factured reproducibly to specifications. It is possible that the effectiveness of the polyoxyethylated glycerides may lie in the complexity of the mixtures which are obtained in the synthesis.

Future Developments

Detergency, emulsification, wetting, and foaming are composite properties derived from the more fundamental surfactant properties of surface-energy lowering, adsorption, solubility, etc. Present uses for nonionics are principally in aqueous systems and utilize the composite properties just referred to. It is anticipated that new inventions will disclose many new uses for nonionic surfactants which will require different composites of properties, including more extensive use of these compounds in non-aqueous systems. Cases in point are the recent description of a process for using nonionic surfactants as flocculating agents for clays in oil-well-drilling fluids, and the discovery of iodophors (18).

In the near future nonionics will be generally recognized as comprising two major categories of products. The larger tonnage items will become staple commodities manufactured to standard specifications and available from two or more producers.

Specialty items and patent-protected inventions are expected to increase in number of products and in total volume. In most cases these latter types of materials will be sold by companies specializing in technical service to specific industries.

REFERENCES

1. Shoeller, C., and Wittwer, C., U. S. Patent 1,970,578.
2. Draves, C. Z., Am. Dyestuff Reporter, 35, 643 (1946).
3. Cross, J. M., Soap and Sanitary Chemicals, Special Issue, Off. Proc. CSMA, vol. 26, CSMA 1.
4. Jelinek, C. F., and Mayhew, R. L., Textile Research Journal 24, 765 (1954).
5. Jelinek, C. F., and Mayhew, R. L., Ind. and Eng. Chem., 46, 1930 (1954).
6. Gantz, G. M., Off. Digest, Fed. of Paint and Varnish Prod. Clubs, p. 1, June (1956).
7. Richardson, R. E., Kern, J. G., Murray, R. L., Sudhoff, R. W., P. B. 6684, CIOS No. 22/1(G) (1945).
8. Flory, P. J., J. Am. Chem. Soc., 62, 1561 (1940).
9. Mayhew, R. L., and Hyatt, R. C., J. Am. Oil Chemists' Soc., 29, 357 (1952).
10. Sutton, M. G., and Reynolds, M. M., U. S. Patent 2,759,869.
11. Terry, D. H., and Shelanski, H., Off. Proc. CSMA, Dec. (1951).
12. Wrigley, A. N., Smith, F. D., and Stirton, A. J., J. Am. Oil Chemists' Soc., 34, 39 (1957).
13. Steindorff, A., Platz, C., and Rosenbach, J., U. S. Patent 2,111,820 (1934).
14. Chem. and Eng. News, 32, 708–709 (1954).
15. Vaughn, T. H., Suter, H. R., Lundsted, L. G., and Kramer, M. F., J. Am. Oil Chemists' Soc., 28, 294 (1951).
16. Vaughn, T. H., Jackson, D. R., and Lundsted, L. G., J. Am. Oil Chemists' Soc., 29, 240 (1952).
17. Schuette, H., and Wittwer, M., U. S. Patent 2,174,761.
18. Burdyn, R. F., and Wiener, L. D., Oil and Gas Journal (1956).

Sugar Esters [1]

LLOYD OSIPOW, FOSTER DEE SNELL, and ARTHUR FINCHLER,
Foster D. Snell Inc., New York, New York

PREVIOUSLY REPORTED STUDIES (1) with polyoxyethylene condensates have demonstrated that optimum surfactant properties require the presence of about two ethylene oxide units for every three carbon atoms in the alkyl chain. One could hope that sucrose with 11 oxygen atoms would contribute about the same hydrophilic effect as a polyoxyethylene containing an equal number of oxygen atoms. An effective surfactant derived from sucrose would then require an alkyl group containing about 16 or 17 carbon atoms.

The usual range of carbon atoms in the alkyl chain of a surfactant is 12 to 18. Consequently this would fit into the well-established framework, and it might be expected that useful surfactants would result from the chemical combination of fatty acids and sucrose. This has been demonstrated (3). Glucose and sorbitol, on the other hand, contain an insufficient number of oxygen atoms per molecule. It is necessary to add oxyethylene groups to obtain sufficient water-solubility, with an alkyl chain of adequate size for surface activity.

The physiological properties of the sucrose esters are unique. Sucrose monostearate is nontoxic, odorless, and tasteless. Its solutions do not sting the eyes or cause allergic response when injected intravenously. When ingested, the sugar esters hydrolyze to form normal food products. Not only are these esters assured of a favorable position in food and medicinal applications, but they will create new markets in those industries where none previously existed for synthetic surfactants.

Sucrose is the least expensive material commercially available for use as the hydrophilic portion of a nonionic surfactant. When combined with tallow fatty acids to form sucrose monotallowate, the resulting product is certainly based on low-cost raw materials. If the manufacturing process is also inexpensive, the sugar esters will be competitive in applications where their special physiological properties are not important. Consequently our major effort has been directed toward developing and improving the method of manufacture.

Alcoholysis Reaction

As previously described (4), the reaction between sucrose and fat to form a sucrose ester is a straightforward alcoholysis reaction. However there are numerous complications. Sucrose cannot be heated for prolonged periods at temperatures exceeding 100°C. without caramelizing. At safe operating temperatures the solubility of sucrose in fat is negligible. It is necessary to employ a neutral solvent, one which does not decompose or enter into the reaction. Dimethylformamide and dimethylsulfoxide proved to be suitable solvents.

To effect at least 90% conversion of one of the reactants to the sugar ester, it is necessary to employ either a very large excess of the second reactant or to remove one or more of the products from solution. The use of a large excess of one reactant would require relatively large equipment in relation to product yield and would not be economical. The solubility characteristics of the sugar esters are intermediate between sucrose and fat. There is little likelihood of finding a solvent for sucrose and fat from which the sucrose ester will precipitate. Similarly glycerine will not separate from a solvent for

sucrose. One feasible approach is to substitute for the fat, a fatty acid ester of a volatile alcohol. The product alcohol can be stripped from the system by operating under vacuum. Methyl, ethyl, or isopropyl esters of fatty acids can be conveniently used in the alcoholysis reaction.

With methyl esters, under our usual conditions of operation, the total quantity of methanol produced is about 0.6% of the total weight of solution. The small quantity of methanol present in the reaction mixture at any given time is difficult to remove efficiently when the reaction is carried out in multi-gallon batches. Under these conditions the reaction rate is determined by the rate at which the methanol is removed from the system. Thus we have found that the rate of the reaction can be very substantially increased by recycling the reaction mixture through a turbulent-film evaporator, where stripping of methanol is very efficient. The product methanol and a portion of the solvent are distilled from a continuously-forming film of the solution.

Comparison can be made between three different experiments, where the only differences were in the batch sizes and in the type of equipment. All three experiments were carried out under anhydrous conditions, and each reaction mixture consisted of 6.3% methyl stearate, 21.6% sucrose, 0.42% potassium carbonate, and the remainder dimethylformamide.

In a laboratory run we employed 1.8 liters of solution in a three-neck flask, which was fitted with a stirrer and a six-plate fractionating column. After three hours at 90°C., and appropriate vacuum for refluxing, 7.3% of the methyl stearate had not reacted. After six hours conversion of the methyl stearate was complete.

Standard pilot plant equipment consisting of a reaction vessel, agitator, fractionating column, and condenser was employed for 100-gal. batches. In a typical run in which the reaction mixture was maintained at 90°C. and appropriate vacuum for eight hours, 6% of the methyl ester did not react.

Small pilot plant runs employing five gallons of the reaction mixture continuously circulated through a turbulent-film evaporator demonstrated that the methyl ester could be completely reacted at 90°C. in two hours. Thus, by the use of very efficient stripping conditions in the pilot plant, we were able to carry out the reaction more rapidly than in the laboratory. Results are summarized in Table I.

Effect of Moisture

One of the most serious problems encountered in the manufacture of the sucrose monoesters was the persistent formation of substantial quantities of sucrose diesters. Subsequent study demonstrated the unique effect of trace quantities of water. The rate of alcoholysis reaction, resulting in the formation of

TABLE I
Unreacted Methyl Ester as a Function of Equipment.
Reaction Temperature 90°C.

Reaction time (hours)	Unreacted methyl ester, percentage		
	Laboratory equipment 1.8 liters	Pilot plant 100 gallons	Film evaporator 5 gallons
2	......	......	0
3	7.3	......	......
6	0	......	......
8	......	6.0	......

sucrose esters, decreases when the moisture content is raised above zero percentage. Above about 2.0% moisture the alcoholysis reaction is extremely slow. This is not entirely unexpected. However, when the moisture content is raised to a few hundredths of 1.0%, very little diester or other polyesters of sucrose form, while the rate of formation of sucrose monoesters is still satisfactory. When sucrose polyesters of fatty acids are already present in the system, they react with free sucrose to form sucrose monoesters, at a rate which depends upon the water content. It is most rapid when the level of water is in the range of 0.05 to 0.15% of the entire reaction mixture.

The following experiments typify the effect of moisture on the alcoholysis reaction.

A reaction mixture was prepared consisting of 112.5 g. of methyl stearate, 387 g. of sucrose, and 1,275 milliliters of dimethylformamide. The mixture was placed in a three-neck flask fitted with a thermometer, mechanical stirrer, and a six-plate fractionating column leading to a water-jacketed condenser. After heating the mixture to 120°C., 7.5 g. of potassium carbonate were added and the vacuum was adjusted for vigorous refluxing of the distillate. The reaction was carried out for 1.5 hrs., with samples removed each 0.5 hr. for analysis. Comparison is made between three runs which differ in moisture content (2) as shown. a) All materials were completely dry before adding the anhydrous potassium carbonate catalyst. Analysis showed 0.01% moisture. After 0.5 hr. moisture dropped to 0.00%. b) The moisture content was adjusted initially to 0.08%. It was rechecked every 15 min. and readjusted to 0.08%. c) The moisture content was adjusted initially to 0.15%. It was returned to that level after each 15 min. of reaction time.

TABLE II
Effect of Moisture on the Alcoholysis Reaction at 120°C.

Water content, percentage	Reaction time (hours)	Methyl ester, percentage unreacted	Sugar ester present as monoester, percentage
0.01–0.00	0.5	6.1	62.1
	1.0	0.0	63.6
	1.5	0.0	73.2
0.08	0.5	14.7	78.2
	1.0	14.7	100.0
	1.5	14.7	100.0
0.15	0.5	22.6	91.1
	1.0	22.3	100.0
	1.5	15.1	100.0

Results presented in Table II show that the conversion of methyl ester to sucrose ester is most rapid and most complete in the absence of water. However formation of sucrose monoester occurs to a greater extent with moisture present.

A reaction mixture was prepared, which was identical to that described above, using anhydrous material. After carrying out the reaction for one hour at 120°C. and the appropriate vacuum, the reaction mixture was divided into three parts. One part was adjusted to 0.05% water and a second part to 0.10% water. The third part was anhydrous. The three portions were maintained at 95°C. for one hour without vacuum. Analytical data at the end of this period are shown in Table III.

A repeat experiment with 0.1% moisture present in the final hour resulted in 90.0% monoester based on total sugar esters. These results suggest that

TABLE III

Effect of Moisture on Monoester Formation at 95°C.

Moisture content, percentage	Sucrose ester present as monoester, percentage
0.00	83.0
0.05	91.9
0.10	85.3
0.10 (repeat)	90.0

sucrose polyesters react with free sucrose to form the monoester most rapidly in the presence of about 0.05 to 0.10% water.

Another equilibration experiment was carried out, using sucrose distearate. The sucrose distearate was dissolved in dimethyl formamide, and sufficient sucrose was added to provide a ratio of 2 moles of sucrose (combined and free) per mole of stearoyl radical. Potassium carbonate was employed as catalyst. The reaction mixture was divided into two parts, and the water level was adjusted to 0.15% and 0.30%. The mixtures were maintained at 90°C., under atmospheric pressure, for three hours. At the end of this period the portion with 0.15% moisture contained 68.8% sucrose monoester based on total sugar ester present. The sample with 0.30% water contained 43.6% sucrose monoester on the same basis.

These as well as other experiments we have conducted demonstrate that there is an optimum level of about 0.05 to 0.15% moisture required for the most efficient preparation of the sucrose monoesters of fatty acids.

Pilot Plant Studies

Figure 1 is a schematic drawing showing the combination of equipment employed in the pilot plant preparation of the sucrose esters. The reactants,
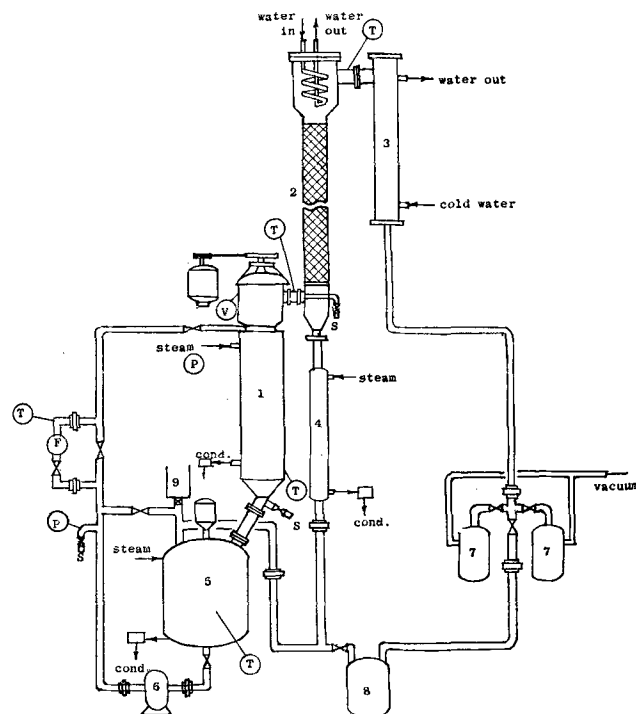

FIG. 1. Pilot plant equipment for preparation of the sugar esters.

1. Turbulent-film evaporator
2. Packed reflux tower
3. Surface condenser
4. Steam-jacketed pipe
5. Reactor vessel
6. Rotary pump
7. Condensate collectors
8. DMF collector
9. Charge pot
T—Temperature indicator
P—Pressure gage
S—Sampling cock
V—Vacuum gage
F—Flow meter

TABLE IV

Comparison of Operating Conditions on Formation of Sucrose Monoester. Reaction Temperature 90°C.

	Sugar ester as monoester, percentage	Unreacted methyl ester, percentage
A		
Equilibration with 0.10% water		
First hour	85	38
Second hour	97	38
Followed by stripping		
30 minutes	100	11
One hour	100	8
B		
Stripping under anhydrous conditions		
30 minutes	58	15
First hour	77	13
Second hour	85	6
Followed by equilibration with 0.10% water		
One hour	94	6

solvent, and catalyst are placed in the reaction vessel (5) in which the conversion from non-sugar ester to sucrose monoester is carried out. The product alcohol and part of the solvent are stripped from the system in the turbulent-film evaporator (1). The product alcohol and solvent are fractionated in the packed reflux tower (2). The solvent is returned to the system through (4) while the alcohol is condensed in (3) and collected in vessels (7).

In carrying out the reaction in the apparatus shown, the sucrose, the solvent, and the non-sucrose esters are placed in the reaction vessel. The agitator is turned on, and heat is applied to bring the mass to about 95°C. After the sucrose and fatty acid esters have dissolved, the moisture content is adjusted to 0.05 to 0.15%, preferably 0.10%, by weight based on the total composition. If the moisture content is initially high, it is lowered by applying vacuum and passing the solution through the heated turbulent-film evaporator to strip off the water. The evaporator is maintained at about 5° to 10°C. above the pot temperature. If the moisture content is low, it is adjusted by the addition of water.

After the moisture content has been adjusted to the proper level, the catalyst is added. The pot temperature is maintained at about 95°C., and the evaporator is kept a few degrees higher. Appropriate vacuum is applied to insure vigorous refluxing. The reaction mixture is constantly pumped through the turbulent-film evaporator, from whence it gravity-flows back to the pot. The volatile alcohol and water are separated from the solvent in the fractionating column. The alcohol and water are condensed and recovered while the solvent is returned to the reaction vessel.

Since water is constantly being removed from the system, it is necessary to feed in replacement water either periodically or continuously. This can be done by manual measurement of the water content, using Karl Fischer Reagent (2) or by the use of automatic control devices. If the equipment is appropriately sized for the batch, the reaction can be completed in about three hours. The solvent is then stripped from the system.

The following is a comparison of results obtained with this equipment, using somewhat different operating conditions. In both experiments the reaction mixture consisted of the following:

Sucrose .... 3,676 g.
Methyl stearate .... 1,069 g.
Potassium carbonate .... 71.2 g.
Dimethylformamide .... 13.7 liters

In one experiment the reaction mixture was adjusted to 0.10% moisture and allowed to equilibrate for two hours at 90°C. The mixture was then cycled through the evaporator for one hour. In the second experiment the anhydrous reaction mixture was first cycled through the evaporator for two hours. The moisture content was then adjusted to 0.10%, and it was allowed to equilibrate for one hour. The pot temperature was maintained at 90°C. Comparison of the results in Table IV reveals that a high ratio of monoester to diester is more readily obtained by equilibrating with water present, prior to stripping of product methanol.

Purification

After completion of the alcoholysis reaction and stripping of the solvent, the sugar ester is separated from unreacted sucrose, which is then recycled. Any one of a large number of solvents can be used to dissolve the sucrose ester without dissolving the sugar. However the sugar recovered by distillation of the reaction solvent is finely divided. Even with the aid of diatomaceous earth, filtration is difficult and occlusion of the sugar ester is excessive. The problem was resolved by the use of a water-insoluble organic solvent in combination with a relatively small amount of water. The quantity of water used is such as to give a sugar solution containing 50 to 60% sugar. At this concentration of sugar the sugar ester is almost completely extracted by the organic solvent. When xylene is employed to take up the sugar ester, the two phases layer rapidly. The xylene is then removed by steam distillation to recover the sugar ester.

Discussion

Pilot plant studies have demonstrated that the sugar esters can be prepared economically, with good yield and purity, using a batch operation. Our pilot plant equipment is presently being modified for the preparation of the sugar esters on a continuous basis. In essence, the equipment will then consist of a series of surge tanks and evaporators. Make-up water will be fed into the surge tanks to maintain the water level at 0.10%. The bulk of the solvent will be removed in the final evaporator, after which the product stream will be blended with xylene and water. This mixture will then be led into a liquid-liquid separator. The xylene and water layers will be fed to separate stills for the recovery of product and unreacted sugar. The latter will be recycled.

Summary

Improvements in the method of manufacture of the sugar esters are described. The use of a turbulent-film evaporator for removal of product methanol reduces reaction time in batch operation from 15 to 3 hrs. The presence of trace quantities of water inhibits diester formation and permits recovery of better than 90% monoester without extensive purification.

Acknowledgment

REFERENCES

1. Ballun, A. T., Schumacher, J. N., Kapella, G. E., and Karabinos, J. V., J. Am. Oil Chemists' Soc., 31, 20 (1954).
2. Mitchell-Smith, Aquametry, 1948.
3. Osipow, Lloyd, Snell, F. D., Marra, D., and York, W. C., Ind. Eng. Chem., 48, 1462 (1956).
4. Osipow, Lloyd, Snell, F. D., York, W. C., and Finchler, A., Ind. Eng. Chem., 48, 1459 (1956).

Ampholytic Surface-Active Agents [1]

D. L. ANDERSEN, General Mills, Inc., Minneapolis, Minnesota

CLASSICALLY, SYNTHETIC DETERGENTS have been categorized electrochemically as anionic, cationic, or nonionic according to whether the surface-active portion (in aqueous solution) is present as an anion, a cation, or an unionized molecule. Only recently has the term ampholytic surfactant been employed to characterize those surface-active agents containing both anionic and cationic groups.
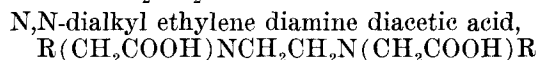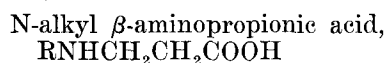
The technology of amphoteric (used interchangeably with ampholytic) surfactants is not new. Products of this type have been known for many years. However, until recently, little practical use has been made of this general class of products. And, until recently, ampholytic surfactants were not commercially available.

With the tremendous technological advances in the utilization of synthetic detergents, competition has increased markedly in the surfactant field. Much more is known about surface-active phenomena such as wetting, detergency, and foaming. Application of existing products is advancing rapidly. The relatively unknown and untried ampholytic surfactants are attempting to keep pace. The technology of these products has advanced to the point where several amphoteric detergents are available commercially. Research and development are directed toward seeking out specific areas where ampholytic products may have a definite advantage over other types. Currently amphoteric surfactants are finding application in such divers fields as the shampoo and cosmetic fields, water emulsion paints, the textile industry, corrosion inhibition, industrial cleaning, and many others.

Chemistry of the Ampholytic Functional Groups

Fundamentally an ampholytic surfactant contains both basic (cationic) and acidic (anionic) groups. These products may be "balanced," i.e., the number of acidic and basic groups are equal, or the product may be "unbalanced," in which case either the acidic or the basic groups are in excess. Typical balanced ampholytics are:

N-alkyl β-aminopropionic acid,
$RNHCH_2CH_2COOH$

N,N-dialkyl ethylene diamine diacetic acid,
$R(CH_2COOH)NCH_2CH_2N(CH_2COOH)R$

Typical unbalanced ampholytic detergents are:

N-alkyl β-iminodiacetic acid,
$RN(CH_2COOH)_2$

N-alkyl N'-carboxymethyl ethylenediamine,
$RNHCH_2CH_2NHCH_2COOH$