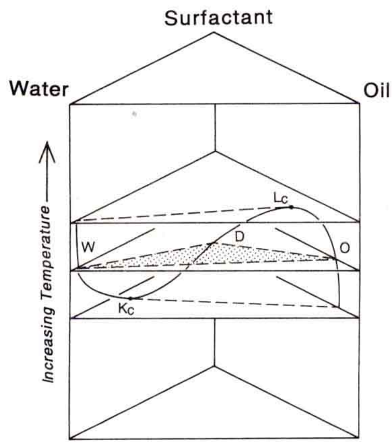
surfactant science series

volume 66

INDUSTRIAL APPLICATIONS OF MICROEMULSIONS



edited by

Conxita Solans

Hironobu Kunieda

INDUSTRIAL APPLICATIONS OF MICROEMULSIONS

edited by

Conxita Solans
Consejo Superior de Investigaciones Científicas
Barcelona, Spain

Hironobu Kunieda
Yokohama National University
Yokohama, Japan

Marcel Dekker, Inc. **New York•Basel•Hong Kong**

Library of Congress Cataloging-in-Publication Data

Industrial applications of microemulsions / edited by Conxita Solans.
Hironobu Kunieda.
p. cm.— (Surfactant science series ; v. 66)
Includes bibliographical references (p. -) and index.
ISBN 0-8247-9795-7 (Hardcover : alk. paper)
1. Emulsions. I. Solans, C. II. Kunieda, Hironobu.
III. Series.
TP156.E6I5 1997
660'.294514—dc20

96-44788
CIP

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This book is printed on acid-free paper.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

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Preface

In recent years microemulsions have attracted a great deal of attention not only because of their importance in industrial applications but also because of their intrinsic interest. They optimize the performance of a wide spectrum of industrial and consumer products and processes.

Microemulsions are isotropic and thermodynamically stable multicomponent fluids composed of water, oil, and amphiphile(s). The characteristic properties of microemulsions include spontaneous formation, optically clear appearance, large interfacial area, low interfacial tension, large solubilization capability, and low viscosity—properties that render these organized solutions unique.

Practical applications of microemulsions preceded their scientific recognition. But the related industrial development was limited for many years due to a lack of basic knowledge of these colloidal solutions. However, the rapid and continuous progress achieved over the past decade has stimulated many novel applications ranging from lubricating fluids to agricultural sprays, drug delivery systems, and reaction media. At present, industrial applications of microemulsions are under active and growing development.

The literature on microemulsions is extensive, and the field has recently experienced rapid progress. In early volumes of the Surfactant Science series, information on microemulsions was scattered throughout a chapter or parts of chapters, whereas more recently whole volumes have been devoted to the exploitation of their basic aspects. Nevertheless, there is still a shortage of information on their applications. An exhaustive review did appear in 1984, in Volume 6 of this series. But in view of the enormous advances in the field of microemulsions in the past few years, there has developed a need for a book devoted to their industrial applications. This publication satisfies that need.

The main objective of this book is to provide a comprehensive description of the most useful industrial applications of microemulsions. It is aimed at scientists, engineers, and students with either industrial or academic interests. It will also stimulate the interest of managers in industry.

The contributors are leading experts from industry and academia. They have been actively engaged in the research and development of various technological applications of microemulsions.

The two introductory chapters focus on basic concepts of microemulsions, which are essential to understanding their industrial significance. These chapters are followed by a comprehensive discussion of relevant technological and industrial applications. The scope of the coverage reflects the state of development and availability of the published material on the subject. Some of the applications (e.g., enhanced oil recovery) are well known and have been extensively reviewed in many previous publications. In such cases, only the major recent developments have been considered. Other well-established applications (e.g., pharmaceuticals, cosmetics, agrochemicals, and lubricants) for which there is not an extensive literature are explored in considerably more depth. This book also contains chapters on the relatively new areas of applications such as biotechnology, foods, textile dyeing, extraction processes, analytical determinations, and preparation of nanostructured materials.

We wish to thank all the contributors for their efforts. We also wish to thank Dr. Martin J. Schick, the editor of this series, for his encouragement in undertaking this task, and production editors, Mr. J. Stubenrauch and Mr. H. Boehm, for their help during the preparation of this volume. We are especially indebted to Mr. and Mrs. Guruswamy and to Mrs. Lidia Beltrán, who provided considerable assistance in helping to edit the book.

Conxita Solans
Hironobu Kunieda

Contributors

Masahiko Abe Faculty of Science and Technology, Science University of Tokyo, Chiba, Japan

Raquel E. Antón Laboratorio FIRP, Facultad de Ingeniería, Universidad de los Andes, Mérida, Venezuela

A. C. Auguet Hispano Química, S.A., Barcelona, Spain

Nuria Azemar Departamento Tecnología de Tensioactivos, Centro de Investigación y Desarrollo, Consejo Superior de Investigaciones Científicas, Barcelona, Spain

Ermanno Barni Dipartimento di Chimica Generale ed Organica Applicata, Università degli Studi di Torino, Turin, Italy

Marc Bavière Reservoir Engineering Department, Institut Français du Pétrole, Rueil-Malmaison, France

Karin Bonkhoff Institut für Angewandte Physikalische Chemie, Forschungszentrum Jülich GmbH, Jülich, Germany

Jean Paul Canselier Institut de Génie des Procédés, Ecole Nationale Supérieure d'Ingénieurs de Génie Chimique, Toulouse, France

Stephanie R. Dungan Departments of Food Science and Technology, and Chemical Engineering and Materials Science, University of California, Davis, Davis, California

Stig E. Friberg Center for Advanced Materials Processing and Department of Chemistry, Clarkson University, Potsdam New York

F. X. Gaillard Hispano Química, S.A., Barcelona, Spain

Maria José García-Celma Departamento de Farmacia, Facultad de Farmacia, Universidad de Barcelona, Barcelona, Spain

Maria Rosa Gasco Dipartimento di Scienza e Tecnologia del Farmaco, Università degli Studi di Torino, Turin, Italy

Francesc Gusi Hispano Química, S.A., Barcelona, Spain

Xiomara Gutiérrez INTEVEP, S.A., Research and Technological Support Center of Petróleos de Venezuela, Caracas, Venezuela

Krister Holmberg Institute for Surface Chemistry, Stockholm, Sweden

Hironobu Kunieda Graduate School of Engineering, Yokohama National University, Yokohama, Japan

M. Arturo López-Quintela Department of Physical Chemistry, University of Santiago de Compostela, Santiago de Compostela, Spain

J. L. Margrave Department of Chemistry, Rice University, Houston, Texas

Hideo Nakajima Basic Research Laboratories, Shiseido Research Center, Yokohama, Japan

Vinod Pillai Center for Surface Science and Engineering, Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, Florida

Ramon Pons Departamento de Tecnología de Tensioactivos, Centro de Investigación y Desarrollo, Consejo Superior de Investigaciones Científicas (CSIC), Barcelona, Spain

José Quibén-Solla Laboratory of R&D, La Artística de Vigo, Vigo, Spain

Hercilio Rivas Production Department, INTEVEP, S.A., Research and Technological Support Center of Petróleos de Venezuela, Caracas, Venezuela

José Rivas Department of Applied Physics, University of Santiago de Compostela, Santiago de Compostela, Spain

Jean-Louis Salager Laboratorio FIRP, Facultad de Ingeniería, Universidad de los Andes, Mérida, Venezuela

Piero Savarino Dipartimento di Chimica Generale ed Organica Applicata, Università degli Studi di Torino, Turin, Italy

Milan J. Schwuger Institut für Angewandte Physikalische Chemie, Forschungszentrum Jülich GmbH, Jülich, Germany

Dinesh O. Shah Center for Surface Science and Engineering, Departments of Chemical Engineering and Anesthesiology, University of Florida, Gainesville, Florida

A. Shukla Department of Chemistry, Southeast College, Houston, Texas

Shyam S. Shukla Department of Chemistry, Lamar University, Beaumont, Texas

Johan Sjöblom Department of Chemistry, University of Bergen, Bergen, Norway

Conxita Solans Departamento de Tecnología de Tensioactivos, Centro de Investigación y Desarrollo, Consejo Superior de Investigaciones Científicas (CSIC), Barcelona, Spain

Günter Subklew Institut für Angewandte Physikalische Chemie, Forschungszentrum Jülich GmbH, Jülich, Germany

Th. F. Tadros Zeneca Agrochemicals, Bracknell, United Kingdom

Guido Viscardi Dipartimento di Chimica Generale ed Organica Applicata, Università degli Studi di Torino, Turin, Italy

José Luis Ziritt Reservoir Engineering Department, INTEVEP, S.A., Research and Technological Support Center of Petróleos de Venezuela, Caracas, Venezuela

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Overview of Basic Aspects of Microemulsions

CONXITA SOLANS and RAMON PONS Departamento de Tecnología de Tensioactivos, Centro de Investigación y Desarrollo, Consejo Superior de Investigaciones Científicas (CSIC), Barcelona, Spain

HIRONOBU KUNIEDA Graduate School of Engineering, Yokohama National University, Yokohama, Japan

I. INTRODUCTION

It is now well established that large amounts of two immiscible liquids (i.e., water and oil) can be brought into a single phase, macroscopically homogeneous but microscopically heterogeneous, by addition of an appropriate surfactant or surfactant mixture. This unique class of optically clear solutions called microemulsions comprises the colloidal systems that have attracted much scientific and technological interest over the past decade. This wide interest stems from their characteristic properties, namely ultralow interfacial tension, large interfacial area, and solubilization capacity for both water- and oil-soluble compounds. These and other properties render microemulsions intriguing from a fundamental point of view and versatile for industrial applications.

Microemulsions had already been used in technological and household applications well before they were scientifically described for the first time as special colloidal dispersions by Hoar and Schulman in 1943 [1]. These authors reported the spontaneous formation of a transport or translucent solution upon mixing of oil, water, and an ionic surfactant combined with a cosurfactant (i.e., a medium chain length alcohol). At first, Hoar and Schulman [1] referred to this new type of colloidal dispersion as an oleophatic hydromicelle, and Bowcott and Schulman [2] referred to it with other names, such as transparent emulsions, at later stages of their studies. In 1959, about 15 years after Schulman's first publication on the subject, Schulman et al. [3] introduced the term microemulsion, the term that has prevailed for these systems.

Microemulsions form under a wide range of surfactant concentrations, water-to-oil ratios, temperature, etc.; this is an indication of the occurrence of diverse structural organizations. The picture that emerged from the earlier work on microemulsions [1–3] was that of spherical water or oil droplets dispersed in either oil (W/O) or water (O/W) with radii of the order of 100 to 1000 Å. In addition to droplet-type structures, the existence of microemulsions with bicontinuous structures in which the surfactant forms interfaces of rapidly fluctuating curvature and both the water and oil domains are continuous was later established [4].

A great deal of debate about the definition of microemulsions originated from the different concepts of the nature of these systems. Whereas Schulman et al. [1–3] viewed microemulsions as two-phase kinetically stable emulsions, Shinoda and Kunieda [5] pointed out that microemulsions could not be considered true emulsions but are one-phase systems with solubilized water or oil, identical to micellar solutions. Phase behavior studies by Friberg et al. [6–9] and Shinoda et al. [10–13] confirmed that most of Schulman's so-called microemulsions fell in the one liquid phase regions of the phase diagrams of the corresponding systems; that is, they were solubilized solutions. Adamson [14] suggested calling the microemulsions "micellar emulsions." The debate concerning thermodynamic stability of microemulsions continued in the 1980s. The definition of microemulsions suggested by Danielsson and Lindman [15] as systems of water, oil, and an amphiphile(s), which are single-phase and thermodynamically stable isotropic solutions, is quite widely accepted. However, other authors consider that the condition of thermodynamic stability is an unnecessary limitation and advocate a definition including, instead, the concept of spontaneous formation as more appropriate [16].

II. HISTORICAL BACKGROUND

A. Applications

The history of the early growth and development of microemulsions of industrial interest was extensively described by Prince [17], a pioneer in the study of theoretical and practical aspects of microemulsions. This has been the source of most of the information given in this section. The industrial development of microemulsions started in the 1930s, about 30 years before the term microemulsions was proposed by Schulman et al. [3]. However, applications of microemulsions at a domestic level were already known earlier. Indeed, it has been reported [18,19] that a very efficient recipe consisting of an oil-in-water microemulsion was widely used for washing wool more than a century ago in Australia. The formulation was made of water, soap flakes, methylated spirits, and eucalyptus oil.

The first marketed microemulsions were dispersions of carnauba wax in water. They were prepared by adding a soap (i.e., potassium oleate) to melted wax followed by incorporation of boiling water in small aliquots. The resulting opalescent formulations were used as a floor polisher and formed a glossy surface on drying. The opalescence of the dispersion obtained was interpreted as due to the presence of very small droplets (below 140 nm). The effectiveness and stability of the liquid wax formulations stimulated the development of many other formulations consisting of either O/W or W/O microemulsions [17]. An example of a particularly successful application of microemulsions of the W/O type was the formulation of cutting oils. Mineral oil-in-water emulsions had been used as effective coolants and lubricants for machine tool operations. However, after several cycles of operation, their efficiency decreased because of emulsion instability. The development of stable cutting oil formulations represented a great improvement in this area. The first formulations consisted of mineral oil (the lubricant), soap, petroleum sulfonate (an emulsifier and corrosion inhibitor), ethylene glycol (a coupling agent), an antifoam agent, and water (the coolant). Generally, the water was added by the user and the "soluble oil," the rest of the ingredients, was the commercial product [17]. Later, other formulations to which the user added both the oil and water were developed.

Simultaneously with the development of the O/W-type microemulsion formulations, a cleaning solution that was a microemulsion of the W/O type was introduced on the market. It consisted of pine oil, wood rosin, sodium oleate, and about 6% water. These solutions can be regarded as a precursor of the modern antiredeposition agents. On addition of this W/O microemulsion formulation to the washing solution, inversion to a microemulsion of the O/W type occurred, provided that the initial concentration of soap was sufficient. Soon afterward, O/W microemulsions (based on pine oil) experienced rapid development as fluid cleaning systems for floors, walls, etc. [17].

In the next decades, the 1940s and 1950s, microemulsion formulations were introduced in several areas of applications, from foods (flavor oils) to agrochemicals (pesticides), detergents (dry textile cleaning), and paints (latex particles). The task of microemulsion formulators was greatly facilitated by the commercial availability of nonionic emulsifiers. Previously, soaps were almost the only emulsifiers used in industry. The high hydrophile-lipophile balance (HLB) of soaps rendered formulation of microemulsions difficult, requiring the presence of long-chain alcohols as cosurfactants.

The application of microemulsions that led to the greatest expectations was, without doubt, that in tertiary oil recovery [20]. A considerable amount of oil is trapped in the porous rocks of oil reservoirs after primary and secondary oil recovery; a surfactant solution is then injected. In order to remove this residual oil successfully, the interfacial tensions between oil and water should be lower than 10^{-2} mN/m. The main advantage of a microemulsion over other surfactant solutions is the ultralow interfacial tension (lower than 10^{-3} mN/m) achieved when it coexists with an aqueous and an oil phase [21,22]. The application of microemulsions in oil recovery offered a large economic potential that stimulated enormously the development of theoretical and experimental research in the field of microemulsions. Even though microemulsions were considered appropriate systems for oil recovery since the early 1940s, increased interest in this application developed in the 1960s. This has been reflected in numerous patents and publications. The early developments of the applications of microemulsions in the area of enhanced oil recovery have been extensively reviewed [20,23]. Chapters 14–16 of this volume describe recent developments.

The main developments of practical applications of microemulsions up to the mid-1980s are described in a comprehensive review by Gillberg [24]. This area has experienced continuous progress. The objective of the various chapters of this book is to provide information about the most significant advances in the field of microemulsion applications in the past decade.