Contents

Preface — v

1 General introduction ----- 1 General classification of surfactants ----- 5 2 2.1 Anionic surfactants ----- 5 Carboxylates ---- 6 2.1.1 2.1.2 Sulfates — 6 2.1.3 Sulfonates ---- 7 2.1.4 Isethionates ----- 8 2.1.5 Taurates — 9 2.1.6 Phosphate-containing anionic surfactants ---- 9 2.2 Cationic surfactants ----- 9 2.3 Amphoteric (zwitterionic) surfactants ----- 11 Nonionic surfactants ----- 12 2.4 Alcohol ethoxylates ----- 12 2.4.1 2.4.2 Alkyl phenol ethoxylates ----- 13 2.4.3 Fatty acid ethoxylates ----- 13 2.4.4 Sorbitan esters and their ethoxylated derivatives (Spans and 2.4.5 Ethoxylated fats and oils ----- 15 2.4.6 Amine ethoxylates — 15 2.4.7 Amine oxides ----- 15 2.5 Speciality surfactants ----- 16 Fluorocarbon and silicone surfactants ----- 16 2.5.12.5.2 Gemini surfactants ----- 17 2.5.3 Surfactants derived from mono- and polysaccharides ----- 17 Naturally occurring surfactants ----- 18 2.5.4 2.5.5 Biosurfactants ---- 22 2.5.6 Polymeric surfactants — 24 3 Aggregation of surfactants, self-assembly structures, liquid crystalline phases ----- 29 3.1 Thermodynamics of micellization — 36 3.1.1 Kinetic aspects — 36 Equilibrium aspects: Thermodynamics of micellization ----- 37 3.1.2 3.2 Enthalpy and entropy of micellization — 39 3.3 Driving force for micelle formation — 40 Micellization in surfactant mixtures (mixed micelles) ----- 42 3.4



viii — Contents

- 3.5 Surfactant self-assembly ----- 45
- 3.5.1 Structure of liquid crystalline phases 45
- 3.5.2 Hexagonal phase ----- 46
- 3.5.3 Micellar cubic phase 47
- 3.5.4 Lamellar phase ----- 47
- 3.5.5 Bicontinuous cubic phases 47
- 3.5.6 Reversed structures ----- 47
- 3.6 Experimental studies of the phase behavior of surfactants 48
- 4 Surfactant adsorption at interfaces ------ 51
- 4.1 Introduction ----- 51
- 4.2 Adsorption of surfactants at the air/liquid (A/L) and liquid/liquid (L/L) interfaces 52
- 4.2.1 The Gibbs adsorption isotherm 53
- 4.2.2 Equation of state approach ----- 57
- 4.2.3 The Langmuir, Szyszkowski and Frumkin equations 58
- 4.3 Interfacial tension measurements 59
- 4.3.1 The Wilhelmy plate method 59
- 4.3.2 The pendent drop method 60
- 4.3.3 The Du Nouy's ring method 61
- 4.3.4 The drop volume (weight) method 61
- 4.3.5 The spinning drop method 61
- 4.4 Adsorption of surfactants at the solid/liquid interface 62
- 4.4.1 Adsorption of ionic surfactants on hydrophobic surfaces 64
- 4.4.2 Adsorption of ionic surfactants on polar surfaces 67
- 4.4.3 Adsorption of nonionic surfactants 69
- 5 Surfactants as emulsifiers 73
- 5.1 Introduction 73
- 5.1.1 Nature of the emulsifier 73
- 5.1.2 Structure of the system 74
- 5.1.3 Breakdown processes in emulsions 74
- 5.2 Physical chemistry of emulsion systems 77
- 5.2.1 The interface (Gibbs dividing line) 77
- 5.2.2 Thermodynamics of emulsion formation and breakdown 78
- 5.2.3 Interaction energies (forces) between emulsion droplets and their combinations 80
- 5.3 Mechanism of emulsification 85
- 5.3.1 Methods of emulsification 86
- 5.3.2 Role of surfactants in emulsion formation 88
- 5.3.3 Role of surfactants in droplet deformation 89
- 5.4 Selection of emulsifiers 92

- 5.4.1 The Hydrophilic-Lipophile Balance (HLB) concept 92
- 5.4.2 The Phase Inversion Temperature (PIT) concept 95
- 5.5 Stabilization of emulsions ---- 97
- 5.5.1 Creaming or sedimentation and its prevention ---- 97
- 5.5.2 Flocculation of emulsions and its prevention 98
- 5.5.3 Ostwald ripening and its reduction ----- 99
- 5.5.4 Emulsion coalescence and its prevention 100

6 Surfactants as dispersants and stabilization of suspensions — 103

- 6.1 Introduction 103
- 6.2 Role of surfactants in preparation of solid/liquid dispersions (suspensions) 103
- 6.2.1 Role of surfactants in condensation methods. Nucleation and growth 104
- 6.2.2 Emulsion polymerization 105
- 6.2.3 Dispersion polymerization 107
- 6.2.4 Role of surfactants in dispersion methods 109
- 6.3 Assessment of wettability of powders 115
- 6.3.1 Sinking time, submersion or immersion test 115
- 6.3.2 Measurement of contact angles of liquids and surfactant solutions on powders ----- 116
- 6.3.3 List of wetting agents for hydrophobic solids in water 116
- 6.3.4 Stabilization of suspensions using surfactants 118

7 Surfactants for foam stabilization — 121

- 7.1 Introduction 121
- 7.2 Foam preparation 121
- 7.3 Foam structure 122
- 7.4 Classification of foam stability 123
- 7.4.1 Drainage and thinning of foam films 124
- 7.4.2 Theories of foam stability 125
- 7.5 Foam inhibitors 129
- 7.5.1 Chemical inhibitors that lower viscosity and increase drainage 130
- 7.5.2 Solubilized chemicals which cause antifoaming 130
- 7.5.3 Droplets and oil lenses which cause antifoaming and defoaming 130
- 7.5.4 Surface tension gradients (induced by antifoamers) 131
- 7.5.5 Hydrophobic particles as antifoamers ----- 131
- 7.5.6 Mixtures of hydrophobic particles and oils as antifoamers 132
- 7.6 Assessment of foam formation and stability 132
- 7.6.1 Efficiency and effectiveness of a foaming surfactant 133

8	Surfactants in nanoemulsions — 135
8.1	Introduction — 135
8.2	Fundamental principles of emulsification — 137
8.2.1	Methods of emulsification and the role of surfactants — 138
8.3	Preparation of nanoemulsions — 139
8.3.1	Use of high pressure homogenizers — 139
8.3.2	Phase inversion principle methods (low energy emulsification) 140
8.4	Steric stabilization and the role of the adsorbed layer thickness — 141
8.5	Ostwald Ripening — 144
8.6	Examples of nanoemulsions —— 145
9	Surfactants in microemulsions —— 153
9.1	Introduction —— 153
9.2	Thermodynamic definition of microemulsions — 154
9.3	Description of microemulsions using phase diagrams — 155
9.4	Thermodynamic theory of microemulsion formation 157
9.5	Characterization of microemulsions using scattering
	techniques —— 159
9.5.1	Time average (static) light scattering — 159
9.5.2	Dynamic light scattering (photon correlation spectroscopy,
	PCS) — 162
9.6	Characterization of microemulsions using conductivity —— 163
9.7	NMR measurements —— 165
9.8	Formulation of microemulsions —— 165
10	Surfactants as wetting agents —— 169
10.1	Introduction —— 169
10.2	The concept of contact angle — 170
10.3	Adhesion tension —— 172
10.4	Work of adhesion W _a 172
10.5	Work of cohesion — 172
10.6	The spreading coefficient S — 173
10.7	Contact angle hysteresis — 173
10.8	Critical surface tension of wetting — 174
10.9	Effect of surfactant adsorption — 175
10.10	Measurement of contact angles —— 176
11	Industrial applications of surfactants — 179
11.1	Surfactants in the home, personal care and cosmetics — 179
11.1.1	Shaving formulations — 184
11.1.2	Bar soaps —— 185

11.1.3 Liquid hand soaps — 185

- 11.1.4 Bath oils ----- 186
- 11.1.5 Foam (or bubble) baths 186
- 11.1.6 After bath preparations 186
- 11.1.7 Skin care products **186**
- 11.1.8 Hair care formulations 188
- 11.1.9 Sunscreens ----- 191
- 11.1.10 Make-up products ----- 193
- 11.2 Surfactants in pharmacy 196
- 11.2.1 Surface active drugs 197
- 11.2.2 Naturally occurring micelle-forming systems 198
- 11.2.3 Biological implications of the presence of surfactants in pharmaceutical formulations 200
- 11.2.4 Solubilized systems 201
- 11.2.5 Pharmaceutical aspects of solubilization 202
- 11.3 Surfactants in agrochemicals 202
- 11.4 Surfactants in paints and coatings 212
- 11.5 Surfactants in detergents ----- 217

Index — 221