

Contents

Preface XI

List of Contributors XIII

1	Emulsion Formation, Stability, and Rheology	1
	<i>Tharwat F. Tadros</i>	
1.1	Introduction	1
1.1.1	Nature of the Emulsifier	1
1.1.2	Structure of the System	2
1.1.3	Breakdown Processes in Emulsions	3
1.1.4	Creaming and Sedimentation	3
1.1.5	Flocculation	4
1.1.6	Ostwald Ripening (Disproportionation)	4
1.1.7	Coalescence	4
1.1.8	Phase Inversion	4
1.2	Industrial Applications of Emulsions	4
1.3	Physical Chemistry of Emulsion Systems	5
1.3.1	The Interface (Gibbs Dividing Line)	5
1.4	Thermodynamics of Emulsion Formation and Breakdown	6
1.5	Interaction Energies (Forces) between Emulsion Droplets and Their Combinations	8
1.5.1	van der Waals Attraction	8
1.5.2	Electrostatic Repulsion	9
1.5.3	Steric Repulsion	12
1.6	Adsorption of Surfactants at the Liquid/Liquid Interface	14
1.6.1	The Gibbs Adsorption Isotherm	14
1.6.2	Mechanism of Emulsification	17
1.6.3	Methods of Emulsification	19
1.6.4	Role of Surfactants in Emulsion Formation	21
1.6.5	Role of Surfactants in Droplet Deformation	22
1.7	Selection of Emulsifiers	26
1.7.1	The Hydrophilic–Lipophilic Balance (HLB) Concept	26
1.7.2	The Phase Inversion Temperature (PIT) Concept	29
1.7.3	The Cohesive Energy Ratio (CER) Concept	31

1.7.4	The Critical Packing Parameter (CPP) for Emulsion Selection	32
1.8	Creaming or Sedimentation of Emulsions	35
1.8.1	Creaming or Sedimentation Rates	36
1.8.2	Prevention of Creaming or Sedimentation	37
1.9	Flocculation of Emulsions	40
1.9.1	Mechanism of Emulsion Flocculation	40
1.9.1.1	Flocculation of Electrostatically Stabilized Emulsions	41
1.9.1.2	Flocculation of Sterically Stabilized Emulsions	42
1.9.2	General Rules for Reducing (Eliminating) Flocculation	43
1.10	Ostwald Ripening	44
1.11	Emulsion Coalescence	45
1.11.1	Rate of Coalescence	46
1.11.2	Phase Inversion	47
1.12	Rheology of Emulsions	48
1.12.1	Interfacial Rheology	48
1.12.1.1	Interfacial Tension and Surface Pressure	48
1.12.1.2	Interfacial Shear Viscosity	49
1.12.2	Measurement of Interfacial Viscosity	49
1.12.3	Interfacial Dilational Elasticity	50
1.12.4	Interfacial Dilational Viscosity	51
1.12.5	Non-Newtonian Effects	51
1.12.6	Correlation of Emulsion Stability with Interfacial Rheology	51
1.12.6.1	Mixed Surfactant Films	51
1.12.6.2	Protein Films	51
1.13	Bulk Rheology of Emulsions	53
1.13.1	Analysis of the Rheological Behavior of Concentrated Emulsions	54
1.14	Experimental $\eta_r - \phi$ Curves	57
1.14.1	Experimental $\eta_r - \phi$ Curves	58
1.14.2	Influence of Droplet Deformability	58
1.15	Viscoelastic Properties of Concentrated Emulsions	59
1.15.1	High Internal Phase Emulsions (HIPEs)	61
1.15.2	Deformation and Breakup of Droplets in Emulsions during Flow	66
	References	73
2	Emulsion Formation in Membrane and Microfluidic Devices	77
	<i>Goran T. Vladislavljević, Isao Kobayashi, and Mitsutoshi Nakajima</i>	
2.1	Introduction	77
2.2	Membrane Emulsification (ME)	78
2.2.1	Direct Membrane Emulsification	78
2.2.2	Premix Membrane Emulsification	79
2.2.3	Operating Parameters in Membrane Emulsification	80
2.2.4	Membrane Type	80
2.2.4.1	Surfactant Type	80
2.2.4.2	Transmembrane Pressure and Wall Shear Stress	81
2.3	Microfluidic Junctions and Flow-Focusing Devices	82

2.3.1	Microfluidic Junctions	82
2.3.2	Microfluidic Flow-Focusing Devices (MFFD)	83
2.4	Microfluidic Devices with Parallel Microchannel Arrays	85
2.4.1	Grooved-Type Microchannel Arrays	86
2.4.2	Straight-through Microchannel Arrays	88
2.5	Glass Capillary Microfluidic Devices	89
2.6	Application of Droplets Formed in Membrane and Microfluidic Devices	93
2.7	Conclusions	93
	Acknowledgments	94
	References	94
3	Adsorption Characteristics of Ionic Surfactants at Water/Hexane Interface Obtained by PAT and ODBA	99
	<i>Nenad Mucic, Vincent Pradines, Aliyar Javadi, Altynay Sharipova, Jürgen Krägel, Martin E. Leser, Eugene V. Aksenenko, Valentin B. Fainerman, and Reinhard Miller</i>	
3.1	Introduction	99
3.2	Experimental Tools	99
3.3	Theory	101
3.4	Results	102
3.5	Summary	107
	Acknowledgments	107
	References	107
4	Measurement Techniques Applicable to the Investigation of Emulsion Formation during Processing	109
	<i>Nima Niknafs, Robin D. Hancocks, and Ian T. Norton</i>	
4.1	Introduction	109
4.2	Online Droplet Size Measurement Techniques	112
4.2.1	Laser Systems	112
4.2.2	Sound Systems	115
4.2.3	Direct Imaging	115
4.2.4	Other Techniques	118
4.3	Techniques Investigating Droplet Coalescence	121
4.4	Concluding Remarks	123
	References	125
5	Emulsification in Rotor–Stator Mixers	127
	<i>Andrzej W. Pacek, Steven Hall, Michael Cooke, and Adam J. Kowalski</i>	
5.1	Introduction	127
5.2	Classification and Applications of Rotor–Stator Mixers	128
5.2.1	Colloid Mills	129
5.2.2	In-Line Radial Discharge Mixers	130
5.2.3	Toothed Devices	131

5.2.4	Batch Radial Discharge Mixers	132
5.2.5	Design and Arrangement	133
5.2.6	Operation	136
5.3	Engineering Description of Emulsification/Dispersion Processes	138
5.3.1	Drop Size Distributions and Average Drop Sizes	138
5.3.2	Drop Size in Liquid–Liquid Two-Phase Systems – Theory	140
5.3.3	Maximum Stable Drop Size in Laminar Flow	141
5.3.4	Maximum Stable Drop Size in Turbulent Flow	142
5.3.5	Characterization of Flow in Rotor–Stator Mixers	143
5.3.5.1	Shear Stress	143
5.3.5.2	Average Energy Dissipation Rate	144
5.3.5.3	Power Draw	144
5.3.6	Average Drop Size in Liquid–Liquid Systems	145
5.3.7	Scaling-up of Rotor–Stator Mixers	147
5.4	Advanced Analysis of Emulsification/Dispersion Processes in Rotor–Stator Mixers	152
5.4.1	Velocity and Energy Dissipation Rate in Rotor–Stator Mixers	153
5.4.1.1	Batch Rotor–Stator Mixers	154
5.4.1.2	In-Line Rotor–Stator Mixers	157
5.4.2	Prediction of Drop Size Distributions during Emulsification	160
5.5	Conclusion	163
	Nomenclature	163
	References	165
6	Formulation, Characterization, and Property Control of Paraffin Emulsions	169
	<i>Jordi Esquena and Jon Vilasau</i>	
6.1	Introduction	169
6.1.1	Industrial Applications of Paraffin Emulsions	170
6.1.2	Properties of Paraffin	170
6.1.3	Preparation of Paraffin Emulsions	172
6.2	Surfactant Systems Used in Formulation of Paraffin Emulsions	174
6.2.1	Phase Behavior	175
6.3	Formation and Characterization of Paraffin Emulsions	178
6.4	Control of Particle Size	181
6.5	Stability of Paraffin Emulsions	185
6.5.1	Stability as a Function of Time under Shear (Orthokinetic Stability)	185
6.5.2	Stability as a Function of Freeze–Thaw Cycles	186
6.5.3	Stability as a Function of Electrolytes	189
6.6	Conclusions	195
	Acknowledgments	196
	References	196

7	Polymeric O/W Nano-emulsions Obtained by the Phase Inversion Composition (PIC) Method for Biomedical Nanoparticle Preparation	199
	<i>Gabriela Calderó and Conxita Solans</i>	
7.1	Introduction	199
7.2	Phase Inversion Emulsification Methods	200
7.3	Aspects on the Choice of the Components	201
7.4	Ethylcellulose Nano-Emulsions for Nanoparticle Preparation	202
7.5	Final Remarks	204
	Acknowledgments	205
	References	205
8	Rheology and Stability of Sterically Stabilized Emulsions	209
	<i>Tharwat F. Tadros</i>	
8.1	Introduction	209
8.2	General Classification of Polymeric Surfactants	210
8.3	Interaction between Droplets Containing Adsorbed Polymeric Surfactant Layers: Steric Stabilization	212
8.3.1	Mixing Interaction G_{mix}	213
8.3.2	Elastic Interaction G_{el}	214
8.4	Emulsions Stabilized by Polymeric Surfactants	216
8.4.1	W/O Emulsions Stabilized with PHS-PEO-PHS Block Copolymer	219
8.5	Principles of Rheological Techniques	220
8.5.1	Steady State Measurements	220
8.5.1.1	Bingham Plastic Systems	221
8.5.1.2	Pseudoplastic (Shear Thinning) System	221
8.5.1.3	Herschel–Bulkley General Model	222
8.5.2	Constant Stress (Creep) Measurements	222
8.5.3	Dynamic (Oscillatory) Measurements	223
8.6	Rheology of Oil-in-Water (O/W) Emulsions Stabilized with Poly(Vinyl Alcohol)	226
8.6.1	Effect of Oil Volume Fraction on the Rheology of the Emulsions	226
8.6.2	Stability of PVA-Stabilized Emulsions	229
8.6.3	Emulsions Stabilized with an A-B-A Block Copolymer	236
8.6.4	Water-in-Oil Emulsions Stabilized with A-B-A Block Copolymer	240
	References	245
	Index	247