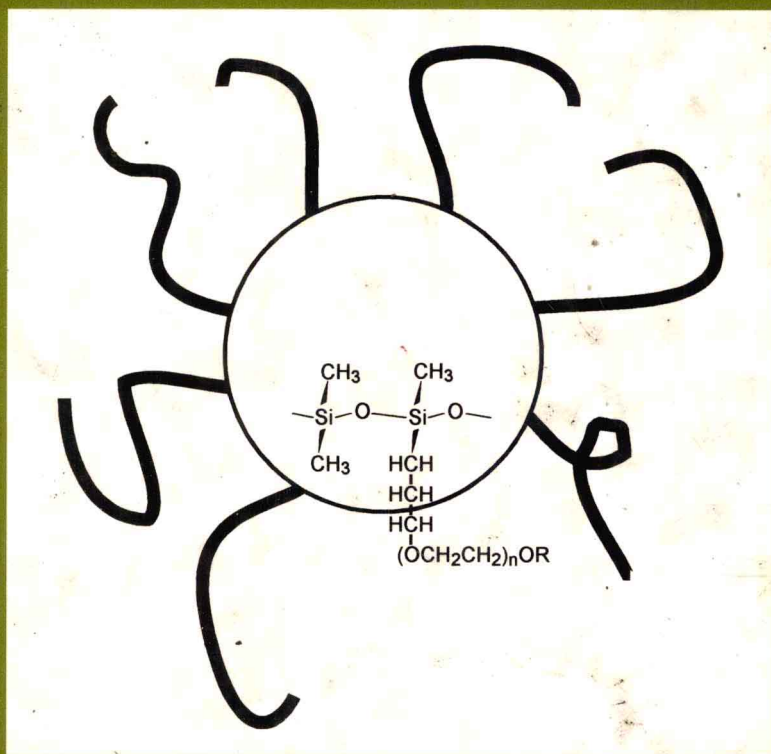


surfactant science series  
volume **86**

# SILICONE SURFACTANTS



edited by  
Randal M. Hill

# SILICONE SURFACTANTS

edited by  
Randal M. Hill

*Dow Corning Corporation  
Midland, Michigan*



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## Preface

Although silicone surfactants are a commercially important class of novel surfactants with numerous applications—ranging from their use in the manufacture of polyurethane foam to applications in coatings, household and personal care products, and foam control and as exceptional wetting agents—the literature on their properties and applications is limited and widely scattered among many journals, patents, and trade publications. Judging from the rapidly growing number of recent publications, the interest in this class of surfactants is increasing dramatically. The intent of the current volume is to bring together in one place a comprehensive introduction to the preparation, uses, and physical chemistry of silicone surfactants. As such, it should be of value both as an introduction to and as a reference source for this fascinating class of surfactants.

Polydimethyl siloxane and many copolymers containing dimethyl siloxane groups are surface active in a variety of aqueous and nonaqueous media. This book focuses primarily on those silicone polyoxyalkylene copolymers that are surface active in aqueous systems, but also includes chapters on two important nonaqueous systems—polyurethane foam and polymer blend compatibilizers. The book begins with an introductory chapter that overviews the preparation, physical chemistry, and applications of silicone surfactants. This broad perspective is followed by detailed discussions of each of these areas. Chapters 2 and 3 cover the synthesis and analysis of silicone surfactants including a number of novel silicone surfactants. Chapter 4 details the surface activity and aggregation behavior of silicone surfactants. Chapters 5–10 discuss specific applications including polyurethane foam manufacture, personal care, coatings, fabric finishes and polymer surface modifiers, foam control, and agricultural adjuvancy. Chapters 11 and



12 deal with two areas of significant recent activity—the unusual wetting behavior of the trisiloxane surfactants and the ternary phase behavior of mixtures of silicone surfactants with water and silicone oils. The emphasis throughout the volume is on understanding and insight rather than formulary presentations.

A variety of authors were enlisted to contribute different perspectives to the work, including representatives from each of the major manufacturers and academic specialists who have studied the surfactancy of silicone surfactants. Thus the work represents the collective effort and knowledge of an international group of scientists and technologists. I hope it will be valuable to those seeking to make use of silicone surfactants in diverse applications as well as to researchers seeking to better understand fundamental surfactancy phenomena by examining the differences and similarities between hydrocarbon and silicone surfactants.

*Randal M. Hill*

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## Siloxane Surfactants

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## I. INTRODUCTION

Siloxane surfactants consist of a permethylated siloxane group coupled to one or more polar groups. This class of surfactants finds a variety of uses in applications where other types of surfactants are relatively ineffective [1–3]. Siloxane surfactants have certain unique properties:

1. Their hydrophobic group is silicone, so that
2. They are able to lower surface tension to  $\approx 20$  dyn/cm compared with  $\approx 30$  dyn/cm for typical hydrocarbon surfactants, causing them to be
3. Surface active in both aqueous and nonaqueous media.

In addition,

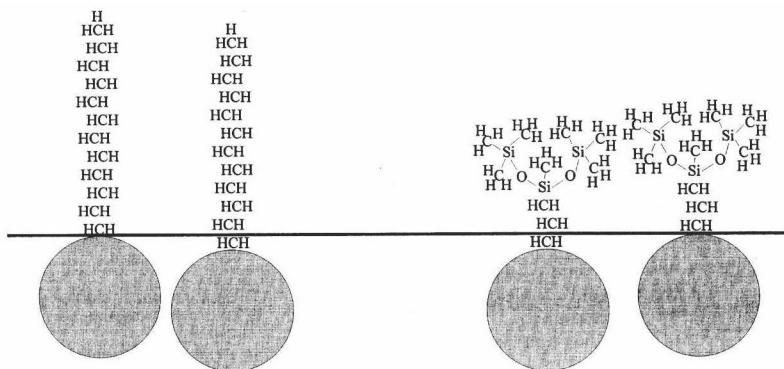
4. They are prepared by different chemistries, yielding molecular structures of different types and ranges [4,5], which are often fluid to very high molecular weights [6].

Siloxane surfactants were introduced to the marketplace in the 1950s for the manufacture of polyurethane foam [7]. Soon afterward other applications were invented for them [8]. Nonaqueous surface activity is the basis for their use in polyurethane foam manufacture, as demulsifiers in oil production, and as defoamers in fuels. Their ability to lower surface tension leads to wetting and spreading applications. Different molecular structures and high molecular weights make them useful as novel emulsifiers. Silicones impart a unique dry-lubricity feel to surfaces such as textiles, hair, and skin. Since siloxane surfactants incorporate silicone in a water-soluble or water-dispersible form, they represent a convenient means for putting silicone on a surface by way of an aqueous formulation.

The molecular origin of the principal difference between hydrocarbon and siloxane surfactants is illustrated in Fig 1. The surface active character of siloxane surfactants is due to the methyl groups, the  $\text{—O—Si—O—Si—}$  backbone simply serves as a flexible framework on which to attach the methyl groups [9–12]. The surface energy of a methyl-saturated surface is about 20 dyn/cm [9], and this is

$-\text{CH}_2-$  groups dominate the interface, 30-32 dynes/cm

$-\text{CH}_3$  groups dominate the interface, 20-21 dynes/cm



**FIG. 1** Comparison of the surface character of hydrocarbon versus siloxane surfactants.

also the lowest surface tension achievable using siloxane surfactants. In contrast, most hydrocarbon surfactants consist of alkyl, or alkylaryl hydrophobes, which contain mostly  $-\text{CH}_2-$  groups, and pack loosely at the air-liquid interface. The surface energy of such a surface is dominated by the methylene groups, and for this reason hydrocarbon surfactants typically achieve surface tensions of about 30 dyn/cm or higher [9]. Thus, the lower surface tensions given by siloxane surfactants can be traced directly to molecular structure, the unusual flexibility of the siloxane backbone, and the different surface energies of  $-\text{CH}_3$  versus  $-\text{CH}_2-$ .

Siloxane surfactants are similar to hydrocarbon surfactants in many common features of surfactancy [2,13-15]:

1. There is a break in their surface tension versus log concentration curve reflecting the onset of self-association (such as micelle formation).
2. Critical aggregation concentrations (cac) vary with molecular structure in the same way—within a homologous series, proportionately larger hydrophobic groups lead to smaller cac values.
3. They show similar patterns of self-association in aqueous solution, forming aggregates and liquid crystal phases, of the same types and following the same trends with molecular structure.
4. Siloxane surfactants incorporating polyoxyalkylene groups also show inverse temperature solubility and cloud points.

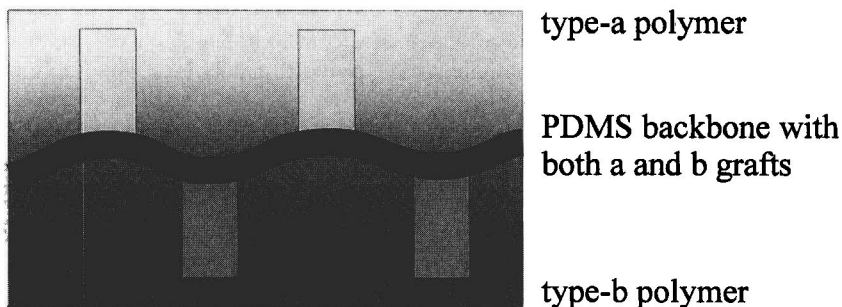
This last point requires some clarification: in the dilute concentration range, many siloxane surfactants form cloudy lamellar phase dispersions that are unrelated to the existence of a cloud point as it is usually understood [13].



Substantial advances in our understanding of this class of surfactants in recent years have covered their aqueous aggregation behavior, their ternary phase behavior with silicone oils, and their ability to promote rapid wetting of hydrophobic substrates. This chapter attempts to describe the structure, preparation, and surfactancy properties of this fascinating class of surfactants incorporating these recent advances. A brief discussion of some common applications also is given to illustrate how the unusual properties of siloxane surfactants are used. Detailed treatments of synthesis, superwetting, aqueous aggregation, and ternary phase behavior, and selected application topics are given elsewhere in this volume.

## II. MOLECULAR STRUCTURES AND NOMENCLATURE

Polydimethylsiloxane (PDMS) is itself surface active [16]. Gruning and Koerner [4] suggest a broad definition of siloxane surfactants to include all surface active copolymers containing a siloxane entity. We prefer to limit the scope to molecules with well-defined and well-separated hydrophilic and hydrophobic parts. Copolymers and terpolymers based on the PDMS backbone can be used to modify interfacial properties (one such use is illustrated in Fig. 2) and could be included under the umbrella of siloxane surfactants. There is a significant literature on such materials [17–23], and they are discussed by Yilgor in this volume [24]. This introduction focuses primarily on siloxane surfactants that are useful in aqueous systems. Most siloxane surfactants are copolymers of PDMS and polyalkylene oxides of intermediate molecular weight. Nonaqueous surface chemistry is briefly discussed, as well as a selection of nonaqueous applications. The primary nonaqueous application, polyurethane foam manufacture, is reviewed elsewhere in this volume.



**FIG. 2** Silicone terpolymer used as a polymer blend compatibilizing agent.