

CONTENTS

Preface	xi
1. INTRODUCTION TO SURFACTANTS	1
Surfactants Adsorb at Interfaces	1
Surfactants Aggregate in Solution	3
Surfactants are Amphiphilic	3
Surface Active Compounds are Plentiful in Nature	5
Surfactant Raw Materials may be Based on Petrochemicals or Oleochemicals	6
Surfactants are Classified by the Polar Head Group	8
The Ecological Impact of Surfactants is of Growing Importance	23
Some Important Development Trends	26
Bibliography	31
2. ASSOCIATION OF SURFACTANTS	33
Different Amphiphile Systems	33
Surfactants Start to Form Micelles at the CMC	33
CMC Depends on Chemical Structure	37
Temperature and Cosolutes Affect CMC	40
The Solubility of Surfactants may be Strongly Temperature Dependent	44
Driving Forces of Micelle Formation and Thermodynamic Models	46
The Association Process and Counterion Binding can be Monitored by NMR	49
Hydrophobic Compounds can be Solubilized in Micelles	51
Micelle Size and Structure may Vary	52
A Geometric Consideration of Chain Packing is Useful	54
Kinetics of Micelle Formation	55
Surfactants may Form Aggregates in other Solvents than Water	56
General Comments on Amphiphile Self-Assembly	58
Bibliography	60
3. PHASE BEHAVIOUR OF CONCENTRATED SURFACTANT SYSTEMS	61
Micelle Type and Size Vary with Concentration	61

Micellar Growth is Different for Different Systems	63
Surfactant Phases are Built Up by Discrete or Infinite Self-Assemblies	67
Micellar Solutions can Reach Saturation	70
Structures of Liquid Crystalline Phases	70
How to Determine Phase Diagrams	74
Binary and Ternary Phase Diagrams are Useful Tools: Two Components	76
Binary and Ternary Phase Diagrams are Useful Tools: Three Components	79
Surfactant Geometry and Packing Determine Aggregate Structure: Packing Parameter and Spontaneous Curvature of the Surfactant Film are Useful Concepts	82
Polar Lipids show the Same Phase Behaviour as other Amphiphiles	85
Liquid Crystalline Phases may Form in Solvents other than Water	89
Bibliography	89
4. PHYSIOCOCHEMICAL PROPERTIES OF SURFACTANTS AND POLYMERS CONTAINING OXYETHYLENE GROUPS 91	
Polyoxyethylene Chains make up the Hydrophilic Part of many Surfactants and Polymers	91
CMC and Micellar Size of Polyoxyethylene-Based Surfactants are Strongly Temperature Dependent	92
Temperature Dependence can be Studied using Phase Diagrams	94
The L ₃ or 'Sponge' Phase	97
Sequence of Self-Assembly Structures as a Function of Temperature	97
The Critical Packing Parameter and the Spontaneous Curvature Concepts are Useful Tools	97
Clouding is a Characteristic Feature of Polyoxyethylene-Based Surfactants and Polymers	103
Physicochemical Properties of Block Copolymers Containing Polyoxethylene Segments Resemble those of Polyoxyethylene-Based Surfactants	105
Temperature Anomalies of Oxyethylene-Based Surfactants and Polymers are Ubiquitous	107
Temperature Anomalies are Present in Solvents other than Water	111
Bibliography	113
5. MIXED MICELLES 115	
Systems of Surfactants with Similar Head Groups Require no Net Interaction	115
General Treatment of Surfactants Mixtures Requires a Net Interaction	120

The Concept of Mixed Micelles can also be Applied to Amphiphiles not Forming Micelles	126
Mixed Surfactant Systems at Higher Concentrations Show Interesting Features	126
Mixed Surfactant Systems are used Technically	128
Appendix	132
Bibliography	133
6. INTERMOLECULAR INTERACTIONS	135
Pair Potentials Act between Two Molecules in Vacuum	135
The Intermolecular Interaction can be Partitioned	137
Effective Pair Potentials Act between Two Molecules in a Medium	144
Bibliography	152
7. COLLOIDAL FORCES	153
Electric Double-Layer Forces are Important for Colloidal Stability	153
Other Types of Forces Exist	158
Colloidal Forces can be Measured Directly	167
Bibliography	169
8. POLYMERS IN SOLUTION	171
Polymer Properties are Governed by the Choice of Monomers	171
Molecular Weight is an Important Parameter	173
Dissolving a Polymer can be a Problem	174
Polymers in Solution can be Characterized by Viscosity Measurements	175
Polymer Solutions may Undergo Phase Separation	176
Polymers Containing Oxyethylene Groups Phase-Separate upon Heating in Aqueous Systems	177
Surfactants and Electrolytes have Large Effects on Polymer Solutions	177
The Solubility Parameter Concept is a Useful Tool for finding the Correct Solvent for a Polymer	178
The Theta Temperature is of Fundamental Importance	180
Polyelectrolytes are Charged Polymers	182
Polymer Configurations Depend on Solvent Conditions—A Scaling Approach	184
Bibliography	190
9. REGULAR SOLUTION THEORY	191
Bragg-Williams Theory can Describe Non-ideal Mixtures	191
Flory-Higgins Theory Describes the Phase Behaviour of Polymer Solutions	197
Bibliography	200

10. SURFACE ACTIVE POLYMERS	201
Surface Active Polymers can be Designed in Different Ways	201
Polymers may have a Hydrophilic Backbone and Hydrophobic Side Chains	202
Polymers may have a Hydrophobic Backbone and Hydrophilic Side Chains	205
Polymers may Consist of Alternating Hydrophilic and Hydrophobic Blocks	213
Polymeric Surfactants have Attractive Properties	217
Bibliography	217
11. SURFACTANT-POLYMER SYSTEMS	219
Polymers can Induce Surfactant Aggregation	219
Attractive Polymer-Surfactant Interactions Depend on both Polymer and Surfactant	223
Surfactant Association to Surface Active Polymers can be Strong	225
The Interaction between a Surfactant and a Surface Active Polymer is Analogous to Mixed Micelle Formation	227
Phase Behaviour of Polymer-Surfactant Mixtures Resembles that of Mixed Polymer Solutions	230
Phase Behaviour of Polymer-Surfactant Mixtures in Relation to Polymer-Polymer and Surfactant-Surfactant Mixtures	240
Polymers may Change the Phase Behaviour of Infinite Surfactant Self-Assemblies	241
There are many Technical Applications of Polymer-Surfactant Mixtures	242
Bibliography	244
12. SURFACE TENSION AND ADSORPTION AT THE AIR-WATER INTERFACE	247
Surface Tension is due to Asymmetric Cohesive Forces at a Surface	247
Solutes Affect Surface Tension	249
Dynamic Surface Tension is Important	250
The Surface Tension is Related to Adsorption	250
Surfactant Adsorption at the Liquid-Air Surface is Related to the Critical Packing Parameter	253
Polymer Adsorption can be Misinterpreted	255
Measurement of Surface Tension	256
The Surface and Interfacial Tensions can be Understood in Terms of Molecular Interactions	258
Surface Tension and Adsorption can be Understood in Terms of the Regular Solution Theory	261
Bibliography	264

13. ADSORPTION OF SURFACTANTS AT SOLID SURFACES	265
Surfactants Adsorption is Governed both by the Nature of the	
Surfactant and the Surface	265
Model Surfaces and Methods to Determine Adsorption	267
Analysis of Surfactant Adsorption is Frequently Carried Out in Terms	
of the Langmuir Equation	269
Surfactants Adsorb on Hydrophobic Surfaces	272
Surfactants Adsorb on Hydrophilic Surfaces	279
Competitive Adsorption is a Common Phenomenon	286
Bibliography	294
14. INTERACTION OF POLYMERS WITH SURFACES	295
The Adsorbed Amount Depends on Polymer Molecular Weight	296
The Solvent has a Profound Influence on the Adsorption	299
Electrostatic Interactions Affect the Adsorption	301
Polyelectrolyte Adsorption can be Modelled Theoretically	306
Polyelectrolytes Change the Double-Layer Repulsion	308
Polymer Adsorption is Practically Irreversible	317
The Acid–Base Concept can be Applied to Polymer Adsorption	318
Measurement of Polymer Adsorption	321
Bibliography	324
15. FOAMING OF SURFACTANT SOLUTIONS	325
There are Transient Foams and Stable Foams	325
Two Conditions must be Fulfilled for a Foam to be Formed	326
There are Four Forces Acting on a Foam	328
The Critical Packing Parameter Concept is a Useful Tool	330
Particles and Proteins can Stabilize Foams	333
Various Additives are Used to Break Foams	334
Bibliography	336
16. POLYMERIZABLE SURFACTANTS	337
The Surfactant Effect is Sometimes Undesirable	337
The Surfactant may Polymerize in Different Ways	338
Polymerizable Surfactants are of Interest for a Variety of Applications	341
Bibliography	349
17. USE OF SURFACTANTS AS EMULSIFIERS	351
Emulsions need to be Stabilized	351
The HLB Concept	352
The HLB Method of Selecting Emulsifier is Crude but Simple	353
The PIT Concept	356
The PIT Method of Selecting Emulsifier is often Useful	357

Different Types of Non-ionic Surfactants can be used as Emulsifiers	358
Bancroft's Rule may be Explained by Adsorption Dynamics of the Surfactant	360
Bancroft's Rule may be Related to the Surfactant Geometry	361
Hydrodynamics may Control what Type of Emulsion will Form	362
Bibliography	363
18. MICROEMULSIONS	365
The Term Microemulsion is Misleading	365
Phase Behaviour of Oil–Water–Surfactant Systems can be Illustrated by Phase Diagrams	365
The Choice of Surfactant is Decisive	370
Ternary Phase Diagrams can be Complex	372
How to Approach Microstructure?	372
Molecular Self-Diffusion can be Measured	373
Confinement, Obstruction and Solvation Determine Solvent Self-Diffusion in Microemulsions	374
Self-Diffusion Gives Evidence for a Bicontinuous Structure at Balanced Conditions	377
The Microstructure is Governed by Surfactant Properties	378
Bibliography	380
19. MICROEMULSIONS FOR OIL AND SOIL REMOVAL	391
Microemulsions can be the Solution to Enhanced Oil Recovery	391
Surfactant-Based Cleaning Formulations may act by <i>in situ</i> Formation of Microemulsion (Detergency)	396
Microemulsion-Based Cleaning Formulations are Efficient	397
Bibliography	399
20. CHEMICAL REACTIONS IN MICROEMULSIONS	401
Microemulsions can be Used as Minireactors for Chemical Reactions	401
Surface Active Reagents may be Subject to Micellar Catalysis	402
Microemulsions are Good Solvents for Organic Synthesis	405
Microemulsions are Useful as Media for Enzymatic Reactions	409
Microemulsions can be Used to Prepare Nanosized Lattices	414
Nanosized Inorganic Particles can be Prepared in Microemulsions	419
Bibliography	422
Appendixes	425
Index	433