

0647 M996 E.3

SURFACTANT SCIENCE AND TECHNOLOGY

THIRD EDITION

Drew Myers





WILEY-INTERSCIENCE
A JOHN WILEY & SONS, INC., PUBLICATION

Copyright © 2006 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey. Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-646-8600, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

Library of Congress Cataloging-in-Publication Data:

Myers, Drew, 1946Surfactant science and technology/Drew Myers. – 3rd ed. p. cm.
Includes bibliographical references and index.
ISBN-13 978-0-471-68024-6 (cloth)
ISBN-10 0-471-68024-9 (cloth)
1. Surface chemistry. 2. Surface active agents. I. Title.
QD506.M94 2006
541'.33-dc22 2005007004

Printed in the United States of America

SURFACTANT SCIENCE AND TECHNOLOGY

To friends gone, but not forgotten—

Johnny B.

Paul G.

Alan B.

此为试读,需要完整PDF请访问: www.ertongbook.com

Preface to the Third Edition

When a book reaches the third edition, it must be assumed that (1) the work has been useful to someone or (2) the publisher has lost its collective mind. As a simple matter of ego, I must assume that reason 1 is true in this case. For that reason, I have tried to maintain the same basic philosophy with regard to the style and content of the book, while endeavoring to incorporate new material where indicated. A good deal of the information presented is "old" in the sense that it represents work done many years ago by the virtual founders of the science of surface and colloid chemistry. In the mid-1950s a few names stood out as the "gurus" of the field—today the names are too numerous to mention, and the body of published literature is enormous. Surfactants and their applications continue to fill books and patents.

Important advances in the tools available for studying the activity of surfactants has significantly increased our understanding of what is happening at interfaces at the molecular level in both model and practical systems, although there is still a lot be learned. New knowledge obtained in the years since the publication of the second edition has added greatly to our understanding of the nature of the molecular interactions of surface-active materials and the consequences of their presence on system characteristics and performance. The basic concepts and principles, however, remain pretty much the same.

In this edition, some topics have been reduced or moved around and several new themes added. Two cases, those of phase transfer catalysis (PTC) and aerosols, are not directly related to surfactants, but their real or potential importance prompted me to include some introductory material related to them.

Without changing the fundamental philosophy and goals of the previous editions, this third edition was prepared with three major ideas in mind: (1) to maintain the basic content of the work, (2) to maintain the "readability" of the book for nonspecialists, and (3) to improve the book's utility as a source of basic concepts concerning surfactants and their applications. A limited number of problems are provided at the end of each chapter (except Chapter 1) to illustrate some of the concepts discussed. In some cases, the problems provided may not have a unique solution, but are posed to stimulate imaginative solutions on the part of the reader. Some may also require some searching on the part of the problem solver to find missing pieces. While exact literature references are not provided, the Bibliography at the end of the book includes many of the better resources for more detailed information on each specific subject. It should serve as a useful guide to more detailed coverage for the interested reader.

xvi PREFACE TO THE THIRD EDITION

I would like to thank my two "best friends," Adriana and Katrina, for their constant love and support, and the crew at ALPHA C.I.S.A.—Lucho, José, Guillermo, Lisandro, Gabriel, Soledad, Alberto, Carlos, Enrique, Rudi, and all the rest—for putting up with my presence and my absence. Gracias por haber soportado mi presencia y mi ausencia.

DREW MYERS

Contents

Pre	reface to the Third Edition				
1	An (Overview	of Surfactant Science and Technology	1	
	1.1	A Brie	f History of Surfactant Science and Technology	3	
	1.2	The Ec	conomic Importance of Surfactants	5	
	1.3	Some 7	Traditional and Nontraditional Applications of Surfactants	7	
		1.3.1	Detergents and Cleaners	7	
		1.3.2	Cosmetics and Personal Care Products	8	
		1.3.3	Textiles and fibers	9	
		1.3.4	Leather and furs	10	
		1.3.5	Paints, Lacquers, and Other Coating Products	10	
		1.3.6	Paper and Cellulose Products	11	
		1.3.7	Mining and Ore Flotation	12	
		1.3.8	Metal-Processing Industries	12	
		1.3.9	Plant Protection and Pest Control	13	
		1.3.10	Foods and Food Packaging	13	
		1.3.11	The Chemical Industry	14	
		1.3.12	Oilfield Chemicals and Petroleum Production	14	
		1.3.13	Plastics and Composite Materials	15	
			Pharmaceuticals	15	
			Medicine and Biochemical Research	16	
		1.3.16	Other "Hi-Tech" Areas	16	
	1.4	Surfacta	ant Consumption	17	
	1.5		onomic and Technological Future	20	
	1.6	Surfacta	ants in the Environment	21	
	1.7	Petroch	emical versus "Renewable"		
		Oleoche	emical-Based Surfactants	23	
	1.8	A Surfa	actant Glossary	25	
2	The	Organic	Chemistry of Surfactants	29	
	2.1	Basic S	urfactant Building Blocks	30	
		2.1.1	Basic Surfactant Classifications	31	
		2.1.2	Making a Choice	32	

viii CONTENTS

2.2	The Generic Anatomy of Surfactants				
	2.2.1	The Mar	ny Faces of Dodecane	34	
	2.2.2	Surfactar	nt-Solubilizing Groups	38	
	2.2.3		Surfactant Hydrophobic Groups	39	
		2.2.3.1	The Natural Fatty Acids	40	
		2.2.3.2	Saturated Hydrocarbons or Paraffins	41	
		2.2.3.3	Olefins	41	
		2.2.3.4	Alkyl Benzenes	42	
		2.2.3.5	Alcohols	43	
		2.2.3.6	Alkyl Phenols	44	
		2.2.3.7	Polyoxypropylenes	44	
		2.2.3.8	Fluorocarbons	45	
		2.2.3.9	Silicone Surfactants	46	
		2.2.3.10	Miscellaneous Biological Structures	47	
2.3			Classification of Surfactants	47	
2.4	Anioni	c Surfactar	nts	48	
	2.4.1	Sulfate E	Esters	50	
		2.4.1.1	Fatty Alcohol Sulfates	51	
		2.4.1.2	Sulfated Fatty Acid Condensation Products	51	
		2.4.1.3	Sulfated Ethers	52	
		2.4.1.4	Sulfated Fats and Oils	54	
	2.4.2	Sulfonic	Acid Salts	54	
		2.4.2.1	Aliphatic Sulfonates	55	
		2.4.2.2	Alkylaryl Sulfonates	56	
		2.4.2.3	α-Sulfocarboxylic Acids and	50	
			Their Derivatives	58	
		2.4.2.4	Miscellaneous Sulfoester and	20	
			Amide Surfactants	60	
		2.4.2.5	Alkyl Glyceryl Ether Sulfonates	63	
		2.4.2.6	Lignin Sulfonates	63	
	2.4.3	Carboxyl	ate Soaps and Detergents	64	
	2.4.4		ric Acid Esters and Related Surfactants	65	
2.5	Cationi	c Surfactar		66	
2.6			ic Surfactants		
	2.6.1	Polyoxyethylene-Based Surfactants			
	2.6.2		res of Polyglycerols and Other Polyols	69 70	
	2.6.3		ppolymer Nonionic Surfactants	73	
	2.6.4		neous Nonionic Surfactants	73	
2.7	Amphoteric Surfactants				
2.7	2.7.1		Imidazoline Derivatives		
	2.7.1		Active Betaines and Sulfobetaines	74	
	2.7.2		ides and Related Amphoteric Surfactants	76	
Probl		тноѕрнас	ides and Related Amphoteric Surfaciants	77	
11001	-1110			78	

					CONTENTS	ix
3	Fluid	Surface	s and Interfa	aces		80
	3.1	Molecu	les at Interfac	ces		83
	3.2	Interfac	es and Adsor	rption Phenomena		84
		3.2.1	A Thermody	ynamic Picture of Adsorption		85
		3.2.2		Interfacial Tensions		88
		3.2.3	The Effect of	of Surface Curvature		90
	3.3	The Sur	face Tension	of Solutions		91
		3.3.1	Surfactants	and the Reduction of Surface T	Pension	94
		3.3.2	Efficiency, I	Effectiveness, and Surfactant St	ructure	95
	Probl	ems				105
4	Surfa	ctants in	Solution: M	Aonolayers and Micelles		107
	4.1	Surfacta	nt Solubility			108
	4.2		-	of Surfactants in Solution		112
	4.3	The His	tory and Dev	velopment of Micellar Theory		116
		4.3.1	Manifestatio	ons of Micelle Formations		117
		4.3.2		amics of Dilute Surfactant Solu	tions	121
		4.3.3		neories of Micelle Formation		122
		4.3.4		of Micellization		124
	4.4			and the Formation of Associat	ion Colloids	125
	4.5			vations of Micellar Systems		129
		4.5.1		gregation Numbers		129
		4.5.2		Micelle Concentration		130
		4.5.3		hobic Group		131
		4.5.4 4.5.5	The Hydrop			140
		4.5.6		Effects on Micellization	D	142
		4.5.0		of Additives on the Micellization		143
				lectrolyte Effects on Micelle Fo	rmation	144
				he Effect of pH		146
		4.5.7		he Effects of Added Organic M		147
	16			of Temperature on Micellization	1	149
	4.6 4.7			Mixed Surfactant Systems		150
	4.7			Nonaqueous Media		153
		4.7.1 4.7.2		in Polar Organic Solvents		153
	Proble		Micelles in	Nonpolar Solvents		154
	110010	21115				157
5	Higher-Level Surfactant Aggregate Structures: Liquid Crystals, Continuous Biphases, and Microemulsions					50.45 max.
	Conti		_			160
	5.1			urfactant Phase Information		161
	5.2	Amphip	hilic Fluids			162

x CONTENTS

		5.2.1	Liquid Crystalline, Bicontinuous, and Microemulsion	
			Structures	163
		5.2.2	"Classical" Liquid Crystals	166
		5.2.3	Liquid Crystalline Phases in Simple Binary Systems	167
	5.3		rature and Additive Effects on Phase Behavior	170
	5.4		Current Theoretical Analyses of Novel Mesophases	171
	5.5		s and Bilayer Membranes	172
		5.5.1	Vesicles	174
		5.5.2	Polymerized Vesicles	176
	5.6	_	cal Membranes	177
		5.6.1	Some Biological Implications of Mesophases	178
		5.6.2	Membrane Surfactants and Lipids	180
	5.7	Microe	mulsions	182
		5.7.1	Surfactants, Cosurfactants, and Microemulsion Formation	186
			5.7.1.1 Ionic Surfactant Systems	187
			5.7.1.2 Nonionic Surfactant Systems	188
		5.7.2	Applications	188
	Proble		Applications	189
	11001			
6	Solub	oilizatior	and Micellar and Phase Transfer Catalysis	191
	6.1	Solubil	ization in Surfactant Micelles	192
		6.1.1	The "Geography" of Solubilization in Micelles	194
		6.1.2	Surfactant Structure and the Solubilization Process	196
		6.1.3	Solubilization and the Nature of the Additive	199
		6.1.4	The Effect of Temperature on Solubilization	
			Phenomena	201
		6.1.5	The Effects of Nonelectrolyte Solutes	203
		6.1.6	The Effects of Added Electrolyte	204
		6.1.7	Miscellaneous Factors Affecting Solubilization	205
	6.2		ar Catalysis	206
		6.2.1	Micellar Catalysis in Aqueous Solution	206
		6.2.2	Micellar Catalysis in Nonaqueous Solvents	208
	6.3	Phase '	Transfer Catalysis	209
		6.3.1	Cross-phase Reactions	210
		6.3.2	Some Examples of PTC Applications	213
			6.3.2.1 Alkylnitrile Synthesis	213
			6.3.2.2 Dihalocyclopropanes	215
		6.3.3	Some Notes on the Use of PTC	216
		6.3.4	Some Requirements for a Successful PTC Reaction	216

xi

7	Polymeric Surfactants and Surfactant-Polymer Interactions				220	
	7.1	Polym	neric Surfactants and Amphiphiles			
	7.2	Some	Basic Che	Basic Chemistry of Polymeric Surfactant Synthesis		
		7.2.1	Modification of Natural Cellulosics, Gums,			
			and Pro		223	
		7.2.2		c Polymeric Surfactants	223	
	7.3			etants at Interfaces: Structure		
	7.4		ethodology		229	
	7.4	7.4.1		Normal" Surfactants with Polymers	230	
		7.4.1		nt–Polymer Complex Formation c Polymers	232	
		7.4.3		lymers and Proteins	235 237	
	7.5			tants, and Solubilization	240	
	7.6			ner Interactions in Emulsion Polymerization	240	
	Probl		,	and the second s	243	
					273	
8	Foan	ns and L	iquid Aeı	cosols	245	
	8.1	The Ph	ysical Bas	sis for Foam Formation	246	
	8.2	The Ro	ole of Surf	actant in Foams	250	
		8.2.1	Foam Fo	ormation and Surfactant Structure	253	
		8.2.2		nilic Mesophases and Foam Stability	256	
		8.2.3	Effects of	of Additives on Surfactant Foaming Properties	257	
	8.3		nhibition		259	
	8.4				261	
	8.5	of Add		ne Foaming and Antifoaming Activities		
	8.6			nefficient	262	
	8.7	1 8			263 265	
		8.7.1		nation of Liquid Aerosols	265	
			8.7.1.1	Spraying and Related Mechanisms of Mist	203	
			0.7.1.1	and Fog Formation	266	
			8.7.1.2	Nozzle Atomization	267	
			8.7.1.3	Rotary Atomization	268	
		8.7.2	Aerosol	Formation by Condensation	270	
		8.7.3	Colloida	Properties of Aerosols	272	
			8.7.3.1	The Dynamics of Aerosol Movement	273	
			8.7.3.2	Colloidal Interactions in Aerosols	275	
	Proble	ems			277	
9	Emul	sions			280	
	9.1	The Lic	uid–Liaui	d Interface	281	
					201	

xii CONTENTS

	9.2	General Cons	siderations of Emulsion Stability	282
		9.2.1 Lifet	imes of Typical Emulsions	286
		9.2.2 Theo	ories of Emulsion Stability	289
	9.3	Emulsion Typ	be and Nature of the Surfactant	290
	9.4	Surface Activ	ity and Emulsion Stability	293
	9.5		tant Systems and Interfacial Complexes	298
	9.6		Mesophases and Emulsion Stability	302
	9.7		ructure and Emulsion Stability	305
			ophile-Lipophile Balance (HLB)	306
			e Inversion Temperature (PIT)	311
			ication of HLB and PIT in Emulsion Formulation	312
			ets of Additives on the "Effective" HLB	214
	9.8			314
	9.0	Multiple Emu		315
			enclature for Multiple Emulsions	316
		1	aration and Stability of Multiple Emulsions	316
			ways for Primary Emulsion Breakdown actants and Phase Components	318
	Proble		actants and mase components	319
	110010	1115		321
10	Solid	Surfaces and	Dispersions	323
	10.1	The Nature o	f Solid Surfaces	323
	10.2		Solid Surfaces	327
	10.3	Adsorption at	the Solid-Liquid Interface	329
			orption Isotherms	329
		10.3.2 Mecl	nanisms of Surfactant Adsorption	331
		10.3.	2.1 Dispersion Forces	332
		10.3.	1	333
		10.3.	2.3 Electrostatic Interactions	334
			Electrical Double Layer	335
	10.4		es of Surfactant Adsorption	337
			rption and the Nature of the Adsorbent Surface	338
			polar, Hydrophobic Surfaces	338
			, Uncharged Surfaces	339
	10.5		ices Having Discrete Electrical Charges	340
	10.5		ucture and Adsorption from Solution	342
			ces Possessing Strong Charge Sites	343
			rption by Uncharged, Polar Surfaces	346
	10.6		ctants at Nonpolar, Hydrophobic Surfaces	347
	10.6		sorption and the Character of Solid Surfaces	347
	10.7		Related Phenomena	349
		10.7.1 Surfa	ctant Manipulation of the Wetting Process	352

		CONTENTS	xiii
	10.7.2	Some Practical Examples of Wetting Control	
		by Surfactants	355
	10.7.3	Detergency and Soil Removal	355
	10.7.4	The Cleaning Process	355
	10.7.5	Soil Types	357
	10.7.6	Solid Soil Removal	357
	10.7.7	Liquid Soil Removal	358
	10.7.8	Soil Redeposition	360
	10.7.9	Correlations of Surfactant Structure and Detergency	361
	10.7.10	Nonaqueous Cleaning Solutions	363
10.8	Enhance	ed Oil Recovery	364
10.9			366
Proble	ems		367
Bibliograp	ohy		370
Index			375

1 An Overview of Surfactant Science and Technology

Rapid evolution in the chemical-based nature of our modern society has made it increasingly difficult for scientists, engineers, regulators, and managers to remain abreast of the latest in the technologies impacting their work. The scientific and technical journals published worldwide number in the thousands, and this number increases yearly. Paralleling the proliferation of the scientific literature in general has been an apparent divergence into fields of "pure" science-studies in which the principal goal is a general advancement of human knowledge with no particular "practical" aim in mind-and "applied" science and technology, in which the research is driven by some anticipated application, quite often, but not always, profit-related. Few areas of chemistry have exhibited this growing dichotomy of purpose more than the study of surface and colloid science, especially as applied to surface activity and surface-active materials. Even the nomenclature used in discussing materials showing surface activity is widely varied, depending on the context of the discussion. It is not surprising, then, that the world of surface activity and surface-active agents, or surfactants, can appear complex and confusing to those not intimately involved in it on a day-to-day basis.

When one considers the impact of surface science in general, and emulsions, dispersions, foaming agents, wetting agents, and other related compounds in particular, in our day-to-day routines, the picture that develops reveals the great extent to which these areas of chemistry and chemical technology permeate our lives. From the fundamental aspects of biological membrane formation and function in living cells, which vividly illustrates the spontaneity and importance of colloidal phenomena, to the more "far out" problem of how liquids wet the walls of a rocket's fuel tank in a low-gravity environment, the physical chemistry of the interactions among various phases at interfaces lies at the root of much of our modern lifestyle.

Industrial concerns, whose very lifeblood may be intimately linked to application of the basic principles of interfacial interactions, often ignore the potential benefits of fundamental research in these areas in favor of an empirical trial-and-error approach, which may lead to a viable process but that possibly could be better understood and even significantly improved by the application of more fundamental science. In many cases the prevailing philosophy seems to be, to paraphrase an old

adage, "A dollar in the hand is worth two in the laboratory." Unfortunately, such an approach often results in more dollars down the drain than many management-level decisionmakers care to admit. Academic researchers, on the other hand, are sometimes guilty of ignoring the potential practical aspects of their work in favor of experimental sophistication and the "Holy Grail" of the definitive theory or model. Neither philosophy alone truly satisfies the needs of our technological existence. Each approach makes its valuable contribution to the overall advancement of human knowledge; however, it sometimes appears that a great deal is lost in the communication gap between the two.

The science and the technology of surfactants have possibly suffered a double blow from the functional divergence of academic and applied research. Academic interest in surfactants, while increasing, has generally concentrated on highly purified, homogeneous materials [quite often limited to a few materials such as sodium dodecylsulfate (SDS), or cetyltrimethylammonium bromide (CTAB)] and elegant analytical techniques. While providing a wealth of useful information related to the particular system under investigation, the application of such information to more complex practical materials and processes is often less than obvious, and is sometimes misleading. The sad fact of life is that real surfactant systems are almost always composed of mixed chemical isomers, contaminants, and added materials that can dramatically alter the effects of a given surfactant on a system. High purity is necessary for the interpretation of delicate laboratory experiments, but requires the use of techniques that may be impractical at the industrial level.

In the results-oriented industrial environment, with some significant exceptions, surfactant research is often carried out on a "Make it work and don't worry about why!" basis. The industrially interesting materials are usually complex mixtures of homologs and structural isomers, or contain impurities resulting from chemical side reactions, unreacted starting materials, residual solvents or byproducts, and so on. Such "contamination" of the desired product is not only common, but commonly variable from batch to batch. For example, particularly significant surface property changes can be induced by the presence of such impurities as inorganic salts or long-chain alcohols remaining after processing. While the presence of such impurities and mixtures will often produce superior results in practice, analysis of the process may be difficult because of the unknown or variable nature of the surfactant composition. Considering the limitations imposed by each school of surfactant research, it is not surprising to find that a practical fusion of the two approaches can be difficult to achieve.

The different views of surfactant science and technology have spawned their own distinctive terminologies and literatures. While the academic or fundamental investigator may probe the properties of surface-active agents, surfactants, tensides, or amphiphiles, the industrial chemist may be concerned with the characteristics of soaps, detergents, emulsifiers, wetting agents, and similar compounds. The former group may publish their results primarily in the Journal of Physical Chemistry, Colloids and Surfaces, Langmuir, or the Journal of Colloid and Interface Science, the latter in the Journal of the American Oil Chemists Society, the Journal of Dispersion Science and Technology, or one of the other technologically specialized

publications aimed at specific areas of application (foods, cosmetics, paints, etc.). All too often, the value of the results to each community can become lost in the sea of manuscripts and the philosophical and operational gulf that sometimes develops between the two, not to mention the almost impossible task of being abreast of all the information published in all the relevant literature.

Before beginning a discussion of specific aspects of the chemistry of surface-active materials and surfactant action, it may be useful to have some idea of the history of surfactants and how their synthesis and use have evolved through the years. Because of parallel developments in various areas of the world, the secrecy of industrial research efforts, and the effects of two world wars, the exact details of the evolution of surfactant science and technology may be subject to some controversy regarding the specific order and timing of specific developments. In any case, the major facts are (hopefully!) correct.

1.1. A BRIEF HISTORY OF SURFACTANT SCIENCE AND TECHNOLOGY

The pedigree of the synthetic surfactant industry is reasonably well documented, unlike that of the more ancient "natural" alkali soaps. However, it is not an easy task to pinpoint the exact time when the industry came into being. In a strictly chemical sense, a soap is a compound formed by the reaction of an essentially water-insoluble fatty acid with an alkali metal or organic base to produce a carboxylic acid salt with enhanced water solubility, sufficient to produce useful surface activity. Since the soaps require some form of chemical modification to be useful as surfactants, they could be considered to be synthetic; however, custom dictates that they not be classified in the same category as the materials prepared by more "elegant" synthetic routes.

The alkali metal soaps have been used for at least 2300 years. Their use as articles of trade by the Phoenicians as early as 600 B.C. has been documented. They were also used by the Romans, although it is generally felt that their manufacture was learned from the Celts or some Mediterranean culture. Early soap producers used animal fats and ashes of wood and other plants containing potassium carbonate to produce the neutralized salt. As the mixture of fat, ashes, and water was boiled, the fat was saponified to the free fatty acids, which were subsequently neutralized.

The first well-documented synthetic (nonsoap) materials employed specifically for their surface-active properties were the sulfated oils. Sulfonated castor oil, produced by the action of sulfuric acid on the castor oil, was originally known as "turkey red oil." It was introduced in the late nineteenth century as a dyeing aid and is still used in the textile and leather industries today. The first surfactants for general application that have been traditionally classified as synthetic were developed in Germany during World War I in an attempt to overcome shortages of available animal and vegetable fats. Those materials were short-chain alkylnaphthalene sulfonates prepared by the reaction of propyl or butyl alcohol with