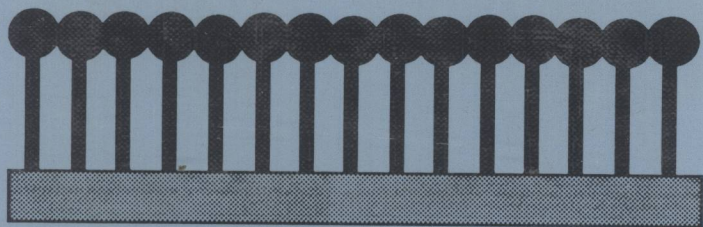
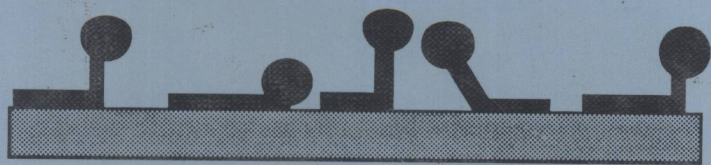
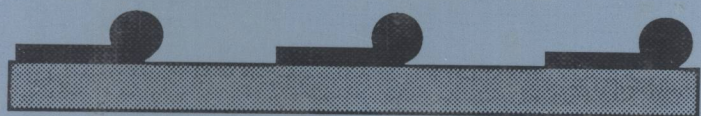


SURFACTANT SCIENCE AND TECHNOLOGY

Drew Myers



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**SURFACTANT SCIENCE
AND TECHNOLOGY**

“For Ruby and Sarge”

PREFACE

Surface science, surface activity, and surfactant technology have historically been relegated to a rather minor position in the overall scheme of the physical sciences. In fact, most undergraduate physical chemistry courses make little more than passing references to the unique nature of surfaces and interfaces. Even the majority of graduate programs, with a few notable exceptions, ignore the subject or offer some introduction on an elective basis. It should not be surprising, then, that most scientific and technical professionals have very little familiarity with the nature of surfaces, or with the properties of surface-active materials or surfactants. They often have problems, therefore, recognizing the need for such materials in their processes or in identifying the surfactant properties that will satisfy the needs of the process. In spite of the large volume of literature covering the fundamental and practical aspects of surface science and surfactant technology, it can be difficult for the nonspecialist to correlate the available information in a way that facilitates its application to a specific system or process.

In the literature of surface science related to the actions of materials at interfaces, the terms "surfactant" and "surface active agent" are encountered. The former term is most popular in North America, while the latter is more common in Europe and is often more acceptable to many workers in the field. In the interest of evenhandedness, these terms will be employed interchangeably throughout the work.

The number of surface active materials available commercially today reaches into the thousands. Even if relatively pure materials are considered, the number of compounds exceeds 700. It is easy to understand, therefore, why many chemists, engineers, biologists, and others having the need to employ surfactants may feel daunted by the prospect of plowing through the literature to find the best material for their purpose. Even if inclined to do so, they may face the investment of inordinate amounts of time and effort without guarantee of success.

A comprehensive coverage of a subject as broad and complex as

the science and technology of surfactants is not possible in a single volume of reasonable length. One has only to look at the extensive "Surfactant Science Series" published by Marcel Dekker to appreciate what such a project involves. There are, however, some basic principles of the science and art of surfactant action, for art it can be at times, that can help the uninitiated to make "educated guesses" as to a preferred material or materials for a particular application - hopefully helping to avoid lengthy and expensive empirical processes. The aim of this work, therefore, is to present in a very basic way the concepts of surface activity and surfactant action that relate the molecular structure of surfactants to their activity and utility at various interfaces.

If one examines the more fundamental scientific literature on surface activity, it is apparent that exhaustive measures are usually taken to ensure that the materials being studied are of the highest possible purity. Such measures are necessary, of course, to isolate the basic chemical and physical phenomena occurring in a system, and to facilitate proper interpretation of the data. Most applications of surfactants and surface activity, on the other hand, do not involve the use of such pure materials. In fact, it is often found that high purity is a disadvantage in the application of many surfactants, since the presence of certain contaminants or mixtures may greatly enhance the desired interfacial effects. In addition, the steps required to obtain high purity surface active materials can be tedious as well as expensive, making such processes economically unfeasible. Because of this dichotomy in the scientific and technological aspects of surface activity, it is becoming more and more difficult for nonspecialists to quickly and intelligently choose surfactants to fit their needs.

Because the goal of this work is to provide a narrow bridge between the basic, theoretical aspects of surfactant science and the less well defined and more empirical world of its applications, it is necessary to make many compromises as to the material included and the way in which it is presented. The theoretical material, for example, is limited to that which seems most useful for the presentation of a clear picture of the chemical and physical principles under consideration. For the reader desiring a more in-depth discussion, there exists a large body of general reference material that covers the theoretical aspects of surface activity in detail. Many such references are provided in the Bibliography for each chapter. A similar approach is used in relation to the more practical applications being considered. Since the volume of literature on surfactants and surface activity is so large and is growing so rapidly, no particular attempt has been made to offer the "latest word" on a specific subject. Reference is generally made to works which seem to clearly illustrate the concept under discussion, with no regard as to the chronological position of the work.

The book has been organized to facilitate its use as a quick reference as well as a general information source. Chapter One, for example, includes some historical and economic information covering

the development and application of surface active materials, and an introduction to some key terms and conventions. Chapter Two presents a discussion of the organic chemistry of surface active agents, including general classifications based upon chemical structure and raw materials sources, and a general discussion of some synthetic methods employed in surfactant preparation. Finally, Chapters Three through Eight cover the most significant physical phenomena associated with surface activity, relating surfactant structure and activity to the nature of the various interfaces encountered. Because of the complexity of many surfactant applications, it is not possible to provide valid generalizations related to structure/performance relationships. However, from the material presented, it may be possible to eliminate many "dead end" trails and, as a result, to save a great deal of time and money in an increasingly competitive world.

Because of the constantly increasing number of publications on surfactants, their synthesis, purification, characterization, and applications, any attempt to produce a truly current literature review is destined to become a case of "the faster I go, the 'behinder' I get." With the introduction of newer, more sensitive experimental techniques, we now have the ability to look at surfactant-related phenomena at the molecular level to an extent impossible just 10 years ago. All of this newly accessible knowledge has clearly added a great deal to our understanding of many of the fundamental molecular forces and processes underlying macroscopic interfacial phenomena. It is not as obvious, however, that such intimate knowledge of interfacial properties is of immediate, vital importance to the understanding of the macroscopic properties and applications of surfactants. At the possible risk of offending some basic research interests, I have generally omitted reference to and discussion of many recent developments in our understanding of surfactants and their activity that seem to be more detailed than required by the scope of this work. Such omission is certainly not intended as a judgment on the value of the research, but rather as a necessary editorial decision. After wading through a mountain of reference material supplied by a computer search of published literature on surfactants and their applications, that decision also resulted out of concern for the mental health of the author!

Works of this kind can seldom be prepared without the assistance of a variety of people. I take this opportunity to thank the many people who have contributed to this work, either by direct input and comment, or through their moral support and material assistance, particularly Drs. Nissim Garti, Ravi Sharma, and Brad Coltrain, and Ms. Kim Goppert. I also wish to thank the management of the Eastman Kodak Company Research Laboratories for supporting the drafting of the original manuscript. A very special thanks goes to Graciela, Adriana, and Katrina who managed to survive it all.

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CHAPTER ONE

SURFACTANT SCIENCE AND TECHNOLOGY: AN OVERVIEW

INTRODUCTION

The rapid evolution in the chemical nature of our modern society has made it increasingly difficult for scientists, engineers, regulators, and managers to remain abreast of the latest in the technologies impacting their work. The volume of scientific and technical journals published worldwide number in the thousands, and this volume increases yearly. Paralleling the proliferation of the scientific literature in general has been an apparent divergence into fields of "pure" science (ie, studies with their principal goal being the general advancement of human knowledge) and "applied" science and technology (in which the research is driven by some anticipated application). Few areas of chemistry have exhibited this growing dichotomy of purpose more than the study of surface and colloid science, especially as applied to surface activity and surface active materials. Even the nomenclature used in discussing materials showing surface activity is widely varied, depending on the context of the discussion. It is not surprising, then, that the world of surface activity and surface active agents, or surfactants, can appear complex and confusing to those not intimately involved in it on a day-to-day basis.

When one considers the impact of surface science in general, and emulsions, dispersions, foaming agents, wetting agents, etc, in particular, on our day-to-day existence, the picture that develops reveals the overwhelming extent to which these areas of chemistry and chemical technology permeate our lives. From the fundamental aspects of biological membrane formation and function in living cells, to the more "far out" problem of how liquids wet the walls of a rocket's fuel tank in a low gravity environment, the physical chemistry of the interactions among various phases at interfaces lies at the root of much of our modern life style.

Industrial concerns, whose very life-blood may be intimately linked to the application of the basic principles of interfacial interactions, often ignore the potential benefits of fundamental research in these areas in favor of an empirical "trial-and-error" approach, which may lead to a viable process but which could possibly be better understood and even significantly improved by the application of more fundamental science. In many cases the prevailing philosophy seems to be, to paraphrase an old adage, "A dollar in the hand is worth two in the laboratory." Unfortunately, such an approach often results in more dollars down the drain than many management level decision makers care to admit. Academic researchers, on the other hand, are sometimes guilty of ignoring the potential practical aspects of their work in favor of experimental sophistication and the "Holy Grail" of the definitive theory or model. Neither philosophy alone truly satisfies the needs of our technological existence. Each approach makes its valuable contribution to the overall advancement of human knowledge; however, it sometimes appears that a great deal is lost in the translation between the two.

The science and the technology of surfactants have possibly suffered a double blow from the functional divergence of academic and applied research. Academic interest in surfactants, while increasing in recent years, has generally concentrated on highly purified, homogeneous materials (quite often limited to a few materials such as sodium dodecylsulfate, SDS, or cetyltrimethylammonium bromide, CTAB), and elegant analytical techniques. While providing a wealth of useful information related to the particular system under investigation, the application of such information to more complex practical materials and processes is often less than obvious, and is sometimes misleading. In the results-oriented industrial environment, with some significant exceptions, surfactant research is often carried out on a "make it work and don't worry about why!" basis. The industrially interesting materials are usually complex mixtures of homologs and isomers, or contain impurities resulting from chemical side reactions or unreacted starting materials. Particularly significant surface property changes can be induced by the presence of such impurities as inorganic salts from the sulfonation of aromatic materials or long-chain alcohols remaining after incomplete sulfation. While the presence of such impurities and mixtures will often produce superior results in practice, analysis of the process may be difficult because of the unknown or variable nature of the surfactant composition. Considering the limitations imposed by each school of surfactant research, it is not surprising to find that a practical fusion of the two approaches can be difficult to achieve.

The different views of surfactant science and technology have spawned their own distinctive terminologies and literatures. While the academic or fundamental investigator may probe the properties of surface active agents, surfactants, tensides, or amphiphiles, the industrial chemist may be concerned with the characteristics of soaps, detergents, emulsifiers, wetting agents, etc. The former group may publish their

results primarily in the Journal of Physical Chemistry, Colloids and Surfaces, Langmuir, or the Journal of Colloid and Interface Science, the latter in the Journal of the American Oil Chemists Society, the Journal of Dispersion Science and Technology, or one of the other technologically specialized publications. All too often, the value of the results to each community can become lost in the sea of manuscripts, and the philosophical and operational gulf that sometimes develops between the two schools.

Before beginning a discussion of specific aspects of the chemistry of surface active materials and surfactant action, it may be useful to have some idea of the history of surfactants and how their synthesis and use have evolved through the years. Because of parallel developments in various areas of the world, the secrecy of industrial research efforts, and the effects of two world wars, the exact details of the evolution of surfactant science and technology may be subject to some controversy regarding the specific order and timing of specific developments. In any case, the major facts are (hopefully!) correct.

A BRIEF HISTORY OF SURFACTANT SCIENCE AND TECHNOLOGY

The pedigree of the synthetic surfactant industry is reasonably well documented, unlike that of the more ancient "natural" alkali soaps. However, it is not an easy task to pinpoint the exact time when the industry came into being. In a strictly chemical sense, a soap is a compound formed by the reaction of an essentially water insoluble fatty acid with an alkali metal or organic base to produce a carboxylic acid salt with enhanced water solubility, sufficient to produce surface activity. Since the soaps require some form of chemical modification to be useful as surfactants, they could therefore be considered to be synthetic; however, custom dictates that they not be classified in the same category as the materials prepared by more elegant synthetic routes.

The alkali metal soaps have been used for at least 2300 years. Their use as articles of trade by the Phoenicians as early as 600 B.C. has been documented.¹ They were also used by the Romans, although it is generally felt that their manufacture was learned from the Celts or some Mediterranean culture. Early soap producers used animal fats and ashes of wood and other plants containing potassium carbonate to produce the neutralized salt. As the mixture of fat, ashes, and water was boiled, the fat was saponified to the free fatty acids, which were subsequently neutralized.

The first synthetic (nonsoap) materials employed specifically for their surface active properties were the sulfated oils.¹ Sulfonated castor oil, also known as Turkey-red oil, was first introduced in the late nineteenth century as a dyeing aid, and is still used in the textile and leather industries today.² The first surfactants for general application that have been traditionally classified as synthetic were developed in

Germany during World War I in an attempt to overcome the developing shortage of available animal and vegetable fats. Those materials were short-chain alkyl naphthalene sulfonates prepared by the reaction of propyl or butyl alcohol with naphthalene followed by sulfonation. The products proved to be only marginally useful as detergents, but showed good wetting characteristics and are still in use as such. They are still sold under their original trade name Nekals, as well as other names, in Europe and the United States.

In the late 1920s and early 1930s, the sulfation of long-chain alcohols became common and the resulting products were sold as the sodium salt. Also in the early 1930s, long-chain alkylaryl sulfonates with benzene as the aromatic group appeared in the United States. Both the alcohol sulfates and the alkylbenzene sulfonates were used as cleaning agents at that time, but made little impact upon the general surfactant or detergent markets.³ By the close of the World War II alkylaryl sulfonates had almost entirely overwhelmed the alcohol sulfates for use as general cleaning agents, but the alcohol sulfates were beginning to emerge as preferred components in shampoo and other personal care formulations.

In common with other chemical developments during that time, progress in the area of surfactants and detergents was not limited to one family of materials. The explosion of new organic chemical processes and raw materials led to the development of a wide variety of new surface active compounds and manufacturing processes. In a particular country, the limiting factor was almost always the availability of raw materials from which to prepare the desired product.

Concurrent with the advance of alkylaryl sulfonates, activities in the United States and Germany led to the development of the taurine (2-aminoethane-1-sulfonic acid) derivatives (eg, Igepon-T, sodium oleyl tauride) and the alkane sulfates (Mersolates), respectively. In the United Kingdom, secondary olefin sulfates (Teepols) derived from petroleum fractions were produced in large quantities. Each of those raw materials had its own special advantages and disadvantages; but in evaluating their feasibility, the producer had to consider such factors as the availability and cost of raw materials, ease of manufacture, the economics of manufacture and distribution, and overall product stability. As a result of its ease of manufacture and versatility, the alkylbenzene sulfonates very quickly gained a strong position in the world market. After World War II, the propylene tetramer (PT, primarily a branched C_9H_{19} alkyl) coupled to benzene became a predominant material. Thus, sulfonated PT-benzenes very rapidly displaced all other basic detergents and for the period 1950-1965 constituted more than half of all detergents used throughout the world.³

Propylene tetramer benzenesulfonate held almost undisputed reign as the major ingredient used in washing operations until the early 1960s. Around that time it was noted that sewage effluents were producing ever greater amounts of foaming in rivers, streams, and lakes throughout the world. In addition, where water was being drawn from