
Detergents and Cleaners

A Handbook for Formulators

K. Robert Lange



Detergents and Cleaners

A Handbook for Formulators

Edited by K. Robert Lange



Hanser Publishers, Munich Vienna New York

Hanser/Gardner Publications, Inc., Cincinnati

The Editor:

Dr. K. Robert Lange, 805 Lombard Street, Philadelphia, PA 19147, USA

Distributed in the USA and in Canada by

Hanser/Gardner Publications, Inc.

6600 Clough Pike, Cincinnati, Ohio 45244-4090, USA

Fax: +1 (513) 527-8950

Distributed in all other countries by

Carl Hanser Verlag

Postfach 86 04 20, 81631 München, Germany

Fax: +49 (89) 98 12 64

The use of general descriptive names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone.

While the advice and information in this book are believed to be true and accurate at the date of going to press, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Library of Congress Cataloging-in-Publication Data

Detergents and cleaners : a handbook for formulators / edited by K.

Robert Lange.

p. cm.

Includes bibliographical references (p. -) and index.

ISBN 1-56990-167-8

1. Detergents, Synthetic. 2. Cleaning compounds. I. Lange, K. Robert.

TP992.5.D39 1994

668'.14—dc20

93-49047

Die Deutsche Bibliothek - CIP-Einheitsaufnahme

Detergents and cleaners : a handbook for formulators / ed. by

K. Robert Lange. - Munich ; Vienna ; New York : Hanser ;

Cincinnati : Hanser/Gardner, 1994

ISBN 3-446-17307-2 (Hanser)

ISBN 1-56990-167-8 (Hanser/Gardner)

NE: Lange, K. Robert [Hrsg.]

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the publisher.

© Carl Hanser Verlag, Munich Vienna New York, 1994

Typeset in the USA by pageAbility, Willseyville

Printed and bound in Germany by Schoder Druck GmbH & Co. KG, Gersthofen

Detergents and Cleaners

Preface

When first considering this task, I wanted to write an article on formulating, in general. Having spent many years formulating products and supervising chemists, my sympathy for the bench chemist's problems, and respect for the ingenuity shown, had led me to write a series of articles for my employer's house organ, explaining the field to the layperson. Editing and contributing to a book meant for the bench chemist is a different matter entirely. For this a focus is needed, one that will attract readers. The topic of detergency provides such a focus because it is of universal interest.

Whatever the industrial or home environment, people have a need for cleanliness. This includes their bodies, their clothing, and the equipment they use. Today there is a strong emphasis on keeping the entire environment preserved, and cleaners play their role in this effort. To these ends the chemical process industry develops formulated products, based on synthetic detergents, that are expected to attack soils of every imaginable type, regardless of water hardness or the conditions of use. Governments around the world monitor and regulate these efforts while encouraging cleanliness through campaigns and laws. Cleanliness is a major worldwide industry.

This book provides methodology for formulators generally, through the medium of detergency. Formulating principles are general, and this volume might just as well be on corrosion inhibitors or pie-baking; but the publisher produces *Tenside*, that fine journal devoted to detergency, and has a German-language handbook by Stache on that subject, among other things. Hanser's desire to produce a book on this topic for the North American market coincided with my own views of the appropriate field to use as the focus of a book for formulators.

The intended audience for this volume is the bench chemist or senior technician, working in a small to medium-sized laboratory, who wants to have a book of convenient size for daily reference and as a guide to the more theoretical, multivolume tomes in the library. My hope is that this book will fill a need between the two extremes of the theoretical texts and the fine trade magazines, which offer much useful information but can be difficult to use in terms of retrieval.

The authors of the various chapters have all overcome the daily pressures of their jobs to share their knowledge here. Working with them has been a pleasure, and I thank them for their efforts. I also thank the following for their cooperation: H.L. Williams, vice president at Monsanto; A.F. Hidalgo, vice president at Colgate Palmolive; and A.F. Burns, technical director at PQ, who were instrumental in recommending members of their staffs to author chapters.

K.R. Lange

Introduction

Every chemical product that reaches the ultimate consumer (with the possible exception of sugar) is, in some degree, a formulated product.* This being the case, it is somewhat mysterious to note the low esteem the formulation process possesses in both academia and industry. Certainly, no college department of chemistry or chemical engineering offers a course entitled *Formulation 101*. And, although formulation is often considered to be an arcane art, its practitioners are often referred to as “mere formulators.” (One wonders, indeed, what the effect of calling a designer of perfumes and scents a “mere” perfumer would be!)

One of the reasons for this low esteem probably is the notion that formulation is largely Edisonian in nature and, therefore, does not possess the cachet that surrounds “real” research. First of all, it should be pointed out that there is nothing in principle wrong with the Edisonian approach to discovery, as long as it is applied with intelligence. Many important discoveries (even in basic science) have resulted from Edisonian methods, although this is often concealed by referring to serendipity.

A number of years ago, I presented a talk with the title *Philosophy of Formulation*.† Although, as the title of the symposium at which the talk was delivered suggests, my remarks were directed mostly to pesticide formulations, I made the point that formulation was *not* particularly Edisonian, but bore many similarities to what is commonly referred to as basic research.

On the other hand, formulation research is carried out for reasons different from those of the so-called basic research. Among those reasons might be listed the following:

- To render the use of application of the active component more effective.
- To enable the consumer to use the product more readily.
- To improve the stability of the product.
- Last—but not least—to improve the aesthetics of the product.

As I pointed out in my talk, to do it properly, one must plan the formulation study. This may involve answering a series of questions. For the formulation of pesticides, these questions were suggested:

- What is the active ingredient and what is its form?
- In what type of system will it be delivered (e.g., solution, dispersion, emulsion)?
- If a solution or dispersion, dissolved or dispersed in what?
- If an emulsion, o/w or w/o—and what is in the aqueous phase—what is the oil phase?

*Table salt, which one might think of as unformulated, is commonly “iodized” and additionally contains an anticaking compound.

†Becher, P. In *Pesticide Formulations and Application Systems*, Vol. 8, D.A. Hovde and G.B. Beestman, Eds., American Society for Testing and Materials, Philadelphia, 1989, p. 13.

- How is it to be applied to the system: If a herbicide—dusted, sprayed? If a drug—applied topically, swallowed, injected?
- What is the desired composition (e.g., if an emulsion, what are the phase ratios)?
- If an emulsion or dispersion, what surface active agents should be used? What restrictions are imposed by safety considerations?
- What physical properties must the system have (e.g., viscosity, density)? In dispersions and emulsions, what is the effect of particle size distribution? If the system is viscoelastic, what effect does this have?
- How do we make it? What types of mixing or blending equipment? How about scale-up?
- Finally, how do we evaluate the system? What degree of stability is required? How is stability determined? What about quality assurance?

These questions can be restated to apply to any kind of formulation problem, and, no doubt, other questions will occur to the worker.

This brings us to an important point. It will not have escaped the eye of the reader that this book to a large extent emphasizes formulation of detergent species. This is simply a matter of convenience. From the foregoing, it should be obvious that the lessons and techniques discussed here can be transferred to any other field with only a modest effort. In other words, this book will be useful to *any* formulator, whether the problem at hand involves, among others, pharmaceuticals, cosmetics, paints, or—yes—pesticides. The authors and the editor are to be commended.

Paul Becher

Contents

Introduction	xvii
1 Basic Surfactant Concepts	1
<i>Eric W. Kaler</i>	
1.1 Introduction	1
1.2 Surfactant Mechanisms	3
1.3 Surfactant Microstructures	4
1.3.1 Micelles	6
1.3.2 Liquid Crystals	9
1.3.3 Vesicles	10
1.3.4 Inverted Structures	11
1.3.5 Other Structures	12
1.3.6 Molecular Packing	12
1.4 Surfactant Phase Diagrams	14
1.5 Microemulsions	18
1.6 Surfactant Properties at Interfaces	22
1.7 Emulsions	25
1.8 Bibliographic Notes	27
Acknowledgments	27
References	28
2 Mechanisms of Soil Removal	29
<i>Guy Broze</i>	
2.1 Introduction	29
2.2 Types of Soils	30
2.2.1 Water-Soluble Soils	30
2.2.2 Oily and Greasy Soils	30
2.2.3 Particulate Soils	31
2.2.4 Oxidizable or Bleachable Soils	31
2.2.5 Proteins and Starchy Soils	32
2.3 Major Mechanisms of Soil Removal	32
2.3.1 Oily-Greasy Soils	32
2.3.1.1 Roll-Up	32
2.3.1.2 Emulsification	34
2.3.1.3 Solubilization of Oil	35
2.3.2 Particulate Soils	36
2.3.3 Bleachable Soils	36

2.3.4	Protein and Starchy Soils	37
2.4	Second-Order Challenges	37
2.4.1	Soil Redeposition	37
2.4.1.1	Electrostatic Repulsion	38
2.4.1.2	Steric Stabilization ("Colloid Protection")	39
2.4.2	Encrustation	40
References		41
3	Surfactants	43
	<i>Michael F. Cox</i>	
3.1	Introduction: What Is a Surfactant?	43
3.2	Basic Surfactant Performance	44
3.2.1	Wetting	45
3.2.2	Soil Removal	46
3.2.3	Suspend Material (Solubilize/Emulsify)	47
3.2.4	Stabilize Foam	50
3.2.5	Adsorb on Surfaces/Amend Surface Properties	50
3.2.6	Bactericide	50
3.2.7	Terminology	50
3.2.8	Surfactant Classification by Charge	51
3.2.9	Surfactant Classification by Feedstock	51
3.2.10	Preview of Sections 3.3–3.5	51
3.3	Anionic Surfactants	52
3.3.1	LAS (Linear Alkylbenzenesulfonate, or Linear Alkylate Sulfonate)	52
3.3.1.1	Description of Hydrophobe	52
3.3.1.2	Description of Hydrophile	54
3.3.1.3	Properties and Characteristics	55
3.3.1.4	Applications	55
3.3.1.5	Availability	56
3.3.2	Alcohol Sulfates (or Alkyl Sulfates)	56
3.3.2.1	Description of Hydrophobe	56
3.3.2.2	Description of Hydrophile	59
3.3.2.3	Properties and Characteristics	59
3.3.2.4	Applications	60
3.3.2.5	Availability	60
3.3.3	Alcohol Ether Sulfates (AES) or Alkyl Ether Sulfates or Alcohol Ethoxysulfates	60
3.3.3.1	Description of Hydrophobe	61
3.3.3.2	Description of Hydrophile	61
3.3.3.3	Properties and Characteristics	62
3.3.3.4	Applications	63
3.3.3.5	Availability	64
3.3.4	Soap (Sodium or Potassium Salts of Long-Chain Fatty Acids)	64
3.3.4.1	Description of Hydrophobe	64
3.3.4.2	Description of Hydrophile	64
3.3.4.3	Properties and Characteristics	64
3.3.4.4	Applications	65
3.3.4.5	Availability	65
3.3.5	Secondary Alkanesulfonates (SAS)	66
3.3.5.1	Description of Hydrophobe	66
3.3.5.2	Description of Hydrophile	66

3.3.5.3	Properties and Characteristics	66
3.3.5.4	Applications	67
3.3.5.5	Availability	67
3.3.6	α -Olefinsulfonate (AOS)	67
3.3.6.1	Description of Hydrophobe	68
3.3.6.2	Description of Hydrophile	68
3.3.6.3	Properties and Characteristics	68
3.3.6.4	Applications	69
3.3.6.5	Availability	69
3.3.7	Methyl Ester Sulfonate (MES)	69
3.3.7.1	Description of Hydrophobe	69
3.3.7.2	Description of Hydrophile	70
3.3.7.3	Properties and Characteristics	70
3.3.7.4	Applications	71
3.3.7.5	Availability	71
3.4	Nonionic Surfactants	71
3.4.1	Alcohol Ethoxylates, or Alkylpoly(ethylene Oxides), or Alkyl-Poly Oxyethylene Ethers	71
3.4.1.1	Description of Hydrophobe	71
3.4.1.2	Description of Hydrophile	72
3.4.1.3	Properties and Characteristics	75
3.4.1.4	Applications	76
3.4.1.5	Availability	77
3.4.2	Alkylphenol Ethoxylates (APEs)	77
3.4.2.1	Description of Hydrophobe	77
3.4.2.2	Description of Hydrophile	78
3.4.2.3	Properties and Characteristics	78
3.4.2.4	Applications	79
3.4.2.5	Availability	79
3.4.3	Ethylene Oxide/Propylene Oxide (EO/PO) Block Copolymers	79
3.4.3.1	Description of Hydrophobe	80
3.4.3.2	Description of Hydrophile	80
3.4.3.3	Properties and Characteristics	80
3.4.4	Alkyl Polyglycoside	81
3.4.4.1	Description of Hydrophobe	81
3.4.4.2	Description of Hydrophile	81
3.4.4.3	Properties and Characteristics	82
3.4.4.4	Applications	82
3.4.4.5	Availability	83
3.5	Nitrogen-Based Surfactants	83
3.5.1	Description of Hydrophobe	83
3.5.2	Description of Hydrophile	83
3.5.2.1	Alkanolamides	84
3.5.2.2	Amine Ethoxylates	84
3.5.2.3	Quaternary Ammonium Salts	85
3.5.2.4	Amine Oxides	86
3.5.2.5	Amphoteric Surfactants	86
3.5.2.6	Polyamines	87
3.6	Getting More Information	88
3.6.1	Surfactant Suppliers	88
3.6.2	Industry Associations	88
3.6.3	Surfactant Publications	88

3.6.4	Annual Meetings/Short Courses	89
References		89
4	Bleaches and Optical Brighteners	91
	<i>Olina G. Raney</i>	
4.1	Bleaches	91
4.1.1	Introduction	91
4.1.2	Hypochlorite Bleaching Agents	92
4.1.3	Peroxygen Bleaching Agents	93
4.1.4	Bleach Activators	95
4.1.5	Peroxycarboxylic Acids	97
4.1.6	Metal-Catalyzed Bleaching Systems	99
4.1.7	Factors Affecting Bleach Performance, Formulation Stability, and Choice of Bleach System	100
4.1.7.1	Temperature	100
4.1.7.2	Rate of Solution	100
4.1.7.3	Concentration	100
4.1.7.4	pH	100
4.1.7.5	Activator/Bleach Ratio	100
4.1.7.6	Chain Length	101
4.1.7.7	Stains	101
4.1.8	Formulating Bleaches	101
4.1.9	Performance	102
4.2	Optical Brighteners	103
4.2.1	Introduction	103
4.2.2	Types of Optical Brighteners	103
4.2.3	Performance and Selection of Optical Brighteners	105
4.2.3.1	Laundry Product Composition	105
4.2.3.2	Laundry Product Type	107
4.2.3.3	Ease of Incorporation into the Formulation	108
4.2.3.4	Solubility of the Optical Brightener	108
4.2.3.5	Rate of Solution of the Optical Brightener	108
4.2.3.6	Laundry Product Whitening	108
4.2.3.7	Washing Conditions	109
4.2.3.8	Fabric Types Present in Wash Load and Optical Brightener Affinity to Fabric Surface	109
4.2.3.9	Effect of Soil	109
4.2.3.10	Bleach Stability	109
4.2.3.11	Fastness of the Optical Brightener	109
4.2.3.12	Use Concentration of the Optical Brightener	109
4.2.3.13	Toxicity	110
4.2.3.14	Hue of Whiteness Produced	110
4.2.3.15	Cost	110
References		110
5	Polymers in Cleaners	113
	<i>David Witiak</i>	
5.1	Polymer Types	113

5.2	Polymer Functions	114
5.2.1	Preventing Inorganic Salt Precipitation	114
5.2.2	Increasing Soil Removal	116
5.2.3	Preventing Particulate Soil Redeposition	116
5.2.4	Other Benefits	117
5.2.4.1	Soil Release	117
5.2.4.2	Dye Transfer Inhibition	118
5.3	End-Use Applications	118
5.3.1	Home Laundry	118
5.3.2	Dishwashing	119
5.3.2.1	I&I Dishwashing	119
5.3.2.2	Home Dishwashing	120
5.3.3	I&I Laundry	122
5.3.4	Food Process Cleaners	124
5.3.5	Hard-Surface Cleaners	124
5.4	Polymer Properties	126
5.4.1	Molecular Weight	126
5.4.2	Percent Solids	127
5.4.3	Degree of Neutralization (pH)	127
5.4.4	Physical Form	127
5.4.5	Sequestration and Clay Dispersancy	128
5.4.6	Caustic Solubility	129
5.4.7	Hypochlorite Stability	130
5.5	Thickeners/Stabilizers	131
5.5.1	Nonassociative	131
5.5.2	Associative	131
5.5.3	Physical Form	131
	References	132

6 Laundry Products 133

Thomas Christ, William W. Morgenthaler, and Frank Pacholec

6.1	Introduction	133
6.2	Detergent Ingredients	133
6.2.1	Surfactants	134
6.2.2	Builders	136
6.2.3	Auxiliary Ingredients	136
6.2.3.1	Bleach Ingredients	136
6.2.3.2	Optical Brighteners	137
6.2.3.3	Enzymes	137
6.2.3.4	Antiredeposition Agents	138
6.2.3.5	Foam Regulators	138
6.2.3.6	Corrosion Inhibitors	138
6.2.3.7	Dyes	138
6.2.3.8	Perfumes	139
6.2.3.9	Fillers/Formulation Aids	139
6.3	Formulation Considerations	139
6.3.1	Product Types	139
6.3.1.1	Market Niche	140
6.3.1.2	Types of Soils and Stains	142
6.3.1.3	Wash Variables	143

6.3.1.4	Fabric Types	145
6.3.2	Watch-Outs: Safety	146
6.4	Detergent Processing	146
6.4.1	Introduction	146
6.4.2	Powder Detergent Processing	146
6.4.2.1	Dry Mixing	147
6.4.2.2	Spray-Drying	148
6.4.2.3	Agglomeration	149
6.4.2.4	Alternative Production Techniques	151
6.4.2.5	Summary	153
6.4.3	Liquid Detergent Processing	154
6.4.3.1	Clear Liquid Products	154
6.4.3.2	Structured and Nonaqueous Liquids	154
6.4.4	Typical Formulations	155
6.5	Product Form and Packaging	157
6.5.1	Introduction	157
6.5.2	Dry Products	157
6.5.2.1	Spray-Dried Detergents	157
6.5.2.2	Tablets and Bars	158
6.5.2.3	Pouches and Sheets	158
6.5.2.4	Concentrated Products	158
6.5.3	Liquid Products	159
6.6	Performance Testing	160
6.6.1	Introduction	160
6.6.2	Laboratory Testing	160
6.6.3	Practical Testing	161
6.6.4	Consumer Testing	161
6.7	Detergent Usage and Cost Performance	161
	References	162
7	Hard-Surface Cleaners	165
	<i>Timothy C. Morris</i>	
7.1	Introduction	165
7.2	In Situ Cleaners (Clean-in-Place)	166
7.2.1	Conventional Hard Surfaces	166
7.2.2	Glass Cleaners	171
7.2.3	Oven Cleaners	171
7.2.4	General-Purpose Cleaners	173
7.3	Dishwash Detergents	175
7.3.1	Hand Dishwash Detergents	176
7.3.2	Machine Dishwash Detergents	178
7.3.2.1	Automatic Dishwash Detergents	178
7.3.2.2	Machine Dishwash Detergents	181
7.4	Vehicle Wash Cleaners	184
7.5	Metal Cleaners	187
7.5.1	Cleaning Systems	188
	References	191

8	Textile Industry Applications	193
	<i>K. Robert Lange</i>	
8.1	Introduction	193
8.2	Cotton	194
	8.2.1 Scouring	194
	8.2.2 Size Removal and Scouring	195
8.3	Polyacrylics	197
	8.3.1 Modacrylics	197
	8.3.2 Scours	198
8.4	Polyamides	198
	8.4.1 Scours	199
8.5	Polyesters	199
	8.5.1 Scours	200
8.6	Polyolefins	200
	8.6.1 Scours	201
8.7	Rayons	201
	8.7.1 Acetate	201
	8.7.2 Scours	201
8.8	Wool	202
	8.8.1 Scours	202
	8.8.2 Proteolytic Enzymes	203
8.9	The Role of Cationic Surfactants	204
	References	204
9	The Detergent Regulatory and Environmental Situation	205
	<i>Edwin A. Matzner</i>	
9.1	Introduction	205
9.2	United States	206
	9.2.1 General Regulations	206
	9.2.2 FTC Environmental Claim Guidelines	207
	9.2.3 Surfactant Regulation	207
	9.2.4 Boron Regulation	208
9.3	U.S. State and Local Regulations	208
	9.3.1 State and Local Phosphate Regulations: Enacted	208
	9.3.1.1 Akron, Ohio (population 660,000)	210
	9.3.1.2 Austin, Texas (population 380,000); LaGrange, Texas (population 3800)	210
	9.3.1.3 Branson, Missouri (population 2500)	211
	9.3.1.4 Chicago, Illinois (population 2,784,000)	211
	9.3.1.5 District of Columbia (population 598,000)	212
	9.3.1.6 Georgia (population 6,623,000)	212
	9.3.1.7 Idaho Municipalities (estimated population 91,000)	213
	9.3.1.8 Indiana (population 5,610,000)	213
	9.3.1.9 Maine (population 1,235,000)	214
	9.3.1.10 Maryland (population 4,860,000)	214
	9.3.1.11 Michigan (population 9,368,000)	214
	9.3.1.12 Minnesota (population 4,432,000)	215
	9.3.1.13 Monroe County, Florida (estimated population 70,000)	215
	9.3.1.14 Montana	216

9.3.1.15	New York State (population 18,058,000)	216
9.3.1.16	North Carolina (population 6,737,000)	216
9.3.1.17	Northern Ohio (estimated population 6,000,000)	217
9.3.1.18	Oregon (population 2,922,000)	218
9.3.1.19	Pennsylvania (population 11,961,000)	218
9.3.1.20	South Carolina (population 3,560,000)	219
9.3.1.21	Spokane, Washington (population 177,000)	220
9.3.1.22	Vermont (population 567,000)	220
9.3.1.23	Virginia (population 6,286,000)	220
9.3.1.24	Wharton, Texas (population 9000)	221
9.3.1.25	Wisconsin (population 4,955,000)	223
9.3.2	State and Local Phosphate Regulations: Not Enacted	223
9.4	Results of Phosphate Regulation	223
9.4.1	Effects on Water Quality	223
9.4.2	Effects on Sewage Treatment Plants	224
9.4.3	Other Effects of Phosphate Bans	225
9.5	Surfactant Biodegradation	225
9.6	pH Regulation	226
9.7	NTA Regulation	226
9.8	Waste and Solvent Regulations	227
9.8.1	California	227
9.8.2	Florida Solvents Tax	228
9.8.3	Volatile Organic Compound Regulation	228
9.8.4	Household Hazardous Waste Regulation	228
9.9	Trends in the United States	229
9.9.1	Animal Testing Regulations	229
9.9.2	Fragrance Regulation	229
9.9.3	Media Image: Eco-Marketing	229
9.9.4	Certification Programs	230
9.9.5	Definition Problems	230
9.10	Canada	231
9.10.1	Phosphate Regulation	231
9.10.2	Surfactant Regulation	231
9.10.3	Right-to-Know Law	231
	References	231
	Bibliography	232
10	Hints for the Formulator	235
	<i>K. Robert Lange</i>	
10.1	Introduction	235
10.2	Solid Formulations	236
10.2.1	Setting or Segregation	236
10.2.2	Caking	237
10.2.3	Color	237
10.2.4	Corrosion	238
10.2.5	Dusting	238
10.3	Liquids	239
10.3.1	Solutions	240
10.3.1.1	Drop-Out	240
10.3.1.2	Splits	240

10.3.1.3 Corrosion	241
10.3.2 Emulsions	242
10.3.2.1 Stability	242
10.3.2.2 Viscosity	243
10.3.2.3 Manufacturing Emulsions	244
10.4 Slurries	244
10.4.1 Viscosity Increase	245
10.5 Quality Assurance	246
10.5.1 Ingredients	246
10.5.2 Testing	247
10.6 Getting the Product out of the Laboratory	247
References	248
Additional Reading	248
Appendix	249
Glossary	261
Index	265

Basic Surfactant Concepts

Eric W. Kaler

This chapter introduces the fundamental ideas that guide the production of successful surfactant formulations. First the major features of surfactant molecules are discussed, and the kind of microstructures that form (micelles, vesicles, liquid crystals) reviewed. Next the general patterns of surfactant phase behavior are presented, and in particular the basic ideas needed to formulate microemulsions are summarized. The interfacial aspects of surfactants and their relation to spreading coefficients are reviewed, and the final section describes the basic properties of emulsions.

1.1 Introduction

Surfactant solutions exhibit many phenomena of scientific and technological interest. For example, surfactants are of primary importance in detergency, separation techniques, agriculture, and the pharmaceutical industry. Naturally occurring surfactants such as phospholipids are the main components of cell membranes and thus play a vital role in organizing the chemical reactions that sustain life. There are an enormous number of natural and synthetic surfactants available for applications, and choosing the optimal kind of surfactant for a given use can be a remarkable challenge.

Intelligent and rational use of surfactants in formulations for carrying hydrophobic materials such as drugs or pesticides into water, as well as in formulating cleaning products for textiles or hard surfaces, draws on principles from physical chemistry and thermodynamics. Moreover, the ultimate success or failure of a formula also often depends on the *kinetics* of solubilization or wetting. This introductory chapter describes a few of the most important properties of surfactants and shows in outline some of the unifying concepts in surfactant science. Useful references for further reading are given in the bibliography.

A surfactant (surface active agent) lowers the equilibrium interfacial tension between the medium in which it is dissolved and any other contacting fluid. Interfacial tensions are thermodynamic properties, like density and heat capacity, and so can be measured under given conditions and tabulated. If temperature and pressure are held constant, the value of the interfacial tension represents the work (and change in Gibbs free energy) necessary to create more interface. Since dispersing any material to colloidal size scales generates an enormous amount of interface, the ability of surfactants to reduce interfacial tensions is critical to such applications as the preparation of emulsions and the wetting and dispersal of powders in liquids. These interfacial properties of surfactants are discussed further in Section 1.6.

Eric W. Kaler, Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering, Colburn Laboratory, University of Delaware, Newark, Delaware 19716, U.S.A.