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Stability of Emulsions Containing Sucrose Esters[1]

LLOYD OSIPOW, FOSTER DEE SNELL, and MURRAY FERENCZ, Foster D. Snell Inc., New York, New York

A SERIES of sucrose esters of fatty acids has recently been developed for use as nontoxic detergents and emulsifying agents (3). Commercial materials became available in the midspring of 1957. These sucrose esters are manufactured by an alcoholysis reaction which involves the methyl ester of a fatty acid and sucrose, in a mutual solvent, in the presence of an alkaline catalyst. Sucrose monoesters, diesters, and higher esters of sucrose can be produced by using essentially the same process but varying the ratio of methyl ester to sucrose. Sucrose monoesters of fatty acids containing 12 to 18 carbon atoms are water-soluble, hydrophilic emulsifiers while the diesters of these fatty acids are oil-soluble, hydrophobic emulsifiers.

During the manufacture of the sucrose monoesters some diester is invariably produced. Careful control of manufacturing conditions, or subsequent purification, is required to obtain a product that is substantially free from sucrose diester.

It is well known that certain selected pairs of emulsifying agents, consisting of a hydrophilic and a hydrophobic emulsifier in the correct proportions for the specific system, will produce more stable emulsions than will either emulsifier used alone.

Emulsion stability is here considered as the ability of the dispersed phase to resist coalescence. Creaming is not regarded as an indication of emulsion instability. In general, emulsion stability depends upon the formation of an interfacial film which resists displacement. A complicating factor is the size of the emulsion droplets since it will ordinarily require substantially more time for very fine droplets than for larger droplets to form a coalesced layer. With the identical work input the emulsion system that gives the smallest interfacial tension will produce the smallest droplets.

It was recently reported that mixtures of sucrose monopalmitate and glyceryl monostearate produced more stable oil-in-water emulsions, with both silicone oil and mineral oil, than did either emulsifier used alone (3). It was not determined whether the observed differences in stability resulted from differences in droplet size or from interaction between the emulsifier pair to produce an interfacial film that was more difficult to desorb than the film produced by either agent alone.

In this study, combinations of sucrose monostearate and distearate were investigated with preformed mineral oil-in-water emulsions. Consequently the effect of variations in droplet size was eliminated. Similar studies were made with combinations of sucrose monostearate, containing 10% distearate, and glyceryl monostearate. The latter combinations were also investigated with emulsions milled after the introduction of all of the emulsifier. The series involving milling after introduction of the entire emulsifier introduces the complicating factor of variations in droplet size for different systems. However it is representative of commercial emulsions.

Experimental

Sucrose monostearate and sucrose distearate were prepared from commercial methyl stearate (about 55% palmitate, 45% stearate) by a procedure previously described (3). They were purified by precipitation from acetone to give products which analyzed as follows:

sucrose monostearate: 90% mono-, 10% di-
sucrose distearate: 17% mono-, 83% di-

The glyceryl monostearate was obtained from the Kessler Chemical Company Inc. It is designated glyceryl monostearate, pure (Saponification No. 168–176, Acid No. 3.0 max., Iodine No. 3.0 max.).

An emulsion was prepared by adding 400 ml. of Klearol mineral oil (L. Sonneborn Sons Inc.), previously purified by passing through an activated alumina column, to an aqueous solution consisting of 1.0 g. of sucrose monostearate dissolved in 1.6 liters of distilled water. The emulsion was preformed by mechanical stirring. It was then passed through a Gifford-Wood laboratory colloid mill, first at a clearance of 0.005 in., then at 0.001 in.

The emulsion was then divided into sixteen 100-ml. portions, and each portion was diluted with an equal volume of an aqueous solution or dispersion of sucrose monostearate and sucrose distearate at a range of concentration levels. The remaining 400 ml. of the emulsion were discarded. Thus each of the 16 emulsions prepared in this manner contained 10% of mineral oil and was withdrawn from a single emulsion concentrate.

A second two-liter batch of mineral oil emulsion containing 1.0 g. of sucrose monostearate was prepared in an identical manner. It was divided into sixteen 100-ml. portions, and each portion was diluted with an equal volume of an aqueous solution or dispersion of sucrose monostearate and glyceryl monostearate at a range of concentration levels.

Approximately 150 ml. of each of the 16 emulsions prepared in this second series were passed through the colloid mill twice at a clearance of 0.001 in. The remaining 50 ml. of each of these emulsions were not milled.

The stability of the three series with 16 emulsions in each series was determined on 25-ml. portions, which were transferred to stoppered test tubes and stored at room temperature. The coalesced oil was removed periodically with a hypodermic syringe and

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weighed. With the systems based on sucrose monostearate-sucrose distearate, the remainder of the emulsions was also stored at room temperature until broken. In some cases it was necessary to centrifuge for prolonged periods or to store the creamed layers at 43°C. for many weeks to accelerate coalescence. The amount of sucrose distearate dissolved in the coalesced oil was determined by optical rotation (3). Surface and interfacial viscosity measurements were also made on the separated oil and water phases, using a modified MacMichael viscosimeter.

Results

The compositions of the three series of emulsions containing 10% (V/V) mineral oil in water are given in Tables I and II. The stability of the emulsions can be expressed in the form

$$\frac{1}{S_E} = \frac{\int_0^t O_t dt}{t}$$

where S_E is the stability of the emulsion and O_t is the weight of oil separated after time t measured in days. The aging period for the sucrose monostearate-sucrose distearate series was 28 days while the aging period for the two series of sucrose monostearate-glyceryl monostearate emulsions was 30 days. Values of S_E for each of the 48 emulsions were determined by graphic integration. Results are presented in the last columns of Tables I and II.

Data on the concentration of sucrose distearate in the oil phase of the emulsions showed that in all cases the oil phase was not saturated with diester. The solubility of sucrose distearate in the mineral oil is 0.66% at 25°C.

Interfacial viscosity values for the sucrose monostearate-sucrose distearate systems were essentially the same in all cases. None of the combinations tested produced a condensed surface-film.

Discussion

The method of preparation of the emulsions from an initial oil emulsion concentrate would be expected to produce a situation somewhat as follows. The initial emulsion containing 20 volume percentage of mineral oil and about 0.05% of sucrose monostearate would be sufficiently coarse to provide essentially complete coverage of the emulsion droplets by adsorbed sucrose monostearate, above the critical micelle concentration. Microscopic examination of the emulsion showed that most of the droplets were in the range of one to five microns in diameter. Calculation of the number of moles of sucrose monostearate required to cover the surface of droplets of one micron radius in 100 ml. of solution, assuming an average area of 200 Å^2 per adsorbed molecule, indicates a requirement of 10^{-5} moles. Since 10^{-4} moles of sucrose monostearate are present and the critical micelle concentration is 10^{-7} moles (2), this requirement is satisfied.

Dilution of the emulsion with solutions or dispersions of sucrose monostearate and/or sucrose distearate must result in a shift in the distribution of the two emulsifiers between oil and water phases and the interface. The stability of the emulsions will depend

TABLE I
Comparison of the Stability of Preformed Emulsions Containing 10% Mineral Oil-in-Water at Various Fractions of Sucrose Monostearate in Sucrose Monostearate-Distearate Mixtures

Emulsion	Total sugar esters (g./100 cc. emulsion)	Sucrose monostearate, *fraction of* total sugar esters	Emulsion stability, S_E
A	0.525	0.76	65.0
B	—	0.62	36.4
C	—	0.48	2.9
D	—	0.34	0.7
E	0.275	0.90	230.0
F	—	0.77	94.0
G	—	0.64	33.8
H	—	0.50	2.3
I	—	0.37	0.9
J	—	0.24	1.1
K	0.150	0.90	230.0
L	—	0.78	50.0
M	—	0.65	29.2
N	—	0.53	3.7
O	—	0.41	1.1
P	—	0.29	0.5

TABLE II
Comparison of the Stability of Preformed and Milled Emulsions Containing 10% Mineral Oil-in-Water at Various Weight Fractions of Sucrose Monostearate in Sucrose Monostearate-Glyceryl Monostearate Mixtures

Emulsion	Emulsifier conc. *(g./100 cc.* emulsion)	Sucrose mono-stearate, *fraction of* emulsifiers present	Glyceryl mono-stearate, *fraction of* emulsifiers present	Emulsion stability, S_E	
				Not milled	Milled
A-1	0.525	0.73	0.19	1.5	1.7
B-1	—	0.56	0.38	2.8	5.0
C-1	—	0.39	0.57	1.5	>100.0
D-1	—	0.22	0.76	3.0	4.2
E-1	0.275	0.90	0.00	5.5	6.7
F-1	—	0.74	0.18	1.7	2.7
G-1	—	0.58	0.36	0.9	2.6
H-1	—	0.40	0.55	1.0	2.1
I-1	—	0.24	0.73	0.9	2.8
J-1	—	0.08	0.91	0.6	1.4
K-1	0.150	0.90	0.00	4.2	2.5
L-1	—	0.77	0.14	1.3	1.3
M-1	—	0.60	0.33	0.8	0.8
N-1	—	0.45	0.50	0.7	0.7
O-1	—	0.30	0.67	0.6	0.6
P-1	—	0.15	0.83	0.6	0.6

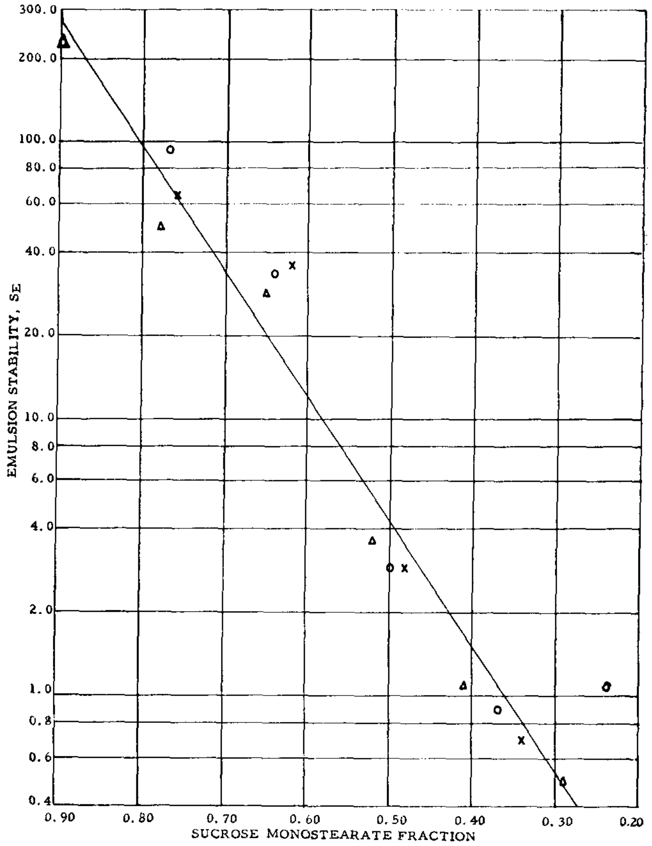

FIG. 1. Emulsion stability, S_E, of preformed emulsions, as a function of the fraction of sucrose monostearate present based on total sucrose stearate. ×, 0.525% sucrose stearate; ○, 0.275% sucrose stearate; △, 0.150% sucrose stearate.

upon the energy required for desorption of the surfactants from the interface.

Desorption into the dispersed phase of a surfactant soluble in that phase does not ordinarily involve a large energy-term. This is shown by the fact that oil-soluble emulsifiers produce unstable oil-in-water emulsions, while water-soluble emulsifiers give unstable water-in-oil emulsions. The stability of an emulsion then depends primarily upon the energy necessary for desorption, into the continuous phase, of the surfactant soluble in that phase. In the case of specific surfactant pairs that produce more stable emulsions than either surfactant alone, interaction between the two surfactants increases the energy required for desorption.

The stability of an emulsion is related exponentially to the energy required for desorption of the surface film (1)

$$S_E \sim e^G$$

where S_E is the stability of the emulsion and G is the energy required for desorption of the surface film.

If we assume that the energy required for desorption is proportional to the surface excess of monoester and this in turn is proportional to the ratio of monoester to total sugar ester in the emulsion system, then

$$\log S_E \sim \frac{C_m}{C_m + C_d}$$

where C_m and C_d refer respectively to the concentration of monoester and diester in the emulsion.

Figure 1 is a plot of log S_E *versus*

$$\frac{C_m}{C_m + C_d}$$

for the sucrose monostearate-sucrose distearate series. Within experimental error all values fall on the same line.

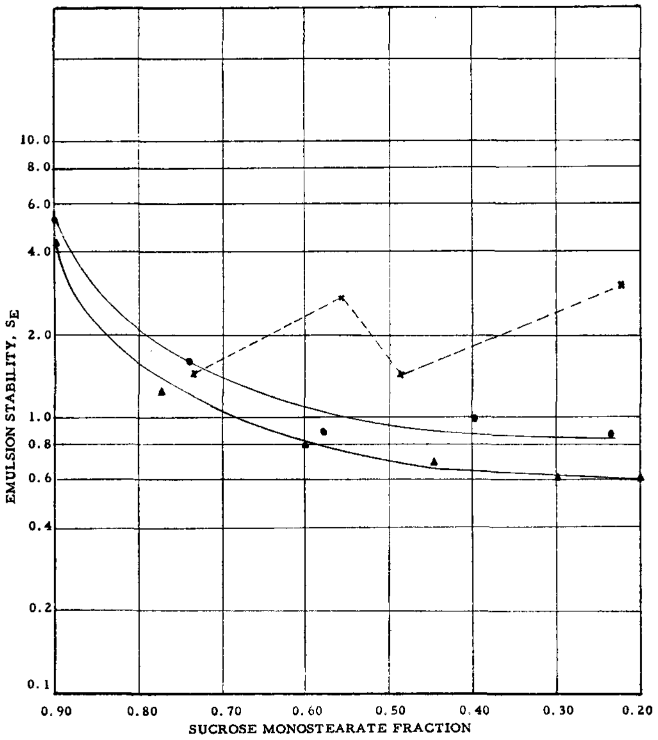

FIG. 2. Emulsion stability, S_E, of preformed emulsions, as a function of the fraction of sucrose monostearate present based on total sucrose and glyceryl esters. ×, 0.525% emulsifiers; ○, 0.275% emulsifiers; △, 0.150% emulsifiers.

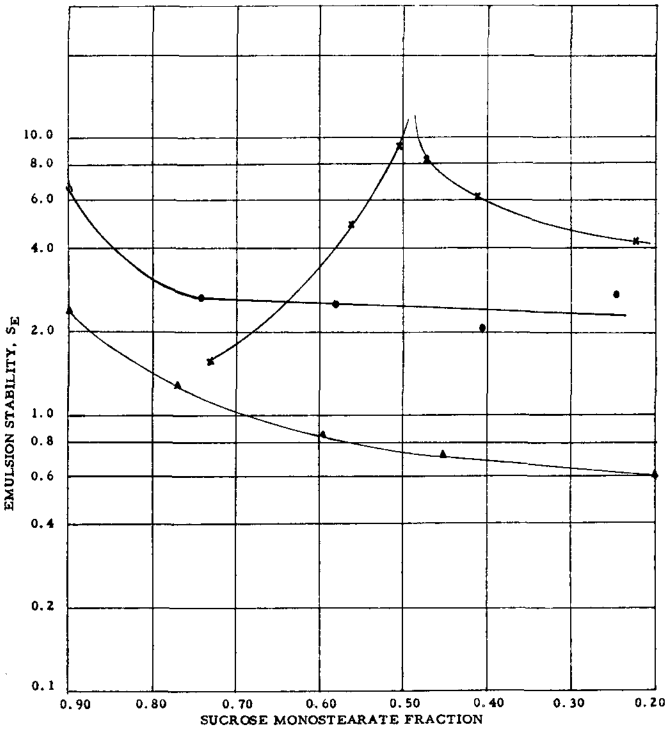

FIG. 3. Emulsion stability, S_E, of milled emulsions, as a function of the fraction of sucrose monostearate present based on total sucrose and glyceryl esters. ×, 0.525% emulsifiers; ○, 0.275% emulsifers; △, 0.150% emulsifiers.

The same reasoning can be applied to the series of emulsions containing sucrose monostearate and glyceryl monostearate, where the bulk of the emulsifiers was added after formation of the emulsion. In this case we obtain a different curve for each concentration level, as shown in Figure 2. The curves corresponding to 0.275 and 0.150% emulsifier are similar. They are consistent with the theory advanced if it is assumed that sucrose monostearate is preferentially displaced at the oil-water interface by glyceryl monostearate. The results suggest that at these low emulsifier concentration levels the sucrose monostearate is completely displaced from the interface when 25 to 30% of the emulsifier is glyceryl monostearate. At higher levels of glyceryl monostearate the emulsions behave as though glyceryl monostearate is the only emulsifier present.

The effect of milling the emulsions containing glyceryl monostearate, subsequent to the addition of the emulsifiers, is shown in Figure 3. At the two lower concentration levels of emulsifiers, the curves have the same form as that shown in Figure 2. Breaks in the curve occur at about 20 to 25% glyceryl monostearate. At 0.275% emulsifier the curve is shifted toward greater emulsion stability. This is undoubtedly because smaller droplets result from repeated milling with additional emulsifier present. With 0.150% emulsifier the decrease in droplet size is probably insufficient to influence emulsion stability.

The curve representing emulsions containing 0.525% emulsifier in Figure 3 shows a substantial increase in emulsion stability with approximately equal parts of sucrose monostearate and glyceryl monostearate present in the system. Since combinations of sucrose monostearate and glyceryl monostearate with preformed oil droplets do not appear to increase the stability of the emulsions over that obtained with sucrose monostearate alone, it must then be supposed that selected combinations of sucrose monostearate and glyceryl monostearate, above some minimum concentration, are capable of producing smaller size droplets and consequently more stable emulsions.

A satisfactory explanation of the behavior of unmilled emulsions containing 0.525% emulsifier, as plotted in Figure 2, is not evident.

Conclusions

The presence of either sucrose distearate or glyceryl monostearate will decrease the stability of preformed mineral oil-in-water emulsions containing sucrose monostearate. With adequate concentrations of emulsifier present the emulsion stability of milled emulsions passes through a maximum as the ratio of glyceryl monostearate to sucrose monostearate is increased. The data suggest that this increased stability results from a decrease in droplet size rather than from the formation of a more tenuous interfacial film.

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Indian Stillingia Oil and Tallow

S. A. NARANG[1] and SADGOPAL,[2] Forest Research Institute, New Forest, Dehra Dun, India

STILLINGIA OIL AND TALLOW are obtained from the fruits of the tree *Sapium sebiferum* Roxb. (fam. *Euphorbiaceae*). The tree is indigenous to China and has been reported to be growing wild in northern India (24). In India it is known as *tarcharbi* (Dehra Dun) and *pahari-shishim* (Saharanpur) (6). The fruits are borne in small clusters. At maturity the outer brown husks split open and expose three oval seeds about one-half inch in diameter, weighing about 0.15 g. The thick mesocarp contains a fatty substance commonly known as vegetable tallow. The kernel oil is a drying oil known as stillingia oil in English (24) or "Tse-ieene" or "tung-yu" in Chinese (20).

The earliest information on the physico-chemical characteristics of the Chinese stillingia oil were reported by Tortelli and Buggeri (23), Nash (20), Bolton (3), and by the Imperial Institute of London (4). By conventional methods Jamieson *et al.* (15) and Kaufmann *et al.* (17) found 26–29% linolenic, 46–59% linoleic, 9–16% oleic, and 6–9% saturated fatty acids and noted abnormally high saponification values. In 1946 Potts (21) observed that one of the acidic components of the oil had an unusual ultraviolet spectrum. The observation was confirmed by Huang *et al.* (14) in 1949 who however did not reach a conclusion about the structure of the new acid. Only recently Hilditch (8), Hilditch and Crossley (9), and Devine (5) were able to isolate about 5% of a deca-2:4-dienoic acid having a characteristic absorption band at about 260 mμ. This acid has been found to be absent in the Indian stillingia oil which has a saponification value of 205.7. The tallow has been studied by Hilditch *et al.* (13), Jamieson (16), and Armstrong *et al.* (1).

All of these workers studied stillingia oils and tallows from seeds grown in China, Florida, or South Texas. It was therefore of interest to examine Indian varieties also.

Experimental

The external fatty and fibrous coating was easily broken and removed by vigorously stirring the seeds in warm water (50° to 55°C.) for two hours. The decorticated seeds were separated, dried, and extracted with petroleum ether or ethyl ether. Characteristics of the oils extracted by these two solvents were practically identical although yields were not the same (see below). Physico-chemical values are summarized in Table I for comparison with those reported by previous workers.

Fibrous matter and tallow were recovered by filtering off the water and then were dried. Tallow was obtained by extracting the dried, powdered material with benzene. The Indian stillingia tallow has the following characteristics: specific gravity 0.8905^{60°, refractive index 1.4560^{60°, acid value 0.75, saponification value 203.9, iodine value (Wij's) 24.1, acetyl value 1.9, unsaponifiable matter 1.5%, and Hehner value 93.03.

By the above procedure the percentage yields from the seeds were tallow 19.3, fibrous matter 12.5, hulls 37.45, and kernels 30.75. Based on the weight of seeds, extraction with petroleum ether (40–60°) gave an oil yield of 18.27% as compared with 16.91% obtained with ether. Based on the weight of kernels, the oil yields were 59.4 and 55.0%, respectively. The oil had a pale yellow color with pleasant odor.

Characterization of Fatty Acids

Fatty acids were isolated in the usual manner by saponification of the oil or tallow. The yield of fatty acids from the oil was 91.2% and from the tallow 93.0%. The fatty acids were resolved into solid and liquid fractions by Twitchell's lead-salt-alcohol method (10). Results of these separations are shown in Table II.

The liquid and solid fatty acid fractions were separately converted into their methyl esters, which were then systematically fractionated by distillation under vacuum. The percentage of saturated acids in each ester fraction was calculated by means of Charnley's formula (11). The amounts of C_{18} mono-, di-, and trienoic acids and unsaponifiable matter were estimated on the basis of iodine and thiocyanogen values according to the equations of Baughman and Jamieson (2). The results of the ester fractionations are given in Table III.

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[1] Now Research Fellow, Indian Association for the Cultivation of Science, Calcutta.

[2] Now Deputy Director (Chemicals), Indian Standards Institution, Delhi.