Surface Activity of Sucrose Palmitates[1]

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ABSTRACT AND SUMMARY

Interfacial tension data are presented for cottonseed oil-water and paraffin oil-water systems containing purified sucrose palmitates of different degrees of acylation. Both the monopalmitates and dipalmitates effectively reduced interfacial tension. To be effective, the monoesters had to be dissolved in water, the diesters in oil. Although nearly inactive alone, sucrose tripalmitate was active in mixtures with the mono- and dipalmitates. Efficiencies of the sucrose palmitates were also excellent. In general, mixtures of sucrose palmitates were as effective as the most active component. When dissolved in water, the efficiency of sucrose palmitate mixtures was proportional to the monoester content, but when dissolved in oil mono-, di-, and triesters contributed to the efficiency.

INTRODUCTION

In the course of developing improved surface active agents from carbohydrates and fatty acids for use in foods, data on the performance of sucrose palmitates in vegetable oil-water systems were needed. Existing data on surface activity of sucrose palmitates are limited to water (1) and water-hydrocarbon (2,3) systems. In most cases, the products tested were not adequately characterized, due in part to lack of a simple method for separating moderate amounts of sucrose esters on the basis of degree of acylation. With such a method available (4), an evaluation of surface activity of the purified sucrose palmitates in cottonseed oil-water systems was undertaken.

EXPERIMENTAL PROCEDURES

The interfacial tension (IFT) of the oil-water systems was measured with a Cenco-du Nouy tensiometer equipped with a hot water bath for heating the sample. Measurements usually were made at 60 C, 2 min after the interface was formed. Sometimes a second measurement was made on a fresh sample 30 min after formation of the interface. Harkins and Jordan's (5) corrections were made.

Sterile, distilled water from freshly opened bottles was used. Before use, the cottonseed oil was passed through a silicic acid column to remove residual soaps (6). White paraffin oil, Saybolt viscosity 125/135, was used without further purification.

Solutions having the highest concentration of sucrose esters to be tested were prepared by dissolving the required weight of esters in the selected phase at about 100 C. Lower concentrations were prepared by diluting these stock solutions. The concentration of emulsifier required to lower the interfacial tension of the system by 20 dynes/cm [delta-20 (7)], and the critical micelle concentration (CMC) were estimated from plots of interfacial tension vs concentration.

Sucrose mono-, di-, and tripalmitates were isolated from a mixture of sucrose palmitates prepared by a sodium carbonate-catalyzed interesterification of pure methyl palmitate and sucrose, 2:1 mole ratio in dimethylformamide solution (8). After dissolving the reaction product in 1-butanol and destroying the soaps with citric acid (0.67 mole citric acid/mole of soaps), the unreacted sucrose and sodium salts were removed by washing with a 10% solution of sodium chloride in water (8). After most of the butanol was removed, the product was precipitated from acetone to obtain sucrose palmitate product M-1, considered to be the equivalent of commercial sucrose dipalmitates. Product M-1 contained 25% mono-, 40% di-, 25% tri-, 3% tetra-, and 6% higher palmitates.

A portion of product M-1 was fractionated by forced-flow, solvent-gradient liquid chromatography on silica gel (4). Similar fractions were composited, precipitated from acetone, and dried before use. Purity of the final ester fractions was checked by thin layer chromatography (TLC) (9). The sucrose dipalmitates and tripalmitates each gave a single TLC spot and a sharp melting point by differential scanning calorimetry (DSC). On the basis of its melting point, 108 C, the sucrose dipalmitate fraction consisted essentially of the 6,6′ isomer, m.p. 107-108 C (1). The precipitated monopalmitate was free from higher esters and sucrose, but it was obviously a mixture of isomers, with no melting point detectable by DSC. DSC data were obtained using ca. 3 mg samples in a Perkin-Elmer Model DSC-1 differential scanning calorimeter.

A crude sucrose ester product (M-2C) made by the potassium and lithium oleate-catalyzed interesterification of molten sucrose and mixed palmitins to demonstrate the effectiveness of a purification process (10) was also examined for surface activity, together with two products obtained from crude product by purification. Product M-2C contained only 12% sucrose esters of palmitic and oleic acids, the remainder being composed of ca. 39% glycerides, 29% free sucrose, and 20% soaps. The weight ratio of palmitic to oleic acid in the product was ca. 75:25. A semi-refined product, M-2SR, was obtained by washing an acidified 1-butanol solution of M-2C with a sodium chloride solution and then removing the 1-butanol and residual sodium chloride. Product M-2SR contained 10% sucrose monoesters, 7% sucrose di- and higher esters, 55% glycerides, and 28% free fatty acids. Further purification of product M-2SR by passage through a column of adsorbent (10) yielded product M-2P, which contained ca. 44% sucrose monoesters, 32% sucrose diesters, and 24% sucrose tri- and higher esters.

RESULTS AND DISCUSSION

In comparing surfactants or emulsifiers by surface or interfacial tension measurements, two factors, efficiency and effectiveness, need to be considered. Rosen (7) suggests that a good measure of efficiency is the amount of a surfactant required to reduce the tension by 20 dynes/cm ($\Delta 20$). In previous work on sugar esters, efficiency was reported as the concentration at which the break occurred in a tension-concentration curve (critical micelle concentration or CMC). The minimum tension obtainable with the surfactant measured its effectiveness.

To obtain stable, minimum values, Wachs (2) recommended waiting over 3 hr before taking the reading, but we believe readings taken on fresh interfaces are more significant. The IFT obtained after long aging is a function of surface-to-volume ratio, as well as bulk concentration, of the phase containing the emulsifier. This ratio is low under the conditions used for measurement of IFT, but high when the emulsifiers are used in food. Furthermore, the performance of the emulsifier during the mixing process, when fresh interfaces are being formed continuously, is particularly important. Estimates of efficiency and effectiveness

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TABLE I

Interfacial Tension between Water and Cottonseed Oil Containing Sucrose Dipalmitates

	Interfacial tension, dynes/cm after	
Conc., %	2 min	30 min
0	33	27
0.001	29	19
0.002	25	15
0.005	13	8
0.010	3	1.6
0.030	2.2	1.6

given in this paper are based on readings taken 2 min after formation of the interfaces. Because of the time required to form the interface and make the measurement, it was impractical to get reproducible readings in less time.

Typical IFT data used for estimating effectiveness and efficiency are given in Table I for solutions of sucrose dipalmitate in cottonseed oil against water. Similar data were obtained with sucrose monopalmitate in the aqueous phase, but low solubility made it impractical to obtain complete data for the tripalmitate. The viscosity of the cottonseed oil made it difficult to get reliable IFT readings at room temperature, so the measurements were made at 60 C. As previously observed (2), IFT decreased as the interface aged. The decrease with time was most pronounced in the concentration range where IFT was roughly proportional to the concentration. The decrease on aging is caused by migration of emulsifier from the bulk of the solution to the interface.

Efficiency and effectiveness of the three purified sucrose palmitates are compared in Table II. By either criterion (Δ20 or CMC), the monopalmitate was about ten times as efficient as the dipalmitate, but it was a little less effective. The tripalmitate was both inefficient and ineffective. A saturated solution in cottonseed oil (ca. 0.1%) had an IFT of only 23 dynes/cm after 2 min. The data for tripalmitate in Table II are from 30 min readings. Use of 30 min readings for the other two esters gave slightly lower values than those obtained with the 2-min readings, but the relationships among the values were similar. Since the tripalmitate was so poor, higher esters were not tested. IFT measurements were also made on saturated solutions (ca. 0.01%) of sucrose monopalmitate in cottonseed oil and of sucrose dipalmitate in water. The IFT was 16 dynes/cm for the monoester and 18 dynes/cm for the diester; hence each must be used in the correct phase to be effective.

Use of mixtures containing sucrose esters having different degrees of acylation, or even crude reaction products, has obvious economic advantages. For this reason the surface activities of four such mixtures were determined in cottonseed oil-water systems (Table III). Product M-1 is similar to commercial sucrose dipalmitates. The others are three stages of purification of an experimental sucrose monopalmitate product. In these tests only two concentrations were used for each product. Except for M-2C, all of the mixtures were as effective as the best purified ester in at least one of the phases. Product M-2SR was very effective

TABLE II

Effect of Sucrose Palmitates on Interfacial Tension (IFT) between Cottonseed Oil and Water

	Δ_{20}[a]		CMC[b]	
Palmitates	%	Moles/l	%	Moles/l
Mono-, in water[c]	0.3×10^{-3}	0.5×10^{-5}	0.9×10^{-3}	1.5×10^{-5}
Di-, in oil[d]	2.5×10^{-3}	3.0×10^{-5}	7.5×10^{-3}	9.0×10^{-5}
Tri-, in oil	3.0×10^{-2}	3.0×10^{-4}	-	-

[a] Concentration required to decrease IFT by 20 dynes/cm.

[b] Critical micelle concentration.

[c] Minimum IFT was 3 dynes/cm.

[d] Minimum IFT was 1.6 dynes/cm.

TABLE III

Effect of Sucrose Palmitate Products on Interfacial Tension between Cottonseed Oil and Water

	Concentration		
Product	%	Phase	Interfacial tension, dynes/cm
M-1[a]	0.002	Oil	18
	0.01	Water	8
	0.02	Oil	2
M-2C[b]	0.001	Water	16
	0.01	Water	6
	0.01	Oil	15
	0.10	Oil	5
M-2SR[c]	0.001	Water	15
	0.005	Oil	19
	0.01	Water	3
	0.05	Oil	3
M-2P[d]	0.001	Water	5
	0.01	Water	3
	0.01	Oil	9
None			33

[a] 25% mono-, 40% di-, 25% tri, and 9% higher palmitates.

[b] 12% sucrose esters, 39% glycerides, 29% sucrose, and 20% soaps.

[c] 17% sucrose esters, 55% glycerides, and 28% free fatty acids.

[d] 44% mono-, 32% di-, and 24% tri- and higher esters of sucrose.

in either phase. The apparent ineffectiveness of M-1 in water and M-2P in oil may be due to poor solubility. Since 13 dynes/cm corresponds to $\Delta 20$ (IFT = 33 dynes/cm with no additive), a rough estimate of efficiency could be made from these limited data. In all cases, efficiencies were at least similar to those of the purified esters when allowance was made for the concentration of active material in the products. In other words, the inactive components just acted as diluents. In the aqueous phase, the $\Delta 20$ for M-1 and M-2P occurred at about $3 \times 10^{-4}\%$ monopalmitate, so the higher esters contributed very little. On the other hand, in cottonseed oil the $\Delta 20$s for M-1 and M-2P corresponded to 1×10^{-3} and $2.7 \times 10^{-3}\%$ dipalmitates, respectively. Since these values are only about 1/5 and 1/2 of the value for pure dipalmitates, sucrose mono- and tripalmitates showed surface activity in the mixture. The apparent high efficiency of M-2C and M-2SR may be due to the presence of surface-active impurities, but it may just reflect difficulties in getting accurate values for sugar ester content on such impure products.

Since Gros and Feuge (11) found that monopalmitin was much more efficient in mineral oil than in cottonseed oil, some of the sucrose palmitates were also evaluated in a mineral oil-water system. In contrast to monopalmitins, sucrose palmitates were only a little more efficient in the mineral oil-water system (Table IV) than they were in the cottonseed oil-water system. In mineral oil, M-1 was more active than pure sucrose dipalmitates. Apparently, sucrose monopalmitate is very active in the oil, but this activity is obscured by poor solubility when the pure ester is tested. Wachs and Hayano (2) reported similar efficiency ($\Delta 20$ of $8 \times 10^{-4}\%$), but much lower effectiveness (minimum IFT of 12 dynes/cm) for a commercial dipalmitate in decalin at 20 C.

Only limited comparison of these products with other emulsifiers is possible because few have been tested in a vegetable oil-water system. Both sucrose mono- and dipalmitates are about as effective as monopalmitin, and are much more efficient. Gros and Feuge (11) reported a minimum IFT of about 2 dynes/cm for monopalmitin in cottonseed oil against water, but the $\Delta 20$ was about 2%. The sucrose esters are a little less effective, but more efficient, than glycerol glucoside palmitates, for which Feuge et al. (6) reported a minimum IFT of 1.3 dynes/cm and $\Delta 20$ of $1.5 \times 10^{-2}\%$ in the same system.

In the case of the sucrose monopalmitates, reduction of the surface tension of water can also be used for estimating surface activity. On this basis, $\Delta 20$ was $3 \times 10^{-4}\%$ (5×10^{-6} molar), CMC was $8 \times 10^{-4}\%$, and minimum surface tension was 32 dynes/cm at 60 C. These values are lower than those reported in the literature. Wachs (2) reported a CMC of $3 \times 10^{-3}\%$ and a minimum surface tension of 33 dynes/cm at 50 C. Reinefeld (1) and Osipow (3) report 34 dynes/cm for the minimum surface tension of 20 C. The latter pointed out that sucrose monopalmitate was a little less effective in lowering surface tension than sodium dodecylsulfonate, but more effective than nonionic surfactants such as tall oil polyoxyethylene condensate. Of 38 surfactants reported by Rosen (7), only 4 had $\Delta 20$ less than 10^{-5} molar based on surface tension. The lowest was 4×10^{-6} molar. Therefore, the efficiency of sucrose monopalmitate is excellent.

TABLE IV

Effect of Sucrose Palmitates on Interfacial Tension (IFT) between Paraffin Oil and Water[a]

Surface active agent	$\Delta 20$s[b], %	Minimum IFT Conc., %	Minimum IFT Value, dynes/cm
Mono-, in water	2×10^{-4}	5×10^{-3}	6
Di-, in oil	2×10^{-3}	2×10^{-2}	1.3
Product M-1, in oil	5×10^{-4}	1×10^{-1}	1

[a] IFT = 55 dynes/cm.

[b] Concentration required to reduce IFT by 20 dynes/cm.

Although purification of sucrose esters is not necessary to obtain good surface activity, it is desirable in order to get light colored products of optimum solubility. Similarly, the separation of pure mono- or dipalmitates is not necessary but in products designed for use in water, monopalmitates content should be as high as practical. For use in oil, dipalmitates should be the major component, but some mono- and tripalmitates may improve the efficiency.

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