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Surfactants Based on Natural Fatty Acids

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1.1 Introduction and History

Over the last 50 years or so consumer awareness and concern for the environmental impact of various household products has steadily increased, and contributed to consumer preferences in choosing, for example, soaps, detergents, cleaners and so on. Initially this concern was driven by the visible effects of certain products on the environment, for example river water. However, in recent years the interest has moved to the products' global effect on the environment and the 'total carbon load' has become an issue. In combination with the sharp increases in price and the competition for petroleum products, the economic importance of renewable or biological raw materials for the chemical industry has increased. This trend has been most visible in the energy and fuel sector, where the capacity for production of renewable products has increased dramatically. It has also manifested itself in the production of bioplastics. The detergent industry has also in the last decades increasingly turned its attention to natural raw materials to replace petrochemical products, either as hydrophilic or hydrophobic building blocks. Hydrophilic building blocks have been chosen from many different sources, for example sugars, amino acids, cellulose and other carbohydrates (as illustrated in many of the chapters of this book). Even though natural fats and their derivatives are common feed stocks of the detergent industry, efforts to find new hydrophobic materials have increased, mainly because of an awareness that natural hydrophobic compounds can yield properties that are not easily achieved through conventional synthesis from petrochemical products.

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An interesting line of development is the use of unsaturated bonds in fatty acids for simple chemical modification to obtain bulkiness in the hydrophobic moiety of the surfactant [1].

Parallel to the growth of the petrochemical industry, the fats and oils industry has grown, and oleochemistry has become an important area of research and technology in several institutions and industries over the years. A large variety of products based on fats and oils have been developed since then, for different uses, such as low-fat spreads and drinks, emulsifiers and functional food ingredients and specialties for cosmetic and personal care applications [2]. These technological advances have also expanded the possibilities of using derivatives of fats and oils for surfactant synthesis.

The availability of oleochemicals has traditionally been dependent on the food and feed industry, where the oils and fats can be found as side-products (e.g. tallow, soya oil, fish oil) or main products (e.g. oils from rapeseed). The recent years' quest for alternative fuels based on fats and oils has led to an increased production and availability of high-quality oleochemicals for nonfood purposes, typically as methyl esters of fatty acids. The increasing demand, in combination with advances in genetics, biotechnology, process chemistry and engineering, are leading to a new or, rather, a return to an old manufacturing concept for converting renewable biomass to valuable fuels and products, generally known as the *biorefinery* concept. The gradual integration of crop-based materials and biorefinery manufacturing technologies offers a potential for new advances in sustainable biomaterial alternatives [3]. There is increased interest in reassessing and developing the biological materials in several fields of application, for example epoxidized oil as plasticizers and stabilizers for vinyl plastics [4], biobased materials [5, 6], reactive diluents [7, 8], surfactants [9], lubricants [10] and printing inks [11]. In this respect the interest has increased in developing new crops and varieties of old crops with higher yields and better performances in the production and final properties. Furthermore, it has become important to evaluate the environmental impact of bio-based products with respect to their entire life cycle, demonstrating that the choice of the raw material often turns out to be an important parameter influencing the life cycle performance [12].

This chapter will cover recent developments in the production, use and characterization of fatty acids and their derivatives as surface-active materials. However, the chapter will be limited to surfactants where the original, native, fatty acid plays an evident role in the properties of the surfactant and will not include the many surfactant classes in which the hydrocarbon backbone or carboxylic group have been modified (e.g. by epoxidation, hydrogenation, amidation) or where the surfactant properties are mostly decided by the variations in the polar head group (e.g. carbohydrate derivatives, amino acids).

1.2 Fats and Oils as Raw Materials

Most fatty acids are obtained by hydrolysis of oils from various oleochemical sources (animal, marine and plant) and the composition of fatty acids in the oil is determined by its origin and production method. An exception to this is the widely used tall oil fatty acid products, obtained as free fatty acids together with rosin acid from paper pulping. Animal sources, for example lard and tallow, are characterized by high concentrations of saturated fatty acids, while marine sources (fish oils) are characterized by long-chain and unsaturated acids. The fatty acid composition of oils from plant sources varies greatly

Table 1.1 *Typical concentrations of different fatty acids in oils from commercially available variants of common oil crops*

	Palmitic acid C16 : 0	Stearic acid C18 : 0	Oleic acid *cis*C18 : 1	Linoleic acid *cis,cis*C18 : 2	Linolenic acid C18 : 3	Other
'Normal' rapeseed	6		60	21	10	
High erucic rapeseed	4		11	12	9	
'Normal' linseed	10		18	14	58	
Tall oil (Scandinavian)	1	2	30	45		Pinolenic 9% Conjugated C18 : 3 5%
Conventional sunflower	12		19	68		
High oleic sunflower	7		83	10		
Conventional soya bean	15		23	54	8	
Palm oil	55	2.5	30	10		
Tallow	27	33	40	3		

Data collated from References [18] to [20].

depending on the plant origin and cultivar. Commercially exploited seeds such as soya, rape and sunflower have been the subject of many years of breeding programmes to obtain oils with particular fatty acid patterns. The fatty acid composition of a selection of fats and oils can be found in Table 1.1. In addition to breeding efforts on traditional oil crops, work is being done to domesticate alternative oil-rich plants that may yield new, potentially useful, fatty acids [16]. Furthermore, plants and organisms can also contain fatty acids with more unusual functionalities, such as conjugated alkenes, alkyne, epoxy and hydroxyl groups [17]. These unusual fatty acids have been classified by Spitzer [18], but the plants and organisms containing them are not domesticated and the oils and fats are only available in small quantities. However, the genes responsible for the synthesis of some of these have been identified and to some extent transferred to agriculturally useful crops [19, 20]. Modern crop development and genetic engineering approaches may, in the future, contribute to an even greater range of hydrophobic materials available for surfactant synthesis, and an increased need for basic studies of surface-active properties of fatty acids.

Traditionally, industrial oleochemistry has concentrated predominantly on exploiting synthetic methods applied to the carboxylic acid functionality of fatty acids, and less than 10% of the modifications have involved the hydrocarbon backbone of the fatty acid [21]. However, the continued development of oleochemistry opens up for several reaction routes involving selective transformation of the alkyl chain, for example epoxidation, sulfonation, with the potential of producing new highly-branched and charged hydrophobes from abundant natural material [15].

1.3 Fatty Acid Soaps

In the fat-splitting process, fats and oils are hydrolysed to glycerol and fatty acid. Prior to saponification the fatty acids can be purified by, for example, distillation in a specific fraction. Soaps of fatty acids are subsequently produced by the neutralization with various bases, resulting in a acid–soap salt with different positively charged counterions, for example Na, K, NH_4. In contrast to the fatty acids, the soaps are generally water soluble and display strong surfactant properties. The solubility and surface-active properties can be tuned by the nature and combination of fatty acids, counterions and the extent of polarization.

The surface activity and adsorption of fatty acids from a bulk solution to an interface is important in various applications, most importantly in personal cleansing applications where a small amount of the original fat is generally considered to have a beneficial effect on skin. The ability of fatty acid soaps to adsorb selectively to solid particles in aqueous solution is used in many applications, for example lubrication [22], flotation de-inking of paper [23] and purification of minerals [24]. The surface chemical aspects of the process of de-inking has been reviewed by Theander and Pugh [25]. The strong tendency of fatty acids to adsorb to liquid and solid surfaces is a topic of great interest for the more fundamental study of fatty acids. Their behaviour as a two-dimensional monolayer at the air–water interface (Langmuir films) or deposited on a substrate (Langmuir–Blodgett films) display a very rich phase transition behaviour and have been taken as potential models for biological membranes [26] or for fabrication of reliable electronic devices [27].

Many different techniques have been used and developed to study the phase behaviour and association at these monolayers [28, 29]. A large amount of studies have been carried out with various X-ray techniques, and the latest information on ordering and phase behaviour in monolayers using this and other methods have been reviewed by, among others, Schlossman and Tikhonov [30] and Duwez [31]. Dutta [32] surveyed some of the currently available experimental evidence regarding backbone ordering and order–disorder transitions in fatty acid monolayers. Ignes-Mullol *et al.* [33] discussed the rheological responses of the monolayer following various forcing processes.

When the straight-chain fatty acid structure is disturbed the ordering at the monolayer, and the properties, are also significantly altered. Several studies have also been published reporting the effect on the ordering as the fatty acid structure is disrupted by one or several alkyl groups [34], hydroxyl groups [35, 36] or unsaturations [37]. An example of this is the study by Siegel *et al.* [38] on the effect of the OH-group position of hydroxypalmitic acids on the monolayer characteristics. By coupling the results of surface pressure-area isotherm measurements and Brewster angle microscopy (BAM) they were able to demonstrate variations in the temperature dependence, as well as in the long-range orientational order. In the case of OH-substitution near the COOH head group ($n = 2$ or 3), irregular domain growth occurred while at OH-substitution in or near the mid-position ($n = 9$) of the alkyl chain, where regular patterning of the domains indicates high ordering. Alonso and Zasadzinski [39] measured the two-dimensional surface shear viscosity of fatty acid monolayers of different chain lengths. They demonstrated that the viscosity can increase by orders of magnitude at phase boundaries associated with tilted to untilted molecular order, providing that the underlying order is semicrystalline. Hence, untilted, long-range ordered phases are the most viscous films (see Figure 1.1). The association behaviour and adsorption to surfaces in liquids, both in pure water and organic solvents, have been studied by several workers [40–42]. Neys and Joos [43] performed very precise measurements of the surface adsorption of aqueous solutions of a homologous series of fatty acids. Additional information about the behaviour at

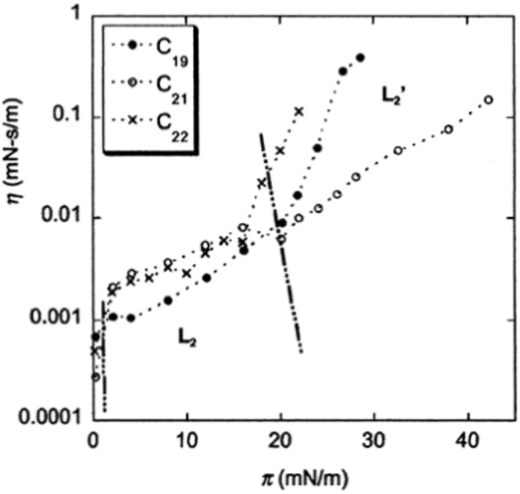

Figure 1.1 *Comparison of the surface shear viscosity η measured as a function of surface pressure for nonadecanoic (C19) at 30 °C, heneicosanoic (C21) at 25 °C and behenic acid (C22) at 20 °C. The temperature of each experiment was adjusted for the monolayers to undergo a transition from a tilted phase (L_2) to an untilted ($L_{2'}$) phase at approximately the same surface pressure. Dashed lines denote phase boundaries. In both the L_2 and $L_{2'}$ phases, the surface viscosity increases exponentially with surface pressure and, hence, with decreasing molecular tilt.*

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the oil–water interface was obtained by Yehia [44], who found that the heat resistance through a monolayer of fatty acids/alcohols at an oil–water interface reaches a minimum at maximum packing of the species at the monolayer.

The relevance of these studies to the behaviour of other surfactants strengthens as the fatty acids become ionized and turn to soaps with an increasing pH. This transition, and its effect on surface-active properties, has consequently been subject to several studies. At low pH values, the predominant molecule is the undissociated fatty acid. At intermediate values (pH 4–8), undissociated acid, anionic carboxylates as well as so called acid soaps, $(RCOO)_2H^-$, coexist in the system. At alkaline pH, carboxylate anions and acid–soap salts, $(RCOO)_2HNa$, dominate the solution and the surface layer [45]. This change in chemical composition causes changes in the steric, electrostatic and bonding interactions between the molecules at the surface, which can be noticed as several phase transitions in the monolayer [46]. Miranda *et al.* [47] investigated the interactions between water and fatty acids as the monolayer changes from neutral to negatively charged soaps and concluded that the fatty acid monolayer is half-ionized at a pH as high as 10.5–12, as compared to the pK_a of acids in bulk water of 4.9. This was attributed to the locally higher pH at the interface, resulting from a higher concentration of protons at the surface, induced by the surface electric field. Wen and Lauterbach [48] measured the density, the molecular level structure and conformation of myristate or myristate/myristic acid monolayer at the air–water interface. At the intermediate pH (pH 9) it was concluded that the adsorbed monolayer contains not only myristate but also substantial amounts of myristic acid. By titrating a homologous series of C18 fatty acids with varying degrees of unsaturation, Kanicky and Shah [49] could conclude that the pK_a was related to the melting point of the fatty acid and area per molecule at the monolayer. The order of these pK_a values were in the same order as area per molecule values of the fatty acids in spread monolayers. This suggests that as area per molecule increases, the intermolecular distance increases and pK_a decreases due to reduced cooperation between adjacent carboxyl groups. Additionally, the same scientists [50] studied how the ionization of fatty acid varied with concentration. Below the critical micelle concentration (CMC), the value of pK_a was found to decrease as the solution was diluted to a lower concentration. Thus, it was concluded that this reduction in pK_a, even at concentrations well below the CMC, is attributed to the effect of submicellar aggregates on the ionization of the polar head group, leading to higher pK_a as compared to that of soap monomers. Mixing of soap molecules of unequal chain length decreases the pK_a of the solution as compared to that of the two individual components because of disorder produced by the unequal chain length. Kralchevsky *et al.* [51] studied how the natural pH and surface tension isotherms of sodium dodecanoate (laurate), $NaC1_2$, and sodium tetradecanoate (myristate), $NaC1_4$, solutions depend on the surfactant concentration at several fixed concentrations of NaCl. Depending on the surfactant concentration, the investigated solutions contain precipitates of definite stoichiometry of alkanoic acids and neutral soaps. The analysis reveals that the kinks in the surface tension isotherms of the investigated solutions correspond to some of the boundaries between the regions with different precipitates in the bulk. The information of the precipitation behaviour and equilibrium between different forms of the acid–soap complex in dilute and concentrated solutions is important for the understanding of bulk properties of soaps in various products, e.g. bars, detergents and liquid cleansing products.

The changing degree of ionization and packing behaviour of soaps as the pH in the solution varies can be observed in many properties of practical relevance. The pH- and pK_a-related phenomena of fatty acid behaviour and their technological applications were described by Kanicky *et al.* [52]. They found that optimum properties in various properties (foam height and stability, bubble lifetime, contact angle, water evaporation rate) were observed at a pH very near the pK_a of sodium laurate at concentrations below the CMC (Figure 1.2). Based on these observations, they proposed that at the pK_a a maximum ion dipole interaction takes place between ionized and unionized species, leading to a minimum in the area per molecule and an optimum in many properties. Similarly, Somasundaran and co-workers [53] found that the flotation of hematite with weakly anionic collectors, such as oleic acid, displays a distinct maximum at a pH of around 8. When the pH is decreased the presence of undissociated acid and acid–soap complexes increases significantly, leading to an increased surface activity of the oleate species and an improved flotation. If the pH is further decreased to the acidic region, the presence of the ionic soap and acid–soap complexes decreases while that of the undissociated acid remains the same, resulting in a decrease in the hematite flotation and an increase in surface tension. Therefore, the greatest number of surface-active species exists in the neutral pH range.

More recently, Novales *et al.* [54] reported the effect of organic counterions on dispersions of a fatty acid and hydroxyl-derivative salts in aqueous solutions that were

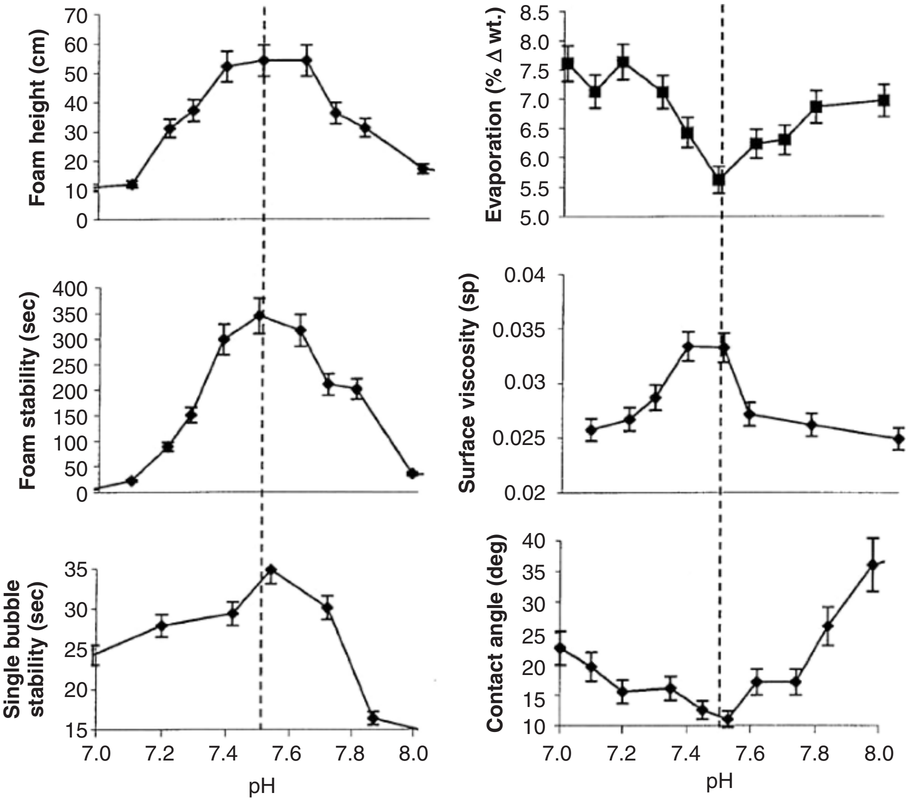

Figure 1.2 Diagrams depicting maxima and minima in various interfacial properties, with respect to pH, of a sodium laurate solution.

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further used to produce foams and emulsions. The tetrabutyl-ammonium salts of palmitic acid, 12-hydroxy stearic acid and 8-hydroxy palmitic acid formed isotropic solutions of micelles, whereas the ethanolamine salts of the same acids formed turbid, birefringent, lamellar solutions. This polymorphism demonstrated the effect of a hydroxyl group within the hydrophobic core layer. Foams and emulsions produced from ethanolamine salt solutions were more stable than those obtained from tetrabutyl-ammonium salt solutions. These results were explained in terms of counterion size, lipid molecular shape and the formation of hydrogen bonds between lipids in the core of the micelles.

Soap is generally not toxic to aquatic organisms. Reported EC50 values of laurates for algae, fish and *Daphnia* are 53.0, 11.0 and 10.2 mg/l, respectively [55]. As the solubility of soap is lower in environmentally relevant waters than well water, the bioavailability of soap is generally lower in environmentally relevant waters. Thus, it is generally accepted that soap is even less toxic in aquatic environments than under laboratory conditions using clean water [56].

1.4 Polyethylene Glycol Fatty Acid Esters

Direct ethoxylation of fatty acids and fats with conventional catalysts yields a complex mixture of mono- and diesters, as well as various polyethylene glycols as by-products, with a wide range in the number of polyethylene glycol units. Despite the inhomogeneity of the composition of the final product, they have found a wide use as emulsifiers in food, feed and technical applications and detailed studies of their emulsification and solubility/dispersibility properties have been carried out [57–59].

The disadvantages of direct ethoxylation have, from the late 1980s onwards, been resolved. Based on experiences of narrow-range ethoxylation catalysis, new catalysts have been developed that enable a direct ethoxylation of short-chain alkyl esters of fatty acids. Cox and Weerasooriya extensively described this alkoxylation technology and the properties of ethoxylated methyl esters of various fatty acids in a series of papers [60–62]. The difference in distribution of ethyleneoxide units between a fatty acid methyl ester ethoxylated with a conventional hydroxide catalyst or a more active Ca/Al catalyst was shown to be drastic (see Figure 1.3, from Reference [61]). The distribution is slightly peaked and the amount of unreacted fatty acid methyl ester significantly reduced. Thratnig [63] later described how a similar effect in the distribution of ethylene oxide (EO)units can be obtained with ethoxylation of fatty acids rather than the methyl ester. Furthermore, the technique has also been shown to be applicable to ethoxylation of several types of fatty acid esters like triglycerides or branched alkyl esters [62, 64], as well as for propoxylation of fatty acid esters [65]. Alejski *et al.* [66, 67] and Bialowas and Szymanowski [68] have contributed to the understanding of how the oxyethylation reaction of fatty acid methyl esters proceeds in stepwise incorporation of the ethylene oxide units. In particular, the ethoxylation of inexpensive methyl esters of common oils like that of rapeseed oil (rapeseed oil methyl ester, or RME) have been attractive, because of the increasing production of this ester as a biodiesel alternative in Europe [69, 70].

Several researchers have described properties of methyl ester ethoxylates [64, 70]. In general, polyoxyethylene esters of fatty acid methyl esters have been found to have good emulsifying, lubricating, dispersing and suspending power and these properties, combined with detergent and antistatic characteristics, provide a potential in a variety of textile processing applications. Good wetting, penetrating and dispersing properties have made them useful in adjuvants in agricultural products [71]. A comparison between fatty acid methyl ester ethoxylates and the corresponding range of alcohol ethoxylates, shows that the CMC is somewhat higher and surface tension at CMC lower for the methyl ester ethoxylates [72]. The methyl terminating EO chain leads to a lower foam profile and a lowering of the cloud points by approximately 10 °C [65]. However, the dishwashing capacity is not so good, due to the low solubilization ability of fats and the low foaming. Nonetheless, Renkin *et al.* [70] reported that the washing performance of rapeseed oil methyl ethoxylates with seven EO units in a laundry formulation could be considered as the equivalent of lauryl alcohol ethoxylates with the same number of EO units. Likewise, Littau and Miller [73] described the benefits of mixing the fatty acid methyl ester ethoxylate with conventional nonionic and anionic surfactants to achieve optimum performance in hard surface cleaning. Hama *et al.* [74] established structure–property

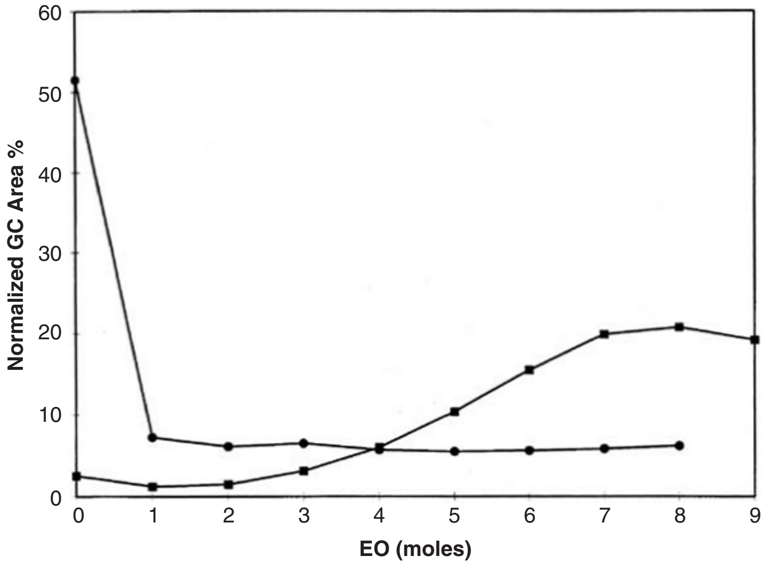

Figure 1.3 *Distribution of ethylene oxide units for tetradecyl methyl ester ethoxylates prepared with conventional catalyst (NaOH) and proprietary catalyst: -●-, conventional catalyst, -■-, proprietary catalyst.* Reproduced with kind permission from Springer Science + Business Media: *J Am Oil Chem Soc.*, Methyl ester ethoxylates, **74**, 1997, 847–859, MF Cox and U Weerasooriya.

relationships by varying fatty acid structure and amounts of EO. Ethoxylated methyllaurate with approximately 60–70% ethyleneoxide was found to be the most suitable as a base surfactant for household detergents.

Various tests have showed that methyl ester ethoxylates have an improved mildness to human skin compared to ordinary alcohol ethoxylates [62, 64]. From the standpoint of environmental properties, fatty acid methyl ester ethoxylates are readily biodegradable and an order of magnitude less toxic than alcohol ethoxylates [70, 75]. However, the beneficial environmental properties, such as rapid biodegradability, also have the drawback of a poorer hydrolytic stability, particularly in high alkaline or acid conditions. After 80 days at 40 °C there was a 4% decomposition at pH 7 and 13.5% at pH [61]. In a typical laundry detergent formulated in the range pH 8.5–10, the hydrolysis after two months' storage is insignificant [70].

1.5 Polyglycerol Fatty Acid Esters

An attractive alternative to ethoxylation, from an environmental point of view, is the possibility of using natural glycerol as the hydrophilic part of the fatty acid surfactant. Partially hydrolysed triglycerides, with one glycerol moiety, represent the most widely used surfactant of this kind, found as emulsifiers in many food and cosmetic products. In addition to these, polyglycerol fatty esters produced through a condensation reaction of fatty acids or partial glycerides with glycerol have been the attention of many studies. However, like the direct ethoxylation described above, this condensation reaction gives rise to a broad distribution in the hydrophilic head group, as well as a distribution of a number of fatty acids attached to the hydrophilic group and various glycerol oligomers as by-products. Hence, the product will consist of many different constituents.

Ishitobi and Kunieda [76] have investigated the effect of the oligoglycerol distribution on the phase behaviour, comparing one product with a broad distribution and one with a more narrow distribution. The phase diagram revealed a micellar region and a hexagonal phase at higher concentrations for both products. The more narrow-range product formed hexagonal phases at higher concentrations, has a higher cloud point, higher surface tension at corresponding concentrations and is a less efficient emulsifier. All effects are explained by the fact that the product with the broader distribution has a smaller effective cross-sectional area per hydrophobic chain and thus can pack more tightly in the interfaces. The challenge of studying these surfactants due to the variation in composition was also addressed by Duerr-Auster *et al.* [77]. They found that a commercial mixture of polyglycerol fatty acid esters (from palmitic and stearic acid) in water formed a lamellar morphology over the whole concentration range investigated. However, it was also found that the commercial mixture contained small amounts of unreacted fatty acid, in a dissociated, anionic, state. This small impurity had a pronounced stabilizing effect on the gel phase. In addition, the phase behaviour of commercial tetraglycerol [78], pentaglycerol [79] and decaglycerol fatty acid esters [80] have been reported.

In contrast, Kato *et al.* [81] prepared a series of purified polyglycerol monolaurates (C12Gn, with n = 2, 3, 4, 5). The phase behaviour and surfactant properties of these were compared with those of n-dodecyl polyoxyethylene monoethers (C12EOn) to examine the function of the hydrophilic part of these compounds. The surfactants followed similar trends in properties like the CMC, surface area at interface, detergency, foam height and stability. However, the foam heights of the glycerol-based surfactants were consistently higher and more stable than those of C12EOn. It was concluded that important surfactant properties, for example detergency, of polyglycerol monolaurates having few glycerol units (di- to tetraglycerol monolaurates) were on the same level as those of C12EOn having more oxyethylene units (hexa- and octaoxyethylene) (see the example in Figure 1.4). If the fatty acid chain is further increased to stearic acid (C18), the surfactant loses water solubility and forms a stable monolayer at the air–water interface [82].

Diglycerol esters of saturated fatty acids have recently been extensively studied by Shrestha and co-workers in both aqueous [83] and nonaqueous [84, 85] systems. The phase behaviour of caprate (C10) and laurate (C12) esters in water were found to be quite different from the solution behaviour of the myristate (C14) and palmitate (C16) esters (see Figure 1.5). In the former, a lamellar liquid crystal phase is present in the surfactant-rich region and it absorbs a substantial amount of water. The melting temperature of this phase is practically constant in a wide range of compositions. For the more hydrophobic surfactant the phases with solids and the extent of water solubilization are increased.

To conclude, polyglycerol fatty acid esters are edible nonionic surfactants, and, in combination with their low solubility in water and high surface activity, many of them are of interest as emulsifiers, dispersants, solubilizers, rheology modifiers in drugs, cosmetics or as specific food ingredients where controlled release is the goal (fragrances, flavourings) [86]. The capability of forming stable α-gel phases makes them useful as stabilizing foams and emulsions in food products [87]. However, like the previously

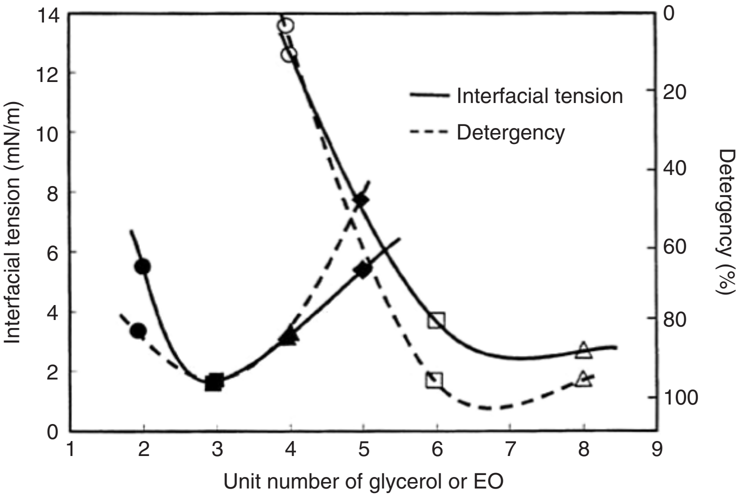

Figure 1.4 *Plots of the interfacial tension of corn oil/surfactant solutions and detergency as a function of the number of glycerol or oxyethylene (EO) units of polyglycerol laurate (filled symbols) and polyoxyethylene lauryl ether (open symbols).*

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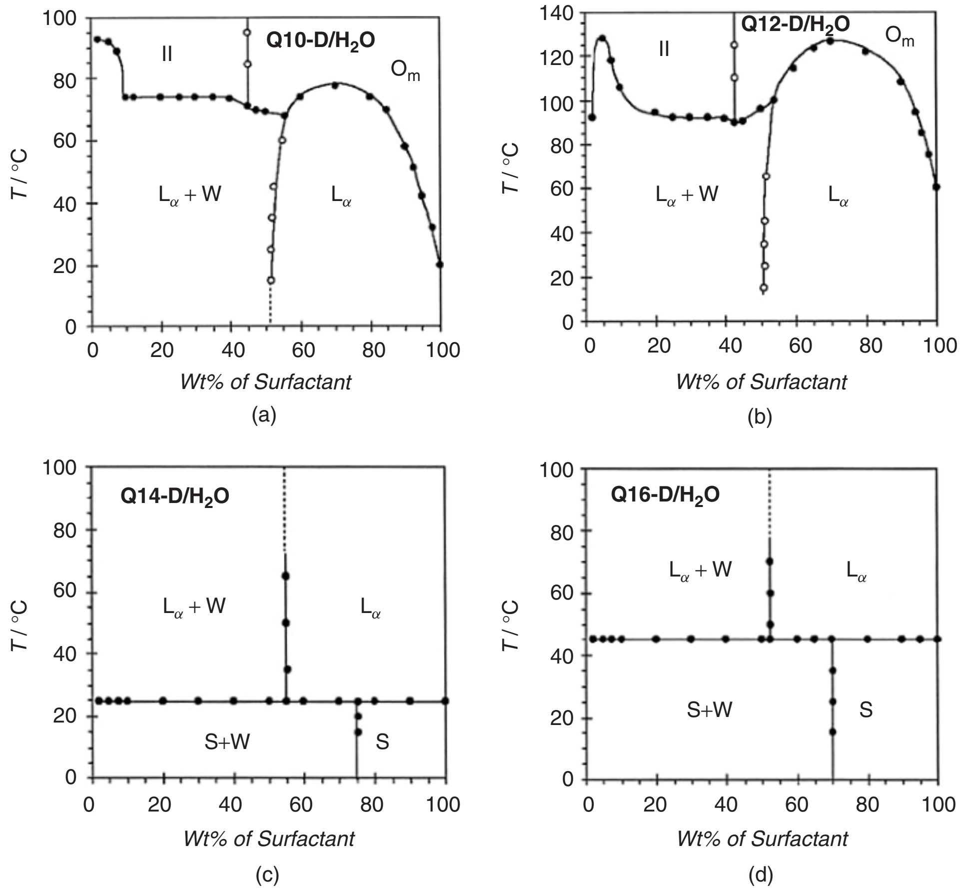
described esters of polyoxyethylene and fatty acid they are susceptible to hydrolysis in strong acid and alkaline environments.

1.6 Conclusions

As is evident from this review, the amount of work being done concerning fatty acids and their derivatives is immense. If the increasing interest in renewable sources for energy purposes in recent years can be combined with a sustainable cultivation and processing, it is expected that fatty acids will continue to grow as a widely available stock for detergents. To understand fully the behaviour and properties of surfactants derived from these fatty acids it is important to expand the studies also of more fundamental properties, such as the association behaviour of fatty acids in Langmuir films. These will, for example, show how basic information of the dissociation behaviour of soaps can be related to practical properties such as foaming and detergency. Another example is the formation of soap–acid complexes and precipitates at higher concentrations and the behaviour of common soap bars.

To overcome the problems with poor solubility in hard water or in the presence of salts and other ions, fatty acids have been used in a rich variety of reactions with polar compounds to produce many different types of surfactants. In this respect, an illustration of the slightest modification would be simple esterification with polar compounds to achieve surfactancy. The simplest of these esters are represented by the polyoxyethylene and glycerol esters. These are characterized by a good biodegradability, low toxicity and mildness to skin, making them useful in cleansing products, agriculture, food and feed



(a) (b) (c) (d)

Figure 1.5 *Binary phase diagrams of diglycerol esters of fatty acids in water: (a) caprylate ester (C10), (b) laurate ester (C12), (c) myristate (C14), (d) palmitate (C16) (L_α = lamellar liquid crystals, W = excess water, II = two-liquid phase region, Om = isotropic reverse micellar solution, S = solid).*

L. K. Shrestha *et al.*, Aqueous phase behavior of diglycerol fatty acid esters, *Journal of Dispersion Science and Technology*, **28**, 2007, 883–891. Reproduced with permission from Taylor & Francis Group, http://www.informaworld.com.

formulations. However, the industrial synthesis of these has not been straightforward, yielding numerous side-products and a distribution of components. The recent years' discovery of a new catalyst for ethoxylation of fatty acid methyl ester has opened up the production of these types of products.

A drawback with ester-based surfactants are their susceptibility to hydrolysis if stored in aqueous formulations. The extent of this problem is not completely clear, but has to be kept in mind for any application of these surfactants. A way to overcome this is to convert the acid to an amide. The properties of this type of surfactant is the topic of another chapter in this book.

References

1. Holmberg, K. (1996) Unsaturated monoethanolamide ethoxylates as paint surfactants. *Prog. Colloid Polym. Sci.*, **101**, 69–74.
2. Hill, K. (2007) Industrial development and application of biobased oleochemicals, *Pure Appl. Chem.*, **79**, 1999–2011.
3. Vemula, P. K. and John, G. (2008) Crops: a green approach toward self-assembled soft materials. *Acc. Chem. Res.*, **41**, 769–782.
4. Bouchareb, B. and Benaniba, M. T. (2008) Effects of epoxidized sunflower oil on the mechanical and dynamical analysis of the plasticized poly(vinyl chloride). *J. Appl. Polym. Sci.*, **107**, 3442–3450.
5. Jin, F. L. and Park, S. J. (2008) Thermomechanical behaviour of epoxy resins modified with epoxidized vegetable oils. *Polym. Int.*, **57**, 577–583.
6. Hong, C. K. and Wool, R. P. (2005) Development of a bio-based composite material from soybean oil and keratin fibres. *J. Appl. Polym. Sci.*, **95**, 1524–1538.
7. Stenberg, C., Svensson, M., Wallström, E. and Johansson, M. (2005) *Surf. Coat. Int. B: Coat. Trans.*, **88**, 119–126.
8. Johansson, K. and Johansson, M. (2007) Fatty acid methyl esters as reactive diluents in coil-coatings. *Polym. Prepr.*, **48**, 857–858.
9. Piispanen, P. S., Persson, M., Claesson, P. and Norin, T. (2004) Surface properties of surfactants derived from natural products. *J. Surf. Detergents*, **7**, 147–159.
10. Sharma, B. K., Perez, J. M. and Erhan, S. Z. (2007) Soybean oil-based lubricants: a search for synergistic antioxidants. *Energy Fuels*, **21**, 2408–2414.
11. Hutchinson, G. H. (2002) Ink technology past, present and future. *Surf. Coat. Int. B: Coat. Trans.*, **85**, 169–176.
12. Hatti-Kaul, R., Tornvall, U., Gustafsson, L. and Borjesson, P. (2007) Industrial biotechnology for the production of bio-based chemicals – a cradle-to-grave perspective. *Trends Biotechnol.*, **25**, 119–124.
13. Biermann, U., Friedt, W., Lang, S. *et al.* (2000) New syntheses with oils and fats as renewable raw materials for the chemical industry. *Angew. Chem. Int. Ed.*, **39**, 2206–2224.
14. Gunstone, F. D. (1997) Major sources of lipids, in *Lipid Technologies and Applications* (eds F. D. Gunstone and F. B. Padley), Marcel Dekker, Inc., New York.
15. Firestone, D. F. (ed.) (1999) *Physical and Chemical Characteristics of Oils, Fats and Waxes*, AOCS Press.
16. Smith, N. O., Maclean, I., Miller, F. A. and Carruthers, S. P. (1997) Crops for Industry and Energy in Europe, European Commission, DG XII E-2, Luxembourg.
17. Metzger, J. O. and Bornscheuer, U. (2006) Lipids as renewable resources: current state of chemical and biotechnological conversion and diversification. *Appl. Microbiol. Biotechnol.*, **71**, 13–22.
18. Spitzer, V. (1999) Screening analysis of unknown seed oils. *FETT-LIPID*, **101**, 2–19.
19. Dyer, J. M., Stymne, S., Green, A. G. and Carlsson, A. S. (2008) High-value oils from plants. *Plant J.*, **54**, 640–655.
20. Dyer, J. M. and Mullen, R. T. (2005) Development and potential of genetically engineered oilseeds. *Seed Sci. Res.*, **15**, 255–267.
21. Hill, K. (2000) Fats and oils as oleochemical raw materials. *Pure Appl. Chem.*, **72**, 1255–1264.
22. Zhang, P., Xue, Q., Du, Z. and Zhang, Z. (2000) The tribological behaviour of LB films of fatty acids and nanoparticles. *Wear*, **242**, 147–151.

23. Borchardt, J. K. (1997) The use of surfactants in de-inking paper for paper recycling. *Curr. Opin. Colloid Interface Sci.*, **2**, 402–408.
24. Quast, K. B. (2000) A review of hematite flotation using 12-carbon chain collectors. *Miner. Engng*, **13**, 1361–1376.
25. Theander, K. and Pugh, R. J. (2004) Surface chemicals concepts of flotation de-inking. *Colloids Surf. A: Physiochem. Engng Aspects*, **240**, 111–130.
26. Edidin, M. (2003) Lipids on the frontier: a century of cell-membrane bilayers. *Nat. Rev. Molec. Cell Biol.*, **4**, 414–418.
27. Akkerman, H. B., Blom, P. W. M., de Leeuw, D. M. and de Boer, B. (2006) Towards molecular electronics with large-area molecular junctions. *Nature*, **441**, 69–72.
28. Loste, E., Díaz-Martí, E., Zarbakhsh, A. and Meldrum, F. C. (2003) Study of calcium carbonate precipitation under a series of fatty acid Langmuir monolayers using Brewster angle microscopy. *Langmuir*, **19**, 2830–2837.
29. Teixeira, A. C. T., Fernandes, A. C., Garcia, A. R. *et al.* (2007) Microdomains in mixed monolayers of oleanolic and stearic acids: thermodynamic study and BAM observation at the air–water interface and AFM and FTIR analysis of LB monolayers. *Chem. Phys. Lipids*, **149**, 1–13.
30. Schlossman, M. L. and Tikhonov, A. M. (2008) Molecular ordering and phase behaviour of surfactants at water–oil interfaces as probed by X-ray surface scattering. *Annu. Rev. Phys. Chem.*, **59**, 153–177.
31. Duwez, A. S. (2004) Exploiting electron spectroscopies to probe the structure and organization of self-assembled monolayers – a review. *J. Electron Spectrosc. Relat. Phenom.*, **134**, 97–138.
32. Dutta, P. (2000) What X-rays tell us about the ordering of molecular and counter ion binding strength are found to decrease as the chain backbones in Langmuir monolayers. *Colloids Surf. A*, **171**, 59–63.
33. Ignes-Mullol, J., Claret, J., Riegada, R. and Sagues, F. (2007) Spread monolayers: structure, flows and dynamic self-organization phenomena, *Phys. Rep.*, **448**, 163–179.
34. Fujii, T., Yuasa, R. and Kawase, T. (1999) Biodetergent. Part 4. Monolayers of corynomycolic acids at the air–water interface. *Colloid Polym. Sci.*, **277**, 334–339.
35. Huda, M. S. (1997) Thermodynamical study of hydroxylated fatty acid monolayer films. *Colloid Surf. B*, **9**, 213–223.
36. Overs, M., Fix, M., Jacobi, S. *et al.* (2000) Assembly of new *vic*-dihydroxyoctadecanoic acid methyl esters at the air–water interface. *Langmuir*, **16**, 1141–1148.
37. Hac-Wydro, K. and Wydro, P. (2007) The influence of fatty acids on model cholesterol/phospholipid membranes. *Chem. Phys. Lipids*, **150**, 66–81.
38. Siegel, S., Vollhardt, D. and Cadenhead, D. A. (2005) Effect of the hydroxy group position on the monolayer characteristics of hydroxypalmitic acids. *Colloids Surf. A: Physicochem. Engng Aspects*, **256**, 9–15.
39. Alonso, C. and Zasadzinski, J. A. (2006) A brief review of the relationshops between monolayer viscosity, phase behaviour, surface pressure and temperature using a simple monolayer viscometer. *J. Phys. Chem. B*, **110**, 22185–22191.
40. Zwierzykowski, W. and Konopacka-Lyskawa, D. (1999) The interactions of saturated fatty acids at the dodecane/water interface and their sodium salts at the air/water interface. *Colloids Surf. A: Physicochem. Engng Aspects*, **160**, 183–188.
41. Bravo, B., Sánchez, J., Cáceres, A. *et al.* (2008) Partitioning of fatty acids in oil/water systems analysed by HPLC. *J. Surfactants Deterg.*, **11**, 13–19.
42. Varma, R. P. and Goel, H. (2000) Conductance behaviour of lithium soaps in aqueous methanol. *J. Surfactants Deterg.*, **3**, 527–532.
43. Neys, B. and Joos, P. (1998) Equilibrium surface tensions and surface potentials of some fatty acids. *Colloids Surf. A*, **143** (5), 467–447.

44. Yehia, A. (1997) Effect of hydrocarbon chain configuration on the surface activity of fatty acids–effect of solution pH. *Afinidad*, **54**, 315–320.
45. Small, D. M. (1986) *The Physical Chemistry of Lipids, Handbook of Lipid Research*, vol. **4**, Plenum Press, New York.
46. Johann, R., Vollhardt, D. and Möhwald, H. (1999) Texture features of long-chain fatty acid monolayers at high pH of the aqueous subphase. *Mater. Sci. Eng. C: Biomimetic Supramol. Syst.*, **8**, 35–42.
47. Miranda, P. B., Du, Q. and Shen, Y. R. (1998) Interaction of water with a fatty acid Langmuir film. *Chem. Phys. Lett.*, **286**, 1–8.
48. Wen, X. Y. and Lauterbach, J. F. (2000) Surface densities of adsorbed layers of aqueous sodium myristate inferred from surface tension and infrared reflection absorption spectroscopy. *Langmuir*, **16**, 6987–6994.
49. Kanicky, J. R. and Shah, D. O. (2002) Effect of degree, type, and position of unsaturation on the p*K*(a) of long-chain fatty acids. *J. Colloid Interface Sci.*, **256**, 201–207.
50. Kanicky, J. R. and Shah, D. O. (2003) Effect of premicellar aggregation on the p*K*a of fatty acid soap solutions. *Langmuir*, **19**, 2034–2038.
51. Kralchevsky, P. A., Danov, K. D., Pishmanova, C. I. *et al.* (2007) Effect of the precipitation of neutral-soap, acid-soap, and alkanoic acid crystallites on the bulk pH and surface tension of soap solutions source. *Langmuir*, **23**, 3538–3553.
52. Kanicky, J. R., Poniatowski, A. F., Mehta, N. R. and Shah, D. O. (2000) Cooperativity among molecules at interfaces in relation to various technological processes: effect of chain length on the p*K*(a) of fatty acid salt solutions. *Langmuir*, **16**, 172 .
53. Somasundaran, P., Ananthapadmanabhan, K. P. and Ivanov, I. B. (1984) Dimerization of oleate in aqueous solutions. *J. Colloid Interface Sci.*, **99**, 128–135.
54. Novales, B., Navailles, L., Axelos, M. *et al.* (2008) Self-assembly of fatty acids and hydroxyl derivative salts. *Langmuir*, **24**, 62–68.
55. Onitsuka, S., Kasai, Y. and Yoshimura, K. (1989) Quantitative structure–toxic activity relationshop of fatty acids and the sodium salts to aquatic organisms. *Chemosphere*, **18**, 1621–1631.
56. Prats, D., Rodriguez, M., Varo, P. *et al.* (1999) Biodegradation of soap in anaerobic digesters and on sludge amended soils. *Water Res.*, **33**, 105–108.
57. Saad, A. L. G., El-Kholy, S. A. and Barakat, Y. (1998) Relaxation behaviour and dipole moment of some nonionics. Part 1. CMC and thermo-complex commercial mixtures that are currently being used in dynamics of ethoxylated oleic acid in nonaqueous medium. *Z. Phys. Chem.*, **203**, 73–85.
58. O'Lenick Jr, A. J. and Parkinson, J. K. (1998) The effect of branching and unsaturation upon some properties of polyoxyethylene glycol diesters. *J. Surfactants Deterg.*, **1**, 529–532.
59. O'Lenick Jr, A. J. (2000) Evaluation of polyoxyethylene glycol esters of castor, high-erucic acid rapeseed, and soybean oils. *J. Surfactants Deterg.*, **3**, 201–206.
60. Cox, M. F. and Weerasooriya, U. (1998) Impact of molecular structure on the performance of methyl ester ethoxylates. *J. Surfactants Deterg.*, **1**, 11–22.
61. Cox, M. F. and Weerasooriya, U. (1997) Methyl ester ethoxylates. *J. Am. Oil Chem. Soc.*, **74**, 847–859.
62. Cox, M. F. and Weerasooriya, U. (2000) Partially saponified triglyceride ethoxylates. *J. Surfactants Deterg.*, **3**, 213–220.
63. Trathnigg, B., Hreczuch, W., Szymanowski, J. *et al.* (2004) Comparison of composition and properties of ethoxylated dodecanoic acid obtained in the presence of various catalysts. *Tenside Surfactant Deterg.*, **41**, 54–61.
64. Hreczuch, W., Trathnigg, B., Dziwinski, E. and Pyzalski, K. (2001) Direct ethoxylation of a longer-chain aliphatic ester. *J. Surfactants Deterg.*, **4**, 167–173.

65. Cox, M. F., Weerasooriya, U., Filler, P. and Mellors, W. (1998) Methyl ester propoxylates. *J. Surfactants Deterg.*, **1**, 167–175.
66. Alejski, K., Bortkowiak, P. and Szymonowski, J. (2004) Modelling of fatty acid methyl ester oxyethylation in a semi-batch reactor with successive dosing of ethylene oxide. *Tenside Surfactant Deterg.*, **41**, 130–134.
67. Alejski, K., Bialowas, E., Hreczuch, W. *et al*. (2003) Oxyethylation of fatty acid methyl esters. Molar ratio and temperature effects. Pressure drop modelling. *Ind. Engng Chem. Res.*, **42**, 2924–2933.
68. Bialowas, E. and Szymanowski, J. (2004) Catalysts for oxyethylation of alcohols and fatty acid methyl esters. *Ind. Engng Chem. Res.*, **43**, 6267–6280.
69. Doll, K. M., Moser, B. R., Sharma, B. K. and Erhan, S. Z. (2006) Current uses of vegetable oil in the surfactant, fuel, and lubrication industries. *Chim. Oggi-Chem. Today*, **24**, 41–44.
70. Renkin, M., Fleurackers, S., Szwach, I. and Hreczuch, W. (2005) Rapeseed methyl ester ethoxylates: a new class of surfactants of environmental and commercial interest. *Tenside Surfactants Deterg.*, **42**, 280–287.
71. Gauvrit, C., Muller, T., Milius, A. and Trouve, G. (2007) Ethoxylated rapeseed oil derivatives as non-ionic adjuvants for glyphosate. *Pest Manage. Sci.*, **63**, 707–713.
72. Makowska, D., Hreczuch, W., Zimoch, J. *et al*. (2001) Surface activity of mixtures of oxyethylated methyl dodecanoate and sodium dodecylbenzenesulfonate. *J. Surfactants Deterg.*, **4**, 121–126.
73. Littau, C. and Miller, D. (1998) Optimization of surfactant systems containing methyl ester ethoxylates. *SÖFW – Seifen, Öle, Fette, Wachse*, **124**, 690–697.
74. Hama, I., Sakaki, M. and Sasamoto, H. (1997) Effects of ethoxylate structure on surfactant properties of ethoxylated fatty methyl esters. *J. Am. Oil Chem. Soc.*, **74**, 823–827.
75. Hama, I., Sasamoto, H., Tamura, T. *et al*. (1998) Skin compatibility and ecotoxicity of ethoxylated fatty methyl ester nonionics. *J. Surfactants Deterg.*, **1**, 93–97.
76. Ishitobi, M. and Kunieda, H. (1998) Effect of chain length distribution on esterification reactions. *J. Surfactants Deterg.*, **1**, 343–344.
77. Duerr-Auster, N., Kohlbrecher, J., Zuercher, T. *et al*. (2007) Microstructure and stability of a lamellar liquid crystalline and gel phase formed by a polyglycerol ester mixture in dilute aqueous solution. *Langmuir*, **23**, 12827–12834.
78. Kawakatsu, T., Tragardh, G., Tragardh, C. *et al*. (2001) The effect of the hydrophobicity of microchannels and components in water and oil phases on droplet formation in microchannel water-in-oil emulsification. *Colloids Surf. A: Physicochem. Engng Aspects*, **179**, 29–37.
79. Izquierdo, P., Acharya, D. P., Hirayama, K. *et al*. (2006) Phase behaviour of pentaglycerol monostearic and monooleic acid esters in water. *J. Dispersion Sci. Technol.*, **27**, 99–103.
80. Ai, S. and Ishitobi, M. (2006) Effects of the number of fatty acid residues on the phase behaviours of decaglycerol fatty acid esters. *J. Colloid Interface Sci.*, **296**, 685–689.
81. Kato, T., Nakamura, T., Yamashita, M. *et al*. (2003) Surfactant properties of purified polyglycerol monolaurates. *J. Surfactants Deterg.*, **6**, 331–337.
82. Kawaguchi, M., Yamamoto, M., Nakamura, T. *et al*. (2001) Surface properties of mono-, di-, and triglycerol monostearate monolayers spread at the air–water interface. *Langmuir*, **17**, 4677–4680.
83. Shrestha, L. K., Shrestha, R. G., Iwanaga, T. and Aramaki, K. (2007) Aqueous phase behavior of diglycerol fatty acid esters. *J. Dispersion Sci. Technol.*, **28**, 883–891.
84. Shrestha, L. K., Shrestha, R. G., Solans, C. and Aramaki, K. (2007) Effect of water on foaming properties of diglycerol fatty acid ester–oil systems. *Langmuir*, **23**, 6918–6926.
85. Shrestha, L. K. and Aramaki, K. (2007) Phase behaviour of diglycerol monomyristate in different nonpolar organic solvent systems. *J. Dispersion Sci. Technol.*, **28**, 1236–1241.

86. Shrestha, L. K., Acharya, D. P., Sharma, S. C. *et al*. (2006) Aqueous foam stabilized by dispersed surfactant solid and lamellar liquid crystalline phase. *J. Colloid Interface Sci.*, **301**, 274–281.
87. Krog, N. (1997) Food emulsifiers, in *Lipid Technologies and Applications* (eds F. D. Gunstone and F. B. Padley), Marcel Dekker, Inc., New York.