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Principles and Applications



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Library of Congress Card No.: Applied for

British Library Cataloguing-in-Publication

Data: A catalogue record for this book is available from the British Library

Bibliographic information published by

Die Deutsche Bibliothek

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available in the Internet at <<http://dnb.ddb.de>>

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Printed in the Federal Republic of Germany
Printed on acid-free paper

Composition Asco Typesetters, Hong Kong

Printing Strauss GmbH, Mörlenbach

Bookbinding Litges & Dopf Buchbinderei GmbH, Heppenheim

ISBN-13: 978-3-527-30629-9

ISBN-10: 3-527-30629-3

*Dedicated to our Grandchildren
Nadia, Dominic, Theodore and Bruno*

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Preface

Surfactants find applications in almost every chemical industry, such as in detergents, paints, dyestuffs, paper coatings, inks, plastics and fibers, personal care and cosmetics, agrochemicals, pharmaceuticals, food processing, etc. In addition, they play a vital role in the oil industry, e.g. in enhanced and tertiary oil recovery, oil slick dispersion for environmental protection, among others. This book has been written with the aim of explaining the role of surfactants in these industrial applications. However, in order to enable the chemist to choose the right molecule for a specific application, it is essential to understand the basic phenomena involved in any application. Thus, the basic principles involved in preparation and stabilization of the various disperse systems used – namely emulsions, suspensions, micro-emulsions, nano-emulsions and foams – need to be addressed in the various chapters concerned with these systems. Furthermore, it is essential to give a brief description and classification of the various surfactants used (Chapter 1). The physical chemistry of surfactant solutions and their unusual behavior is described in Chapter 2. Particular attention was given to surfactant mixtures, which are commonly used in formulations. Chapter 3 gives a brief description of the phase behavior of surfactant solutions plus a description of the various liquid crystalline phases formed. The adsorption of surfactants at the air/liquid and liquid/liquid interface is described in Chapter 4, with a brief look at the experimental techniques that can be applied to measure the surface and interfacial tension. The adsorption of surfactants on solid surfaces is given in Chapter 5, with special attention given to the adsorption of polymeric surfactants, which are currently used for the enhanced stabilization of emulsions and suspensions. The use of surfactants for preparation and stabilization of emulsions is described in Chapter 6, paying particular attention to the role of surfactants in the preparation of emulsions and the mechanisms of their stabilization. The methods that can be applied for surfactant selection are also included, as is a comprehensive section on the rheology of emulsions. Chapter 7 describes the role of surfactants in preparation of suspensions and their stabilization, together with the methods that can be applied to control the physical stability of suspensions. A section has been devoted to the rheology of suspensions with a brief description of the techniques that can be applied to study their flow characteristics. Chapter 8 describes the role of surfactants in foam formation and its stability. Chapter 9 deals with the role of surfactants in formation and stabilization of nano-emulsions – the latter having recently been

applied in personal care and cosmetics as well as in health care. The origin of the near thermodynamic stability of these systems is adequately described. Chapter 10 deals with the subject of microemulsions, the mechanism of their formation and thermodynamic stability, while Chapter 11 deals with the topic of the role of surfactants in wetting, spreading and adhesion. The surface forces involved in adhesion between surfaces as well as between particles and surfaces are discussed in a quantitative manner.

Chapters 12 to 15 deal with some specific applications of surfactants in the following industries: personal care and cosmetics, pharmaceuticals, agrochemicals and the food industry. These chapters have been written to illustrate the applications of surfactants, but in some cases the basic phenomena involved are briefly described with reference to the more fundamental chapters. This applied part of the book demonstrates that an understanding of the basic principles should enable the formulation scientist to arrive at the optimum composition using a rational approach. It should also accelerate the development of the formulation and in some cases enable a prediction of the long-term physical stability.

In writing this book, I was aware that there are already excellent texts on surfactants on the market, some of which address the fundamental principles, while others are of a more applied nature. My objective was to simplify the fundamental principles and illustrate their use in arriving at the right target. Clearly the fundamental principles given here are by no means comprehensive and I provide several references for further understanding. The applied side of the book is also not comprehensive, since several other industries were not described, e.g. paints, paper coatings, inks, ceramics, etc. Describing the application of surfactants in these industries would have made the text too long.

I must emphasize that the references given are not up to date, since I did not go into much detail on recent theories concerning surfactants. Again an inclusion of these recent principles would have made the book too long and, in my opinion, the references and analysis given are adequate for the purpose of the book. Although the text was essentially written for industrial scientists, I believe it could also be useful for teaching undergraduate and postgraduate students dealing with the topic. It could also be of use to research chemists in academia and industry who are carrying out investigations in the field of surfactants.

Berkshire, January 2005

Tharwat Tadros

1

Introduction

Surface active agents (usually referred to as surfactants) are amphipathic molecules that consist of a non-polar hydrophobic portion, usually a straight or branched hydrocarbon or fluorocarbon chain containing 8–18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic). The hydrophilic portion can, therefore, be nonionic, ionic or zwitterionic, and accompanied by counter ions in the last two cases. The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion–dipole interactions. It is this strong interaction with the water molecules that renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the hydrocarbon chain out of the water and hence these chains are referred to as hydrophobic. As we will see later, the balance between hydrophobic and hydrophilic parts of the molecule gives these systems their special properties, e.g. accumulation at various interfaces and association in solution (to form micelles).

The driving force for surfactant adsorption is the lowering of the free energy of the phase boundary. As we will see in later chapters, the interfacial free energy per unit area is the amount of work required to expand the interface. This interfacial free energy, referred to as surface or interfacial tension, γ , is given in mJ m^{-2} or mN m^{-1} . Adsorption of surfactant molecules at the interface lowers γ , and the higher the surfactant adsorption (i.e. the denser the layer) the larger the reduction in γ . The degree of surfactant adsorption at the interface depends on surfactant structure and the nature of the two phases that meet the interface [1, 2].

As noted, surface active agents also aggregate in solution forming micelles. The driving force for micelle formation (or micellization) is the reduction of contact between the hydrocarbon chain and water, thereby reducing the free energy of the system (see Chapter 2). In the micelle, the surfactant hydrophobic groups are directed towards the interior of the aggregate and the polar head groups are directed towards the solvent. These micelles are in dynamic equilibrium and the rate of exchange between a surfactant molecule and the micelle may vary by orders of magnitude, depending on the structure of the surfactant molecule.

Surfactants find application in almost every chemical industry, including detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibres, plastics.

Moreover, surfactants play a major role in the oil industry, for example in enhanced and tertiary oil recovery. They are also occasionally used for environmental protection, e.g. in oil slick dispersants. Therefore, a fundamental understanding of the physical chemistry of surface active agents, their unusual properties and their phase behaviour is essential for most industrial chemists. In addition, an understanding of the basic phenomena involved in the application of surfactants, such as in the preparation of emulsions and suspensions and their subsequent stabilization, in microemulsions, in wetting spreading and adhesion, etc., is of vital importance in arriving at the right composition and control of the system involved [1, 2]. This is particularly the case with many formulations in the chemical industry.

Commercially produced surfactants are not pure chemicals, and within each chemical type there can be tremendous variation. This is understandable since surfactants are prepared from various feedstocks, namely petrochemicals, natural vegetable oils and natural animal fats. Notably, in every case the hydrophobic group exists as a mixture of chains of different lengths. The same applies to the polar head group, for example with poly(ethylene oxide) (the major component of non-ionic surfactants), which consists of a distribution of ethylene oxide units. Hence, products that may be given the same generic name could vary a great deal in their properties, and the formulation chemist should bear this in mind when choosing a surfactant from a particular manufacturer. It is advisable to obtain as much information as possible from the manufacturer about the properties of the surfactant chosen, such as its suitability for the job, its batch to batch variation, toxicity, etc. The manufacturer usually has more information on the surfactant than that printed in the data sheet, and in most cases such information is given on request.

1.1

General Classification of Surface Active Agents

A simple classification of surfactants based on the nature of the hydrophilic group is commonly used. Three main classes may be distinguished, namely anionic, cationic and amphoteric. A useful technical reference is McCutcheon [3], which is produced annually to update the list of available surfactants. van Os et al. have listed the physicochemical properties of selected anionic, cationic and nonionic surfactants [4]. Another useful text is the *Handbook of Surfactants* by Porter [5]. In addition, a fourth class of surfactants, usually referred to as polymeric surfactants, has long been used for the preparation of emulsions and suspensions and their stabilization.

1.2

Anionic Surfactants

These are the most widely used class of surfactants in industrial applications [6, 7] due to their relatively low cost of manufacture and they are used in practically every

type of detergent. For optimum detergency the hydrophobic chain is a linear alkyl group with a chain length in the region of 12–16 carbon atoms. Linear chains are preferred since they are more effective and more degradable than branched ones. The most commonly used hydrophilic groups are carboxylates, sulphates, sulphonates and phosphates. A general formula may be ascribed to anionic surfactants as follows:

- Carboxylates: $C_nH_{2n+1}COO^-X$
- Sulphates: $C_nH_{2n+1}OSO_3^-X$
- Sulphonates: $C_nH_{2n+1}SO_3^-X$
- Phosphates: $C_nH_{2n+1}OPO(OH)O^-X$

with $n = 8\text{--}16$ atoms and the counter ion X is usually Na^+ .

Several other anionic surfactants are commercially available such as sulphosuccinates, isethionates and taurates and these are sometimes used for special applications. These anionic classes and some of their applications are briefly described below.

1.2.1

Carboxylates

These are perhaps the earliest known surfactants since they constitute the earliest soaps, e.g. sodium or potassium stearate, $C_{17}H_{35}COONa$, sodium myristate, $C_{14}H_{29}COONa$. The alkyl group may contain unsaturated portions, e.g. sodium oleate, which contains one double bond in the C_{17} alkyl chain. Most commercial soaps are a mixture of fatty acids obtained from tallow, coconut oil, palm oil, etc. The main attraction of these simple soaps is their low cost, their ready biodegradability and low toxicity. Their main disadvantages are their ready precipitation in water containing bivalent ions such as Ca^{2+} and Mg^{2+} . To avoid such precipitation in hard water, the carboxylates are modified by introducing some hydrophilic chains, e.g. ethoxy carboxylates with the general structure $RO(CH_2CH_2O)_nCH_2COO^-$, ester carboxylates containing hydroxyl or multi $COOH$ groups, sarcosinates which contain an amide group with the general structure $RCON(R')COO^-$.

The addition of the ethoxylated groups increases water solubility and enhances chemical stability (no hydrolysis). The modified ether carboxylates are also more compatible both with electrolytes and with other nonionic, amphoteric and sometimes even cationic surfactants. The ester carboxylates are very soluble in water, but undergo hydrolysis. Sarcosinates are not very soluble in acid or neutral solutions but are quite soluble in alkaline media. They are compatible with other anionics, nonionics and cationics. Phosphate esters have very interesting properties being intermediate between ethoxylated nonionics and sulphated derivatives. They have good compatibility with inorganic builders and they can be good emulsifiers. A specific salt of a fatty acid is lithium 12-hydroxystearic acid, which forms the major constituent of greases.

1.2.2

Sulphates

These are the largest and most important class of synthetic surfactants, which were produced by reaction of an alcohol with sulphuric acid, i.e. they are esters of sulphuric acid. In practice, sulphuric acid is seldom used and chlorosulphonic or sulphur dioxide/air mixtures are the most common methods of sulphating the alcohol. However, due to their chemical instability (hydrolysing to the alcohol, particularly in acid solutions), they are now overtaken by the chemically stable sulphonates.

The properties of sulphate surfactants depend on the nature of the alkyl chain and the sulphate group. The alkali metal salts show good solubility in water, but tend to be affected by the presence of electrolytes. The most common sulphate surfactant is sodium dodecyl sulphate (abbreviated as SDS and sometimes referred to as sodium lauryl sulphate), which is extensively used both for fundamental studies as well as in many industrial applications. At room temperature ($\sim 25\text{ }^{\circ}\text{C}$) this surfactant is quite soluble and 30% aqueous solutions are fairly fluid (low viscosity). However, below $25\text{ }^{\circ}\text{C}$, the surfactant may separate out as a soft paste as the temperature falls below its Krafft point (the temperature above which the surfactant shows a rapid increase in solubility with further increase of temperature). The latter depends on the distribution of chain lengths in the alkyl chain – the wider the distribution the lower the Krafft temperature. Thus, by controlling this distribution one may achieve a Krafft temperature of $\sim 10\text{ }^{\circ}\text{C}$. As the surfactant concentration is increased to 30–40% (depending on the distribution of chain length in the alkyl group), the viscosity of the solution increases very rapidly and may produce a gel. The critical micelle concentration (c.m.c.) of SDS (the concentration above which the properties of the solution show abrupt changes) is $8 \times 10^{-3}\text{ mol dm}^{-3}$ (0.24%).

As with the carboxylates, the sulphate surfactants are also chemically modified to change their properties. The most common modification is to introduce some ethylene oxide units in the chain, usually referred to as alcohol ether sulphates, e.g. sodium dodecyl 3-mole ether sulphate, which is essentially dodecyl alcohol reacted with 3 moles EO then sulphated and neutralised by NaOH. The presence of PEO confers improved solubility than for straight alcohol sulphates. In addition, the surfactant becomes more compatible with electrolytes in aqueous solution. Ether sulphates are also more chemically stable than the alcohol sulphates. The c.m.c. of the ether sulphates is also lower than the corresponding surfactant without EO units.

1.2.3

Sulphonates

With sulphonates, the sulphur atom is directly attached to the carbon atom of the alkyl group, giving the molecule stability against hydrolysis, when compared with the sulphates (whereby the sulphur atom is indirectly linked to the carbon of the hydrophobe via an oxygen atom). Alkyl aryl sulphonates are the most common

type of these surfactants (e.g. sodium alkyl benzene sulphonate) and these are usually prepared by reaction of sulphuric acid with alkyl aryl hydrocarbons, e.g. dodecyl benzene. A special class of sulphonate surfactants is the naphthalene and alkyl naphthalene sulphonates, which are commonly used as dispersants.

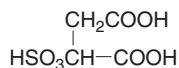
As with the sulphates, some chemical modification is used by introducing ethylene oxide units, e.g. sodium nonyl phenol 2-mole ethoxylate ethane sulphonate, $C_9H_{19}C_6H_4(OCH_2CH_2)_2SO_3^- Na^+$.

Paraffin sulphonates are produced by sulpho-oxidation of normal linear paraffins with sulphur dioxide and oxygen and catalyzed with ultraviolet or gamma radiation. The resulting alkane sulphonic acid is neutralized with NaOH. These surfactants have excellent water solubility and biodegradability. They are also compatible with many aqueous ions.

Linear alkyl benzene sulphonates (LABS) are manufactured from alkyl benzene, and the alkyl chain length can vary from C_8 to C_{15} ; their properties are mainly influenced by the average molecular weight and the spread of carbon number of the alkyl side chain. The c.m.c. of sodium dodecyl benzene sulphonate is $5 \times 10^{-3} \text{ mol dm}^{-3}$ (0.18%). The main disadvantages of LABS are their effect on the skin and hence they cannot be used in personal care formulations.

Another class of sulphonates is the α -olefin sulphonates, which are prepared by reacting linear α -olefin with sulphur trioxide, typically yielding a mixture of alkene sulphonates (60–70%), 3- and 4-hydroxyalkane sulphonates (~30%) and some disulphonates and other species. The two main α -olefin fractions used as starting material are C_{12} – C_{16} and C_{16} – C_{18} .

A special class of sulphonates is the sulposuccinates, which are esters of sulposuccinic acid (1.1).



1.1

Both mono and diesters are produced. A widely used diester in many formulations is sodium di(2-ethylhexyl)sulposuccinate (sold commercially under the trade name Aerosol OT). The diesters are soluble both in water and in many organic solvents. They are particularly useful for preparation of water-in-oil (W/O) micro-emulsions (Chapter 10).

1.2.4

Phosphate-containing Anionic Surfactants

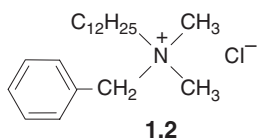
Both alkyl phosphates and alkyl ether phosphates are made by treating the fatty alcohol or alcohol ethoxylates with a phosphorylating agent, usually phosphorous pentoxide, P_4O_{10} . The reaction yields a mixture of mono- and di-esters of phosphoric acid. The ratio of the two esters is determined by the ratio of the reactants and the amount of water present in the reaction mixture. The physicochemical

properties of the alkyl phosphate surfactants depend on the ratio of the esters. Phosphate surfactants are used in the metal working industry due to their anti-corrosive properties.

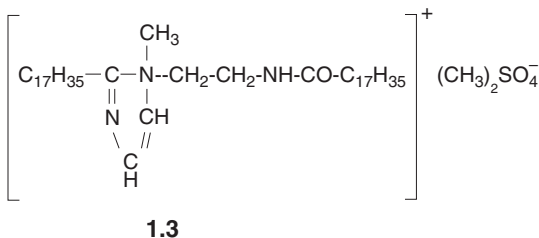
1.3

Cationic Surfactants

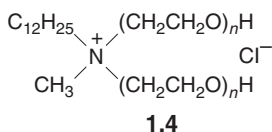
The most common cationic surfactants are the quaternary ammonium compounds [8, 9] with the general formula $R'R''R'''R''''N^+X^-$, where X^- is usually chloride ion and R represents alkyl groups. A common class of cationics is the alkyl trimethyl ammonium chloride, where R contains 8–18 C atoms, e.g. dodecyl trimethyl ammonium chloride, $C_{12}H_{25}(CH_3)_3NCl$. Another widely used cationic surfactant class is that containing two long-chain alkyl groups, i.e. dialkyl dimethyl ammonium chloride, with the alkyl groups having a chain length of 8–18 C atoms. These dialkyl surfactants are less soluble in water than the monoalkyl quaternary compounds, but they are commonly used in detergents as fabric softeners. A widely used cationic surfactant is alkyl dimethyl benzyl ammonium chloride (sometimes referred to as benzalkonium chloride and widely used as bactericide) (1.2).



Imidazolines can also form quaternaries, the most common product being the ditallow derivative quaternized with dimethyl sulphate (1.3).



Cationic surfactants can also be modified by incorporating poly(ethylene oxide) chains, e.g. dodecyl methyl poly(ethylene oxide) ammonium chloride (1.4).



Cationic surfactants are generally water soluble when there is only one long alkyl group. They are generally compatible with most inorganic ions and hard water, but they are incompatible with metasilicates and highly condensed phosphates. They are also incompatible with protein-like materials. Cationics are generally stable to pH changes, both acid and alkaline. They are incompatible with most anionic surfactants, but they are compatible with nonionics. These cationic surfactants are insoluble in hydrocarbon oils. In contrast, cationics with two or more long alkyl chains are soluble in hydrocarbon solvents, but they become only dispersible in water (sometimes forming bilayer vesicle type structures). They are generally chemically stable and can tolerate electrolytes. The c.m.c. of cationic surfactants is close to that of anionics with the same alkyl chain length.

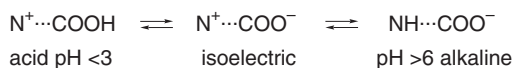
The prime use of cationic surfactants is their tendency to adsorb at negatively charged surfaces, e.g. anticorrosive agents for steel, flotation collectors for mineral ores, dispersants for inorganic pigments, antistatic agents for plastics, other antistatic agents and fabric softeners, hair conditioners, anticaking agent for fertilizers and as bactericides.

1.4

Amphoteric (Zwitterionic) Surfactants

These are surfactants containing both cationic and anionic groups [10]. The most common amphoteric are the N-alkyl betaines, which are derivatives of trimethyl glycine $(\text{CH}_3)_3\text{NCH}_2\text{COOH}$ (described as betaine). An example of betaine surfactant is lauryl amido propyl dimethyl betaine $\text{C}_{12}\text{H}_{25}\text{CON}(\text{CH}_3)_2\text{CH}_2\text{COOH}$. These alkyl betaines are sometimes described as alkyl dimethyl glycinates.

The main characteristic of amphoteric surfactants is their dependence on the pH of the solution in which they are dissolved. In acid pH solutions, the molecule acquires a positive charge and behaves like a cationic surfactant, whereas in alkaline pH solutions they become negatively charged and behave like an anionic one. A specific pH can be defined at which both ionic groups show equal ionization (the isoelectric point of the molecule) (described by Scheme 1.1).



Scheme 1.1

Amphoteric surfactants are sometimes referred to as zwitterionic molecules. They are soluble in water, but the solubility shows a minimum at the isoelectric point. Amphoteric show excellent compatibility with other surfactants, forming mixed micelles. They are chemically stable both in acids and alkalis. The surface activity of amphoteric varies widely and depends on the distance between the charged groups, showing maximum activity at the isoelectric point.

Another class of amphoteric is the N-alkyl amino propionates having the structure $R-NHCH_2CH_2COOH$. The NH group can react with another acid molecule (e.g. acrylic) to form an amino dipropionate $R-N(CH_2CH_2COOH)_2$. Alkyl imidazoline-based products can also be produced by reacting alkyl imidazoline with a chloro acid. However, the imidazoline ring breaks down during the formation of the amphoteric.

The change in charge with pH of amphoteric surfactants affects their properties, such as wetting, detergency, foaming, etc. At the isoelectric point (i.e.p.), the properties of amphoteric resemble those of non-ionics very closely. Below and above the i.e.p. the properties shift towards those of cationic and anionic surfactants, respectively. Zwitterionic surfactants have excellent dermatological properties. They also exhibit low eye irritation and are frequently used in shampoos and other personal care products (cosmetics).

1.5

Nonionic Surfactants

The most common nonionic surfactants are those based on ethylene oxide, referred to as ethoxylated surfactants [11–13]. Several classes can be distinguished: alcohol ethoxylates, alkyl phenol ethoxylates, fatty acid ethoxylates, monoalkanolamide ethoxylates, sorbitan ester ethoxylates, fatty amine ethoxylates and ethylene oxide–propylene oxide copolymers (sometimes referred to as polymeric surfactants).

Another important class of nonionics is the multihydroxy products such as glycol esters, glycerol (and polyglycerol) esters, glucosides (and polyglucosides) and sucrose esters. Amine oxides and sulphinyl surfactants represent nonionics with a small head group.

1.5.1

Alcohol Ethoxylates

These are generally produced by ethoxylation of a fatty chain alcohol such as dodecanol. Several generic names are given to this class of surfactants, such as ethoxylated fatty alcohols, alkyl polyoxyethylene glycol, monoalkyl poly(ethylene oxide) glycol ethers, etc. A typical example is dodecyl hexaoxyethylene glycol monoether with the chemical formula $C_{12}H_{25}(OCH_2CH_2O)_6OH$ (sometimes abbreviated as $C_{12}E_6$). In practice, the starting alcohol will have a distribution of alkyl chain lengths and the resulting ethoxylate will have a distribution of ethylene oxide chain lengths. Thus the numbers listed in the literature refer to average numbers.

The c.m.c. of nonionic surfactants is about two orders of magnitude lower than the corresponding anionics with the same alkyl chain length. The solubility of the alcohol ethoxylates depends both on the alkyl chain length and the number of ethylene oxide units in the molecule. Molecules with an average alkyl chain length