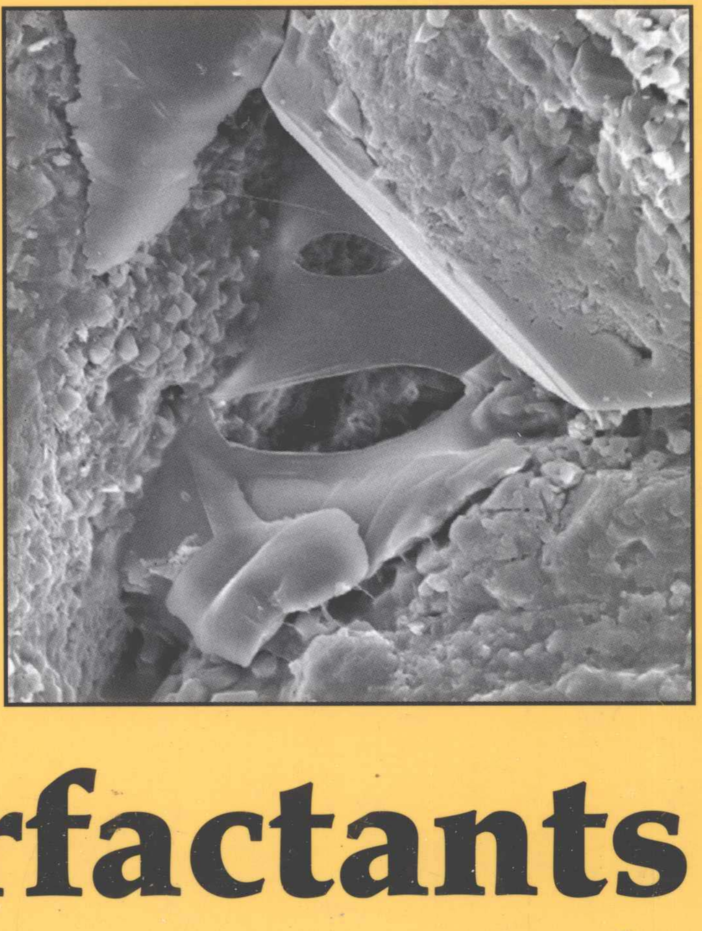

Surfactants

Fundamentals and Applications in the Petroleum Industry

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Surfactants: Fundamentals and Applications in the Petroleum Industry

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Surfactants: Fundamentals and Applications in the Petroleum Industry

This book provides an introduction to the nature, occurrence, physical properties, propagation, and uses of surfactants in the petroleum industry. It is aimed principally at scientists and engineers who may encounter or use surfactants, whether in process design, petroleum production, or research and development.

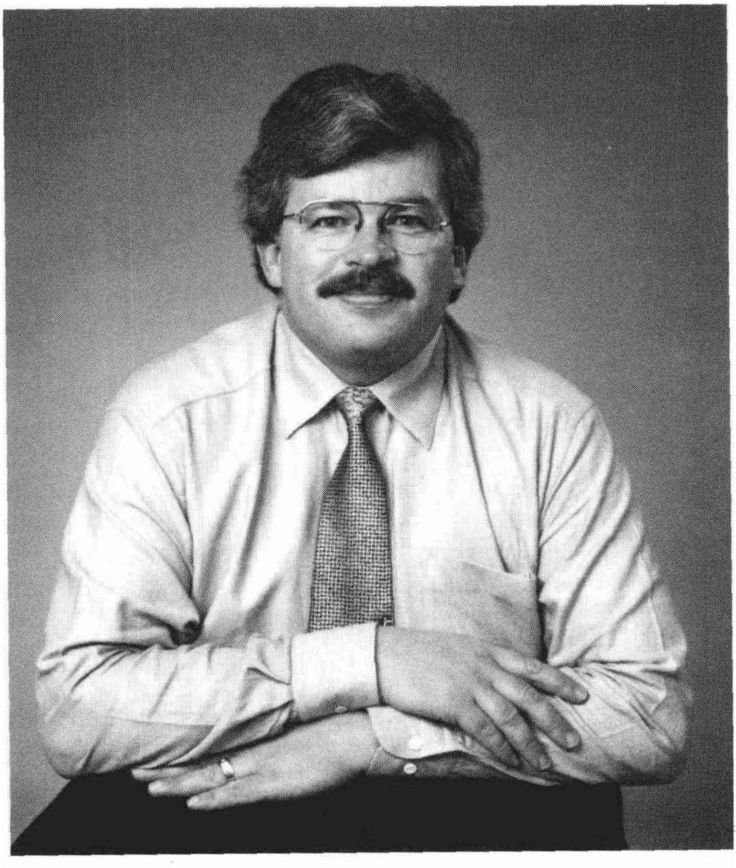
The primary focus is on applications of the principles of colloid and interface science to surfactant applications in the petroleum industry, and includes attention to practical processes and problems. Applications of surfactants in the petroleum industry are of great practical importance and are also quite diverse, since surfactants may be applied to advantage throughout the petroleum production process: in reservoirs, in oil and gas wells, in surface processing operations, and in environmental, health and safety applications. In each case appropriate knowledge and practices determine the economic and technical successes of the industrial process concerned. The book includes a comprehensive glossary, indexed and fully cross-referenced.

In addition to scientists and engineers in the petroleum industry, this book will be of interest to senior undergraduates and graduate students in science and engineering, and to graduate students of surfactant chemistry.

LAURIER L. SCHRAMM is President and CEO at the Petroleum Recovery Institute, and adjunct professor of chemistry at the University of Calgary. Dr. Schramm received his B.Sc. (Hons.) in chemistry from Carleton University in 1976 and Ph.D. in physical and colloid chemistry in 1980 from Dalhousie University, where he studied as a Killam and NRC Scholar. From 1980 to 1988 he held research positions with Syncrude Canada Ltd. in its Edmonton Research Centre. Since 1988 he has held a series of positions, of progressively increasing responsibility, with the Petroleum Recovery Institute.

His research interests have included many aspects of colloid and interface science applied to the petroleum industry, including research into mechanisms of processes for the improved recovery of light, heavy, and bituminous crude oils, such as *in situ* foam, polymer or surfactant flooding, and surface hot water flotation from oil sands. This research has involved the formation and stability of dispersions (foams, emulsions and suspensions) and their flow properties, electrokinetic properties, interfacial properties, phase attachments, and the reactions and interactions of surfactants in solution.

Dr. Schramm has won several national awards for his research, including the Canadian Society for Chemical Engineering – Bayer Award in Industrial Practice and the Natural Sciences and Engineering Research Council of Canada – Conference Board of Canada Award for Best Practices in University–Industry R & D Partnership. He is a Fellow of the Chemical Institute of Canada, a past Director of the Association of the Chemical Profession of Alberta, and a member of the American Chemical Society. He has 100 scientific publications and patents in the open literature and over 220 proprietary research reports for industry. This is his fifth book, following *Emulsions: Fundamentals and Applications in the Petroleum Industry*, *The Language of Colloid and Interface Science*, *Foams: Fundamentals and Applications in the Petroleum Industry*, and *Suspensions: Fundamentals and Applications in the Petroleum Industry*.



PREFACE

This book provides an introduction to the nature, occurrence, physical properties, propagation, and uses of surfactants in the petroleum industry. The primary focus is on applications of the principles of colloid and interface science to surfactant applications in the petroleum industry, and includes attention to practical processes and problems. Books available up to now are either principally theoretical (such as the colloid chemistry texts), much more general (like Rosen's *Surfactants and Interfacial Phenomena*, Myers' *Surfactant Science and Technology*, or Mittal's *Solution Chemistry of Surfactants*), or else much narrower in scope (like Smith's *Surfactant Based Mobility Control*). The applications of surfactants in the petroleum industry area are quite diverse and have a great practical importance. The area contains a number of problems of more fundamental interest as well. Surfactants may be applied to advantage in many parts of the petroleum production process: in reservoirs, in oilwells, in surface processing operations, and in environmental, health, and safety applications. In each case appropriate knowledge and practices determine both the economic and technical successes of the industrial process concerned.

In this volume, a wide range of authors' expertise and experiences are brought together to yield the first surfactant book that focuses on the applications of surfactants in the petroleum industry. Taking advantage of a broad range of authors' expertise allows for a variety of surfactant technology application areas to be highlighted in an authoritative manner. The topics chosen serve to illustrate some of the different methodologies that have been successfully applied. Each of the chapters in this book has been critically peer-reviewed and revised to meet a high scientific and editorial standard.

The target audience includes scientists and engineers who may encounter or be able to use surfactants, whether in process design, petroleum production, or in the research and development fields. It does not assume a knowledge of colloid chemistry, the initial emphasis being placed on a review of the basic concepts important to understanding surfactants. As such, it is hoped that the book will be of interest to senior undergraduate and graduate students in science and engineering as well since topics such as this are not normally part of university curricula.

The book provides an introduction to the field in a very applications oriented manner, as the focus of the book is practical rather than theoretical. The first group of chapters (1 to 3) sets out fundamental surfactant principles, including chemistry and uses. Subsequent groups of chapters address examples of industrial practice with Chapters 4–7 aimed at the use of surfactants in reservoir oil recovery processes, Chapters 8–10 covering some oilwell, near-well, and surface uses of surfactants, Chapters 11–13 addressing several environmental, health, and safety applications, and the Glossary containing a comprehensive and fully cross-referenced dictionary of terms in the field.

A recurring theme in the chapters is the use of the fundamental concepts in combination with actual commercial process experiences to illustrate how to approach planned and unplanned surfactant occurrences in petroleum processes. It also completes a natural sequence, serving as a companion volume to my earlier books: *Emulsions: Fundamentals and Applications in the Petroleum Industry*; *Foams: Fundamentals and Applications in the Petroleum Industry*, and *Suspensions: Fundamentals and Applications in the Petroleum Industry*.

Acknowledgments

I thank all the authors who contributed considerable time and effort to their respective chapters. This book was made possible through the support of my family, Ann Marie, Katherine and Victoria who gave me the time needed for the organization, research, and writing. I am also very grateful to Conrad Ayasse for his consistent encouragement and support. Throughout the preparation of this book many valuable suggestions were made by colleagues, the external reviewers of individual chapters, and by the editorial staff of Cambridge University Press, particularly Simon Capelin and Margaret Patterson.

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GLOSSARY AND INDEXES

SURFACTANT FUNDAMENTALS

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Surfactants and Their Solutions: Basic Principles

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This chapter provides an introduction to the occurrence, properties and importance of surfactants as they relate to the petroleum industry. With an emphasis on the definition of important terms, the importance of surfactants, their micellization and adsorption behaviours, and their interfacial properties are demonstrated. It is shown how surfactants may be applied to alter interfacial properties, promote oil displacement, and stabilize or destabilize dispersions such as foams, emulsions, and suspensions. Understanding and controlling the properties of surfactant-containing solutions and dispersions has considerable practical importance since fluids that must be made to behave in a certain fashion to assist one stage of an oil production process, may require considerable modification in order to assist in another stage.

Introduction

Surfactants are widely used and find a very large number of applications because of their remarkable ability to influence the properties of surfaces and interfaces, as will be discussed below. Some important applications of surfactants in the petroleum industry are shown in Table 1. Surfactants may be applied or encountered at all stages in the petroleum recovery and processing industry, from oilwell drilling, reservoir injection, oilwell production, and surface plant processes, to pipeline and seagoing transportation of petroleum emulsions. This chapter is intended to provide an introduction to the basic principles involved in the occurrence and uses of surfactants in the petroleum industry. Subsequent chapters in this book will go into specific areas in greater detail.

Table 1. Some Examples of Surfactant Applications in the Petroleum Industry

Gas/Liquid Systems
- Producing oilwell and well-head foams
- Oil flotation process froth
- Distillation and fractionation tower foams
- Fuel oil and jet fuel tank (truck) foams
- Foam drilling fluid
- Foam fracturing fluid
- Foam acidizing fluid
- Blocking and diverting foams
- Gas-mobility control foams

Liquid/Liquid Systems
- Emulsion drilling fluids
- Enhanced oil recovery *in situ* emulsions
- Oil sand flotation process slurry
- Oil sand flotation process froths
- Well-head emulsions
- Heavy oil pipeline emulsions
- Fuel oil emulsions
- Asphalt emulsion
- Oil spill emulsions
- Tanker bilge emulsions

Liquid/Solid Systems
- Reservoir wettability modifiers
- Reservoir fines stabilizers
- Tank/vessel sludge dispersants
- Drilling mud dispersants

All the petroleum industry's surfactant applications or problems have in common the same basic principles of colloid and interface science. The widespread importance of surfactants in general, and scientific interest in their nature and properties, have precipitated a wealth of published literature on the subject. Good starting points for further basic information are classic books like Rosen's *Surfactants and Interfacial Phenomena* [*1*] and Myers' *Surfactant Science and Technology* [2], and the many other books on surfactants [3–*19*]. Most good colloid chemistry texts contain introductory chapters on surfactants. Good starting points are references [20–23], while for much more detailed treatment of advances in specific surfactant-related areas the reader is referred to some of the chapters available in specialist books [24–29]. With regard to the occurrence of related colloidal systems in the petroleum industry, three recent books describe the principles and occurrences of emulsions, foams, and suspensions in the petroleum industry [*30–32*].

Definition and Classification of Surfactants[4]

Some compounds, like short-chain fatty acids, are amphiphilic or amphipathic, i.e., they have one part that has an affinity for nonpolar media and one part that has an affinity for polar media. These molecules form oriented monolayers at interfaces and show surface activity (i.e., they lower the surface or interfacial tension of the medium in which they are dissolved). In some usage surfactants are defined as molecules capable of associating to form micelles. These compounds are termed surfactants, amphiphiles, surface-active agents, tensides, or, in the very old literature, paraffin-chain salts. The term surfactant is now probably the most commonly used and will be employed in this book. This word has a somewhat unusual origin, it was first created and registered as a trademark by the General Aniline and Film Corp. for their surface-active products.[5] The company later (ca. 1950) released the term to the public domain for others to use [*33*]. Soaps (fatty acid salts containing at least eight carbon atoms) are surfactants. Detergents are surfactants, or surfactant mixtures, whose solutions have cleaning properties. That is, detergents alter interfacial properties so as to promote removal of a phase from solid surfaces.

The unusual properties of aqueous surfactant solutions can be ascribed to the presence of a hydrophilic head group and a hydrophobic chain (or tail) in the molecule. The polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is solvated via dipole–dipole or ion–dipole interactions. In fact, it is the nature of the polar head group which is used to divide surfactants into different categories, as illustrated in Table 2. In-depth discussions of surfactant structure and chemistry can be found in references [*1, 2, 8, 34, 35*].

The Hydrophobic Effect and Micelle Formation

In aqueous solution dilute concentrations of surfactant act much as normal electrolytes, but at higher concentrations very different behaviour results. This behaviour is explained in terms of the formation of organized aggregates of large numbers of molecules called micelles, in which the

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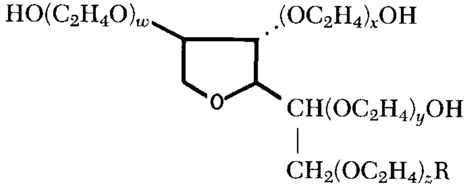
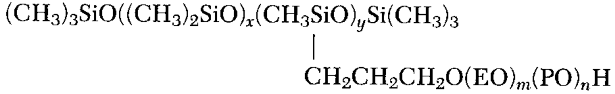
[4] A glossary of frequently encountered terms in the science and engineering of surfactants is given in the final chapter of this book.

[5] For an example of one of GAF Corp's. early ads promoting their trademarked surfactants, see *Business Week*, March 11, 1950, pp. 42–43.

Table 2. Surfactant Classifications

Class	Examples	Structures
Anionic	Na stearate	$CH_3(CH_2)_{16}COO^-Na^+$
	Na dodecyl sulfate	$CH_3(CH_2)_{11}SO_4^-Na^+$
	Na dodecyl benzene sulfonate	$CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+$
Cationic	Laurylamine hydrochloride	$CH_3(CH_2)_{11}NH_3^+Cl^-$
	Trimethyl dodecylammonium chloride	$C_{12}H_{25}N^+(CH_3)_3Cl^-$
	Cetyl trimethylammonium bromide	$CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$
Nonionic	Polyoxyethylene alcohol	$C_nH_{2n+1}(OCH_2CH_2)_mOH$
	Alkylphenol ethoxylate	$C_9H_{19}—C_6H_4—(OCH_2CH_2)_nOH$
	Polysorbate 80 $w + x + y + z = 20$, $R = (C_{17}H_{33})COO$	
	Propylene oxide-modified polymethylsiloxane EO = ethyleneoxy PO = propyleneoxy	 $(CH_3)_3SiO((CH_3)_2SiO)_x(CH_3SiO)_ySi(CH_3)_3$, $CH_2CH_2CH_2O(EO)_m(PO)_nH$
Zwitterionic	Dodecyl betaine	$C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$
	Lauramidopropyl betaine	$C_{11}H_{23}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$
	Cocoamido-2-hydroxy-propyl sulfobetaine	$C_nH_{2n+1}CONH(CH_2)_3N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$

lipophilic parts of the surfactants associate in the interior of the aggregate leaving hydrophilic parts to face the aqueous medium. An illustration presented by Hiemenz and Rajagopalan [22] is given in Figure 1. The formation of micelles in aqueous solution is generally viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavourable contacts with water, and the desire for the polar parts to maintain contact with the aqueous environment.

A thermodynamic description of the process of micelle formation will include a description of both electrostatic and hydrophobic contributions to the overall Gibbs energy of the system. Hydrocarbons (e.g., dodecane) and water are not miscible; the limited solubility of hydrophobic species in water can be attributed to the hydrophobic effect. The hydrophobic Gibbs energy (or the transfer Gibbs energy) can be defined as the difference between the standard chemical potential of the hydrocarbon solute in water and a hydrocarbon solvent at infinite dilution [*36–40*]

$$\Delta G_t^\circ = \mu_{HC}^\circ - \mu_{aq}^\circ \qquad (1)$$

where μ_{HC}° and μ_{aq}° are the chemical potentials of the hydrocarbon dissolved in the hydrocarbon solvent and water, respectively, and ΔG_t° is

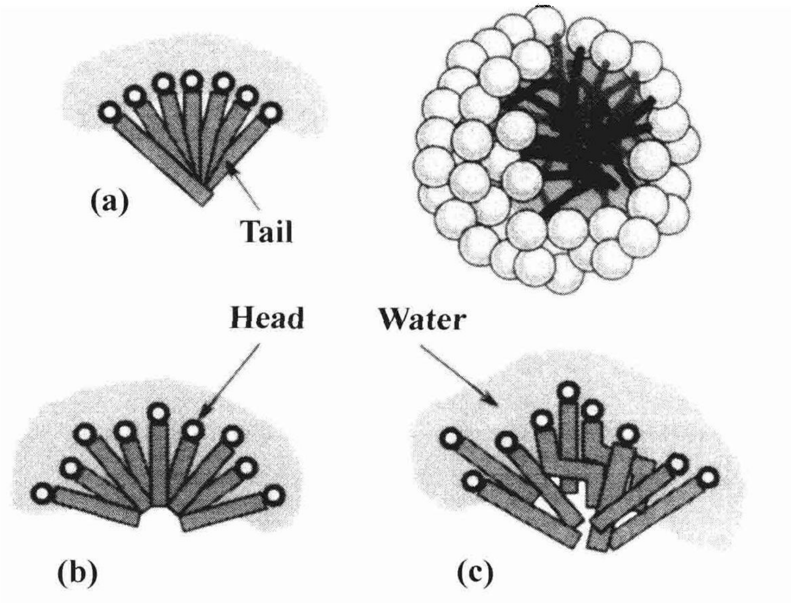


Figure 1. Schematic representation of the structure of an aqueous micelle showing several possibilities: (a) overlapping tails in the centre, (b) water penetrating to the centre, and (c) chains protruding and bending. (From Hiemenz and Rajagopalan [22]. Copyright 1997 Marcel Dekker Inc., New York.)

the Gibbs energy for the process of transferring the hydrocarbon solute from the hydrocarbon solvent to water. In a homologous series of hydrocarbons (e.g., the *n*-alcohols or the *n*-alkanes), the value of ΔG_t° generally increases in a regular fashion

$$\Delta G_t^\circ = (a - bn_c)RT \tag{2}$$

where a and b are constants for a particular hydrocarbon series and n_c is the number of carbon atoms in the chain. The transfer Gibbs energy, ΔG_t°, can be divided into entropic and enthalpic contributions

$$\Delta G_t^\circ = \Delta H_t^\circ - T\Delta S_t^\circ \tag{3}$$

where ΔH_t° and ΔS_t° are the enthalpy and entropy of transfer, respectively. A significant characteristic of the hydrophobic effect is that the entropy term is dominant, i.e., the transfer of the hydrocarbon solute from the hydrocarbon solvent to water is accompanied by an increase in the Gibbs transfer energy ($\Delta G > 0$) [*41*]. The decrease in entropy is thought to be the result of the breakdown of the normal hydrogen-bonded structure of water accompanied by the formation of differently structured water, often termed icebergs, around the hydrocarbon chain. The presence of the hydrophobic species promotes an ordering of water molecules in the vicinity of the hydrocarbon chain. To minimize the large entropy effect, the "icebergs" tend to cluster [38], in order to reduce the number of water molecules involved; the "clustering" is enthalpically favoured (i.e., $\Delta H < 0$), but entropically unfavourable. The overall process has the tendency to bring the hydrocarbon molecules together, which is known as the hydrophobic interaction. Molecular interactions, arising from the tendency for the water molecules to regain their normal tetrahedral structure, and the attractive dispersion forces between hydrocarbon chains, act cooperatively to remove the hydrocarbon chain from the water "icebergs", leading to an association of hydrophobic chains.

Due to the presence of the hydrophobic effect, surfactant molecules adsorb at interfaces, even at low surfactant concentrations. As there will be a balance between adsorption and desorption (due to thermal motions), the interfacial condition requires some time to establish. The surface activity of surfactants should therefore be considered a dynamic phenomenon. This can be determined by measuring surface or interfacial tensions versus time for a freshly formed surface, as will be discussed further below.

At a specific, higher, surfactant concentration, known as the critical micelle concentration (cmc), molecular aggregates termed micelles are formed. The cmc is a property of the surfactant and several other factors, since micellization is opposed by thermal and electrostatic forces. A low cmc is favoured by increasing the molecular mass of the lipophilic part of the molecule, lowering the temperature (usually), and adding electrolyte.