Surfactants from Renewable Resources

Edited by

MIKAEL KJELLIN

YKI, Institute for Surface Chemistry, Stockholm, Sweden

INGEGÄRD JOHANSSON

AkzoNobel Surfactants, Stenungsund, Sweden

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Surfactants from Renewable Resources

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Series Preface

Renewable resources, their use and modification are involved in a multitude of important processes with a major influence on our everyday lives. Applications can be found in the energy sector, chemistry, pharmacy, the textile industry, paints and coatings, to name but a few.

The area interconnects several scientific disciplines (agriculture, biochemistry, chemistry, technology, environmental sciences, forestry, etc.), which makes it very difficult to have an expert view on the complicated interaction. Therefore, the idea to create a series of scientific books, focusing on specific topics concerning renewable resources, has been very opportune and can help to clarify some of the underlying connections in this area.

In a very fast changing world, trends are not only characteristic for fashion and political standpoints, also science is not free from hypes and buzzwords. The use of renewable resources is again more important nowadays; however it is not part of a hype or a fashion. As the lively discussions among scientists continue about how many years we will still be able to use fossil fuels, with opinions ranging from 50 to 500 years, they do agree that the reserve is limited and that it is essential not only to search for new energy carriers but also for new material sources.

In this respect, renewable resources are a crucial area in the search for alternatives for fossil-based raw materials and energy. In the field of energy supply, biomass and renewable-based resources will be part of the solution alongside other alternatives such as solar energy, wind energy, hydraulic power, hydrogen technology and nuclear energy.

In the field of material sciences, the impact of renewable resources will probably be even bigger. Integral utilization of crops and the use of waste streams in certain industries will grow in importance, leading to a more sustainable way of producing materials.

Although our society was much more (almost exclusively) based on renewable resources centuries ago, this disappeared in the Western world in the nineteenth century. Now it is time to focus again on this field of research. However, it should not mean a *retour à la nature*, but it should be a multidisciplinary effort on a highly technological level to perform research towards new opportunities and to develop new crops and products from renewable resources. This will be essential to guarantee a level of comfort for a growing number of people living on our planet. It is ‘the’ challenge for the coming generations of scientists to develop more sustainable ways to create prosperity and to fight poverty and hunger in the world. A global approach is certainly favoured.

This challenge can only be dealt with if scientists are attracted to this area and are recognized for their efforts in this interdisciplinary field. It is therefore also essential that consumers recognize the fate of renewable resources in a number of products.

Furthermore, scientists do need to communicate and discuss the relevance of their work. The use and modification of renewable resources may not follow the path of the genetic engineering concept in view of consumer acceptance in Europe. Related to this aspect, the series will certainly help to increase the visibility of the importance of renewable resources.

Being convinced of the value of the renewables approach for the industrial world, as well as for developing countries, I was myself delighted to collaborate on this series of books focusing on different aspects of renewable resources. I hope that readers become aware of the complexity, the interaction and interconnections, and the challenges of this field and that they will help to communicate the importance of renewable resources.

I certainly want to thank the people of Wiley from the Chichester office, especially David Hughes, Jenny Cossham and Lyn Roberts, in seeing the need for such a series of books on renewable resources, for initiating and supporting it and for helping to carry the project to the end.

Last, but not least, I want to thank my family, especially my wife Hilde and children Paulien and Pieter-Jan, for their patience and for giving me the time to work on the series when other activities seemed to be more inviting.

Christian V. Stevens,
Faculty of Bioscience Engineering
Ghent University, Belgium
Series Editor '*Renewable Resources*'
June 2005

Preface

Surfactants are molecules that consist of one hydrophilic (water-loving) part and one hydrophobic (water-hating or oil-loving) part. The production of a surfactant is essentially a question of joining different types of these two categories with one another. Renewability refers to the sources for the hydrophilic and the hydrophobic groups.

There has been a substantial development during the last century to construct molecules that are more efficient than the fatty acid soaps that have been produced for over 2000 years. As pointed out in the chapter on surfactants (Oleochemical and Petrochemical Surfactants: An Overall Assessment) in the first book in the series about renewable products (*Renewables-Based Technology*: *Sustainability Assessment*), most surfactants today are readily biodegradable and low-toxic to the aquatic environment, which are the two criteria for ‘green surfactants’. The majority of these surfactants are, however, synthesized from petroleum, which of course is non-renewable. This book will focus on renewable sources for surfactants that are also readily biodegradable and how an increased use of renewable sources might be achieved.

When it comes to the hydrophobic part of a surfactant, the natural oleochemical source predominantly offers straight hydrophobic chains with even amounts of carbon atoms. These structures are not always optimal and it has been shown that some branching that does not destroy the biodegradability is preferable from a performance point of view in many applications like cleaning, wetting, etc. On the hydrophilic side, one of the most interesting structural elements that forms the non-ionic surfactants as well as some of the anionic surfactants is ethylene oxide, which at present is made from petroleum sources, i.e. ethylene.

In both cases there are ways of making building blocks from ‘natural’ sources, for instance from ethanol from fermentation processes using ‘green chemistry’. There are activities reviving the processes that were used as late as in the 1950s to produce a whole range of small and larger building blocks from ethanol, starting with acetaldehyde and condensing that to larger branched aldehydes, as well as producing ethylene that could be polymerized to polyethene or oxidized to ethylene oxide.

One could argue that the high-tech surfactants that we use today offer much less burden for the environment than the less efficient, more primitive versions of renewable surfactants that were made earlier, e.g. from fatty acid. Developing the ‘green routes’ to these advanced surfactants via green building blocks is then an important task for the future and efforts in this direction are thus reported in this book.

Another stumbling block on the road to renewable sources for surfactants are the market issues that come as a consequence of an increasing use of oleochemicals as fuels such as biodiesel. Due to subsidies the market is very much influenced by the support from governments, resulting in an increasing price for the classical hydrophobe sources. Not only cost but also availability is influenced, which in the end might result in a decrease in possible raw material amounts. This development is illustrated in Figure 1 where the price level for fatty acids is followed through the years 2004–2008. There is an obvious dependence on the diesel price which makes the level vary in an unforeseeable way.

Yet another complication is the property demand on the structure of the hydrocarbon chain, which is totally different when the oleochemical is used as an energy source from when it is used as the hydrophobic part of a surfactant. To produce energy through combustion you just need a certain amount of carbon material, but for a surfactant the behaviour is mostly determined by the length and structure of the hydrophobe. This means that, for example, tallow oil cannot be easily substituted by, for instance, palm oil to get the same surfactant properties. Therefore, if a couple of major power plants choose to use tallow oil for their combustion, they could easily consume the total amount produced in Europe. This would be a rather attractive option for the tallow producers, having to deal with only a couple of large-scale customers prepared to pay premium

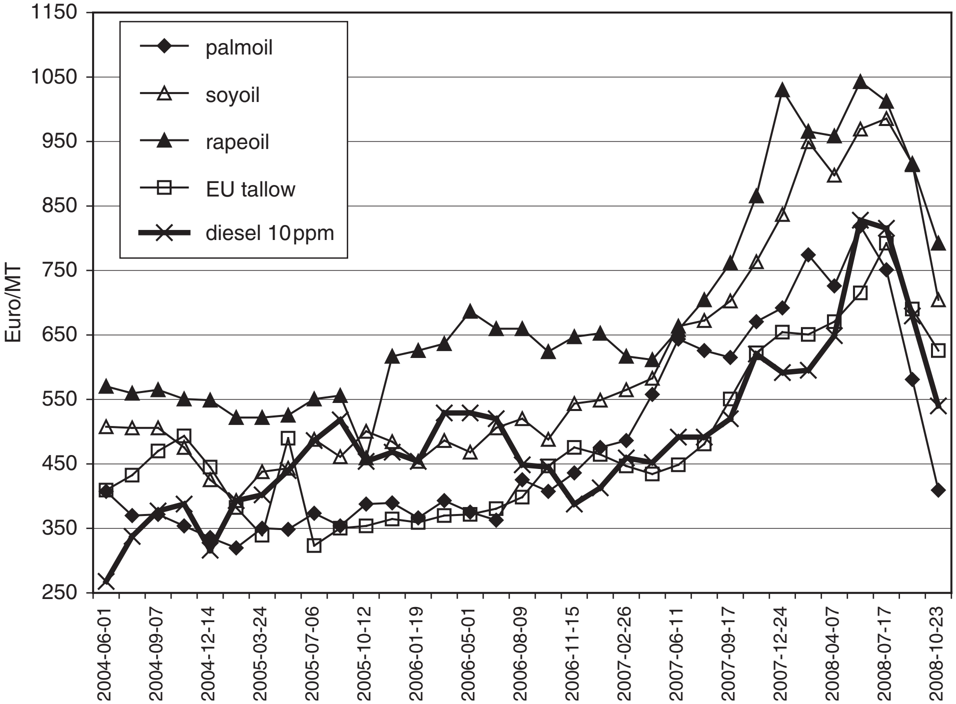

Figure 1 *Correlation between the prices for different raw materials between 2004 and 2008.*
Source: AkzoNobel

prices, having fewer delivery points, lower demands on quality and higher prices due to subsidies. The market might then be forced to go back to petroleum-based sources for surfactant production, i.e. synthetic fatty alcohols – a development that is not wished for by anyone.

It is thus important to create knowledge and awareness of the complicated issues involved in the raw material source uses when the market is driven by forces other than natural competition.

In this book you will find reviews treating both the traditional sources for hydrophobic as well as hydrophilic parts of surfactants, and some newer attempts. We have chosen to concentrate on issues that have an obvious potential for large-scale use and not the more academic investigations, however interesting they might be.

In the first part of the book we treat surfactant raw materials from different sources, crops, animals and wood, touching upon the biorefinery concept including carbohydrates and amino acids and short carboxylic acids like lactic acid, citric acid, etc.

The rest is devoted to different ways of creating new resources, i.e. green ethylene from green ethanol and complex mixtures from waste biomass. A high-flying concept like using algae as a new source is only mentioned very briefly since large-scale experience and knowledge is still lacking.

On top of that, green ways of using these raw materials, for instance in enzymatic processes or microorganism systems, are treated. An example of the use of living cells is the production of sophorolipids and rhamnolipids to be integrated in new 'green' detergents that have found their way to the market in the last 10–15 years and thus can be considered to be an established type of biosurfactant.

A few surface-active structures can be extracted directly from nature, such as lecithin and saponin. They are reviewed in separate chapters, showing that these historic types of surface-active materials are still in use in important areas like food and feed production and various cleaning applications.

Finally, the area is enlarged a bit by looking at larger surface-active molecules that one could describe as surface-active polymers or polymeric surfactants. Here mature types of products like cellulose derivatives and lignosulfonates, as well as the newer inulin products, are treated.

Mikael Kjellin
Ingegärd Johansson
Stockholm/Stenungsund, Sweden
2009

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The editors for this book met in 1995 when the Centre for Surfactants Based on Natural Products (SNAP) started. Mikael was then a PhD student in surface chemistry at the Royal Institute of Technology and Ingegärd an industrial research leader at AkzoNobel Surface Chemistry in Stenungsund. In total, six academic and thirteen industrial partners collaborated within SNAP with the common goal to explore properties and applications of the next-generation environmentally friendly surfactants. The main outcome of the centre activities was 22 PhDs and over 200 scientific publications.

The networks between academic and industrial researchers created during the lifetime of SNAP also laid the foundation for future research collaborations. Two ongoing examples are the Controlled Delivery and Release Centre (CODIRECT) at the Institute for Surface Chemistry (YKI) and the Supramolecular Biomaterial Center (SuMo Biomaterials) at Chalmers University of Technology.

We thank our employers, the Institute for Surface Chemistry (YKI) and AkzoNobel Surface Chemistry, for giving us the opportunity to work with this book, which we feel covers an important topic for the future. We would also particularly like to thank all the authors for their contributions and for answering all our questions on top of all their other duties in their company or academic surroundings.

List of Contributors

Edgar Joel Acosta Department of Chemical Engineering & Applied Chemistry, University of Toronto, Canada

Patrick Adlercreutz Department of Biotechnology, Lund University, Sweden

David Grant Allen Department of Chemical Engineering & Applied Chemistry, University of Toronto, Canada

Kris Arvid Berglund Division Chemical Engineering, Luleå University of Technology, Sweden

Dirk W. G. Develter Ecover Belgium NV, Malle, Belgium

Steve J. J. Fleurackers Ecover Belgium NV, Malle, Belgium

Ralph Franklin AkzoNobel Surfactants, Brewster, USA

Flor Yunuen García-Becerra Department of Chemical Engineering & Applied Chemistry, University of Toronto, Canada

Stig Are Gundersen Borregaard LignoTech, Sarpsborg, Norway

Arafa Hamed Department of Botany, Aswan Faculty of Science, South Valley University, Aswan, Egypt

Rajni Hatti-Kaul Department of Biotechnology, Lund University, Sweden

Karlheinz Hill Cognis GmbH, Monheim, Germany

Thomas Hjertberg Borealis AB, Stenungsund, Sweden

David B. Hodge Division Chemical Engineering, Luleå University of Technology, Sweden

Bjarne Holmbom Process Chemistry Centre, Åbo Akademi University, Finland

Maria Rosa Infante Instituto de Química Avanzada de Cataluña, Barcelona, Spain

Leif Karlson AkzoNobel Functional Chemicals, Stenungsund, Sweden

Rolf Andreas Lauten Borregaard Corporate R&D, LignoTech Group, Sarpsborg, Norway

Bart Levecke Beneo Bio Based Chemicals, a Division of Beneo-Remy NV, Leuven-Wijgmaal, Belgium

Anna Lundgren Stiftelsen Chalmers Industriteknik, Gothenburg, Sweden

Carmen Moran Chemistry Department, Coimbra University, Coimbra, Portugal

Bernt O. Myrvold Borregaard Corporate R&D, LignoTech Group, Sarpsborg, Norway

Willem van Nieuwenhuyzen Lecipro Consulting, Limmen, The Netherlands

Wieslaw Oleszek Institute of Soil Science and Plant Cultivation, State Research Institute, Pulawy, Poland

Lourdes Perez Instituto de Química Avanzada de Cataluña, Barcelona, Spain

Aurora Pinazo Instituto de Química Avanzada de Cataluña, Barcelona, Spain

Ramon Pons Instituto de Química Avanzada de Cataluña, Barcelona, Spain

Ulrika Rova Division Chemical Engineering, Luleå University of Technology, Sweden

Anders Strand Process Chemistry Centre, Åbo Akademi University, Finland

Anna Sundberg Process Chemistry Centre, Åbo Akademi University, Finland

Martin Svensson Lantmännen Food R&D AB, Stockholm, Sweden

Tharwat Tadros Consultant, Wokingham, UK

Part 1

Renewable Hydrophobes

1

Surfactants Based on Natural Fatty Acids

Martin Svensson
Lantmännen Food R&D AB, Stockholm, Sweden

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

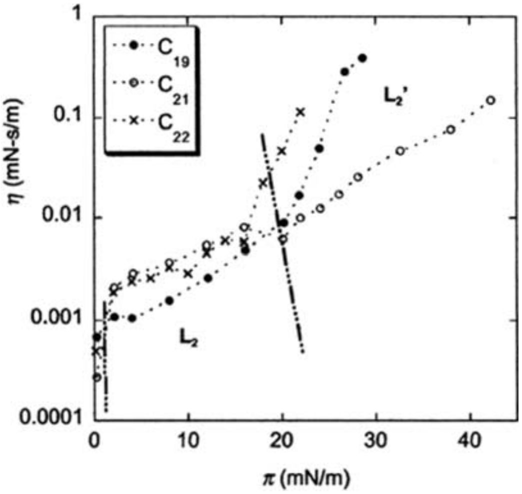

Figure 1.1 Comparison of the surface shear viscosity η measured as a function of surface pressure for nonadecanoic (C19) at 30 °C, heneicosanoic (C21) at 25 °C and behenic acid (C22) at 20 °C. The temperature of each experiment was adjusted for the monolayers to undergo a transition from a tilted phase (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.

Reprinted with permission from C Alonso and J A. Zasadzinski, A brief review of the relationships between monolayer viscosity , phase behaviour, surface pressure and temperature using a simple monolayer viscometer, *J. Phys. Chem. B*, **110**, 22185–22191. Copyright 2006 American Chemical Society.

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