

BIODEGRADABILITY OF SURFACTANTS

Edited by
D.R. Karsa
and
M.R. Porter



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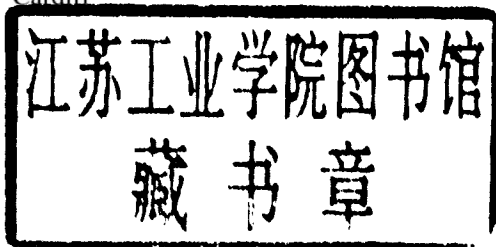
Biodegradability of Surfactants

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Preface

The awareness and development of 'biodegradable' surfactants pre-dates current pressures by the environmental movement by nearly three decades, wherein a responsible industry mutually agreed to replace 'hard', non-biodegradable components of household detergents by 'soft', biodegradable alternatives, without course to legislation.

The only requirement at that time was for surfactants used in detergents to exhibit a 'primary biodegradability' in excess of 80%; this referring to the disappearance or removal from solution of the intact surface active material as detected by specified analytical techniques. This proved useful, as observed environmental impacts of surfactants, e.g. visible foam on rivers, are associated with the intact molecule. Test methods for 'primary biodegradability' were eventually enshrined in EU legislation for nonionic surfactants (Directive 82/242/EEC, amended 73/404/EEC) and for anionic surfactants (Directive 82/243/EEC, amended 73/405/EEC). No approved test methods and resultant legislation have been developed for cationic and amphoteric surfactants to date.

The environmental classification of chemical substances, which of course includes surfactants, and associated risk assessment utilises a second criterion – 'ready biodegradability'. This may be assessed by a number of methods which monitor oxygen uptake (BOD), carbon dioxide production or removal of dissolved organic carbon (DOC). Some surfactants which comply with the above Detergents Directive are borderline when it comes to 'ready biodegradability'.

The publication of this book coincides with biodegradability legislation standing at a cross-roads, with some uncertainty as to the way in which it may develop. The European Commission has indicated a desire to develop and introduce ultimate biodegradability legislation or mineralisation into the Detergents Directive, underlining the already existing assessment of ultimate biodegradability by major surfactant end-users regardless of standardised test methods or any legislation being in place. Likewise, attention has also been focused more recently on industrial cleaning applications and some areas of industry where surfactants are used as process aids to assess their biodegradability and potential impact on the environment.

Whereas there is general agreement that surfactants should be subject to some environmental acceptance criteria, there is a growing lobby that suggests that surfactants should no longer require an exceptional role as compared with other chemical compounds released into the environment. Eventually, there may be a valid case to deregulate as far as surfactant biodegradability is concerned and to subject the acceptance of surfactants particularly for use in washing, rinsing and cleaning to an environmental risk assessment which is required as a matter of

principle for all new and existing substances (EU directives 93/67/EEC and 793/93/EEC, respectively). Only time will tell as to which approach will be accepted.

Set against such a background, this volume provides a state-of-the-art review of surfactant biodegradability mechanisms, test methods, legislative requirements and individual consideration of the four ionic classifications of surfactant, namely anionics, nonionics, cationics and amphoterics. Each chapter is written by acknowledged experts in their particular field, which should ensure that this book will provide a valuable addition to our knowledge of surfactant biodegradability and become a significant reference work on this subject.

Acknowledgements

The editors would like to record their special thanks to the individual authors of each chapter for their time, patience and hard work which has resulted in a volume of substance in which all contributors can take pride. For those working in industry or academia, we would also like to extend our thanks to their individual companies or universities for their support.

Finally, we would thank the publishers for their unlimited patience and understanding, as the gestation period for this particular work proved to be somewhat longer than originally anticipated. We trust the final product has been worth waiting for.

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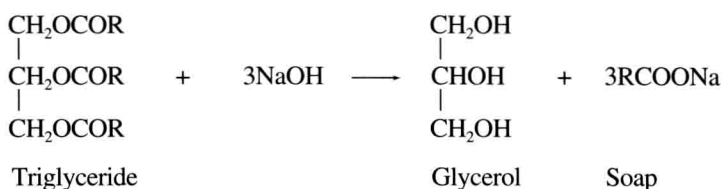
1 Introduction to surfactant biodegradation

D. BROWN

1.1 Introduction

The term surfactant, or surface active agent, is applied to organic molecules whose function is to promote mixing or dispersion between phases of a mixture by lowering the interfacial tension between these phases. For most applications one of these phases is water and the other phase is hydrophobic. Thus, surfactants can be used in a whole range of technical and industrial products where it is required to disperse hydrophobic materials in water or *vice versa*. The major use of surfactants, in terms of the quantities used, is as a component in cleaning preparations or detergents. Such cleaning operations usually result in the discharge of an aqueous effluent, and it is the biodegradability of the surfactants in that effluent, which is the subject of this book.

The earliest known manufactured surfactants are soaps which are the sodium salts of natural, saturated and unsaturated fatty acids formed from the alkaline hydrolysis of animal and plant triglycerides (fats and oils). Recipes for soap manufacture have been found on papyri and clay tablets from ancient civilisations in Egypt and the Tigris/Euphrates (Bock and Stache 1982) and the science of soap-making has progressed through the soap boilers' guilds of the Middle Ages to the sophisticated products of present day commerce.



Soaps and other synthetic surface active agents used for cleaning purposes are molecules in which there is a hydrophobic group and a hydrophilic group. The nature of the hydrophilic group and the balance between the hydrophilic and hydrophobic parts of the molecule determine which particular surfactants are appropriate.

An often used broad classification of surfactants is based on the charge characteristics of the hydrophilic part of the molecule. Anionic surfactants have a negatively charged hydrophile and include soaps, sulphonates, sulphates; non-ionic

surfactants have an uncharged hydrophile often a polyglycol; cationic surfactants are often based on a quaternary ammonium hydrophile while the fourth main class is the amphoteric where the hydrophile contains both positive and negative charges, e.g. an amino carboxylic acid. A more comprehensive description of the different surfactant types is contained in subsequent chapters of this book and has been described by Porter (1991).

As previously mentioned, the major use of surfactants is as a component of cleaning preparations and in this application and several others, essentially all the surfactant is discharged to drain. The major end-uses have been reviewed by Richtler and Knaut (1988) and, as well as home use for personal hygiene, washing and cleaning, these uses include industrial cleaning, textile and leather auxiliaries, emulsifiers, paint additives, oilfield chemicals, etc. These same authors give detailed statistics and trends in consumption and point out the major difference in annual use of cleaning compounds in Western Europe and the USA (10 kg/person per year) compared with the world average (4 kg/person per year).

The estimated 1987 total surfactant consumption (Richtler and Knaut, 1988) for USA (45%), Western Europe (38%) and Japan (17%) is 6.6 M tonne/year with an approximately 1:1 split between household and other uses. Six surfactants together make up approximately 60% of this total consumption, soap (1.5 M tonne/year), linear alkylbenzene sulphonates (1 M tonne/year), alcohol ethoxylates (0.5 M tonne/year), alkyl phenol ethoxylates (0.47 M tonne/year), alcohol ether sulphates (0.35 M tonne/year) and alcohol sulphates (0.25 M tonne/year). Clearly without biodegradation the environmental burden would be enormous.

1.2 Biodegradability and the replacement of soap in detergent products

As mentioned in the introduction, soaps have been manufactured and used by mankind for thousands of years and are still very widely employed for personal hygiene and other washing purposes. The statistics above show that soap is the major surfactant in Western Europe, USA and Japan and is even more dominant in the developing countries. Why then did the biodegradability of detergents only become an issue in the middle of the 20th century when the use of soap as the main surfactant in domestic detergents began to be replaced by alternative products?

From the viewpoint of the 1990s, where awareness of environmental issues is sharply focused, two general answers to this question may be made. Firstly, the biodegradability of all substances released to the environment (including soap) is an important factor in defining the levels of a substance in the environment and hence assessing its potential for causing environmental damage (environmental risk assessment). Secondly, based on the so-called precautionary principle, where very major quantities of a substance are released to the environment, regardless of whether the anticipated levels in the environment appear likely to

cause harm, the substance should be biodegradable to safeguard against the possibility of future harm due to build-up in the environment.

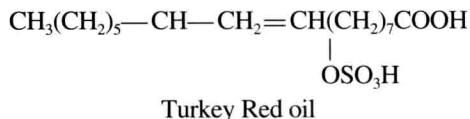
However, in earlier times and specifically for synthetic surface active agents in the post-World War II period, environmental problems were tackled on an *ad hoc* basis and in general attention was paid only where problems were manifest. The problem which became all too manifest with certain synthetic surface-active agents was foam. Foam at sewage works, foam on rivers and indeed in certain localised areas, below waterfalls, even foam spreading from the rivers to the street (Standing Technical Committee on Synthetic Detergents (STCSD), 1958).

This problem of foam due to the synthetic surface agents being introduced into domestic detergents was certainly not confined to any one country and major investigations into the cause of the problem, delineation of adverse effects other than foam and ways to rectify the situation were made in the USA, Germany, France, the UK and other industrial countries. In fact, this problem was probably the first example of a specific environmental problem attributable to a particular type of material as opposed to general air or water pollution problems caused by the discharge of domestic or industrial wastes direct to the environment.

Two particular attributes of soap, as opposed to the synthetic surface active agents introduced post-World War II, were quickly identified as being the explanation of why foaming problems had not been caused by soap formulations. Soap, as the sodium salt of a fatty acid, reacts with the calcium and magnesium ions in natural waters to form insoluble calcium and magnesium soap (seen as 'scum' in hardwater areas), a major drawback to its use in domestic laundry applications where large amounts of polyphosphate are necessary to prevent deposition of these insoluble soaps in the fabrics being washed. This property of soap, in forming water-insoluble materials with bivalent ions, also means that, once released into water either direct or via a sewage works, it will be immediately and effectively removed as a surface active material. Furthermore, based on our present knowledge of what is, or is not, likely to be easily biodegraded, soap as the sodium salt of fatty acids is expected to be well degraded and indeed a high level of degradation of soap has been demonstrated (Swisher, 1987). Interestingly, however, Swisher makes the comment that the lack of any foaming problems attributable to soap is more due to the insolubility of the calcium and magnesium salts than to biodegradability. To put this Swisher comment into context, it is not being suggested that soap is poorly biodegradable, but rather that even if it were, the chemistry of soap is such that foaming would not be a problem. This, in a more generic sense, is useful in drawing our attention to the fact that biodegradability is not the sole environmental property of consequence in assessing environmental risk.

The sulphation and sulphonation chemistry necessary to replace soap with anionic surfactants which did not suffer the drawback (to the user, if not to the environment) of forming insoluble calcium and magnesium salts began to be developed in the latter part of the 19th century. The sulphation of unsaturated

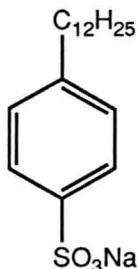
oils such as castor oil by reaction with concentrated sulphuric acid to give the so-called Turkey Red oil was developed around 1860 (Fieser, 1950) although this product was not technically suitable as a domestic detergent ingredient.



Further developments in Germany and the USA prior to World War II gave sulphated and sulphonated products primarily based on natural alcohols and oils. However, as the availability of hydrocarbon feedstocks and the ability of synthetic chemists and chemical engineers increased so did the availability of a particularly cost-effective replacement for soap in the domestic detergent market, namely the material known as tetrapropylene benzene sulphonate (TPBS) or sometimes more generally as alkyl benzene sulphonate (ABS). The use of this product became very widespread in most industrialised countries around 1950 and in the United States, at this time, TPBS was used for most laundry detergents (Swisher, 1987).

TPBS is made by the alkylation of benzene with propylene tetramer using Friedel–Crafts type catalysts followed by sulphonation of the alkyl benzenes so produced. This process gives a whole mixture of isomeric and homologous materials. A gas chromatogram of the alkylbenzene indicates at least 100 components (Kaelbe, 1963) and the sulphonation process, although predominantly at the *para* position, will also give other isomers. Faced with this large mixture of chemical entities, a situation also found with many other synthetic surfactants including those in use today, scientists wishing to investigate the biodegradability and environmental levels of the product had to adopt approaches rather different from those of classical organic analysis where single compounds are studied.

The analytical methods used to follow the biodegradation of surfactants (or indeed any other organic substance) play a fundamental role in defining what is



Tetrapropylene benzene sulphonate (TPBS).

meant by 'biodegradability' in any particular test method or environmental situation. In a historical context, it is important to appreciate that the commonly used MBAS (methylene blue active substance) and BiAS (bismuth active substance) analytical methods for anionic and non-ionic surfactants, respectively, are limited both in the types of anionic and non-ionic surfactant which respond to those methods, and also limited in terms of what is meant by 'biodegradability' when surfactants which do respond are assessed by these methods. These remarks will be elaborated further in following sections of this chapter.

1.3 Biodegradation, biodegradability testing and interpretation of results

The three questions, what is biodegradation, how do you measure it and how do you interpret the results, form an exponential cascade of complexity in terms of the difficulty with which answers can be given. This section is aimed at giving the reader at least some insight into the issues for surfactants (and other organic materials) which those questions attempt to address.

1.3.1 Biodegradation

This, in its simplest definition, is the breakdown of an organic substance by living organisms but for most purposes, and certainly for the purpose of this book, this definition is narrowed to the breakdown of an organic substance by microorganisms. Even with this rather narrower definition, four other questions immediately open up, namely 'breakdown to what?', 'under what conditions?', 'with what microorganisms?' and 'at what rate?'.

Within the science of biodegradation the 'breakdown to what' question is usually answered in one of two, or possibly three, ways.

'Primary' biodegradation is effectively defined as the breakdown of the substance as measured by a substance-specific analytical method. To take a simple example, an analytical method such as gas chromatography (GC) or high performance liquid chromatography (HPLC) might be set up to monitor the primary biodegradation of a substance such as phenol by the disappearance of the phenol from the chromatograph. With phenol, as with many other single compound substances, it is possible to measure 100% primary biodegradation using compound-specific analytical methods. With complex mixtures, other analytical methods, which will be described later for surfactants, may be used. Alternatively, loss of a key property, such as surface activity/foaming potential, may be used as an indicator of primary biodegradation.

'Ultimate' biodegradation is the second main way in which the 'breakdown to what' question may be answered and 'ultimate' biodegradation may be defined as the complete breakdown of an organic substance to wholly inorganic materials and natural cellular material. That is, to show the complete ultimate degradation of phenol, it would be necessary to demonstrate not only the disappearance of the

specific analytical response of phenol, but also that no other organic metabolites resistant to the particular biodegradation conditions are being formed. This analytical task is extremely difficult even for a simple substance such as phenol, and to be carried out with full scientific rigour requires the synthesis of carbon-14 labelled material and rather elaborate experimentation. In practice, ultimate biodegradability is generally assessed in an aerobic system by measuring carbon dioxide produced, by measuring the oxygen consumed during the biodegradation process ('biochemical oxygen demand' or BOD) or by measuring the level of organic carbon remaining in solution during the time course of the biodegradation study. Each such method has its own intrinsic problems leaving aside any experimental problems associated with the measurements themselves.

The measurement of carbon dioxide production or the expression of BOD is a positive indication that some measure of ultimate degradation has occurred. However, microorganisms, like higher organisms, use biodegradable organic materials not only as an energy source but also as a food source to build up their cellular mass. Depending on the nature of the substance in question and the food supply available to the microorganisms (the more food, the more they 'put on weight'), only approximately 60–70% of the theoretical carbon dioxide production or BOD will be found for even a very easily biodegradable substance such as sodium acetate.

The measurement of dissolved organic carbon (DOC) in solution as an indication of ultimate degradation can both in principle and in practice indicate high levels of biodegradation since any of the substrate converted into cellular biomass will be removed by filtration or centrifugation. However, it is not applicable to substances which are sparingly soluble in water or strongly sorptive, and can also be misleading where sparingly soluble or sorptive metabolites are formed. A combination of a high level of ultimate biodegradation as shown by DOC removal (say 95%+) and a high level of ultimate degradation as indicated by carbon dioxide production or BOD (say 60%+) does provide confidence that a high level of ultimate degradation has taken place.

A third way in which the 'breakdown to what' question may be answered is sometimes answered explicitly or implicitly in terms of 'environmentally acceptable' biodegradation. In practice, the methods developed to determine the biodegradation for surfactants implicitly define the biodegradation measured as 'environmentally acceptable'. However, before dealing with the ways in which the biodegradability of surfactants has been and is assessed, some more general elaboration of what is meant by 'environmentally acceptable' will be given.

Many substances of interest and use to mankind are considerably more complex in chemical structure than simple molecules such as phenol, sodium acetate, etc. which can relatively easily be shown to undergo essentially complete and rapid ultimate biodegradation in simple test systems. Furthermore, many of these more complex substances are multi-compound mixtures and, as has already been mentioned, many surfactants of commercial interest fall into