Chapter 10

Synthesis of Surfactants from Vegetable Oil Feedstocks

Ronald A. Holser

USDA, ARS, NCAUR, Food and Industrial Oils Research Group, Peoria, Illinois 61604

Introduction

Triglycerides obtained from domestic oilseed crops such as soybean represent a renewable source of medium chain length fatty acids (FA) that are suitable for the preparation of surfactants and related products (1). These compounds find numerous industrial applications as detergents, dispersants, emulsifiers, softeners, and wetting agents (2). The hydrolysis of vegetable oil yields FA and glycerol. The FA provide the chemical structures that are the building blocks of surfactants. A FA combines an alkyl structure that imparts hydrophobic properties with a carbonyl or other solubilizing structure that imparts hydrophilic properties. Both attributes are essential to surfactant performance (3). The length of the alkyl chain determines the hydrophobic character while the solubilizing group determines the hydrophilic character, e.g., anionic, cationic, or non-ionic (4). The presence and location of substituent groups further influence surfactant properties and performance in a particular application (5). For example, the tropical oilseeds—coconut and palm kernel—are rich sources of lauric and myristic acids which are used in the production of detergents, whereas the derivatives of longer chain FA perform better as dispersants or emulsifiers (6).

FA may be neutralized with base to produce the corresponding salts. Such salts or soaps combine the hydrophilic and hydrophobic functionalities that are characteristic of surfactant compounds. However, the performance and production of soaps is surpassed by the ether, ester, and amide derivatives that can be prepared from FA (7).

Oilseed crops are an attractive source of FA since they represent a renewable and sustainable raw material that can replace petrochemicals for industrial synthesis. A surfactant will exhibit the same physical and chemical properties whether prepared from oleochemical or petrochemical raw materials. In fact, certain structures may be more advantageously prepared from an oleochemical raw material. For example, the fatty alcohols that are commonly used in the preparation of surfactants may be produced by the reduction of FA obtained from oilseed triglycerides. Other factors that affect the choice of oleochemical or petrochemical feedstocks include availability, consumer preference, cost, process economics, and purity.

Additionally, initiatives to promote the development of biobased products that can replace products currently derived from petroleum sources have been implemented by the U.S. government and the European Union over the past several years. In the U.S., the Biomass Research and Development Act of 2000 and executive order 13134, "Developing and promoting bio-based products and bio-energy," have established the goal to significantly increase the use of agricultural materials as a source for the production of consumer goods, industrial chemicals, lubricants, and alternative fuels. Historically, agricultural materials were used in this capacity prior to the development of petroleum as a raw material for the chemical industry. The shift from agriculture to petroleum as the source of industrial raw materials occurred due to the availability of inexpensive petrochemicals. A return to agricultural sources may be expected as petroleum prices increase.

Agricultural Raw Materials in Industrial Applications

The current interest in agricultural raw materials for industrial applications is a response to both economic and environmental concerns associated with petroleum. The reserves of petroleum and other fossil fuels are finite, in contrast to renewable sources of oleochemicals, such as those obtained from oilseed crops. The cost of petroleum is expected to increase as the supply is depleted, while the corresponding cost of a sustainable agricultural raw material should remain relatively stable. In addition, the use of domestically produced oleochemical materials instead of petrochemical feedstocks helps to conserve the global supply of fossil resources while reducing the dependence of the U.S. on foreign petroleum supplies. The U.S. currently imports the majority of petroleum it uses. Much of this supply is located in politically sensitive regions such as the Middle East, where a change in the social order can interrupt the production of petroleum and lead to price fluctuations or shortages. Reducing the levels of imported petroleum offers a strategic benefit and promotes domestic economic security. The U.S. Department of Energy has recognized this and established goals to increase the use of biomass as a source of raw materials for the chemical industry (8).

The domestic petroleum resources in the U.S. are located in environmentally fragile areas where development remains extremely controversial, such as the Coastal Plain of the Arctic National Wildlife Refuge, and offshore regions of the Gulf and the Pacific coasts. Leasing and drilling activities in these areas would provide only a temporary solution to a long-term problem.

In contrast, agricultural raw materials offer a renewable alternative with distinct economic advantages to replace petrochemical feedstocks for industrial applications. The domestic production of industrial agricultural crops promotes a stable and secure supply of the raw materials obtained from these sources. This presents both economic and strategic benefits to the U.S. There is an economic benefit to the farmers and local processors involved in the production and post-harvest handling of the crop. Additional economic stability exists for the farmer who is supplying a crop with both edible and industrial applications. For example, a decline in the price of a crop or derivative agricultural material in the edible market may be offset by the price in the industrial market. This stability improves the rural economy and stimulates diversity in the agricultural marketplace. The national economy also benefits from this stability. The increased agricultural production of oilseed crops for industrial oleochemicals will provide a secure source of raw materials for the chemical process industry and reduce dependence on imported petroleum.

The economic benefit associated with substituting an agricultural raw material for a petrochemical raw material may not be measured simply by the raw material cost or through evaluation of conventional direct production costs. A more accurate life-cycle analysis must be evaluated for each particular case. Comprehensive life-cycle assessments are not trivial to perform and the results obtained for one crop do not necessarily transfer to a similar crop (9). Such analyses must consider the agronomic expenses of fertilizer, pesticides, cultivation, harvest, transport, and storage of the crop plus the additional post-harvest processing that may be required to recover or prepare the agricultural material for use as an industrial raw material. For example, crushing, expelling, or refining operations are necessary to recover the natural oils from an oilseed crop followed by hydrolysis or transesterification of the component FA.

The strategic plan prepared by the Biomass Research and Development Board in response to the Biomass Research and Development Act of 2000 and executive order 13134 (which set the national goal of "tripling the use of biobased products and bioenergy by 2010") proposed the coordination of federal, state, and industrial activities to accelerate the commercialization of biobased products and technologies without adversely affecting environmental and public health (10). The environmental aspects of developing biobased products and implementing the corresponding production technologies need to be evaluated critically.

Life-cycle analyses have also been performed to evaluate the environmental impact of manufacturing a particular product from agricultural raw materials versus one manufactured from petrochemicals. A review performed in Germany found that the use of vegetable oils, specifically rapeseed oil, to produce surfactants presented definite advantages both in the reduction of greenhouse gases such as carbon dioxide, and energy requirements (11).

Surfactants

Surfactants are applicable to both edible and industrial products. Edible applications include use as emulsifiers or thickening agents. The monostearate and oleate glycerides are used in the highest volume in the food industry where these compounds act as viscosity modifiers and stabilizers that provide texture to processed foods (12). Industrial applications of surfactants are numerous. Surfactants are important components in formulations of agrochemicals, corrosion inhibitors, cosmetics, detergents, lubricants, metal working and oil drilling fluids, polymers, and textile finishes (3). They can act as emulsifiers, dispersants, stabilizers for oil-in-water (o/w) or water-in-oil (w/o) emulsions, viscosity modifiers or flocculents. Surfactants can impart foaming, leveling, release, or wetting properties to formulations. The attributes of the surfactant that make it suitable for a specific application are determined by the chemical structure which can be designed for optimal performance in a particular formulation.

Surfactants are classified as anionic, cationic, amphoteric, or non-ionic based on the ionization of the structure in an aqueous system. Surfactants from all of these classes may be produced from vegetable oils. The typical surfactant structure consists of a hydrophilic group attached to a hydrophobic moiety. Common hydrophiles include the carboxylate, sulfate, sulfonate, or phosphate groups for anionic surfactants and amine or ammonium groups for cationic surfactants. Common hydrophobes or lipophiles include the linear hydrocarbons of medium chain length (C12–C18). FA obtained from natural fats and oils provide this structure, and their salts were some of the earliest surface active compounds prepared. However, FA may be easily converted into a variety of derivative compounds with a wider range of surfactant properties through reaction of the carboxylic acid group (13). The FA may undergo amidation, esterification, or ethoxylation to produce derivative structures with specific surfactant properties. Alternatively, the FA may be reduced to the fatty alcohol which is another important material for the production of surfactants. Fatty alcohols produced from vegetable oils in this way compete directly with those obtained from petrochemical sources.

In some instances the alkyl portion of the FA may contain hydroxyl or epoxide functionalities. The presence of such functional groups permits chemical modifications to be made along the hydrocarbon chain that can further alter the surfactant characteristics. If these functionalities do not occur naturally in the FA they may be introduced by addition reactions at unsaturated sites. Several important surfactant compounds that may be synthesized from vegetable oils are described in the following sections.

Esters

FA esters are formed by the condensation of an alcohol with the free FA or by transesterification of the triglyceride in the presence of an acid or base catalyst. Esters of primary and secondary alcohols such as methyl, ethyl, isopropyl, butyl, octyl, decyl, myristyl, and cetyl are commonly used in cosmetic and personal care products (14). These compounds act as excipients, lubricants, plasticizers, softeners, solubilizers, and wetting agents in cleansing creams, lipsticks, insect repellants, nail varnishes, perfumes, bath oils, creams, lotions, antiperspirants, and deodorant formulations. The methyl esters are also intermediates for the synthesis of other surfactants such as the α-sulfonates.

Esters produced by reaction of the FA with polyhydroxy alcohols such as glycol, glycerol, pentaerythritol, or sorbitol produce compounds with greater hydrophilic characteristics (15). These materials act as emulsifying, opacifying, thickening, dispersing, pearling, and anti-foaming agents that find applications in the preparation of o/w and w/o emulsions, absorption bases, pomades, emollient creams, and shampoos.

Sucrose esters display high biodegradability and physiological inertness (16). The best detersive performance is reportedly obtained with saturated C18 FA. These compounds find applications in cosmetic and detergent formulations.

Esters prepared with polyethylene glycol (PEG) provide a non-ionic o/w emulsifier for cosmetic and pharmaceutical formulations. The emulsifier is used as a thickening agent in creams, a suspension agent for solid substances, and a stabilizer in formulations with a high proportion of electrolytes. It has also been used as an anti-static agent for plastics.

Ester Sulfonates. A sulfonated FA methyl ester is prepared by the transesterification of a vegetable oil to obtain the corresponding methyl esters followed by sulfonation with sulfur trioxide. The hydrophilic sulfonate group increases the water solubility while the linear hydrocarbon moiety provides the necessary lipophilic character. Ester sulfonates exhibit favorable wetting, emulsifying, and dispersant properties (17,18). This is an efficient method for the production of these anionic surfactants (19). These compounds have been prepared from coconut oil and compare favorably to C12–C14 fatty alcohol ether sulfates and C14–C16 olefin sulfonates (20,21).

Yields greater than 95% are obtained when the vegetable oil is hydrogenated prior to sulfonation. If the oil is unsaturated then numerous reaction products are generated. Further reaction of the sulfonate with diethanolamine (DEA) or triethanolamine (TEA) produces improved foaming characteristics (22). The sodium DEA and TEA salts of α-sulfomyristate exhibit better detergency than sodium lauryl sulfate with less irritation in physiological tests (23).

Ester Ethoxylates. Fatty ester ethoxylates are prepared by catalytic ethoxylation of the FA methyl esters. These ethoxylates are comparable to the alcohol ethoxylates but with increased water solubility (24). Glycerol esters prepared with 7 moles of ethoxylate are used as dispersing and solubilizing agents. These non-ionic ethoxylates promote the solution of other lipid ingredients in alcoholic formulations. Applications include emulsifying, opacifying, thickening and dispersing agents for in oil-in-water emulsions.

Sorbitan esters prepared with 4–20 moles of ethoxylate also act as emulsifying, dispersing, and solubilizing agents for vitamins, essential oils, fragrances, tannins, and other lipid components in cosmetic formulations and topical medicinal preparations.

Amides

FA or their methyl esters can react with primary and secondary amines such as monoethanolamine (MEA) and diethanolamine (DEA) to produce the corresponding amides (25). However, the reaction of FA with MEA or DEA can produce unwanted ester by-products, whereas reaction of the corresponding methyl ester with MEA or DEA produces the desired alkanolamide with over 90% yield.

Amido alkoxylated ammonium compounds are also prepared from either the FA or the triglyceride by reaction with diethylamine triamine followed by ethoxylation and conversion to the methyl sulfate derivative with dimethyl sulfate (26). The amido imidizolines are produced by a similar reaction scheme but at elevated temperatures cyclization occurs (27). These compounds are used industrially as fabric softeners, flotation agents, corrosion inhibitors (13,28).

The amides also serve as intermediates for structures such as the betaines which exhibit good foaming power and favorable skin tolerance. The reaction of a FA with an amino acid such as N-methyl glycine produces the important class of N-acyl-sarcosine surfactants. Additional condensation products may be obtained by reaction of FA with protein hydrolysates. These compounds have diverse properties, and applications including use as rust inhibitors, fuel oil additives, and emulsifiers.

Alcohols

Fatty alcohols are not produced in significant quantities by commodity oilseed crops although some specialty crops such as jojoba produce wax esters rather than triglycerides. However, it would not be practical to obtain fatty alcohols from jojoba oil because of the value of the oil. Alternatively, fatty alcohols may be produced by the hydrogenation of the triglycerides, FA, or FA esters obtained from vegetable oil (29,30). The resulting fatty alcohols provide an alternative to the petrochemical source. The fatty alcohol is reacted to form ethoxylated, sulfated, or aminated surfactant compounds. The alcohol ethoxylates are prepared by reacting the fatty alcohol with ethylene oxide. The ethylene oxide chain provides the hydrophilic character for these non-ionic surfactants. These compounds are biodegradable and are used in formulating low foaming degreasers and liquid cleansers (31–33).

Subsequent sulfation of these alcohol ethoxylates produces biodegradable surfactants that exhibit exceptional foaming and detergency, and are used in shampoos. The fatty alcohol may also be sulfated directly with sulfur trioxide to provide the alcohol sulfates which are used extensively as foaming agents in personal care products (34,35).

Amines

Amines can be produced by the reaction of fatty alcohols with alkylamines or by reduction of the fatty nitrile (36). Primary, secondary, tertiary, and quaternary amines are prepared *via* the fatty nitrile which is formed by the reaction of the FA with ammonia, followed by hydrogenation to produce the corresponding fatty amine. Amine oxides can be prepared from the fatty amine by heating with hydrogen peroxide. These compounds are mild with good foaming properties, and are used in shampoos and cosmetic products.

Summary

Clearly, a variety of vegetable oil-based surfactants can be prepared from the reaction of FA or the corresponding methyl esters with various alcohols or amines. A surfactant of every type is represented, such as anionic, cationic, non-ionic, and amphoteric, with applications in personal care products, household detergents, and industrial cleansers. Surfactants are essential components in formulations in such diverse areas as emulsion polymerization, textile treatments, agrochemicals, paper and textile finishes, coatings, metal working fluids, and corrosion inhibitors.

Currently, the consumer has expressed interest in bio-based products. In response, initiatives for using renewable raw materials have been established by the federal government. Similarly, applicable industries will evaluate the economic benefits of using natural raw materials to replace petrochemicals.

References

1. Gervasio, G.C., FA and Derivatives from Coconut Oil, in *Bailey's Industrial Oil & Fat Products*, 5th ed., edited by Y.H. Hui, Wiley Interscience, NY, 1996, Vol. 5, pp. 33–91.
2. Heidrich, J.F., Oleochemicals: Feedstock or Auxiliary, *J. Am. Oil Chem. Soc. 61*: 271–275 (1984).
3. Lynn, Jr., J.L., and B.H. Bory, Surfactants, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., edited by Kirk-Othmer, Wiley Interscience, NY, 1997, Vol. 23, pp. 478–541.
4. Klevens, H.B., Structure and Aggregation in Dilute Solution of Surface Active Agents, *J. Am. Oil Chem. Soc. 30*: 74–80 (1953).
5. Mankowich, A.M., Micellar Molecular Weights of Selected Surface Active Agents, *J. Phys. Chem. 58*: 1027–1030 (1954).
6. Ogoshi, T., and Y. Miyawaki, Soap and Related Products: Palm and Lauric Oil, *J. Am. Oil Chem. Soc. 62*: 331–335 (1985).
7. Borghetty, H.C., and C.A. Bergman, Synthetic Detergents in the Soap Industry, *J. Am. Oil Chem. Soc. 27*: 88–90 (1950).
8. US DOE: Plant/Crop-based Renewable Resources 2020—A Vision to Enhance U.S. Economic Security Through Renewable Plant/Crop-Based Resource Use, DOE/G-10098–3385, 1998.
9. Zemanek, G., and G.A. Reinhardt, Notes on Life-Cycle Assessments of Vegetable Oils, *Fett/Lipid 101*: 321–327 (1999).
10. *Fostering the Bio-Economic Revolution in Biobased Products and Bioenergy: An Environmental Approach*, Biomass Research and Development Board, 2001, pp. 1–20.
11. Patel, M., G.A. Reinhardt, and G. Zemanek, Vegetable Oils for Biofuels Versus Surfactants: An Ecological Comparison for Energy and Greenhouse Gases, *Fett/Lipid 101*: 314–320 (1999).
12. Van Haften, J.L., Fat-Based Food Emulsifiers, *J. Am. Oil Chem. Soc. 56*: 831A–835A (1979).

13. Maag, H., Fatty Acid Derivatives: Important Surfactants for Household, Cosmetic and Industrial Purposes, *J. Am. Oil Chem. Soc. 61*: 259–267 (1984).
14. Meffert, A., Technical Uses of Fatty Acids, *J. Am. Oil Chem. Soc. 61*: 255–258 (1984).
15. McIntyre, R.T., Polyglycerol Esters, *J. Am. Oil Chem. Soc. 56*: 835A–840A (1979).
16. Schwartz, A.M., and C.A. Rader, Performance Characteristics of Sucrose Ester Detergents, *J. Am. Oil Chem. Soc. 42*: 800–804 (1965).
17. Stirton, A.J., J.K. Weil, and R.G. Bistline, Jr., Surface-active Properties of Salts of Alpha-Sulfonated Acids and Esters, *J. Am. Oil Chem. Soc. 31*: 13–16 (1954).
18. Stirton, A.J., R.G. Bistline, Jr., J.K. Weil, W.C. Ault, and E.W. Maurer, Sodium salts of Alkyl Esters of α-Sulfo Fatty Acids. Wetting, Lime Soap Dispersion, and Related Properties, *J. Am. Oil Chem. Soc. 39*: 128–131 (1962).
19. Stein, W., and H. Baumann, α-Sulfonated Fatty Acids and Esters: Manufacturing Process, Properties, and Applications, *J. Am. Oil Chem. Soc. 52*: 323–329 (1975).
20. Knaggs, E.A., J.A. Yeager, L. Varenyi, and E. Fischer, Alpha Sulfo Fatty Esters in Biologically Soft Detergent Formulations, *J. Am. Oil Chem. Soc. 42*: 805–810 (1965).
21. Stirton, A.J., R.G. Bistline, E.A. Barr, and M.V. Nunez-Ponzoa, Salts of Alkyl Esters of α-Sulfopamitic and α-Sulfostearic Acids, *J. Am. Oil Chem. Soc. 42*: 1078–1081 (1965).
22. Weil, J.K., A.J. Stirton, and R.G. Bistline, Jr., Amides of α-Sulfonated Palmitic and Stearic Acid, *J. Am. Oil Chem. Soc. 37*: 295–297 (1960).
23. Stirton, A. J., α-Sulfo Fatty Acids and Derivatives. Synthesis, Properties, and Use, *J. Am. Oil Chem. Soc. 39*: 490–496 (1962).
24. Ballun, A.T., J.N. Schumacher, G.E. Kapella, and J.V. Karabinos, Comparative Detergency of Several Built Polyethenoxy Alkanoates, *J. Am. Oil Chem. Soc. 31*: 20–23 (1954).
25. Linfield, W.M., Fatty Oxazolines and Imidazolines, *J. Am. Oil Chem. Soc. 61*: 437–441 (1984).
26. Egan, R.R., Cationic Surface Active Agents as Fabric Softeners, *J. Am. Oil Chem. Soc. 55*: 118–121 (1978).
27. Ferm, R.J., and J.L. Riebsomer, The Chemistry of the 2-Imidazolines and Imidizolidines, *Chem. Rev. 54*: 593–613 (1954).
28. Micich, T.J., and W.M. Linfield, Nonionic Surfactant Amides as Soil Wetting Agents, *J. Am. Oil Chem. Soc. 63*: 1385–1391 (1986).
29. Kreutzer, U.R., Manufacture of Fatty Alcohols Based on Natural Fats and Oils, *J. Am. Oil Chem. Soc. 61*: 343–348 (1984).
30. Voeste, T., and H. Buchold, Production of Fatty Alcohols from Fatty Acids, *J. Am. Oil Chem. Soc. 61*: 350–352 (1984).
31. Karabinos, J.V., G.E. Bartels, and G.E. Kapella, Comparative Detergency of Several Built Polyethenoxy Aliphatic Ethers, *J. Am. Oil Chem. Soc. 31*: 419–420 (1954).
32. Tamura, T., Y. Kaneko, and M. Ohyama, Dynamic Surface Tension and Foaming Properties of Aqueous Polyoxyethylene n-Dodecyl Ether Solutions, *J. Colloid Interface Sci. 173*: 493–499 (1995).
33. Knaebel, D.B., T.W. Federle, and J.R. Vestal, Mineralization of Linear Alkylbenzene Sulfonate and Linear Alcohol Ethoxylate in 11 Contrasting Soils, *Environ. Toxicol. Chem. 9*: 981–988 (1990).
34. Feitkenhauer, H., and U. Meyer, Anaerobic Digestion of Alcohol Sulfate (Anionic Surfactant) Rich Wastewater—Batch Experiments. I. Influence of the Surfactant Concentration, *Bioresour. Technol. 82*: 115–121 (2002).

35. Feitkenhauer, H., and U. Meyer, Anaerobic Digestion of Alcohol Sulfate (Anionic Surfactant) Rich Wastewater—Batch Experiments. II. Influence of the Hydrophobic Chain Length, *Bioresour. Technol. 82*: 123–129 (2002).
36. Billenstein, S., and G. Blaschke, Industrial Production of Fatty Amines and Their Derivatives, *J. Am. Oil Chem. Soc. 61*: 353–357 (1984).