Biobased Surfactants and Detergents

Synthesis, Properties, and Applications

Editors

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Biobased Surfactants and Detergents

Synthesis, Properties, and Applications

Introduction

For the majority of the 20th century, petroleum was utilized as the main feedstock for transportation and other fuels, chemical intermediates, and many co-products. The Surfactants and Detergents industrial sector, like many others, relied heavily upon petroleum as its main feedstock.

It is now clear that the relative abundance of petroleum is decreasing, leading to increased prices, as experienced during 2008. In addition, it is generally accepted that the heavy utilization of petroleum results in an increased emission of carbon dioxide into earth's atmosphere, which may lead to severe climate change throughout our planet. More sustainable feedstocks for fuels and chemical intermediates are necessary. The consumer is becoming aware of the potential danger of climate change and has interest in products derived from more sustainable starting materials and processing methods.

Due to the reasons discussed above, Surfactants and Detergents manufacturers have increased interest in the utilization of biobased feedstocks. The primary motivation is the rising costs of petroleum relative to oleochemical feedstocks, with the gap in the price of the two anticipated to further narrow in the upcoming years. Of note, the manufacturing costs associated with petrochemical and biobased feedstocks are generally equal.

This book was prepared to highlight for the community of Surfactant and Detergent developers, formulators, and designers in industry, academia, and government-sponsored laboratories throughout the world on the current industrial status of biobased surfactants, new biobased surfactants being developed, the potential for the "green" manufacturing of biobased surfactants via a biocatalytic route, and novel applications for biobased surfactants. We hope this book will further the employment of biobased surfactants in commercial products and inspire scientists worldwide to develop new biobased surfactants and applications for their use.

The authors who prepared the chapters of this book are experts in their respective fields, and thus are supplying the reader with a full, current, and critical evaluation of biobased surfactant preparation and applications. We recognize that several research groups are active in the research and development of biobased surfactants in addition to those represented by this book's authorship.

The book has been divided into four sections. The first section, "Introduction, Importance, and Relevance of Biobased Surfactants," consisting of Chapter 1, reports on the motivation and current use for biobased surfactants, particularly in the industrial sector, and to serve as an introductory chapter to the remainder of the book, moreover, to highlight the other chapters in relation to biobased surfactant research and development. The second section, "Biosurfactants: Biosynthesis and

Applications," consisting of Chapters 2–6 focuses upon biosurfactants, biobased surfactants produced by living cells, particularly their fermentative production and novel applications. The third section "Biobased Surfactants in Biomedical Applications," Chapters 7–9 describes the development of biobased lung surfactant formulations, important for the treatment of several pulmonary diseases such as acute respiratory distress syndrome, and the applications of biosurfactants in medicine. Of relevance to Section 2, Chapter 9 also contains a thorough review of biosurfactant preparation and utilization. The fourth section ("Sugar–, Polyol–, and Amino–Based Lipids: Biodegradable and Biocompatible Surfactants," Chapters 10–16) focuses upon the preparation of sugar- and amino acid-based surfactants, with several chapters describing their preparation by enzymatic synthesis, and their applications.

The genesis for this book was "Biobased Surfactants and Oleochemicals," a symposium chaired and organized by the Editors at the 98th American Oil Chemists' Society (AOCS) Annual Meeting and Exposition, May 13–16, 2007, in Québec City, Canada. The meeting was co-sponsored by the Japan Oil Chemists' Society (JOCS). Many of this book's authors participated in the symposium, or in a symposium of the same title at the 99th AOCS Annual Meeting and Exposition, May 18–21, 2008, in Seattle, USA.

Therefore, we are grateful to both organizations, the AOCS (and the Biotechnology and Surfactants and Detergents Divisions in particular) and the JOCS, for their support in enabling the above-mentioned symposia. We also are very appreciative of the staff of AOCS Press for their kind assistance and leadership in the preparation and printing of this book. Last but not least, we thank the authors of this book's chapters for their willingness to contribute, and their time and diligence in preparing the chapters. It is their expertise, shared in the pages of this book, which we hope will make it a valuable resource for the reader.

Douglas G. Hayes
Dai Kitamoto
Daniel K. Y. Solaiman
Richard D. Ashby

February 13, 2009

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PART 1

Introduction, Importance, and Relevance

1

Biobased Surfactants: Overview and Industrial State-of-the-Art

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What Is a Biobased Surfactant?

"Biobased products" are defined as "commercial or industrial products (other than food or feed) that are composed in whole or in significant part of biological products or renewable domestic agricultural materials (including plant, animal, and marine materials) or forestry materials" (U.S. Senate Committee on Agriculture, Nutrition, and Forestry, 2006). Biobased products do not contain components which are toxic or endanger the environment; their use results in the following benefits: increased safety for users, a low impact on the environment, a reduction of petroleum usage, and an enhancement of the economy on both a domestic and local level, particularly for the rural regional sector (Biobased US, 2007). Of the three broad categories attributed to biobased products: biochemicals, biofuels, and biomaterials, biobased surfactants best belong to biochemicals and, more specifically, to the following subcategories: cleaning agents, paints and coatings, foods, personal-hygiene and cosmetics products, lubricants, and pharmaceutical agents (Biobased US, 2007). An additional category, a niche market, would be surfactants for environmental remediation or environmentally-sensitive applications, such as tertiary oil recovery, particularly well-suited for "biosurfactants" (Lu & Somasundaran, 2007; Quadri et al., 2008), where the latter term refers to "surface-active substances synthesized by living cells" (Rahman & Gakpe, 2008), and exists as a subset of biobased surfactants. (See also McInerney et al., "Lipopeptide Surfactants and Their Use in Oil Recovery, within this book.) Metal-working fluids are a subcategory of lubricants where mixtures of anionic and nonionic biobased surfactants are desired to replace synthetic surfactants to greatly enhance their environmental profile. (See Zhao et al., "Design of Vegetable Oil Metalworking Fluid Microemulsions Using Biobased Surfactants" in this book.)

Studies in 2003 and 2005 reported that the global surfactant industry produced 8.6 MMT and 12.5 MMT of surfactant, respectively, and was worth about $14 billion and $28 billion, respectively, with annual growth being near 0.5 MMT (Anonymous, 2006; Chemistry in Britain, 2003; Patel, 2004). In the United States, of the 3.5 MMT of surfactants produced, roughly 35% were biobased (U.S. Department of Energy, 1999). The value of the laundry, personal-care, and dishwashing-detergents industries, the major users of surfactants and detergents, was $70 billion globally in 2005, with the projected value in 2010 expected to be $78 billion (Phillips et al., 2007). The total market value of the soaps and detergents industry within the European Union (EU) countries in 2007 was 40.8 billion Euros ($64 billion) [International Association of Soaps, Detergents, and Maintenance Products (AISE), 2007], with the EU consisting roughly of one-third of the surfactant market (Chemistry in Britain, 2003).

Biobased feedstocks employed for surfactants are mainly used to form the hydrophobe. The most common feedstock is seed oil, particularly from a source rich in acyl groups of chain lengths of 12–16, such as palm, palm-kernel, particularly palm stearine, a palmitic acyl-rich by-product from the purification and fractionation of palm-kernel oil (Santosa, 2008), and coconut oils (Edser, 2004). Animal wastes, such as lard or tallow, may be an additional source (e.g., cationic surfactants for fabric softeners produced by Evonik, Essen, Germany) (McCoy, 2008b). Cuphea, a potentially valuable new U.S. crop with an oil enriched in C_{12}–C_{16} fatty acyl groups, may serve as a future feedstock (Pandey et al., 2000). Other potentially valuable sources of fatty acyl groups for surfactants and detergents include algal oils and oils from jatropha and soapnut (*Sapindus mukorossi*) (Chetri et al., 2008; Chisti, 2007; Scheibel, 2007). Many surfactants and emulsifiers require hydroxy fatty acids, particularly ricinoleic acid from castor oil, and perhaps also, in the future, lesquerolic and dimorphecolic acids from the seed oils of lesquerella and dimorphotheca, potential new crops in the United States and the EU, respectively (Hayes, 2004). Epoxidized seed oils (or their methyl esters), readily prepared from common oils such as soybean, are potentially useful surfactant feedstocks (see Doll and Erhan, "Polyol and Amino Acid-Based Biosurfactants, Builders, and Hydrogels," in this book). In addition to the oil's triglyceride species, methyl ester derivatives, common intermediates in an oleochemical biorefinery due to their use as a biodiesel feedstock (further discussed below), would likely be employed (Ahmad et al., 2007). Sterols, minor components of seed oils, also serve as effective surfactant hydrophobes (Svensson & Brinck, 2003). Furthermore, lignin, a co-product from the conversion of lignocellulosic biomass to biofuels, may be an additional feedstock for a surfactant's hydrophobe (Holladay et al., 2007; Johansson & Svensson, 2001).

Biobased feedstocks may also become more commonly employed as the sources of a surfactant's hydrophilic moiety, particularly for nonionic surfactants. Currently, mono- and disaccharides (and their derivatives: sugar alcohols such as sorbitol and xylitol and oxidation products such as furfuryl and levoglucosanyl compounds), and glycols (produced via fermentation), derived from starches, cellulose, and other naturally-derived polysaccharides, are becoming increasingly popular as "head group" moieties of alkyl glycosides and esters (Werpy & Petersen, 2004). An additional feedstock is glycerine, an inexpensive co-product from the manufacture of biodiesel, a hydrophilic building block of mono- and diacylglycerols, common surfactants in food and cosmetics products (discussed below). In addition, glycerine can be converted into other "head group" moieties: 1,2-propanediol or propylene glycol (1,3-propanediol), the former via a catalytic process—a technological approach under development by Dow, Huntsman, and others—and the latter, 1,3-propanediol, through a fermentation process developed by DuPont Tate and Lyle LLC (Loudon, TN) (Shelley, 2007); and, polyglycerol, through homogeneous or heterogeneous catalysis (Barrault et al., 2004). Amino acids also serve as a feedstock for the hydrophilic moiety (Xia et al., 2001). In addition, amino acids can be converted into ethanolamine and isopropylamine (from serine and threonine, respectively), important intermediates for cationic surfactants (Scott et al., 2007). (See Rosa Infante et al., "Synthesis, Aggregation Properties and Applications of Biosurfactants Derived From Arginine," and Otero, "Selective Enzymatic Synthesis of Alcoholamine Emulsifiers," in this book.) Surfactants with DNA hydrophiles were recently reported (Bilalov et al., 2004; Leal et al., 2006; Xu et al., 2005). Alternatively, renewable resources serve as surfactant feedstocks indirectly by serving as the carbon-energy source of biosurfactant synthesis from microorganisms (Lang, 2003; Lu et al., 2007). (See "Production and Modification of Sophorolipids from Agricultural Feedstocks," Ashby et al., in this book.) Biosurfactants include trehalose esters, rhamnolipids and sophorolipids (see chapters written by Ashby et al. and Pinzon et al. in this book), mannosylerythritol lipids (chapter by Rau and Kitamoto, "Mannosylerythritol Lipids: Production and Downstream Processing"), other glycolipids, phospholipids, and lipopeptides (chapter by McInerney et al.) (Lang, 2003; Lu et al., 2007). For synthetic nonionic surfactants employed today, the major source of hydrophile is polyethylene glycol (or equivalently, polyethylene oxide, or "ethoxylate"), which is derived from petroleum; however, one can potentially derive it from bioethanol through the synthesis of ethylene as an intermediate (Gielen et al., 2008). Ethylene oxide, the starting material, is carcinogenic, mutagenic, highly flammable, volatile, and reactive. Therefore, for the reasons given above, biobased hydrophiles for surfactants and detergents will become more commonly employed. Perhaps polymerization products of bioderived 1,2- or 1,3-propanediol or polyglycerol may become future substitutes.

Motivation for Biobased Surfactants

Since the press time of this book, petroleum crude oil prices have reached their highest levels in recorded history ($140/bbl), and an increased replacement by oleochemical or other biobased feedstocks is being pursued by the surfactants and detergents industry (Phillips et al., 2008). The use of oleochemical feedstocks makes further sense since the production cost per mass for biobased materials is roughly equivalent to petroleum-based materials (U.S. Department of Energy, 1999). The projected growth has already begun; for example, the "[g]lobal crude palm oil output has increased from less than 3 million tonnes in 1974/75 to almost 40 million tonnes in 2006/07, [representing] an average annual growth rate of more than 8%" (Carter et al., 2007). However, before their more extensive utilization can occur, oleochemical feedstocks must become lower in cost, at least equal to that of petroleum-based alternatives, with a lower degree of price fluctuations; and their supply must be more reliable and readily available (Patel, 2004; Schalitz, 2007). In fact, oleochemical prices have soared in recent months. For example, palm, soybean, and corn oils have achieved record-high prices, due in part to the increased demand for biofuels and increased transportation costs (Brasher, 2008; Lewis, 2008; Phillips et al., 2008). But, genetic engineering approaches are anticipated to enhance the supply-related issues in the intermediate-to-long term by leading to an increased yield of oil and the ability to tailor the chemical properties of the oil, such as acyl chain length, to meet product needs (Gressel, 2008; Jambhulkar, 2007).

Another motivating factor is the desire of consumers to purchase eco-friendly products, moreover, commodities that utilize renewable resources, employ sustainable technologies for their manufacture, and result in a low environmental impact (McCoy, 2007a,b; Watkins, 2007). This area currently exists as a "niche market" that targets environmentally-conscious consumers who are willing to pay for higher-priced items that provide more ecological benefits. However, due to increased public concern [and acceptance (Baum, 2008)] of the linkage of increased CO_2 and other greenhouse gas production with climate change and the socioeconomic issues relating to petroleum usage, which in turn will probably lead to increased government-imposed regulations, this market will continue to grow. Many manufacturers are now seeking certification for their products to be labeled as "biobased" or "green" or "eco-friendly" or "sustainable," reflecting a trend of increased cooperation between environmental organizations and manufacturers (McCoy, 2008a). A good description of sustainability, provided by The Natural Step, an environmental nonprofit organization with the mission of integrating sustainability practices into businesses, is: "[n]ature should not be subject to increasing concentrations of substances extracted from the Earth's crust, to high concentrations of substances produced by society, or to physical degradation..." (McCoy, 2008a).

No universal set of standards or definitions exists that one can employ to achieve certification on either a national or international level; moreover, several organizations certify (Table 1.1). However, criteria for certification, even though (in many cases) based partially on International Organization for Standardization protocols ISO 14024 (environmental labels and declarations) and 14001 (environmental management system), differ significantly from each other and change regularly (McCoy, 2008b; Schalitz, 2007). This makes difficult both the job of producers to tailor their products and to decide between certification labels, and comparison shopping for consumers (Coons & Phillips, 2008). In addition, many manufacturers believe insufficient evidence is available to support the claim that biobased surfactants are more degradable than petroleum-based alternatives, particularly if the feedstocks undergo a significant amount of chemical modification (McCoy, 2007a). Furthermore, the increased use of biobased feedstocks can have detrimental environmental effects resulting from the increased acreage of oleochemical-yielding crops—such as deforestation and animal habitat loss, which have already occurred in Malaysia and Indonesia as a result of palm-oil production—and a loss of biodiversity for oilseed-bearing plants (McCoy, 2007a,b; Patel, 2004). However, sustainability certification is also being addressed for feedstocks to prevent the occurrence of such events. The Roundtable for Sustainable Palm Oil serves as an example (Roundtable for Sustainable Palm Oil—RSPO, 2008).

An important aspect of eco-friendliness is reduced environmental impact. Several environmentally-related issues are facing the surfactants and detergents industry that may be effectively addressed by using biobased surfactants (Table 1.2). The need to replace alkylphenyl ethoxylates (APEs), nonionic surfactants commonly used in cleaning products, was accelerated by the recent decision of Walmart to place APEs on a list of "chemicals of concern" that its laundry product suppliers must replace before 2010 (McCoy, 2007a) and by the request of the Sierra Club (Washington, DC) to the U.S. EPA (Environmental Protection Agency) to ban the use of APEs (Sissell, 2007). Linear and branched alkyl ethoxylates, which one can manufacture from petroleum and/or biobased feedstocks, are the leading substitution candidates (McCoy, 2007a). The increased demand for cold water laundry detergents will provide an opportunity for the use of methyl ester sulfonates (MESs), which are derived from fatty acid methyl esters (FAMEs) (described below) (Roberts et al., 2008). For

Table 1.1. Certification Labels for Biobased Surfactants

Name of certification	Product type
BioPreferred (U.S. Dept. Agriculture, Ames, IA)	Household, industrial cleaning, and laundry products
CleanGredients (GreenBlue, Charlottesville, VA) [a]	Surfactants for household cleaning and laundry products
Design for the Environment (DfE; U.S. Environmental Protection Agency, Washington, DC)	Household and industrial cleaning products
EcoCert (L'Isle Jourdain, France)	Detergents, cosmetics
EcoLogo (Environmental Choice Program, Ottawa, Canada)	Industrial and household cleaning products
EU Flower/Eco-Label (European Union, Ivry-sur Seine, France)	Household and industrial cleaning products
Green Seal (Washington, DC)	Cleaning products and paints/coatings
GREENGUARD (Greenguard Environmental Institute, Marietta, GA)	Indoor air quality
Leadership in Energy and Environmental Design (LEED; U.S. Green Building Council, Washington, DC)	Industrial cleaners
Nordic Swan (Nordic Ecolabelling Board, Stockholm, Sweden)	Household and industrial cleaning products

[a] Does not certify, but provides a reference database of "green" and biobased ingredients. available for formulators.

example, the Japanese oleochemical manufacturer, Lion, is manufacturing MES to include in the formulation of the Care Coldwash product by Danlind (Holstebro, Denmark) (McCoy, 2008b). The growing demand for more concentrated liquid laundry detergents, also driven by Walmart's specifications, may lead to the increased use of short-chain alkyl polyglucosides (described below) to provide cleaning activity while enhancing the solubilization of other ingredients in the concentrated solution (Watkins, 2007). Furthermore, a recent report states that "[i]n the last few years, oleochemical surfactants have contributed more to the development of compact detergents and the reduction of washing temperatures than petrochemical surfactants have" (Patel, 2004). Phosphates, used as "builders" for laundry detergents, help inactivate hard water cations, provide pH buffering, and prevent redeposition of dirt; however, their bioaccumulation in waterways leads to a temporary surge of algal and bacterial growth, followed by oxygen depletion due to the thick "slime" layer that forms at the water–air interface which blocks oxygen and light transport from the air. This results in the loss of life for fish and aquatic wildlife and a source of drinking water. (Further information is given in Doll and Erhan, "Polyol and Amino Acid-Based Biosurfactants, Builders, and Hydrogels" in this book.) Recent industrial practice has involved replacing phosphates with a blend of nonionic ethoxylated/propoxylated fatty alcohol surfactants (Plurafac; BASF, Ludwigshafen, Germany), chelation agents, and hydrophilic polymers (McCoy, 2007a). Biobased amino acid derivatives may be important detergent builders as well (see chapter by Doll and Erhan). Regarding the need to replace solvents in cleaning products, several companies are developing blends of nonionic and cationic surfactants to replace ethylene glycol butyl ether, a volatile organic compound commonly used in spray cleaners.

Table 1.2. Environmental Goals for the Surfactants and Detergents Industry

Environmental goal	Rationale
Reduce carbon-dioxide emissions	Reduce climate change
Replacement of alkylphenyl ethoxylates (APEs)	Produce toxic biodegradation products; may promote reproductive problems
Use of cold-water-compatible laundry detergents	Reduce household-energy consumption
Increased concentration of liquid laundry detergents	Reduce packaging and shipping costs
Replacement of phosphates and zeolites as builders for dishwasher detergent	Reduce phosphate eutrophication in lakes and rivers; zeolites are nondegradable solids
Replacement of formaldehyde-releasing biocides	Nasopharyngeal cancer agent
Replacement of solvents (e.g., ethylene glycol butyl ether in spray cleaners)	Decrease volatile organic compounds; possible asthma agent
Replacement of quaternary ammonium compounds	Possible asthma agent

McCoy, 2007a,b; Watkins, 2007.