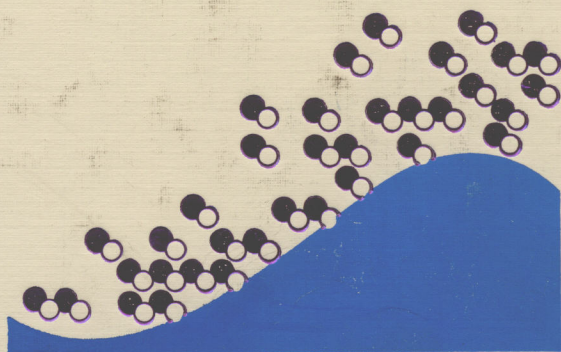


# Mixed Surfactant Systems



EDITED BY  
**Paul M. Holland and  
Donn N. Rubingh**

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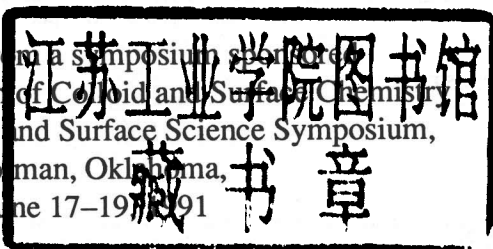
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# Mixed Surfactant Systems

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## Foreword

THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of this series is to publish comprehensive books developed from symposia, which are usually "snapshots in time" of the current research being done on a topic, plus some review material on the topic. For this reason, it is necessary that the papers be published as quickly as possible.

Before a symposium-based book is put under contract, the proposed table of contents is reviewed for appropriateness to the topic and for comprehensiveness of the collection. Some papers are excluded at this point, and others are added to round out the scope of the volume. In addition, a draft of each paper is peer-reviewed prior to final acceptance or rejection. This anonymous review process is supervised by the organizer(s) of the symposium, who become the editor(s) of the book. The authors then revise their papers according to the recommendations of both the reviewers and the editors, prepare camera-ready copy, and submit the final papers to the editors, who check that all necessary revisions have been made.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

*M. Joan Comstock*  
Series Editor

## Preface

MIXED SURFACTANT SYSTEMS ARE ENCOUNTERED in nearly all practical applications of surfactants. This situation is due to the inherent difficulty of preparing chemically pure surfactants and the performance advantage or synergism that often results from deliberately mixing different surfactant types, and it has led to considerable theoretical and experimental work to understand the properties and behavior of these complex systems. Six years ago, volume 311 in this series, *Phenomena in Mixed Surfactant Systems*, was the first to address this topic in book format. Now, expanded interest and additional work in this field lead us to reexamine this topic.

The present volume is divided into six sections dealing with various aspects of mixed surfactant systems. First, the overview section introduces the topic with a review of mixed surfactant systems, a basic introduction to modeling, and comments on the terminology used to describe nonideal mixing. The second section examines different approaches to modeling mixed surfactant aggregates based on thermodynamics, geometry, and molecular interactions. This section includes two new molecular modeling approaches, as well as a pseudophase approach for modeling polydisperse mixtures. Because mixed micelle formation exerts a controlling influence on the behavior of mixed surfactant systems, the third section addresses mixed micellar solutions and associated phenomena. Included are thermodynamic studies of mixed micellization, electron spin resonance (ESR) and NMR studies of mixed micelles, partitioning from micellar solution into an oil phase, and the effect of mixed micelles on chemical reaction rates. The fourth section covers mixtures containing unusual surfactant types, such as fluorocarbon, siloxane, bolaform, and bile salt surfactants. These surfactants often exhibit marked differences in behavior compared with standard hydrocarbon surfactants. Most practical benefits of surfactants arise from their effects on interfacial properties, and the fifth section deals with the adsorption of mixed surfactants at interfaces. Topics include synergism at various interfaces, modeling of contact angles and Langmuir monolayers, and experimental studies of adsorption at solid-liquid interfaces. The final section of the book deals with phase boundaries and solubilization in mixed surfactant systems. These topics include both precipitation and cloud point phenomena, as well as the solubilization of insoluble surfactants into mixed surfactant aggregates.

This volume is the result of the collective effort and expertise of many leading specialists in the area of mixed surfactant systems. We hope that by summarizing progress in this challenging area the book will benefit those developing new surfactant technology, students wishing to learn about the effects of surfactant mixtures, and other researchers in colloid and surface science seeking to advance understanding of these complex systems.

We wish to express our appreciation to the many authors who participated in this effort and without whom this volume could not have been completed. We would also like to acknowledge the organizers of the 65th Colloid and Surface Science Symposium, and we thank John Scamehorn for both encouraging the sessions on which this book is based and leading the way with his previous volume.

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## OVERVIEW

# Chapter 1

## Mixed Surfactant Systems

### An Overview

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The properties and behavior of mixed surfactant systems are discussed in the context of experimental techniques and modeling. The overview begins with a general description of mixed surfactant solutions, followed by a more detailed examination of mixed micelles, surfactant mixtures at interfaces, and the phase behavior of mixed systems. Topics include experimental measurements, approaches to modeling, nonideality, unusual surfactant types, micellar demixing, adsorption at various interfaces, chemical reactions in micelles, precipitation, cloud point phenomena and perspectives on the direction of future research on mixed surfactant systems.

Mixed surfactant systems are encountered in nearly all practical applications of surfactants. These mixtures arise from several sources. First is the natural polydispersity of commercial surfactants which results from impurities in starting materials and variability in reaction products during their manufacture. These are less expensive to produce than isomerically pure surfactants and often provide better performance. Second is the deliberate formulation of mixtures of different surfactant types to exploit synergistic behavior in mixed systems or to provide qualitatively different types of performance in a single formulation (e.g. cleaning plus fabric softening). Finally, practical formulations often require the addition of surfactant additives to help control the physical properties of the product or improve its stability.

Because of the growing theoretical interest and practical importance of mixed surfactant systems, this topic has seen much activity in recent years. Previous comprehensive overviews (1,2) and a book devoted to mixed surfactant systems (3) are now several years old, and a more recent book chapter is focused primarily on mixed systems which contain cationic surfactants (4). This overview is intended to provide both an overall introduction to the many areas discussed in detail by the authors of the chapters which follow, and an up-to-date general survey of work on the topic of mixed surfactant systems.

## General Description of Mixed Surfactant Solutions

Aqueous solutions of surfactants, whether mixtures or single surfactants, exhibit a variety of interesting and useful phenomena. Even at low concentrations of surfactant in water, significant effects can be observed at interfaces with the solution. The most pronounced effect is a lowering of interfacial tension due to preferential adsorption of surfactant molecules at solution interfaces. With increasing surfactant concentration, the experimentally measured decrease in surface tension becomes linear with the logarithm of the surfactant concentration and surfactant monolayers or bilayers are formed at solution interfaces. Finally, a concentration is reached where this linear decrease in surface tension suddenly stops and striking changes occur in the light scattering in solution. At this critical micelle concentration (CMC), surfactant molecules undergo cooperative self-association to form large surfactant aggregates (micelles) with the hydrophobic chains of the molecules residing in the interior of the aggregates and the hydrophilic head groups at the surface in contact with aqueous solution. In this process both ideal and nonideal mixing contributions may occur. Since the hydrophobic effect (5) which drives the overall process is not specific to surfactant "head" group, the formation of randomly mixed surfactant aggregates will tend to be favored. This can be viewed as leading to the "ideal" component of mixing in the aggregate. In the case of mixtures with different surfactant types, electrostatic interactions between "head" groups can provide the basis for the "nonideal" component of mixing in the aggregate.

A mixed micellar solution is schematically illustrated in Figure 1 where a mixture of two surfactant types is indicated by open and filled circles representing the head groups. Shown are representations of a mixed micelle, mixed monolayer at the air/solution interface, and mixed bilayer aggregate at the solid solution interface. Rapid equilibrium between monomers and micelles establishes the concentration of each of the surfactant species in solution and thereby controls their chemical potential. The chemical potentials in turn represent the thermodynamic driving force for processes such as interfacial tension lowering and contact angle changes, and at equilibrium establish a thermodynamic link between surfactant molecules at interfaces and the mixed micellar solution.

Mixtures of different surfactant types often exhibit synergism in their effects on the properties of the system (6-14). The observed synergism can be attributed to nonideal mixing effects in the aggregates, and results in substantially lower CMCs and interfacial tensions than would be expected based on the properties of the unmixed surfactants alone. This situation has led to both theoretical and practical interest in developing a quantitative understanding of the behavior of mixed surfactant systems, and can be exploited in applications such as detergency (14-16), enhanced oil recovery (17) and mineral flotation (18). We begin with the topic of mixed micelles, since monomer-micelle equilibrium exerts a key controlling influence on the behavior of the overall mixed surfactant system.

### Mixed Micellar Solutions

Mixed micellar systems involving a wide range of surfactant types have been studied. These include all combinations of typical nonionic, anionic, and cationic surfactant

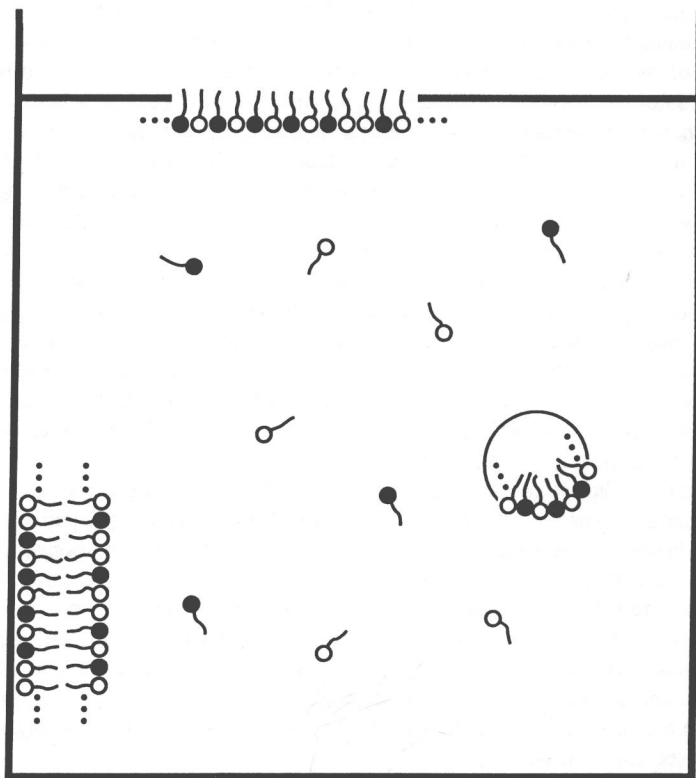


Figure 1. Schematic representation of phenomena in a mixed micellar solution of two surfactant types, illustrated by open and filled head groups. Shown are representations of surfactant monomers, a mixed micelle, mixed monolayer at the air/solution interface, and a mixed bilayer aggregate at the (hydrophilic) solid-solution interface (see text).



types, as well as binary mixtures of each of these with zwitterionic surfactant types. Some examples of these types of mixtures (9-12,19-26) are listed and discussed in Chapter 2 of this volume (27). Mixtures containing various surfactants with unusual hydrophobic groups and molecular structures have also been studied, and are covered in a separate section below.

**Experimental Mixed CMC Measurements.** Measurements show that the formation of mixed micelles in aqueous solution leads to striking changes in solution properties such as surface tension and light scattering. Among the experimental techniques routinely used for measuring mixed CMCs are surface tension measurements, conductivity, dye solubilization and light scattering. Other methods have also been demonstrated including calorimetry and oil-solution interfacial tension measurements.

The most widely used technique for the determination of mixed CMCs employs surface tension measurements. Here, the surface tension of a solution is measured at a number of concentrations both above and below the CMC and results plotted against the logarithm of surfactant concentration. The CMC is then taken as the "break point" or intersection of straight lines drawn through data representing the limiting surface tension above the CMC and the linear slope below the CMC (22). Measurement of surface tensions for this purpose have been performed using tensiometers with du Nouy ring (21,28-30) or Wilhelmy plate (6,22,31,32) and the sessile-drop method (33,34). A closely related technique has been demonstrated using interfacial tension at the oil-solution interface and the spinning-drop method (35,36).

Conductivity measurements (28,36-38) have also been employed in measurements of mixed CMCs but are necessarily limited to mixtures which contain ionic surfactants. Here, a break in the plot of conductivity versus concentration is taken to be the CMC. A related method which involves the use of specific ion electrodes to monitor the activity of counterions has also been used (29,39,40).

The dye solubilization method is a traditional technique that was used in much of the early work for determining mixed CMCs (41,42). It is currently not widely used for measuring mixed CMCs however, due in part to the potential problem of solubilized dye interacting with surfactant in the micelles and affecting the value of the CMC.

Light scattering measurements can also be applied for the determination of mixed CMCs (32). The most common technique is to measure the intensity of scattered light perpendicular to the incident beam at different surfactant concentrations. Since the intensity of scattered light increases significantly upon micellization, the CMC can be determined from the intersection of the linear regions above and below this discontinuity. An added benefit of using the light scattering technique is that it is possible to determine the micelle molecular weight provided other optical constants of the solution are available. This application is covered in a separate section below.

A related light scattering technique, known as quasi-elastic light scattering (QELS), measures the spectral distribution of the incident single frequency light upon scattering. The spectral half-width is proportional to the diffusion coefficient of the particle doing the scattering and hence also changes abruptly at the CMC when micelles are formed. The application of QELS to mixed micelles is discussed elsewhere in this volume (43).

Titration calorimetry has also been demonstrated for the measurement of mixed

CMCs (20,44), but has seen little use to date. Here, an isoperibol titration is employed to monitor the heat of demicellization of a concentrated mixed micellar solution as it is diluted. When the CMC is reached, a sharp break is observed. Good results for mixed CMCs can be obtained as long as sufficient heats of micellization are present.

**Monomer Concentration and Micelle Composition.** Fewer experimental measurements of monomer concentrations and micelle composition have been carried out in mixed micellar systems. If either of these is known at a given surfactant concentration, the other can be calculated using the mixed CMC. One of the primary techniques for determining monomer concentrations and micelle composition is ultrafiltration using membranes with molecular weight cutoffs which allow surfactant monomers to pass the filter but prevent micelles from passing. This has been applied to various anionic-nonionic (21,45,46) and zwitterionic (20) hydrocarbon surfactant mixtures, as well as fluorocarbon-hydrocarbon mixtures (47). A similar approach using gel filtration has been applied to fluorocarbon-hydrocarbon surfactant mixtures (48).

A very promising new development is the use of surfactant selective electrodes to study mixed surfactant systems. This experimental approach has been applied in a detailed thermodynamic study of cationic-sulfobetaine mixtures reported in this volume by Hall et al. (49).

Micelle compositions have also been probed using NMR self-diffusion measurements (50), and surfactant activities in "mixed" protonated/unprotonated amine-oxide micelles determined from titrations (51). A new technique based on the decay of hydrated electrons has been developed to measure monomer concentrations of fluorocarbon surfactants in mixed anionic fluorocarbon-hydrocarbon surfactant systems. This is discussed in this volume (52). Structural details of various mixed anionic-nonionic, cationic-nonionic and anionic-cationic micelles have been probed using electron spin echo modulation and electron spin resonance techniques and this is also discussed in this volume (53).

**Micelle Size and Aggregation Numbers.** Various techniques have been applied to experimentally determining mixed micelle sizes, with those based on the scattering of photons (or other particles) most widely used. Binary mixed micelles of hydrocarbon surfactants studied by light scattering include nonionic-nonionic (54), anionic-nonionic (54-56), cationic-nonionic (54) and zwitterionic-anionic (32) mixtures. Mixed fluorocarbon-hydrocarbon surfactant systems have been studied by light scattering (56), and small angle neutron scattering studies have been made on both mixed micelles of anionic-nonionic (57) and cationic-nonionic (58) hydrocarbon surfactants and anionic-anionic fluorocarbon-hydrocarbon surfactant mixtures (59). A fluorescence probing technique has also been used to investigate micelle sizes in both anionic-nonionic hydrocarbon surfactant mixtures (60), and fluorocarbon-hydrocarbon anionic-nonionic (60,61), nonionic-anionic (61), nonionic-nonionic (61) and anionic-anionic (60) surfactant systems.

**Mixtures with Unusual Surfactant Types.** Mixed micellar solutions containing unusual surfactant types present an interesting area for study. These mixtures include