

## Contents

**Preface** XIII

**List of Contributors** XV

<b>1</b>	<b>Emulsion Science and Technology: A General Introduction</b>	<b>1</b>
	<i>Tharwat F. Tadros</i>	
1.1	Introduction	1
1.2	Industrial Applications of Emulsions	3
1.3	The Physical Chemistry of Emulsion Systems	4
1.3.1	The Interface (Gibbs Dividing Line)	4
1.4	The Thermodynamics of Emulsion Formation and Breakdown	5
1.5	Interaction Energies (Forces) Between Emulsion Droplets and Their Combinations	7
1.5.1	Van der Waals Attraction	7
1.5.2	Electrostatic Repulsion	9
1.5.3	Steric Repulsion	11
1.6	Adsorption of Surfactants at the Liquid/Liquid Interface	12
1.6.1	The Gibbs Adsorption Isotherm	13
1.6.2	Mechanism of Emulsification	16
1.6.3	Methods of Emulsification	18
1.6.4	Role of Surfactants in Emulsion Formation	19
1.6.5	Role of Surfactants in Droplet Deformation	21
1.7	Selection of Emulsifiers	25
1.7.1	The Hydrophilic-Lipophilic Balance (HLB) Concept	25
1.7.2	The Phase Inversion Temperature (PIT) Concept	27
1.7.3	The Cohesive Energy Ratio (CER) Concept	29
1.7.4	The Critical Packing Parameter for Emulsion Selection	31
1.8	Creaming or Sedimentation of Emulsions	32
1.8.1	Creaming or Sedimentation Rates	33
1.8.2	Prevention of Creaming or Sedimentation	35
1.9	Flocculation of Emulsions	37
1.9.1	Mechanism of Emulsion Flocculation	38

1.9.1.1	Flocculation of Electrostatically Stabilized Emulsions	38
1.9.1.2	Flocculation of Sterically Stabilized Emulsions	40
1.9.2	General Rules for Reducing (Eliminating) Flocculation	41
1.10	Ostwald Ripening	41
1.11	Emulsion Coalescence	43
1.11.1	Rate of Coalescence	44
1.11.2	Phase Inversion	45
1.12	Rheology of Emulsions	46
1.12.1	Interfacial Rheology	46
1.12.2	Measurement of Interfacial Viscosity	47
1.12.3	Interfacial Dilational Elasticity	47
1.12.4	Interfacial Dilational Viscosity	48
1.12.5	Non-Newtonian Effects	49
1.12.6	Correlation of Interfacial Rheology with Emulsion Stability	49
1.12.6.1	Mixed Surfactant Films	49
1.12.6.2	Protein Films	49
1.12.7	Bulk Rheology of Emulsions	50
1.12.8	Rheology of Concentrated Emulsions	51
1.12.9	Influence of Droplet Deformability on Emulsion Rheology	53
1.12.10	Viscoelastic Properties of Concentrated Emulsions	53
	References	55
<b>2</b>	<b>Stabilization of Emulsions, Nanoemulsions and Multiple Emulsions Using Hydrophobically Modified Inulin (Polyfructose)</b>	<b>57</b>
	<i>Tharwat F. Tadros, Elise Vandekerckhove, Martine Lemmens, Bart Levecke, and Karl Booten</i>	
2.1	Introduction	57
2.2	Experimental	58
2.2.1	Materials	58
2.2.2	Methods	58
2.2.2.1	Preparation of Emulsions, Nanoemulsions and Multiple Emulsions	58
2.2.2.2	Investigation of Emulsion Stability	59
2.3	Results and Discussion	59
2.3.1	Emulsion Stability Using INUTE <sup>®</sup> SP1	59
2.3.2	Nanoemulsion Stability Using INUTE <sup>®</sup> SP1	60
2.3.3	Multiple Emulsion Stability Using INUTE <sup>®</sup> SP1	64
2.4	Conclusions	65
	References	65
<b>3</b>	<b>Interaction Forces in Emulsion Films Stabilized with Hydrophobically Modified Inulin (Polyfructose) and Correlation with Emulsion Stability</b>	<b>67</b>
	<i>Tharwat Tadros, Dotchi Exerowa, Georgi Gotchev, Todor Kolarov, Bart Levecke, and Karl Booten</i>	
3.1	Introduction	67

3.2	Materials and Methods	68
3.3	Results and Discussion	69
3.4	Conclusions	73
	References	73
<b>4</b>	<b>Enhancement of Stabilization and Performance of Personal Care Formulations Using Polymeric Surfactants</b>	<b>75</b>
	<i>Thanwat F. Tadros, Martine Lemmens, Bart Levecke, and Karl Booten</i>	
4.1	Introduction	75
4.2	Experimental	76
4.3	Results and Discussion	76
4.3.1	Massage Lotion	76
4.3.2	Hydrating Shower Gel	79
4.3.3	Soft Conditioner	80
4.3.4	Sun Spray SPF19	81
4.4	Conclusions	81
	References	81
<b>5</b>	<b>Effect of an External Force Field on Self-Ordering of Three-Phase Cellular Fluids in Two Dimensions</b>	<b>83</b>
	<i>Waldemar Nowicki and Grazyna Nowicka</i>	
5.1	Introduction	83
5.2	The Model	84
5.3	Results and Discussion	85
5.3.1	Energies of Cluster Insertion and Transformation	85
5.3.2	Evolution of the System in a Gravitational Field	90
5.4	Conclusions	93
	References	94
<b>6</b>	<b>The Physical Chemistry and Sensory Properties of Cosmetic Emulsions: Application to Face Make-Up Foundations</b>	<b>97</b>
	<i>Frédéric Auguste and Florence Levy</i>	
6.1	Introduction	97
6.2	Materials and Methods	98
6.2.1	Selection of the Foundations to be Studied	98
6.2.2	Characterization Methods	98
6.3	Experimental Results and Discussion	99
6.3.1	Drying of the Foundation Bulk and Drift in Composition During Drying	99
6.3.2	Evolution of Viscosity During Drying	100
6.3.3	Play-Time and Disposition of Foundation on the Skin	102
6.4	Conclusions	104
	References	104

<b>7</b>	<b>Nanoparticle Preparation by Miniemulsion Polymerization</b>	<b>107</b>
	<i>Man Wu, Elise Rotureau, Emmanuelle Marie, Edith Dellacherie, and Alain Durand</i>	
7.1	Introduction	107
7.2	Experimental	108
7.2.1	Materials	108
7.2.2	Emulsion Preparation	108
7.2.3	Polymerization	108
7.2.4	Size Measurement of the Emulsion Droplets	108
7.2.5	Particle Characterization	109
7.3	Results and Discussion	109
7.3.1	Synthesis of Hydrophobically Modified Dextrans	109
7.3.2	Preparation of O/W Miniemulsions	111
7.3.2.1	Control of Initial Droplet Size by Process Variables	111
7.3.2.2	Influence of Polymer Structure on Initial Droplet Size	112
7.3.3	Stability of Miniemulsions within Polymerization Duration	114
7.3.3.1	Mechanism and Kinetics of Miniemulsion Polymerization	114
7.3.3.2	Mechanism and Rate of Emulsion Aging	116
7.3.3.3	Variation of the Rate of Emulsion Aging with Polymerization Conditions	118
7.3.4	Preparation of Defined Nanoparticles with Various Monomers	123
7.3.4.1	Poly(styrene) Nanoparticles Covered by Dextran	123
7.3.4.2	Poly(butylcyanoacrylate) Nanoparticles	126
7.3.5	Colloidal Properties of the Obtained Suspensions	128
7.4	Conclusions	129
	References	130
<b>8</b>	<b>Recent Developments in Producing Monodisperse Emulsions Using Straight-Through Microchannel Array Devices</b>	<b>133</b>
	<i>Isao Kobayashi, Kunihiko Uemura, and Mitsutoshi Nakajima</i>	
8.1	Introduction	133
8.2	Principles of Microchannel Emulsification	135
8.3	Straight-Through MC Array Device and Emulsification Set-Up	137
8.4	Effect of Channel Shapes on Emulsification Using Symmetric Straight-Through MC Arrays	139
8.4.1	Effect of Channel Cross-Sectional Shape	139
8.4.2	Effect of the Aspect Ratio of Oblong Channels	139
8.4.3	Computational Fluid Dynamics (CFD) Simulation and Analysis	141
8.5	Effect of Process Factors on Emulsification Using Symmetric Straight-Through MC Arrays	144
8.5.1	Effect of Surfactants and Emulsifiers	144
8.5.2	Effect of To-Be-Dispersed Phase Viscosity	146
8.5.3	Effect of To-Be-Dispersed Phase Flux	148
8.6	Scaling-Up of Straight-Through MC Array Devices	149

8.7	Emulsification Using an Asymmetric Straight-Through MC Array	150
8.8	Conclusions and Outlook	152
	References	154
<b>9</b>	<b>Isotropic and Anisotropic Metal Nanoparticles Prepared by Inverse Microemulsion</b>	<b>157</b>
	<i>Ignác Capek</i>	
9.1	Introduction	157
9.1.1	Properties of Nanoscale Particles	157
9.1.2	Production of Nanoparticles and Microemulsions	158
9.2	General Aspects of Microemulsions	159
9.2.1	Droplet Dimensions	160
9.2.2	The Use of W/O Microemulsions	161
9.2.3	Nanoparticle Preparation	162
9.2.4	Surfactant-Based Methods	164
9.2.5	Coprecipitation	166
9.3	Isotropic Nanoparticles	166
9.4	Anisotropic Nanoparticles	167
9.5	Conclusions and Outlook	179
	References	185
<b>10</b>	<b>Preparation of Nanoemulsions by Spontaneous Emulsification and Stabilization with Poly(caprolactone)-<i>b</i>-poly(ethylene oxide) Block Copolymers</b>	<b>191</b>
	<i>Emmanuel Landreau, Youssef Aguni, Thierry Hamaide, and Yves Chevalier</i>	
10.1	Introduction	191
10.1.1	Block Copolymers	192
10.1.1.1	Spontaneous Emulsification	193
10.1.1.2	Biodegradability and Biocompatibility	194
10.1.2	Block Copolymer Micelles	194
10.1.3	Diblock Copolymers	195
10.2	Materials and Methods	195
10.2.1	Materials	195
10.2.2	Synthesis of Block Copolymers (PCL- <i>b</i> -PEO)	196
10.2.3	Methods	196
10.2.4	Emulsification of Oils or PCL	197
10.3	Results and Discussion	197
10.3.1	Emulsions of PCL by Spontaneous Emulsification	198
10.3.1.1	Fabrication of the Emulsions	198
10.3.1.2	Particle Sizes	200
10.3.1.3	Stability of the Emulsions	201
10.3.2	Emulsions of Various Oils by Spontaneous Emulsification	203
10.4	Conclusions	205
	References	206

<b>11</b>	<b>Routes Towards the Synthesis of Waterborne Acrylic/Clay Nanocomposites</b> 209
	<i>Gabriela Diaconu, Maria Paulis, and Jose R. Leiza</i>
11.1	Introduction 209
11.2	Experimental 211
11.2.1	Materials 211
11.2.2	Synthesis of Waterborne (MMA-BA)/MMT Nanocomposites by Emulsion Polymerization 213
11.2.3	Synthesis of Waterborne (MMA-BA)/MMT Nanocomposites by Miniemulsion Polymerization 214
11.2.4	Characterization and Measurements 215
11.3	Results and Discussion 217
11.3.1	Waterborne Nanocomposites by Emulsion Polymerization 217
11.3.2	Waterborne Nanocomposites by Miniemulsion Polymerization 219
11.4	Conclusions 226
	References 226
<b>12</b>	<b>Preparation Characteristics of Giant Vesicles with Controlled Size and High Entrapment Efficiency Using Monodisperse Water-in-Oil Emulsions</b> 229
	<i>Takashi Kuroiwa, Mitsutoshi Nakajima, Kunihiko Uemura, Seigo Sato, Sukekuni Mukataka, and Sosaku Ichikawa</i>
12.1	Introduction 229
12.2	Materials and Methods 230
12.2.1	Materials 230
12.2.2	Preparation of W/O Emulsions Using MC Emulsification 230
12.2.3	Formation of GVs 231
12.2.4	Measurement of Droplet and Vesicle Diameters 232
12.2.5	Determination of Entrapment Yield 232
12.3	Results and Discussion 233
12.3.1	Preparation of GVs Using Monodisperse W/O Emulsions 233
12.3.2	Size Control of GVs and Entrapment of a Hydrophilic Molecule into GVs 234
12.3.3	Formation Characteristics of GVs 237
12.4	Conclusions 240
	References 241
<b>13</b>	<b>On the Preparation of Polymer Latexes (Co)Stabilized by Clays</b> 243
	<i>Ignác Capek</i>
13.1	Introduction 243
13.2	Cloisite Clays and Organoclays 247
13.3	Radical Polymerization 260
13.3.1	Solution/Bulk Polymerization 260
13.3.2	Radical Polymerization in Micellar Systems 263
13.4	Collective Properties of Polymer/MMT Nanocomposites 281

13.4.1	Kinetic and Molecular Weight Parameters	281
13.4.2	X-Ray Diffraction Studies	284
13.4.2.1	Homopolymers	284
13.4.2.2	Copolymers	288
13.4.3	Thermal and Mechanical Properties	290
13.4.3.1	Polystyrene and Poly(methyl methacrylate) Nanocomposites	290
13.4.3.2	Poly(ethylene oxide) Nanocomposites	293
13.5	Polymer–Inorganic Nanocomposites	296
13.6	General	301
13.7	Conclusions and Outlook	302
	References	310
	<b>Index</b>	317