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GEMINI SURFACTANTS

Synthesis, Interfacial and Solution-Phase Behavior, and Applications

edited by

Raoul Zana

Jiding Xia

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Cover: Microstructure of a 1.5 wt% solution of the gemini (dimeric) surfactant 12-2-12 as visualized by cryo-transmission electron microscopy. Additional explanation is given in the legend of Fig. 7 and Ref. 57 in Chapter 7.

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Preface

Surfactants are present in most aspects of our daily life: in the soap or gel we use when showering in the morning, in the creams and cosmetics we spread on our skin, in many of the foods we have from breakfast to night, in the detergents we use in our washing machine and dishwasher, and in some of the medications we may be prescribed. They are also present in the processes used to prepare the clothes we wear, and the metals and plastics in most of the tools, appliances, cars, and so forth, we use. It should therefore not come as a surprise that research on, and developments of, new surfactants has always been very active in spite of the fact that surfactant catalogs list hundreds if not thousands of surfactants of all types—anionic, cationic, zwitterionic, and nonionic. The world production of surfactants is probably close to 10 million tons per year, worth several billions of dollars. Any new surfactant with novel properties or improved performances or capable of improving the economics of a given process would translate into savings of millions of dollars. In addition, new surfactants with lower toxicity or environment-friendly characteristics have a promising future, as new regulations that will most likely be enacted in the coming years will require the surfactants used in formulations to have a lower level of toxicity and less impact on the environment and to be more easily degraded by natural biological processes.

A new type of surfactant, the so-called *dimeric* or *gemini* surfactants, has recently generated much interest in academic circles and among scientists at surfactant-producing companies. These surfactants are made up of two amphiphilic surfactant-like moieties connected at the level of the head groups or very close to the head groups by a spacer group of varied nature. Several reasons can be given for the present interest in gemini surfactants. First their critical micellization concentration (cmc) is generally at least one order of magnitude lower than that of the corresponding conventional (monomeric) surfactants. Second, they are 10–100 times more efficient at reducing the surface tension of water and the interfacial tension of the oil–water interface than conventional surfactants. Third, the aqueous solutions of some dimeric surfactants with a short spacer can have extremely interesting rheological properties (viscoelasticity, shear thickening). Finally, the microstructure of some gemini surfactant solutions shows unexpected but remarkable micellar shapes. In fact, the properties of gemini surfactants are in some respects so unexpected and superior to those of comparable conventional surfactants that Rosen, in a paper published in *Chemtech* in March 1993, referred to gemini surfactants as "surfactants for the nineties." This statement was premature, but certainly gemini surfactants are the surfactants for the future.

Gemini surfactants can be generated with an enormous variety of structures because it is in principle possible to take any two identical or different surfactants among the available ones and connect them by a spacer group that can be hydrophilic or hydrophobic, flexible or rigid, heteroatomic, aromatic, and so on. New properties will probably be discovered for the gemini surfactants that can be synthesized. In addition, the concept of gemini (dimeric) surfactants has been extended to longer homologs, trimeric surfactants made up of three surfactant-like moieties connected by two spacer groups, tetrameric surfactants, etc. The number of possible structures is truly mind-boggling.

Research on gemini surfactants is expanding, both in universities and in chemical companies. Formulations based on anionic dimeric surfactants made by Condea (now Sasol GmbH, Marl, Germany) have reached the market. Because of their superior properties and special performances, gemini surfactants have been suggested in formulating products for more effective wetting, solubilizing, dispersing, thickening, making of microemulsion, antimicrobial activity, and other industrial uses. It thus appeared timely to prepare a volume that would present the state of the art of gemini surfactants for those already doing research work on these surfactants or planning to do so, in both the academic and industrial worlds.

This volume comprises 13 chapters that provide as complete a view of gemini surfactants as possible at the time of the writing of the book. It is hoped that the interesting properties that these surfactants display will draw more people in the field. The help of synthetic organic chemists is much needed for the complicated and challenging synthesis involved in generating gemini surfactants with complex structure. Physicochemists and physicists will follow to study the properties of these new compounds. Industrial surfactant scientists will accompany these developments at all stages.

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GEMINI SURFACTANTS

Contents

1
Introduction

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I. DEFINITION OF GEMINI (DIMERIC) SURFACTANTS AND HISTORIC ASPECTS

Gemini (also called dimeric) surfactants represent a new class of surfactants made up of two identical or different amphiphilic moieties having the structure of conventional (monomeric) surfactants connected by a spacer group [1]. The spacer may be hydrophobic (aliphatic or aromatic) or hydrophilic (polyether), short (two methylene groups) or long (up to 20 and more methylene groups), rigid (stilbene) or flexible (polymethylene chain). Figure 1a gives a schematic representation of a gemini surfactant. At the outset, it must be emphasized that the spacer group must connect the two amphiphilic moieties at the level of, or in close vicinity to, the head groups. If the connection takes place in the middle or toward the end of the alkyl chains of the amphiphilic moieties as in Fig. 1b, the surfactant is then a bolaform surfactant endowed with properties that are inferior to those of conventional surfactants.

Gemini surfactants have been known in the patent literature since 1935. This literature has been recently reviewed [2,3] and is not dealt with here. To the best of our knowledge the first report on gemini surfactants in the scientific literature is that of Bunton et al. in 1971 [4]. These authors synthesized bisquaternary ammonium bromide gemini surfactants and studied how the micelles of these surfactants affect the rate of chemical reactions. This work was followed by that of Devinsky et al. [5] who synthesized bisquaternary ammonium gemini surfactants with a great variety of structures, and that of Okahara et al. [6], who synthesized a large number of anionic gemini surfactants. The variety of gemini surfactants that have been synthesized to this day is already enormous. It includes anionic, cationic, zwitterionic, and nonionic surfactants with all kinds of spacer group. Gemini surfactants with al-

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