

ides. When fed as a mixture, aceto-olein appears to enhance the digestibility of acetostearin.

A number of potential uses of acetoglyceride products as components of foods and cosmetic preparations are mentioned. One possible use of acetostearins appears to be as a protective coating for food products.

## REFERENCES

1. Ambrose, A. M., and Robbins, D. J., *J. Am. Pharm. Assoc., Sci. Ed.*, **45**, 282-284 (1956).
2. Ambrose, A. M., and Robbins, D. J., *Federation Proc.*, **14**, 314-315 (1955).
3. Ambrose, A. M., and Robbins, D. J., *J. Nutrition*, **58**, 113-124 (1955).
4. Augur, V., Rollman, H. S., and Deuel, H. J. Jr., *J. Nutrition*, **33**, 177-186 (1947).
5. Baur, F. J., *J. Am. Oil Chemists' Soc.*, **31**, 147-151 (1954).
6. Baur, F. J. (to Procter and Gamble Co.), U. S. Pat. 2,615,160 (1952).
7. Calloway, D. H., and Kurtz, G. W., *Federation Proc.*, **15**, 545 (1956).
8. Deuel, H. J. Jr., Hallman, L., and Leonard, A., *J. Nutrition*, **20**, 215-225 (1940).
9. Feuge, R. O., Gros, Audrey T., and Vicknair, E. J., *J. Am. Oil Chemists' Soc.*, **30**, 320-325 (1953).
10. Feuge, R. O., Vicknair, E. J., and Lovegren, N. V., *J. Am. Oil Chemists' Soc.*, **29**, 11-14 (1952).
11. Feuge, R. O., Vicknair, E. J., and Lovegren, N. V., *J. Am. Oil Chemists' Soc.*, **30**, 283-287 (1953).
12. Feuge, R. O., Vicknair, E. J., and Markley, K. S. (to the United States of America), U. S. Pat. 2,745,749 (1956).
13. Gros, Audrey T., and Feuge, R. O., *J. Am. Oil Chemists' Soc.*, **31**, 377-383 (1954).
14. Herting, D. C., Ames, S. R., Embree, N. D., and Harris, P. L., *Federation Proc.*, **15**, 556 (1956).
15. Herting, D. C., Ames, S. R., Koukides, M., and Harris, P. L., *J. Nutrition*, **57**, 369-385 (1955).
16. Jackson, F. L., and Lutton, E. S., *J. Am. Chem. Soc.*, **74**, 4827-4829 (1952).
17. Lovegren, N. V., and Feuge, R. O., *J. Agr. Food Chem.*, **2**, 558-563 (1954).
18. Lovegren, N. V., and Feuge, R. O., *J. Agr. Food Chem.*, **4**, 634-638 (1956).
19. McDonough, E. G., and Edman, W. W., *Drug and Cosmetic Ind.*, **76**, 170-171, 252, 254 (1955).
20. Mattson, F. H., Alexander, J. C., Baur, F. J., and Reller, H. H., *J. Nutrition*, **59**, 277 (1956).
21. Mattson, F. H., Baur, F. J., and Beck, L. W., *Federation Proc.*, **14**, 443 (1955).
22. Norman, W., and Ülwerke Germania, G.m.b.H., Ger. Pat. 417,215 (1920).
23. Vicknair, E. J., Singleton, W. S., and Feuge, R. O., *J. Phys. Chem.*, **58**, 64-66 (1954).

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## Interaction of Sucrose Monolaurate with Other Surface-Active Agents<sup>1</sup>

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A PROCESS for the manufacture of sucrose monoesters of fatty acids has reached a stage of development where commercial quantities will soon be made available. These sucrose esters differ fundamentally from ethylene-oxide derived, nonionic surface-active agents in that water solubility is imparted by a multiplicity of hydroxyl groups rather than ether linkages. Data concerning some of the surface-active properties of these sucrose esters have recently appeared (6). Unlike polyoxyethylene derivatives containing an equal number of oxygen atoms, the sucrose esters do not exhibit a cloud point below 100°C.

The present study is concerned with interaction between sucrose monolaurate and other water-soluble, surface-active agents. The problem of interaction between surface-active materials is of considerable importance and has received a great deal of attention. The effect of lauryl alcohol in enhancing the foam stability of sodium lauryl sulfate is well known (1). Interaction between cholesterol and other biologically-active materials and water-soluble, surface-active agents has been investigated (5). Inactivation of phenolic germicides by polyoxyethylene-derived nonionics has also been discussed (2). In general, these studies have been concerned with combinations of water-soluble, surface-active agents and relatively water-insoluble organic compounds.

It appeared possible that the large number of hydroxyl groups present in the sugar esters would contribute sufficient hydrogen-bonding energy for substantial interaction with the polar and ionic groups of other water-soluble, surface-active agents.

### Materials and Methods

Sucrose monolaurate and sucrose monostearate were prepared according to a procedure previously described (6). They were purified by several re-

crystallizations from ethanol. Sodium lauryl sulfate was prepared from fractionated C. P. dodecanol and recrystallized from ethanol. Absence of a minimum in the surface tension-concentration curve for sodium lauryl sulfate indicated that the material was pure. Polyethylene glycol 400 monolaurate (Kessler Chemical Company) and Ninol AA62 Extra (Ninol Laboratories Inc.) are commercial materials. They were used without purification. The former is an ester of lauric acid and an ethylene oxide polymer of average molecular weight 400. Ninol AA62 Extra is a lauroyl diethanolamide with an amide content of 92%.

Surface-tension values were determined by the Du Nouy ring method at  $27.1 \pm 0.1^\circ\text{C}$ . Measurements were made at intervals of a few minutes until the values agreed within 0.2 dynes/cm.

Foam test measurements were made, using the method of Ross and Miles (7). The solutions were maintained at  $27.1 \pm 0.1^\circ\text{C}$ . Duplicate determinations resulted in foam height values, which checked within 5 mm.

A surface viscosimeter was constructed in accordance with details provided elsewhere (1). The deflection of the bob could be read accurately to 0.2 degree. Measurements were made at  $27.0 \pm 0.1^\circ\text{C}$ .

### Results

*Surface Tension.* Surface-tension values for sucrose monolaurate and sucrose monostearate in distilled water are plotted against the logarithm of the concentration in Figure 1. The concentration at which the two linear portions of each curve intersect is considered to represent the CMC value. The uncertainty in determining these CMC values graphically is about 15%. These estimated CMC values are  $34 \times 10^{-5}$  molar for sucrose monolaurate and  $64 \times 10^{-7}$  molar for sucrose monostearate. The accepted value for the lowering of the CMC accompanying an increase in the length of an unbranched alkyl chain is  $2^n$ , where  $n$  is the increase in the number of carbon

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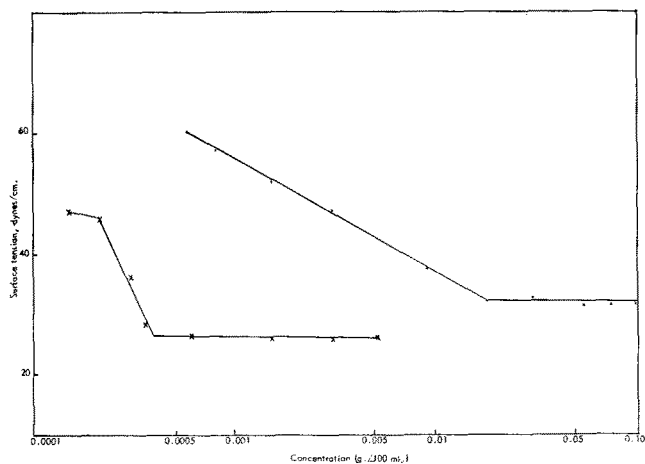


FIG. 1. Surface tension *versus* logarithm of concentration (g./100 ml.) for solutions of sucrose monolaurate ● and sucrose monostearate X in distilled water.

atoms in the alkyl chain (4). Thus the CMC value for sucrose monostearate would be expected to be 1/64 the value for sucrose monolaurate. The value found is 1/53, which is within the experimental error.

Figure 2 shows surface-tension values plotted against the logarithm of the concentration of active agent present in aqueous solutions containing 9 parts by weight of sucrose monolaurate and 1 part by weight of a second surface-active agent. Again the intersection of linear portions of each curve was used to estimate the CMC values. With both sodium lauryl sulfate and polyethylene glycol 400 monolaurate the CMC values are considerably below the value of sucrose monolaurate alone. The presence of lauroyl diethanolamide produced a substantial increase in the CMC value. A pronounced minimum in the surface tension-concentration curves was obtained only when sodium lauryl sulfate was present with sucrose monolaurate.

**Foam.** Foam-height values are plotted against time for several concentrations of the surface-active agents in Figures 3 and 4. Comparison is made between solutions of sucrose monolaurate in distilled water and solutions containing 9 parts by weight of sucrose monolaurate to 1 part by weight of a second

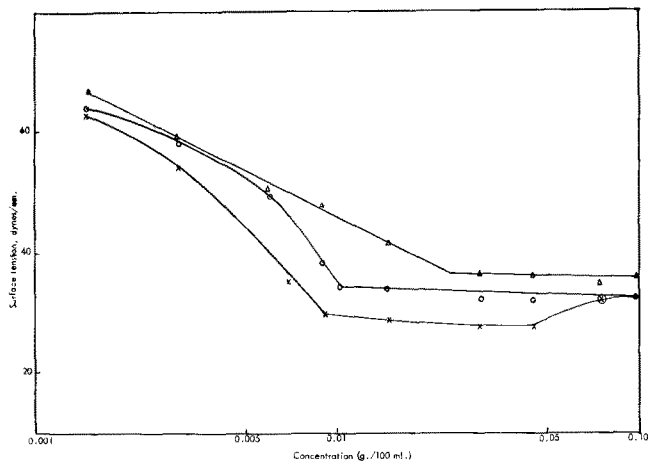


FIG. 2. Surface tension *versus* logarithm of concentration (g./100 ml.) for 9 to 1 aqueous solutions of sucrose monolaurate and sodium lauryl sulfate X, polyethylene glycol 400 monolaurate O, and lauroyl diethanolamide Δ.

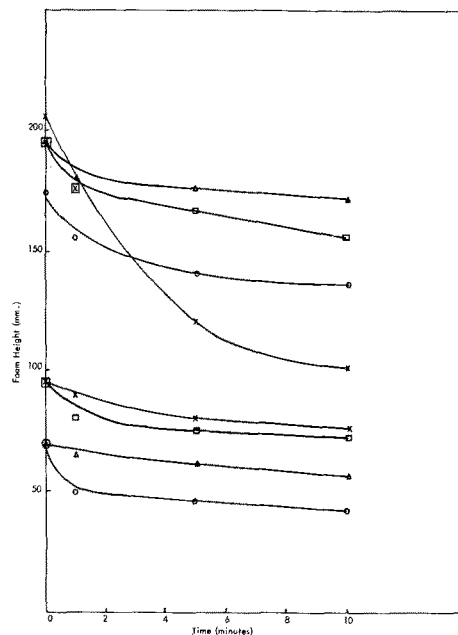


FIG. 3. Foam stability curves for aqueous solutions of sucrose monolaurate alone X, and 9 parts of sucrose monolaurate to 1 part by weight of sodium lauryl sulfate O, lauroyl diethanolamide □, and polyethylene glycol 400 monolaurate Δ. Upper series 0.30 g./100 ml. total active agent, lower series 0.03 g./100 ml. total active agent.

surface-active agent. The stability of the Foam  $S_f$  was estimated by graphic integration of foam height  $H_t$  and time  $t$  over the ten-minute period:  $S_f = \int_0^{10} H_t dt$ . Foam stability values are recorded in Table I.

**Surface Viscosity.** The experimentally determined, force-flow curves are shown in Figure 5, plotted as the rate of rotation (revolutions per minute) of the cup *versus* deflection (degrees) of the bob. All solu-

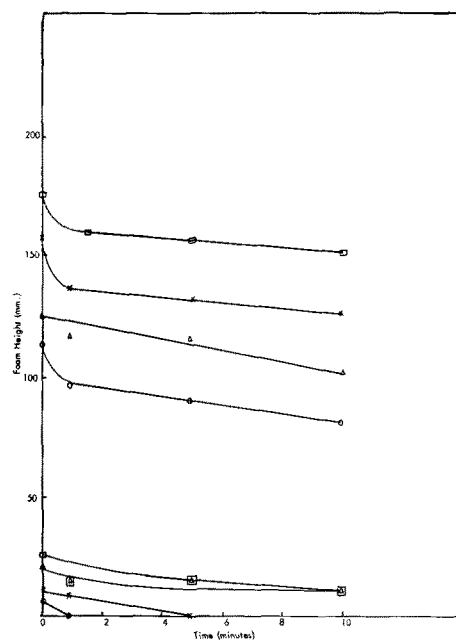


FIG. 4. Foam stability curves for aqueous solutions of sucrose monolaurate alone X, and 9 parts of sucrose monolaurate to 1 part by weight of sodium lauryl sulfate O, lauroyl diethanolamide □, and polyethylene glycol 400 monolaurate Δ. Upper series 0.075 g./100 ml. total active agent, lower series 0.003 g./100 ml. total active agent.

TABLE I  
Foam Stability Values for Solutions of Sucrose Monolaurate Alone  
and Sucrose Monolaurate: Additive = 9:1  
Foam Stability (mm. min.)

Additive	Concentration (g./100 ml.)			
	0.30	0.075	0.030	0.0030
None.....	1300	1346	820	25
Sodium lauryl sulfate.....	1428	844	460	4
Polyethylene glycol 400 monolaurate.....	1662	1560	760	142
Ninol AA62 Extra.....	1750	1112	618	140

tions contained 0.30% surface-active agent in distilled water. Values obtained within one hour after preparation of the solution and also after the solutions had aged for five days were identical. Distilled water and solutions of sucrose monolaurate alone and with other surface-active agents, in the ratio of 9:1, gave values falling on the same curve. Values obtained with a solution containing 0.27% pure sodium lauryl sulfate plus 0.03% lauryl alcohol are shown for comparison. This was the only solution tested with a substantial surface-viscosity and a finite surface-yield value.

### Discussion

Surface tension-concentration curves show that the CMC value of sucrose monolaurate is lowered by the presence of minor amounts of both sodium lauryl sulfate and polyethylene glycol 400 monolaurate. This effect can be ascribed to hydrogen bonding between the sucrose moiety and the sulfate ion in one case and the ether linkages in the other. The increase

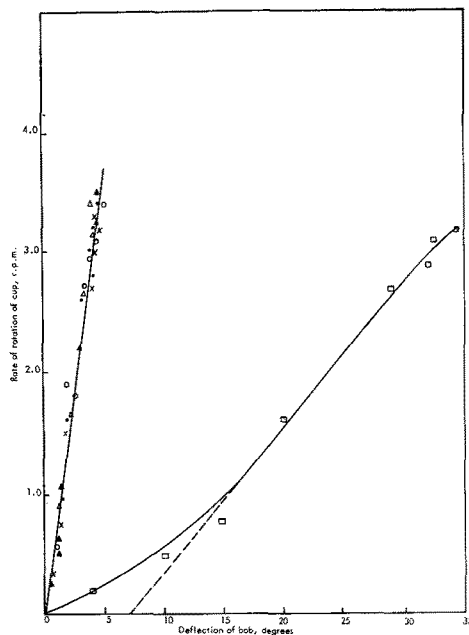


Fig. 5. Surface-viscosity curves for aqueous solutions of sucrose monolaurate alone ●, 9 parts of sucrose monolaurate to 1 part by weight of sodium lauryl sulfate Δ, lauroyl diethanolamide ○, and polyethylene glycol 400 monolaurate ▲. All solutions 0.30 g./100 ml. active agent. Sodium lauryl sulfate 0.277 g./100 ml. plus lauryl alcohol 0.03 g./100 ml. □, distilled water X.

in the CMC value with lauroyl diethanolamide present suggests that the energy of hydrogen bonding between adjacent sucrose groups is greater than between sucrose and the diethanolamide moiety.

Low surface-viscosities and absence of a surface-yield value for solutions of sucrose monolaurate alone and with added sodium lauryl sulfate, polyethylene glycol 400 monolaurate, and lauroyl diethanolamide indicate that these solutions give expanded surface films. Interaction revealed by surface-tension measurements is not sufficient for the formation of a condensed film or even to produce a measurable increase in surface viscosity. Viscosity differences of about  $2 \times 10^{-3}$  surface poises can be distinguished with this apparatus.

Foam stability data reveal the complexity of this phenomenon. The behavior of sucrose monolaurate solutions containing added surface-active agents may be interpreted according to the surface transport theory of Ewers and Sutherland (3), wherein a foam tends to be stabilized by the flow of the surface of the film from a region of low surface-tension to one of high surface-tension. The effect of stretching a portion of the film is primarily to deplete the number of adsorbed molecules per unit area of surface. This will cause a local increase in surface tension, which will in turn cause surface flow toward the stretched portion of the film. The flow of substrate accompanying the flow of the surface film will tend to restore the original thickness of the film. However a competing mechanism is the adsorption of surface-active agent from the solution below the surface. The relatively small size of lauryl sulfate, coupled with the energy of hydrogen bonding with the sucrose moiety, will tend to favor its rapid adsorption and thus prevent restoration of the original film thickness by surface transport. Negative interaction between sucrose monolaurate and the lauroyl diethanolamide, indicated by surface-tension measurements, will tend to retard adsorption and thus favor surface transport. A steric effect, because of the large polyethylene glycol group, may hinder adsorption when polyethylene glycol 400 monolaurate is present in the solution.

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### REFERENCES

1. Brown, A. G., Thurman, U. C., and McBain, J. W., *J. Colloid Sci.*, **8**, 491 (1953).
2. De Navarre, M. G., and Bailey, H. E., *J. Soc. Cosmetic Chemists*, **7**, 427 (1956).
3. Ewers, W. E., and Sutherland, K. L., *Australian J. Sci. Research, Series A, Phys. Sci.*, **5**, 697 (1952).
4. Harkins, W. D., *J. Am. Chem. Soc.*, **61**, 549 (1939).
5. Matalon, R., *J. Colloid Sci.*, **8**, 53 (1953).
6. Osipow, Lloyd, Snell, F. D., Marra, D., and York, W. C., *Ind. Eng. Chem.*, **48**, 1459 (1956).
7. Ross, J., and Miles, G. D., *Oil and Soap*, **18**, 99 (1941).

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