HANDBOOK *of* SURFACTANTS

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Handbook of Surfactants

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Preface

The worldwide consumption of surfactants now exceeds several million tonnes per annum. Six of the major types represent approximately 80% of the volume consumed, whereas the remaining 20% is made up of approximately 40 different chemical types.

Commercially produced surface active agents are not pure chemicals, and within each chemical type there can be tremendous variation. Technical staff who are not familiar with surfactants are frequently bewildered by the enormous variety of different products on the market and the vast body of literature which exists on the composition and properties of surfactants. The selection of the best surfactant for any given use therefore becomes a major problem.

This volume arose from the clear need to have available a simple reference book summarising the different types of surfactants on the market and their properties. The concept and structure of the book evolved from early attempts to define chemical structure/property relationships of all the different types of surfactants commercially available, into a simple handbook providing essential background information for the surfactant user. It is realised that most users will be developing their own data bank of structure/end use property relationships and they will therefore be the experts on end use. What most users seem to lack is an appreciation of the chemical structures of commercial surfactants. They will be purchasing a surfactant which is a mixture of surface active molecules (and possibly also non surface active molecules) from sales people who may have little or no knowledge of the exact composition. The book will also be of value to those who need a clear and straightforward account of the constitution of commercial surfactants, their general properties, and their surface active properties.

Because of the need to discuss broad principles and keep statements simple I have had to make many generalisations. Although there may be instances where these generalisations may not be entirely accurate for every surfactant, overall they will serve the purpose of enabling readers rapidly to improve their knowledge of surfactants and surfactant technology.

I would like this opportunity to thank the very large number of people in the surfactant industry who have willingly supplied data, and who have made many helpful comments and suggestions. Particular thanks are due to David Karsa, who played a key role in the formative thinking which preceded the actual writing of this book, and Enc Lomax who checked the draft on amphoterics.

M.R.P.

Abbreviations

Ac	Acetyl group – CH_3CO
AE	Alcohol ethoxylate
AES	Alcohol ether sulphate
AOS	Alpha-olefin sulphonate
APE	Alkyl phenol ethoxylate
APG	Alkyl polyglycoside
AS	Alcohol sulphate
CD	Coconut diethanolamide
CMC	Critical micelle concentration
DEA	Diethanolamine
EO	Ethylene oxide
EO/PO	Ethylene oxide/propylene oxide co-polymer
Et	Ethyl – C_2H_5
EtOH	Ethanol (ethyl alcohol) – C_2H_5OH
FES	Fatty ester sulphonate
HLB	Hydrophilic lyophilic balance
LABS	Linear alkyl benzene sulphonate
Me	Methyl – CH_3
MEA	Monoethanolamine
MeOH	Methanol (methyl alcohol) – CH_3OH
NPE	Nonyl phenol ethoxylate
O/W	Oil in water emulsion
PE	Phosphate ester
PEG esters	Polyoxyethyleneglycol esters of fatty acids
PO	Propylene oxide
QAC	Quaternary ammonium compound
RT	Room temperature
SAS	Secondary alkane sulphonate (paraffin sulphonate)
ST	Surface tension
TEA	Triethanolamine
W/O	Water in oil emulsion

Contents

1 General introduction

The basic aim of the book is to give practical help to users of surfactants and those people who make formulations with surfactants. The choice of a cost-effective surfactant, although essential, is not easy due to: the bewildering number of surfactants available on the market; insufficient data given by the manufacturers; poorly defined chemical structure/effect relationships. This book attempts to provide some practical help with these problems but also to explain the basic properties of particular types of commercially available surfactants.

The practical help consists of describing the various types of surfactants in terms of their chemical structure, the principal physical properties of that type, the functional properties, the principal end uses and some comments on the requirements for quality control. There are chapters on using surfactants in formulations, the use of surfactant theory, how and where to find information concerning surfactants and their applications, and a broad description of test methods for biodegradation and toxicity. However, the bulk of the book is about the surfactants themselves in a concise, consistent format.

Surfactants are generally described as anionic, non-ionic, cationic or amphoteric. However, these are physical properties of particular chemical structures. To describe a surfactant in these terms gives some very general properties which may, but usually do not, help a user to choose a surfactant. The more important factors in the choice of a surfactant are:

- Is it commercially available?
- Does it perform the function required?
- Is it expensive to use?
- Is the physical form convenient for manufacture and use?
- Is the surfactant stable to storage in its end use?
- Is it safe in manufacture and transport?
- Is it safe to use in the required end use?
- Does it pose any dangers to the ecology?

The last three requirements are becoming the most important. No matter how good or cheap the finished product, if the surfactant (or any other component for that matter) gives a danger, real or imagined, to the end user or the ecology then the product is not saleable. There are no safety or toxicity data given on the various types of surfactants described, the reason being that it is impossible to generalise on toxicity. This is because small changes in the hydrophobic

group can affect the toxicity of products. On environmental grounds, the requirements change so rapidly that statements on environmental safety could be misleading. Factual data such as toxicity tests and biodegradation tests are not useful unless full details of the test protocols are given. Instead a short chapter on this subject has been included to give some background on the various tests for those new to this area. At least the readers may then have a better understanding of the data and statements made by the surfactant manufacturer or supplier who should be the major source of data and advice.

When picking surfactants for a particular end use, a user must bear in mind all these requirements in order to make cost-effective, saleable products, or to use surfactants without problems within his factory. It is only sensible to use those surfactants which will cover all the requirements above. Although there are hundreds of surfactants commercially available, only a small number of chemical types are commercially produced, in large volumes, world-wide. It is obviously preferable to select one or more of these types if possible. However, there can be problems in picking one chemical type. The great majority of surfactants available on the market are not pure but consist of mixtures of chemicals. It is these mixtures which often give the end effect required. This is why there can be variations in performance of surfactants from one manufacturer to another. Although manufacturers may give as full a chemical description as possible, the relationship between chemical structure and performance remains poorly documented and not well understood.

A very large amount of information is available on surfactants in published papers and conference proceedings. The surfactant manufacturer will also have a considerable amount of information on the properties, end use and safety of his products. The majority of published scientific information relates to the properties of the surfactants, whereas details of the use of surfactants in formulations tend to be in the patent literature. Patent literature can often be more confusing than helpful if one is seeking the reason behind the choice of a particular surfactant in a specific end use.

The theoretical basis of surfactants is well-established but is usually insufficient to help formulators in fine detail. Some understanding is therefore necessary. Although the concept of adsorption at a surface need not be mathematically understood, a visualisation does help. The simple concept of McBain for the formation of micelles has been shown to be much more complex with spherical, disc, lamellar and hexagonal micelles in practice. This can explain many of the complex solubility and phase changes encountered in surfactant solutions.

The present tendency to stricter quality control emphasises the need for the routine analysis of the surfactant, plus the analysis of the surfactant in the formulation. Users need to know which tests must be carried out in order to identify significant variations in the composition of the surfactant.

There is now a strong move by consumer groups and some sections of the surfactant producers to move away from petrochemical-based feedstocks.

Surfactants made from natural materials other than petroleum have been neglected but are now making a comeback. It is for this reason that possibly a disproportionate amount of space has been devoted to products whose major raw materials are derived from animal fats, vegetable oils or carbohydrates.

The use of surfactants is extremely widespread both in industry and in the home. There are three major reasons for this:

- The increasing use of water rather than organic solvents in industrial products
- Most mixtures and formulations are applied to solid substrates
- Cleaning is a very common requirement

Most industrial and domestic processes using chemicals involve contact between a liquid and a solid where the solid needs wetting. This is exactly the function of the surfactant. However, there are many products which can easily wet substrates better than water, for example alcohol, hydrocarbons, etc. It is the particular property of surfactants to decrease the surface tension of water using very low concentrations that is so valuable. In practical terms it means that most of the properties of water can be retained and the wetting improved at a very small additional cost. The function of cleaning is extremely common both in consumer use, and in industry. There is no other end use of formulated products which approaches the volume and number of applications involving cleaning or the scientific term 'detergency'. Water is by far the most common medium and all aqueous-based detergents (formulations for cleaning purposes) contain surfactants.

Surfactant is an abbreviation for surface active agent which literally means active at a surface. The surface can be between solid and liquid, between air and liquid or between liquid and a different, immiscible, liquid. The primary property of a surfactant in a solution is that the concentration of the surfactant is higher at the surface than in the bulk of the liquid. Thus the surfactant concentrates at the surface. As this is the point where they are doing a useful function, it is therefore not surprising to find that surfactants can be very economically used. This may be an elementary concept but it does explain the effectiveness of surfactants in many applications, compared to other products which do not show any marked surface active properties. The user is always concerned with the economics of the product which is often dependent upon the basic surface active properties.

What do we mean by a formulated product? Manufacturing industry makes a wide variety of formulations for use both within industry, and as the manufactured product for use in industry or in the home and institutions. Detergents, paints, inks, adhesives, cosmetics, dyes, weedkillers, insecticides, ice cream, are all examples of common formulations. However, inside the manufacturing industry there are many formulations which are not seen by the end consumer, but are essential as processing aids. The textile industry uses scouring aids to clean fibres, aqueous-based lubricants for spinning synthetic

fibres, warp sizes to protect fibres in weaving, defoamers to suppress foam during dyeing, and softening agents to treat fabrics in order to give a soft 'handle'. The paper industry uses defoamers, dispersing aids and release agents. The engineering industry uses lubricants, anticorrosive treatments and metal working lubricants. Practically all these formulations are composed of mixtures of chemicals. Surface active agents are present in all the formulations mentioned so far, and in numerous others.

Although formulations differ from one application to another, there are some factors which are common to every formulation.

1. An active ingredient which carries out the primary function desired by the end user.
2. A medium by which the active ingredient is carried.
3. At least one secondary function which will usually, but not always, be achieved by at least one other ingredient.

It is possible to provide all functions with one chemical product. A good example is soap, which in the bar form provides the active ingredient which washes, the solid medium which is convenient for washing hands, and the good dispersion of the dirt in water for easy disposal. Modern synthetic detergents now contain active washing ingredients which can wash at much lower temperatures, are liquid in form by virtue of their solubility in water (which is now the medium) and provide better dispersion of dirt particularly in hard waters. Although new synthetic organic chemicals have been produced which can give all these improvements in one chemical species, they are very rarely used. The reason is that mixtures of chemicals are easier and cheaper to produce than new molecules, particularly on a large scale. Although soap has not disappeared from the market place, the soap tablet of today is not one chemical, but a carefully formulated product.

Another example is lubricating oils which were at one time a refined fraction of crude petroleum. The oil would provide the essential function of lubricating, it would be its own medium (being liquid and easily handled) and it had secondary functions such as dispersing solids and giving some corrosion resistance. However, modern lubricants are complex mixtures with chemical additives, some giving improved lubrication and others giving improved corrosion resistance and improved dispersibility of solids. It is very much easier and cheaper to provide improved products by mixing rather than by synthesising new chemical molecules with the desired properties. New synthetic organic chemicals (esters, synthetic hydrocarbons, phosphate esters) have been produced which are superior to petroleum-based lubricating oils as lubricants. However, even these synthetic products are now being formulated by the addition of additives to improve their basic properties.

These two examples illustrate the practical effect of using mixtures of chemicals to solve problems. In the great majority of formulations used by industry and in the home, a surfactant or a mixture of surfactants will be used.

The information presented in this book has been obtained from a combination of personal experience, manufacturers' technical information and the patent and scientific literature. There are very few references but a considerable number of generalisations in order to make the book easy to read. If there is no reference it means that there are at least two sources of information which agree, plus the author's own experience. If a reference is given it generally means that the statement is reasonable within the author's knowledge but a secondary independent source cannot be found. The number of generalisations means that exceptions can probably be found, particularly those relating chemical structure and physical/chemical properties. The end uses given, with very few exceptions, have been positively identified as those actually used in practice rather than quotations from patent literature. There will be many uses of particular surfactants which are not mentioned but the author believes that he has identified the major uses of particular types of surfactant. If he is wrong in statements on data or end uses he would be most interested to be provided with appropriate data confirming the error.

2 General approach to using surfactants in formulations

2.1 Introduction

There can be two quite different approaches to formulation because of the very different requirements of the market. There are basically two different market conditions:

1. Where there is a large volume market and the formulation will be sold for several years without significant change, e.g. a household detergent
2. Where the market is small and subject to change

In the first situation the potential profit on a single product can be very large and hence a detailed technical program can be initiated. Planned experiments on end effect, storage stability and environmental acceptability with comprehensive testing of various surfactants and of hundreds of formulations is feasible. Detailed examination of the properties of the surfactant is possible, new methods of analysis can be devised and more information is often obtained than that possessed by the supplier. The formulator then becomes to a large degree independent of the technical help from the supplier.

The picture is very different in the second situation. The potential profit is so much smaller that technical work has to be limited. The formulation is always required quickly, if not by the customer then at least by one's own sales staff. The resources are generally very much more limited. The overall result is that the formulator becomes very dependent upon the supplier. His main contact from the supplier comes via a sales representative and the technical literature published by the company. The formulator will be hoping that someone can tell him all that the formulation requires together with all safety data and environmental acceptability. However in the case of surfactants, the formulator's major problem is finding and choosing the supplier. As surfactants are often similar in effect, most suppliers will be promoting a particular surfactant. This product might well be the best product in that supplier's range but is it the most cost effective product available on the market? In the first situation above, the technical department have the time and resources to search for the best surfactant. In the second situation, the formulator is dependent upon his own (sometimes literally) knowledge and in extreme circumstances has to make decisions in a matter of days.

The information in this book will not enable formulations to be quickly

made up but should help the formulator in choosing the right family of surfactants and posing the right questions to suppliers in order to identify the best surfactant to use.

There will be a reason for a new or modified formulation. This reason should be firmly established with other members of the company, e.g. the marketing department before commencing work as this reason can and does restrict the choice of surfactant. The most common reasons are:

- Meeting a new market requirement in terms of a completely new product
- Changing the physical characteristics of the formulation
- Improving the functional efficiency of a product
- Reducing costs of a formulation to meet competition
- Avoiding problems of human toxicity
- Avoiding problems of environmental acceptability
- Avoiding a patent

However the exact reason for the need of a new formulation may not be clear in detail or quantifiable. 'It dosen't work' or 'it's too expensive' are often the reasons given by the marketing department. They, however, have their problems and it is likely that the customer has been vague with them. There is no substitute for a meeting with the end user, even if the need is for a cheaper product, in order to identify the critical requirements of the product as seen by the user. Thus after the reason, i.e. the overall objective, is established, there is the need to establish the technical and economic target. The main factors are:

- The end effect (or function) desired and the conditions of use
- The costs to be met
- The physical form
- Restriction on safety in manufacture, handling, transport and use

The end effect and costs are generally related, a high cost product can be sold if it is very efficient, i.e. used in smaller quantities than the cheaper formulation.

In the case of changing an existing formulation, the situation can often arise that the original formulation has been unchanged for many years, the original formulator has retired and there are no detailed records of the development work leading to the formulation. This situation often arises where a company places great importance on the confidentiality of the formulations. Particularly where a formulation contains more than one surfactant, the functions performed by each individual surfactant may not be at all clear. There is now considerable evidence to show that mixtures of different surfactants do show synergistic properties so, if mixtures are present, not only must the properties of each surfactant be identified but also the interaction between them. When there is a need to change a complex formula, it may be simpler to start from basics rather than modify by trial and error.

2.2 Systematic approach

The first essential in a systematic approach is to draw up a detailed requirement for the product:

- Identify the end user's requirement in terms of the function of the finished formulation and how to test for that requirement (if possible)
- Identify the physical properties required by the product and user
- Identify toxicity and ecological requirements
- Identify cost limitations
- Identify time limitations, i.e. when is the new formulation required

Experienced formulators will find that this target requirement can often be determined very quickly but the author strongly urges time to be spent on this analysis in order to avoid wasted time and effort. It must also be realised that one or more of these requirements can change during the course of the development of a formulation. Therefore there is a need to update these requirements if there is a time delay in producing a new formulation. An update should be made at a maximum of 3 months.

These targets can be quickly identified but the problems arise in translating the properties required into the type of surfactant which will satisfy the targets. The following approach is suggested:

1. Consider the cost of the formulation and the quantity of surfactant in the formula; if there is a high proportion of surfactant in the formulation then this can often eliminate high priced surfactants.
2. Identify the physical properties required, e.g. solubility, viscosity, pH range stability, chemical stability, compatibility with other components, hard water tolerance. Again this can often eliminate many surfactants.
3. Try to identify the basic functions provided by the surfactant, namely wetting, foaming, emulsifying, solubilisation, dispersing and cleaning. Cleaning is not a basic property but it is included in this category because it demands the right combination of wetting, foaming, emulsifying and dispersing properties. It is also a very common requirement of household and industrial formulations.

The chapters on the different classes of surfactants have been written in such a way that it is easy to determine the physical and functional properties of the various classes of surfactants.

Cost and availability are probably the most important considerations and the next step should be to see if the properties specified so far would be satisfied with those surfactants which are produced in large volume world-wide. Examine whether the following chemical types can satisfy these criteria: soaps; linear alkylbenzene sulphonates (LABS); alcohol ethoxy sulphates (AES); alcohol sulphates (AS); alkane or paraffin sulphonates (SAS); alcohol ethoxylates (AE). There are many other surfactants available in volume but the above families probably represent the cheapest and most commonly available

products world-wide. There is also the added benefit that safety information on these surfactants is available in great detail.

Once a detailed target and also some idea of the surfactant's requirements have been established then it is much easier to search the technical literature and to put the right questions to potential suppliers. Of major help in creating a new formulation is to find internal reports or personal knowledge from someone who has formulated a similar kind of product. Lacking that help, external sources must be used (see Chapter 3). The five main sources of information are: internal reports or verbal help; manufacturers' literature or advice from their technical departments; specialist books; Chemical Abstracts as an index to published articles; patents.

2.3 Practical formulation

In nearly all cases, a meaningful test for the functional use of a formulation is the most difficult to devise. There are laboratory tests for detergents, wetting agents, lubricants, defoamers, dispersing agents etc. but no one laboratory test can simulate the many different end user requirements. Therefore it is preferable to eliminate as many surfactants/formulations as possible with simple, quick and cheap tests which do not attempt to test for functional use. Requirements such as flash point, viscosity, minimum solids content etc. can be quickly checked. As described in Section 2.2 many products can also be eliminated on cost and safety considerations.

With the use of this handbook, the chemical type of surfactant to give the required end effect can usually be identified. However the exact choice of surfactant can only be made following tests for the end use. Such testing is most easily carried out in the laboratory but the essential need is to correlate laboratory tests with actual practice. With many variables, statistically designed experiments are more efficient but rarely carried out in practice.

When a finished formulation is ready for outside testing it is wise to carry out some simple stability tests because surfactants are usually in a state of semi-solution giving separation of phases, thickening, thinning and sometimes loss of activity. Stability tests at higher (40°C) or lower (freezing) temperatures can often quickly identify unsatisfactory formulations. Visual examination is generally adequate for shelf stability tests. When such tests have been carried out, the products can be released for commercial evaluation. Often a considerable length of time will elapse before results are available from outside customers. Such time should not be wasted. Extended storage trials do not involve much extra effort in visual examination once a week. Additional information can be obtained from suppliers on methods of analysis for quality control, which will be needed if the product is successful commercially.

The quantitative analysis of a surfactant in a formulation is often needed for quality control. Analysis of a single surfactant species is relatively easy and well documented but analysis of small quantities of surfactants in mixtures is