An additional mixer was designed and inserted in the circulating system. The circulating paste passing through the mixer and the injected acid mix were subjected to intensive mixing action. Completenesses obtained in the factory with the neutralizer added to the system were equal to those obtained with the best laboratory techniques.

Conclusions

A continuous process has been developed for sulfating fatty alcohols with sulfuric acid up to 100% H_2SO_4 concentration.

The success of the process depends on maintaining a proper balance among the factors of temperature, reaction time, acid strength, and acid usage.

In general, best results accrue from use of as strong acid as is permissible (99% in plant operations), about 160°F. and 10 seconds reaction time.

Neutralization is quite simple, requiring only efficient mixing and adequate heat removal.

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Solubility of Tristearin and Hydrogenated Cottonseed Oil in Certain Aceto- and Butyroglycerides[1]

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THE SOLUBILITY of hard fats in liquid oils is a property of importance in the formulation of commercial fat products like shortening and margarine oil. In such products the proportion of fat crystals which dissolves in the oil or liquid phase over a given temperature range has a decided influence on the consistency of the product. It is recognized, of course, that crystal size and shape and mode of deposition also are important factors, but they are outside the scope of the present discussion.

Solubilities of hard fats in some of the more common liquid oils have been determined by Hofgaard (2), Kraemer and Bailey (5), and Craig *et al.* (1). Possibly others have published data which included isolated determinations of solubility. There appears to be no published information on systems containing aceto-oleins or butyro-oleins.

In the course of earlier work by two of the present investigators (4) it was discovered that the consistency of mixtures of an aceto-olein product and hard fat did not undergo as marked a change with a change in temperature as did the consistency of a mixture of the same hard fat in liquid soybean or similar oil. Some of the mixtures containing an aceto-olein product possessed an almost constant consistency over the temperature range of —15 to 50°C.

The present investigation was undertaken to establish the role of solubility in the consistency of fat mixtures containing acetoglycerides and to obtain fundamental information which could be used in the development of new fat products. The solubility of tristearin and hydrogenated cottonseed oils (iodine values, 1.1 and 29.3) in binary mixtures with aceto-oleins and other liquid fats was measured by the so-called "synthetic method" of Harwood, Ralston, and Selby (3).

Experimental

Materials. The samples of 1,2-diaceto-3-olein and 1,2-dibutyro-3-olein were prepared by a procedure essentially as described by Feuge *et al.* (4). Purified methyl oleate was converted to 1-mono-olein by interesterification, molecular distillation, and fractional crystallization from acetone. The 1-mono-olein (purity about 98%) was mixed with chloroform and pyridine and allowed to react with a slight excess of acetyl or butyryl chloride in chloroform solution. The reaction product in each case was purified by washing with dilute acid and water, bleaching with clay and carbon, and repeated fractional crystallization from commercial hexane. The purified 1,2-diaceto-3-olein had a melting point of —18.3°C., an iodine value of 57.5 (theoretical, 57.6), and a hydroxyl value of 0. The purified 1,2-dibutyro-3-olein had an iodine value of 51.3 (theoretical, 51.1), and a hydroxyl value of 0.

The aceto-olein product which was used was the same as that described previously (4). For its preparation commercial oleic acid was purified to yield a fraction containing about 97% of oleic and iso-oleic acids. This fraction was converted into a glycerol-free, technical grade monoglyceride (62.5% of monoesters) and acetylated with acetic anhydride. The reaction product obtained was washed with water, bleached with clay and carbon, and steam-deodorized. The final product had a melting point of —24.0°C., an iodine value of 63.9, and a hydroxyl value of 6.8.

Triolein was prepared from purified methyl oleate by letting it react with glycerol in the presence of lithium hydroxide and then purifying the reaction product (4). The triolein had a melting point of 5.0°C., and iodine value of 85.3, and a hydroxyl value of 4.9.

The tristearin was prepared by esterifying stearic acid (purity better than 99%) with glycerol, using stannous chloride as a catalyst. The reaction product was first washed with dilute hydrochloric acid, then with a solution of sodium carbonate, and then purified by fractional crystallizations from hexane and absolute ethanol. The final product had a hydroxyl value of 2 and a melting point of 72.3°C. (generally accepted melting point, 72.5°C.).

The cottonseed oil used was a commercial, alkali-refined and bleached oil having an iodine value of

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108.3. Hydrogenation of portions of this oil to iodine values of 29.3 and 1.1 provided the hydrogenated oils used in the experiments.

Apparatus and Method. In making the solubility determinations sealed glass tubes or ampules (10 mm. x 60 mm.), containing known concentrations of binary mixtures of fat and oil, were tumbled end over end in a water bath, and the disappearance of the solid phase for each mixture was observed visually as the temperature of the bath was increased in a step-wise fashion.

The water bath was contained in a double-walled, rectangular, open-top tank measuring 1 ft. x 1 ft. x 3 ft. and fitted with a mechanical stirrer. Completely immersed in the water bath were four vertically placed wheels, each 8 in. in diameter and each fitted with 8 ampule clips which oriented the long axis of the oil-containing ampules along radii of the wheel. The wheels were rotated at 35 r.p.m. To aid in the agitation of the fat and oil mixtures a small glass bead was sealed in each ampule.

The temperature of the water bath was increased step-wise with the aid of manual controls, but the temperature was maintained at each selected level by a mercury-type thermoregulator that activated a Thyratron relay, which in turn controlled either an electrical heater or a pump for circulating a coolant through a coil of copper tubing in the bath. The bath temperature was recorded constantly by a recorder of the potentiometric type. However the temperatures at which the solid phase of the binary mixtures disappeared were measured by a calibrated thermometer inserted in the bath. The thermometer was of the 45-mm. immersion type and was graduated in intervals of 0.2 Centigrade degrees.

Solubility measurements were made on two sets of samples. In the first set the fats and oils were weighed into the ampules, heat was applied to melt completely the hard fat component in each mixture, and the ampules were sealed under vacuum. The ampules, with their contents in the liquid state, were placed in a covered Dewar flask containing hot water. With the aid of an adjustable heating unit the samples were cooled from 75 to 27°C. at a rate of 1° per hour, as measured by an automatic temperature recorder. Subsequent cooling of the Dewar flask and its contents in a refrigerator lowered the temperature of the samples from 27 to 12°C. at an average rate of 0.7° per hour. The solid-containing samples then were transferred to the apparatus for determining solubility. In the first run to determine solubility the temperature was increased in 3°-steps with a time-interval of 1 hr. between steps. In later runs the above-described procedures were repeated except that temperature increments were reduced to 0.5° steps and the holding times between steps were changed from 0.5 to 1 hr. as points of disappearance of the solid phase were approached. These points in all instances were taken as the lowest temperature at which the sample appeared to be perfectly clear when rotation of the wheel was stopped and light was reflected through the sample.

Solubility measurements were made on a second set of oil-fat mixtures. These mixtures were not heated prior to determining the point of disappearance of the solid phase. In these samples the tristearin as obtained by crystallization from solvent and the hydrogenated cottonseed oils as obtained by slow solidification of the melt were added to the liquid oils in the ampules. After the air was displaced with nitrogen, the ampules were sealed, care being exercised not to melt any of the hard fat. This procedure kept the hard fats in the highest melting polymorphic form. In the subsequent solubility determinations temperature changes were in steps of 0.5° with holding times of 1 hr. to 12 hrs. between steps. The amount of time between steps depending whether or not the sample was in the process of melting.

Results and Discussion

The experimental results obtained are recorded in Table I. Each value for the samples in set No. 1 represents an average value obtained from several determinations. It is evident from the data that the points of complete solubility for the two sets of samples generally agree within a fraction of a degree, which is about the limit of accuracy for the method employed. However, when the solubilities are plotted in the conventional manner on semi-logarithmic coordinates, those obtained with the second set of samples tend to fall more nearly on a straight line, possibly because lower heating rates were employed with these samples and they were not subjected to repeated cycles of heating and cooling.

Solubility curves for the data in Table I are plotted in Figure 1. Whenever possible, data obtained with

TABLE I

Percentage of Fat Soluble in Various Binary Solutions of Fat and Oil[a]

Set number of sample	Tristearin in						Hydrogenated cottonseed oil (iodine value, 1.1) in				Hydrogenated cottonseed oil (iodine value, 29.3) in	
	1,2-Diaceto-3-olein		1,2-Dibutyro-3-olein		Triolein		Aceto-olein product		Cottonseed oil		Cottonseed oil	
	%	°C.	%	°C.	%	°C.	%	°C.	%	°C.	%	°C.
2	0.180	42.9	0.199	42.9	0.206	42.2	......	......	......	......	0.221	27.5
2	0.518	47.3	0.531	46.6	0.460	45.8	......	......	......	......	0.644	33.0
1	1.000	49.8	1.050	48.4	0.971	47.3	1.147	44.5	0.936	42.7	......	......
2	......	......	......	......	......	......	......	......	0.940	43.5	0.932	35.1
1	1.995	53.3	2.053	51.4	1.818	51.8	1.903	47.5	1.935	46.7	......	......
2	2.051	52.9	2.036	51.7	2.026	52.2	......	......	1.933	47.2	2.150	39.4
1	4.082	56.2	4.006	54.8	4.006	55.9	4.233	50.9	3.832	50.8	......	......
2	......	......	......	......	......	......	......	......	3.830	50.8	4.096	43.4
1	7.991	58.2	7.947	58.0	7.983	59.8	7.976	53.8	7.751	53.8	......	......
2	7.988	58.8	8.002	57.0	8.028	58.8	......	......	7.753	54.0	7.888	46.6
1	15.776	60.1	16.007	61.6	16.098	63.3	16.456	56.9	15,754	56.7	......	......
2	15.776	59.4	16.007	61.9	16.098	61.9	......	......	15.751	57.3	16.032	50.0
1	28.841	63.7	29.100	63.7	29.988	Leaky	29.622	57.5	29.726	57.5	......	......
2	......	......	......	......	......	......	......	......	29.737	61.0	......	......
2	......	......	......	......	......	......	......	......	......	......	28.596	52.9

[a] Percentage based on total weight of binary solution.

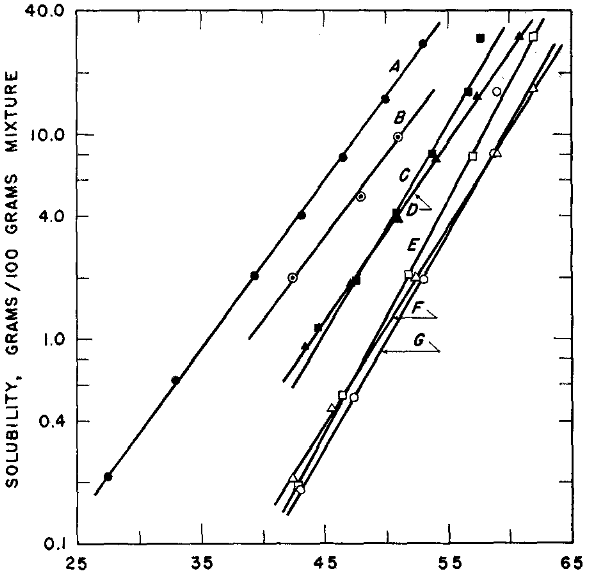

FIG. 1. Solubility of *(A)* hydrogenated cottonseed oil (iodine value, 29.3) in cottonseed oil; *(B)* hydrogenated cottonseed oil (iodine value, 4.6) in cottonseed oil, according to Hofgaard (2); *(C)* hydrogenated cottonseed oil (iodine value, 1.1) in aceto-olein product; *(D)* hydrogenated cottonseed oil (iodine value, 1.1) in cottonseed oil; *(E)* tristearin in 1,2-dibutyro-3-olein; *(F)* tristearin in triolein; and *(G)* tristearin in 1,2-diaceto-3-olein.

the samples of set No. 2 were plotted. Included for comparative purposes is a curve *(B)* obtained by Hofgaard (2) for hydrogenated cottonseed oil (iodine value, 4.6) in cottonseed oil. This curve, which was determined by dilatometric methods, is consistent with the curves for hydrogenated cottonseed oil in cottonseed oil determined in the present investigation.

From Figure 1 it appears that the solubilities of the mixtures containing highly hydrogenated cottonseed oil and tristearin fall into two groups differentiated by the hard fat present rather than by the nature of the oils or liquid components. Within each group the solubilities of the different mixtures are quite similar. Therefore it must be concluded that the longer plastic range of hard fat-acetoglyceride product mixtures as compared to hard fat-natural oil mixtures (4) is not a reflection of different solubility relationships.

The effect of the melting point of the hard fat component on the solubility curve of a fat in oil is indicated on comparing curves *A*, *B*, and *D*, for hydrogenated cottonseed oil in cottonseed oil. As the iodine value of the hydrogenated oil decreases, which means that its melting point increases, the solubility decreases but the slope of the curve is not affected.

While examination of the curves *E*, *F*, and *G* plotted in Figure 1 reveals that on a weight basis the solubility of tristearin was about the same in each of the three oils, 1,2-diaceto-3-olein, 1,2-dibutyro-3-olein, and triolein, the slopes of the three curves do differ slightly. The slope for the triolein curve is the least while that for butyro-olein is the greatest. This indicates, of course, that for a given increase in temperature the proportionate increase in the solubility of tristearin is greatest for 1,2-dibutyro-3-olein, intermediate for 1,2-diaceto-3-olein, and least for triolein.

It is of theoretical interest to compare the actual solubility of tristearin with its ideal solubility curve, which was plotted from values given by Bailey (6). Such a comparison is made in Figure 2. It is apparent that the solubility of tristearin in triolein is greater than ideal, which is also true for the solubility of tristearin in solvents like chloroform, benzene, and ethyl ether. In 1,2-dibutyro-3-olein the solubility is about equal to the ideal, but in 1,2-diaceto-3-olein is less than ideal.

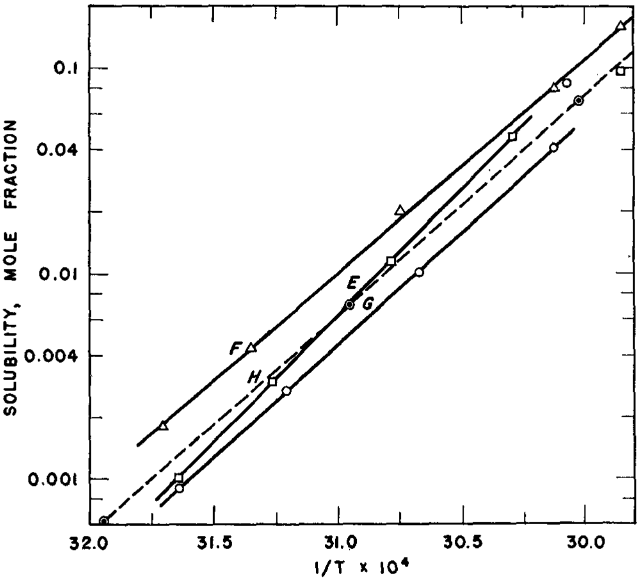

FIG. 2. Solubility of tristearin in terms of mole fractions and a function of the absolute temperature: ideal solubility curve *(H)* and solubility in 1,2-dibutyro-3-olein *(E)*, triolein *(F)*, and 1,2-diaceto-3-olein *(G)*.

Summary

Tristearin, triolein, 1,2-diaceto-3-olein, an aceto-olein product, and 1,2-dibutyro-3-olein were prepared. Also a commercial, refined, and bleached cottonseed oil was hydrogenated to obtain products having iodine values of 29.3 and 1.1. Solubility measurements were made for the mixtures tristearin-triolein, tristearin-1,2-diaceto-3-olein, tristearin-1,2-dibutyro-3-olein, and for hydrogenated cottonseed oils in the aceto-olein product and cottonseed oil.

In mixtures containing from 0.18% to approximately 30% of tristearin the solubility on a weight basis was unaffected by the nature of the oil. On a mole fraction basis the tristearin was most soluble in the triolein and least soluble in the 1,2-diaceto-3-olein. Hydrogenated cottonseed oil appeared to be about equally soluble, on a weight basis, in the aceto-olein product and cottonseed oil.

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