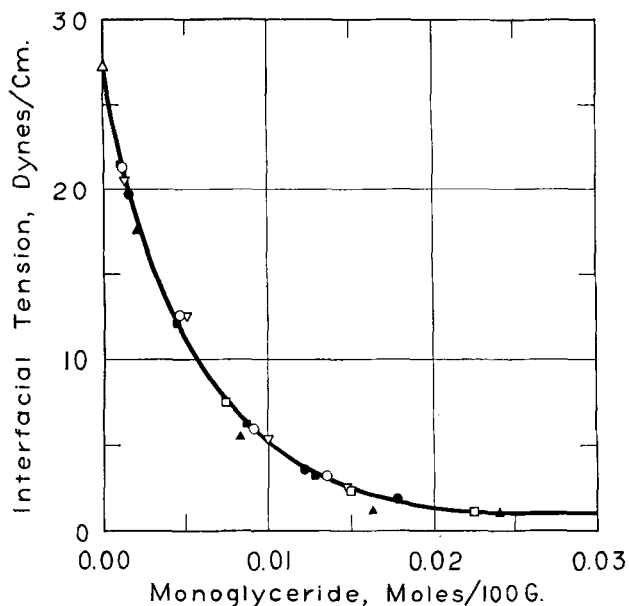


FIG. 4. Molar comparison of the relative effect of saturated monoglycerides on the interfacial tension of cottonseed oil-water systems at 70°C. Each monoglyceride identified as in Figure 3.

eride is the same in both figures. Of the compounds tested, monocaprylin is the only one showing a tendency to deviate from the suggested relationship. The deviation of monocaprylin is slight and detectable only at certain concentrations.

It is probable that when the alkyl chains in the monoglycerides become very short the surface activity of the compounds is influenced by their increas-

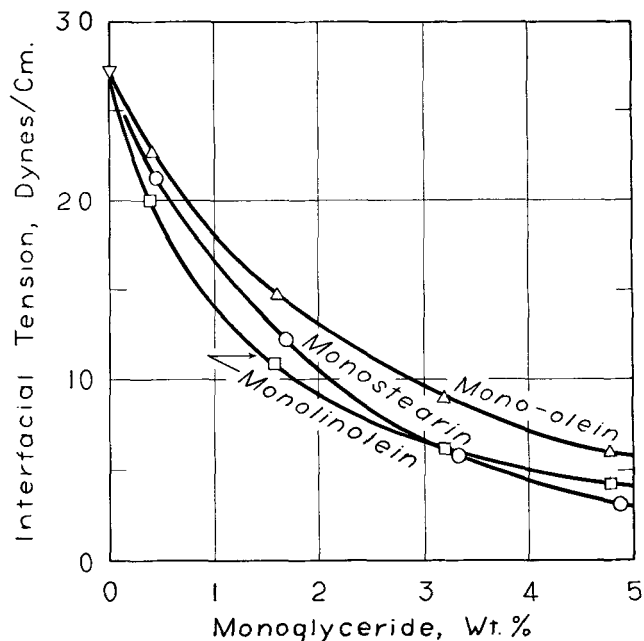


FIG. 5. Effect of degree of unsaturation of monoglycerides on the interfacial tension of cottonseed oil-water systems at 70°C.

ing solubility in water, but this relationship was not investigated in the present series.

The effect of the degree of unsaturation of the fatty acid combined as monoglyceride is shown in Figure 5. Each curve shows the interfacial tension for various percentages of a monoglyceride in the oily phase of a cottonseed oil-water system at 70°C. Apparently the effects of unsaturation are complex. While both mono-olein and monolinolein are less effective than monostearin at low interfacial tension values, the monolinolein behaves more like monostearin than does mono-olein. Mono-olein and monolinolein have an advantage over monostearin because they can be used in relatively large concentrations at low temperatures. At 60°C. less than 5% of monostearin can be dissolved in cottonseed oil.

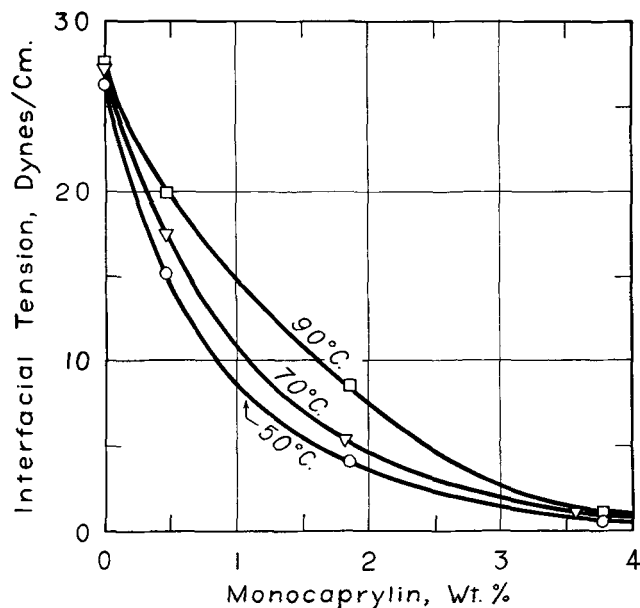


FIG. 6. Effect of temperature on the surface activity of monocaprylin in cottonseed oil-water systems.

The influence of temperature on interfacial tension at the boundary between water and cottonseed oil containing various amounts of monocaprylin is shown in Figure 6. Similar temperature effects were obtained when monostearin was substituted for monocaprylin. For the system represented in Figure 6 the change in interfacial tension per degree change in temperature is not large, generally less than 0.1 dyne per cm. per degree; but when the temperature of the system is changed, for example, from 50°C. to 90°C., the effect becomes important.

Temperature is another variable whose influence is quite complex, and its effect appears to be a function of the concentration of the surface active agent. The interfacial tension between pure cottonseed oil and water decreases 1.8 dynes per cm. as the temperature is decreased from 90°C. to 50°C., but when the cottonseed oil phase contains 1% monocaprylin the decrease is 5.6 dynes per cm. At a 4% concentration of monocaprylin the decrease is only 0.4 dyne per cm.

Mineral Oil-Water Systems. Because the composition and properties of petroleum oils vary widely, data obtained with any one oil are only of limited value. The results of these tests are shown in Figure 7. Each utility, therefore only a few of the tests made with

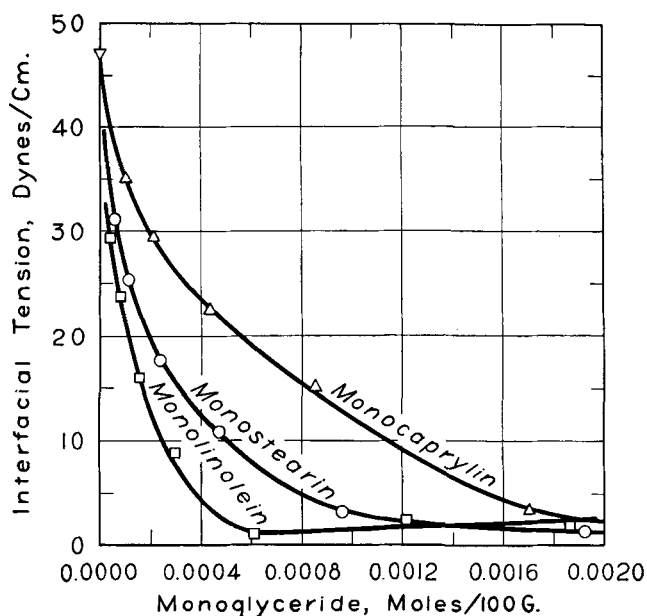


Fig. 7. Effect of monoglycerides in lowering the interfacial tension of mineral oil-water systems at 70°C.

curve represents the interfacial tension, at 70°C., between water and light-bodied, white mineral oil containing the monoglyceride indicated, the concentration of the monoglyceride being calculated as moles per 100 grams of oil phase.

The curves show that in mineral oil-water systems, monoglycerides of the saturated fatty acids are not active to the same degree when compared on a mole basis, which is contrary to their behavior in cottonseed oil-water systems. It was noted that in the mineral oil-water system shown, monostearin is considerably more surface active than monocaprylin on both a mole and weight-for-weight basis.

In mineral oil-water systems, monolinolein shows a marked superiority over monostearin in lowering the interfacial tension which is not true in cottonseed oil-

water systems. In the latter systems monolinolein is slightly superior at low concentrations, but after the interfacial tension has been lowered to about 5 dynes per cm., further additions are relatively ineffective. In mineral oil the monolinolein lowers the interfacial tension to about 1 dyne per cm. before further addition becomes relatively ineffective. In mineral oil there is a perceptible tendency for the interfacial tension to increase as the monolinolein is added beyond a concentration of about 0.0007 mole per 100 grams of oil phase, that is, above about 0.25%.

Summary

Monoglycerides were prepared from methyl oleate and methyl linoleate, and from each of the even-numbered, saturated fatty acids from C_8 to C_{18} by esterification or interesterification with glycerol in the presence of an alkaline catalyst. The reaction products were purified to remove soaps, free fatty acids, and uncombined glycerol; and in some cases they also were concentrated by fractional crystallization from solvents. The interfacial tension of oil-water systems containing purified monoglycerides was investigated.

It was found that the ability of a given monoglyceride to reduce interfacial tension varied widely when the nonaqueous phase consisted successively of mineral oil, cottonseed oil, and amyl acetate. For example, 0.5% of monostearin reduced the interfacial tension between mineral oil and water by 96%, whereas a similar concentration of monostearin reduced the interfacial tension of cottonseed oil and water by only 24%, and of amyl acetate and water by only 1%.

When the monoglycerides of the saturated fatty acids were compared on a molar basis, they were found to be equally effective in lowering the interfacial tension between cottonseed oil and water. This was not true when the nonaqueous phase consisted of mineral oil and the monoglycerides compared were monocaprylin and monostearin. Monostearin was more effective on both a mole- and weight-for-weight basis.

In cottonseed oil-water systems there was no apparent correlation between surface activity and degree of unsaturation of the fatty acids combined in the monoglycerides. Monostearin was approximately as active or more active than mono-olein and monolinolein. In mineral oil, monolinolein was the most active monoglyceride tested.

The effect of temperature on interfacial tension was found to be related to the concentration of the monoglyceride in the nonaqueous phase. The largest temperature effects observed with monocaprylin produced a lowering of the interfacial tension of about 0.1 dyne per cm. per degree.

Acknowledgment

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