

surfactant science series

NONIONIC SURFACTANTS

Chemical Analysis

Volume **19**

edited by

John Cross

NONIONIC SURFACTANTS^{*}

Chemical Analysis

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Soil and Water Studies Centre
Darling Downs Institute of Advanced Education
Toowoomba, Queensland, Australia



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NONIONIC SURFACTANTS

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Preface

The market for nonionic surfactants continues to increase steadily, currently composing over 30% of the total surfactant sector; such materials are replacing anionic surfactants in many laundry products and continually finding new fields of application in their own right. The consumption of alkylphenol oxyethylates was some 140,000 tonnes in the United States alone in 1982.

It has been nearly 20 years since the first of Marcel Dekker, Inc.'s outstandingly successful Surfactant Science series rolled off the presses and into the literature collections of every major surface activity institution around the world. *Nonionic Surfactants*, edited by Martin Schick and published in 1967, has had an enormous impact in the surface science community and even today retains its place as one of the most frequently quoted reference texts on the topics.

Now, with the enormous advances in analytical techniques that have occurred since that time, certain segments of the content which merited only a chapter or two are now deserving of a volume in their own right. The analytical chemistry of these substances unquestionably falls into this category: progress in nuclear magnetic resonance and in separation techniques alone would justify this.

Defining the exact scope of the ideal contents for a volume of this nature is a daunting task indeed. The very term "surface-active agent" suggests that any substance capable of adsorption at an interface should be included. As a class of compounds, nonionic surfactants must be broadly regarded as comprising all surfactants which are not aptly categorized within the well-defined groups of anionic, cationic, and amphoteric types. This makes for an extraordinarily diverse range of structures and applications throughout the whole range of hydrophile-lipophile balance (HLB) values: from surface film producers (e.g., fatty alcohols) through emulsifiers and foam stabilizers (e.g., fatty acid condensates of polyols and alkanolamines) right up to the poly

(oxyethylated) detergents and solubilizers. Beyond the farthest end of the scale lie the polyethylene glycols themselves: free from any hydrophobic moiety whatsoever, they can scarcely be classed as surface active, but since they are common integral components of oxyethylated surfactant samples and also respond to many of the analytical methods used for their surface-active counterparts, they are justifiably included in this treatise.

The authors, representing an international collection of academic institutions and industrial concerns, have not been required to operate within any preconceived framework. Rather, they have been encouraged to concentrate on whatever segments of this broad subject area their particular topic heading and own expertise and interests may dictate. Necessarily some chapters are concerned with oxyalkylates alone.

This book is aimed at practicing chemists possessing a general background knowledge including familiarity with the basic concepts of classical and modern chemical analysis. The reader will be referred to a variety of general texts on modern instrumental analysis and monographs relating to particular techniques. No detailed knowledge of surfactants or surface activity, however, is assumed, although such is necessary particularly if the analysis is to be extended to include minor components and contaminants. Hence this volume commences with a chapter devoted to this aspect.

It is not intended that this volume should function as a laboratory manual, although experimental details are included throughout. Rather it provides an introduction to the basic problems that face the analyst and to the array of weapons, including the literature, on which he can draw in order to formulate an attack. There is seldom any one "right" way to approach a particular analysis; so much depends on the nature of the sample and on the extent of detail and sophistication required by the end user of the results. Combinations of techniques may provide the best approach: not necessarily the formal couplings such as GC/MS but perhaps use of MR to measure aromatic, alkyl, and oxyethylene proton ratios plus GLC to determine chain distributions.

My sincere thanks are extended to the authors for providing their contributions so readily; to Dr. Martin Schick, Consulting Editor for the Surfactant Science series, for his continued interest and support; to the entire Marcel Dekker organization, who so smoothly and patiently guided me along the production road; and finally to my wife for her patience and aid in the preparation of this manuscript.

John Cross

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Part A

Introduction

Introduction to Nonionic Surfactants

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1. NONIONIC SURFACTANTS: CHARACTERISTICS AND GENERAL PROPERTIES

The term *surfactant*, or *surface-active agent* to use the full title, is defined conveniently for the purpose of this work as any substance that when mixed with water will congregate at interfaces rather than in the bulk of the solution (in contrast to the behavior of most solutes, which by virtue of maximizing the solute/solvent interaction, will concentrate in the bulk of the solution, away from surfaces). Such substances may have a very limited solubility in water: those with a high solubility may exist in the bulk phase in aggregates commonly known as micelles. In the vast majority of cases, the adsorption occurring at the interface is accompanied by a substantial decrease in interfacial tension.

The essential structural features of such a molecule are nonpolar hydrocarbon, normally an alkyl chain of not less than 10 carbon atoms, bonded to a polar or ionic group, giving rise to nonionic and ionic surfactants, respectively. The degree of surface activity and type of application depend on the net effects of these polar (hydrophilic) and nonpolar (hydrophobic, lipophilic) sections. Griffin [1] found it possible to quantify the relationship between the two ends on an empirical basis in terms of the hydrophile-lipophile balance (HLB), a value which increases in indirect proportion to the overall polarity of the molecule. These HLB values can be broadly used to indicate the suitability of a particular surfactant to a particular purpose, namely:

HLB range	Application
<3	Surface films
3-6	Water-in-oil emulsifiers
7-9	Wetting agent
8-15	Oil-in-water emulsifiers
13-15	Detergents
15-18	Solubilizers

The analytical chemist might initially be tempted to use this table in reverse, i.e., as a guide to the identity of a surfactant once having determined its function. However, two factors prevent this:

1. A very wide variety of structures give similar values for HLB, and
2. A desired HLB may have been achieved by the blending of two or more surfactants with HLBs either side of the overall value.