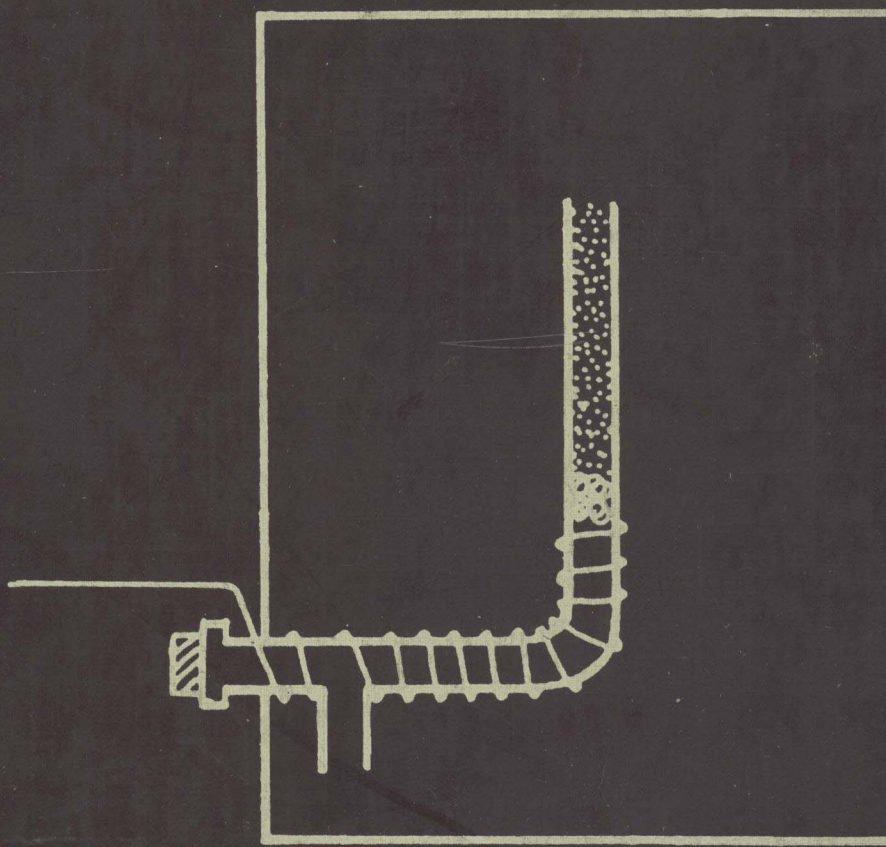
surfactant science series

volume 8

ANIONIC SURFACTANTS - CHEMICAL ANALYSIS



edited by John Cross

Anionic Surfactants-Chemical Analysis

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Anionic Surfactants-Chemical Analysis

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PREFACE

Surface-active agents (surfactants) are currently manufactured in quantities of the order of a million tons per annum, of which about 80% is of the types broadly known as anionic surfactants. This book is part of a series devoted to such compounds and presents a comprehensive coverage of all aspects of analysis, from the measurement of trace quantities in water to quality control during manufacture. It is aimed at readers with a general background of chemistry that includes familiarity with the basic concepts of classical and modern methods of analysis. Consequently, the introduction to analytical techniques has been kept to a minimum. For example, the chapter on gas chromatography contains no discussion on principles of separation, detector choice, etc.; the reader is referred to monographs on the particular technique or to the numerous general texts devoted to modern instrumental methods of chemical analysis for such information. However, no detailed familiarity with surfactants or surface activity is assumed.

The authors, representing an international collection of academic and industrial institutions, have been encouraged to present a critical, up-to-date review of their topic as they themselves see it. In keeping with previous volumes in the series, no attempt has been made to present a group opinion, nor to inhibit the authors by confining them to a fixed format of presentation or a specified range of common surfactants. Each contribution represents a full treatise on a particular aspect of the topic in its own right and consequently readers should find themselves able to use any chapter independently of the remainder. In addition to the material presented in this volume, a chapter on the analysis of raw materials and formulations, automation, and on-stream methods was planned, but unfortunately it was not possible to arrange for coverage of these areas.

Two particular points concerning the contents of this book merit mention in this preface. Firstly, as conceived by Swisher in Volume 3 of this series, the reference section at the end of each chapter contains the titles of the articles in addition to the usual author and location information. Entry to the text via the author index and further reference to the original articles

may thus be on a selective basis. The author index gives the page number on which a particular author's work is cited (even though this name may not necessarily be mentioned in the text), and the page on which the complete reference may be found.

Secondly, as authors, editors, publishers and readers alike are only too aware, research and development work continues during and beyond the time this book was in preparation. I have included in the introduction brief details of the services offered by some of the more prominent organizations dealing with standardization of analytical methods, so that in the years to come, the reader may be able to circumvent conventional literature searching and obtain details of the latest accepted methods from these agencies. This list was not intended to be exhaustive and the omission of reference to a particular organization should not be regarded as indicative that this author considers their work to be of little merit.

My sincere thanks are due to the many individuals and organizations who have supplied me with helpful information, to the management of the Darling Downs Institute of Advanced Education for the availability of facilities and their encouragement to undertake this task, to the authors of each contribution and their companies and finally, but not least, to my wife for her patience and aid in the preparation of the manuscript.

John Cross

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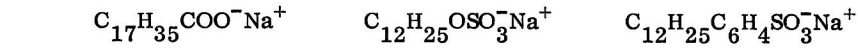
INTRODUCTION

The term "surfactant" is a combination of "surface-active agent" and may be defined as any substance which is strongly adsorbed at a surface or interface. This definition encompasses the majority of substances which function as wetting, cleansing, and emulsifying agents and which are to be found wherever a stable solid-liquid suspension or liquid-liquid emulsion is formed, either during a cleansing process or in the preparation of consumer products such as cosmetics, toilet preparations, mayonnaise, and paints.

Surfactants comprise large molecules containing both nonpolar and polar (or ionic) groups which are referred to as the "hydrophobic" and "hydrophilic" sections, respectively. Traditionally they have been classified into anionic, cationic, nonionic, and ampholytic/zwitterionic types, according to the anture of the hydrophile. Works on the chemical analysis of nonionic and cationic surfactants have been presented elsewhere in this series [1,2]. This volume is devoted solely to the analysis of anionic surfactants, which are commercially the most important, representing about 80% of the total surfactant production. Typical common examples are soaps [1], and salts of sulfated esters of fatty alcohols [2], and alkylbenzenesulfonates [3],



[1] [2] [3]

but a quick survey of the patents in the Surface-active Agent Section of Chemical Abstracts in the last decade will show a formidable array of alternate choices. The chemistry of some of the more important members of this series has been dealt with in a previous volume [3].

As indicated above, anionic surfactants are to be found in a variety of consumer products and consequently in admixture with a wide variety of other substances. For example, in a formulated (or "built") laundry detergent, one would expect to find an anionic surfactant mixed with:

a. Sodium salts such as poly- and monophosphates, nitriloacetates, ethylenediaminetetraacetate, carbonates, and silicates, performing a variety of functions such as binding the surfactant into a free-pouring powder, controlling pH, increasing the ionic strength, preventing corrosion and complexing calcium and magnesium ions

b. Antideposition agents such as sodium carboxymethylcellulose

c. A fluorescent optical brightener

d. Sodium percarbonate or perborate (bleaching agent)

Alternatively the main ingredients of a toothpaste, in addition to a surfactant, are an abrasive (such as calcium carbonate or calcium hydrogen phosphate) slurried, for example, with a glycerol-sorbitol-water mixture to yield the typical viscous paste. Other components would be medicinal ingredients (antiseptics, fluorides, etc.) and flavoring compounds.

The pretreatments required to separate the surfactant from these two types of product will obviously differ considerably and when one considers the vast range of products which contain anionic surfactants, it will be appreciated that specific details for each individual case cannot be provided. Nevertheless, in Chapter 1 an exhaustive collection of methods has been condensed into an authoritative treatise on detection, separation, and isolation of surfactants.

Chapters 1 and 2 describe absorptiometric and some chromatographic methods for the identification of anionic surfactants. Perhaps the term "identification" is too definite, since most commercial products contain a mixture of homologues and isomers of the hydrophobic type, and full identification of each and every component is not always required.

Another system of surfactant classification which has become prominent in the last decade is based upon the susceptibility of the surfactant to degradation by living organisms found in natural waters. Surfactants can be classified as biodegradable (soft) or nonbiodegradable (hard) according to their ability to meet official specifications. A "soft" surfactant is generally one which is at least 80% decomposed within 21 days under specified test conditions; but these requirements may be tightened considerably in the not-too-distant future. Swisher [4], in an exhaustive treatise on surfactant biodegradation, has summarized the susceptibility of a surfactant to biodegradation as

a. Greatly influenced by the nature of the hydrophobe, being deterred by chain-branching in general and by the presence of a terminal t-butyl group in particular

b. Only slightly influenced by the nature of the hydrophile

c. Increased by increased distance between the hydrophile and the end of the hydrophobic chain

Analytical chemistry has played a vital role in the establishment of these principles, and the development of chromatographic methods (Chapters 1 and 3), in particular, has permitted an accurate description of the nature of the alkyl chains.

Chapter 4 describes the application of nuclear magnetic resonance (NMR) spectroscopy to the examination of anionic surfactants. The author has been the principal pioneer into this field that yields complementary information to the standard absorption spectroscopy measurements. A comprehensive collection of correlation tables, spectra, and commentaries are presented.

The rapidly growing concern for the quality of surface waters, that developed as part of the general awakening in environmental matters, has focused attention upon the need for methods for the determination of anionic surfactants at the ppm level or lower. A colorimetric method was first described in 1945 but the road to a technique that showed similar response to a wide variety of anionic surfactants, was relatively unaffected by other components of the sample, and gave consistent results in the hands of independent operators, has been long and arduous. Chapter 5 gives an up-to-date account of the progress of these studies and also introduces some newer, alternative methods. Many organizations are interested in improving and standardizing procedures for the estimation of trace amounts of surfactants in water and also for the collection and preservation of samples. The Water Pollution Control Federation (Washington, D.C.) has a membership of 39 organizations within the United States and is affiliated with 24 overseas organizations; in addition to its regular journal it publishes an annual literature review containing a section on detergents in which one can find references to new developments in trace analysis, and also its well known Standard Methods for Examination of Water and Waste Water (currently in its 13th edition) in which the latest adopted procedures may be found. The U.S. Environmental Protection Agency (EPA) (successor to the Federal Water Pollution Control Administration) has adopted ASTM method D2330-68, based upon the well-known methylene blue extraction technique.

When the concentration of surfactant in a sample can be better expressed in percent than in ppm, the preferred method is volumetric over colorimetric and the most popular methods are based upon the two-phase titration technique. As in the case of colorimetry, a method has been available since the 1940s, but one which satisfies the three criteria mentioned above has not been arrived at easily. In Chapter 6, Heinerth details the work of the Commission Internationale d'Analyses (CIA), of which he was a member, and of the Comité International des Dérivés Tensioactifs (CID), Paris, which has resulted in great improvements over the older methods.

Quality control of manufactured surfactants or surfactant-containing formulations may require determination of a surprising number of common impurities as well as the active ingredient itself. A simple soap, for example, may be tested for unsaponifiable matter, unsaponified matter,

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about the book . . .

Surfactants are currently manufactured in quantities of approximately one million tons per annum; 80% of these are of the type broadly known as anionic surfactants. This volume presents the most comprehensive coverage available of all aspects of analysis of anionic surfactants, containing discussions of their detection, isolation, identification, and estimation in a wide variety of samples in both trace and macro quantities.

Contributors to the volume represent an international collection of academic and industrial institutions and provide critical, up-to-date reviews of their respective topics. Each article is a full treatise on a particular aspect of the subject, complete with extensive references, and readers should be able to use each chapter independently of the remainder. In addition, the editor has included a brief description of the services offered by some of the more prominent organizations dealing with standardization of analytical methods, so that in years to come readers may be able to circumvent conventional literature searching and obtain details of the latest accepted methods from these agencies.

Anionic Surfactants–Chemical Analysis is an invaluable reference for readers with a general chemistry background who are familiar with basic concepts of classical and modern methods of analysis. Workers in the detergent industry and related fields of paints, petroleum, cosmetics, textiles, and metal working will find this volume essential reading, as will those involved in environmental protection.

about the editor . . .

JOHN CROSS lectures in analytical and physical chemistry at the Darling Downs Institute of Advanced Education in Toowoomba, Queensland, Australia. Educated in England, he subsequently joined the Analytical Section of the Distiller's Company Ltd., R and D Department, gaining his first technical qualifications (Higher National Certificate and Graduateship of the Royal Institute of Chemistry) from nearby Kingston Polytechnic. Upon graduation, he joined the Toilet Preparations Division of Unilever Research Laboratory, where he gained experience in surfactant analysis. In 1963 he emigrated to Australia to study at the University of New England, where he was awarded his Masters (1965) and Doctorate (1967) degrees for his work on the mechanisms of gas-phase reactions. Dr. Cross spent two years with The National Research Council of Canada before taking up his current position. He is presently an Associate of the Royal Australian Chemical Institute, and a member of The Royal Institute of Chemistry and The Chemical Society.

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