

Contents

Foreword — XIII

List of Authors — XV

Abbreviations — XXI

List of Symbols — XXVII

Matthias Kraume

1 Motivation and Objectives — 1

- 1.1 Goals and Scientific Concept — 3
- 1.2 Advanced Phase Systems — 5
 - 1.2.1 Thermomorphic Multiphase Systems — 6
 - 1.2.2 Microemulsion Systems — 7
 - 1.2.3 Pickering Emulsions — 7
- 1.3 Material Basis and Reactions — 9
- 1.4 Model Process — 11
- 1.5 Challenges of the Fundamental Investigations — 12
 - 1.5.1 Chemical–Physical Fundamentals — 13
 - 1.5.2 Process Technology — 15
 - 1.5.3 Systems Technology — 18
- 1.6 Structure of the Book — 20
- References — 21

Matthias Kraume

2 State of the Art of the Investigated Phase Systems — 23

- 2.1 Thermomorphic Multiphase Systems — 24
 - 2.1.1 Introduction — 24
 - 2.1.2 Fundamentals and Thermodynamics — 25
 - 2.1.3 Reactions in TMS and Remaining Challenges — 31
- 2.2 Microemulsion Systems — 32
 - 2.2.1 Introduction — 32
 - 2.2.2 Fundamentals — 33
 - 2.2.2.1 Properties and Phase Behavior of Microemulsion Systems — 33
 - 2.2.2.2 Features and Description of the Three-Phase Body — 35
 - 2.2.2.3 Coalescence Behavior and Separation Dynamics — 36
 - 2.2.3 Industrial Applications and Remaining Challenges — 39

2.3	Pickering Emulsions — 40
2.3.1	Introduction — 40
2.3.2	Fundamentals — 40
2.3.2.1	Stabilizing Mechanism — 40
2.3.2.2	Properties of Pickering Emulsions — 41
2.3.3	Reactions in Pickering Emulsions — 42
2.3.4	Remaining Challenges — 42
2.3.4.1	Pickering Emulsion Characterization and Properties — 43
2.3.4.2	Mass Transfer and Location of Catalyst — 44
2.3.4.3	Continuous L/L Separation for Catalyst Retention — 44
2.4	Reaction Indicators — 45
	References — 48

Sabine Enders

3	Thermodynamics, Kinetics, and Mass Transfer — 55
3.1	Thermodynamics — 55
3.1.1	Heterosegmented Perturbed-Chain Statistical Associating Fluid Theory — 56
3.1.2	Lattice Cluster Theory — 57
3.1.3	Phase Equilibria — 58
3.1.4	Interfacial Properties — 71
3.1.5	Reaction Equilibria — 84
3.1.6	Aggregation Formation of Aqueous Surfactant Solutions — 90
3.1.7	Solubilization of Weak Polar Molecules in Aqueous Surfactant Solutions — 96
3.1.8	Conclusion — 100
3.2	Kinetic Modeling of Complex Catalytic Reactions in Multiphase Systems — 101
3.2.1	Introduction — 101
3.2.2	Methodological Approach — 102
3.2.2.1	Reaction Network Investigation — 102
3.2.2.2	Derivation of Explicit Rate Equations — 108
3.2.2.3	Reduction of Kinetic Models — 117
3.2.3	Demonstration of Concept for Coupled Networks — 136
3.2.3.1	Isomerizing Hydroformylation — 137
3.2.3.2	Overall Reaction Network of Tandem Hydroaminomethylation — 142

3.2.4	Thermodynamic Outlook —	144
3.2.5	Summary —	148
3.3	Mass Transfer Processes —	149
3.3.1	Introduction —	149
3.3.2	Experimental Characterization of Multiphase Liquid–Liquid Mass Transport —	150
3.3.2.1	Single Drop Experiments —	150
3.3.2.2	Modified Nitsch Cell —	153
3.3.2.3	Stirred Tank Reactor —	155
3.3.3	Experimental Characterization of Multiphase Gas-Liquid Mass Transport —	156
3.3.3.1	Determination of k_{La} from Pressure Decrease in a Closed System —	156
3.3.3.2	Stirred Tank Reactor —	159
3.3.3.3	Falling Film Contactor —	160
3.3.4	Gas–Liquid Mass Transfer —	162
3.3.5	Effect of Mass Transfer on Reaction Selectivity —	170
	References —	175

Anja Drews, Reinhard Schomäcker

4	Phase Systems Characterization and Process Development —	189
4.1	Thermomorphic Multiphase Systems —	190
4.1.1	Phase System Characterization —	190
4.1.2	Mass Transfer in Thermomorphic Multiphase Systems —	192
4.1.3	Applications —	197
4.1.4	Recent Developments in TMSs —	219
4.1.4.1	Combination of TMSs with Other Reactor Types —	222
4.1.4.2	Improved Online Analytics —	223
4.1.4.3	Application of TMSs for Complex Reactions in Continuous Operation —	224
4.1.4.4	Combined Reaction Separation Processes —	229
4.1.5	Summary and Outlook —	234
4.2	Microemulsion Systems —	236
4.2.1	Phase System Characterization and Systematic Analysis of MES for the Selected Reaction —	239
4.2.1.1	Dispersion Types in Micellar Multiphase Systems —	239
4.2.1.2	Localization of the Catalyst Complex —	241
4.2.1.3	Mass Transfer in Microemulsion Systems —	242

4.2.1.4	Micellar-Enhanced Ultrafiltration and Organic Solvent Nanofiltration —	252
4.2.1.5	Systematic Development and Analysis of Microemulsions for Process Application —	254
4.2.2	Applications —	263
4.2.3	Application Case Study: Hydroformylation of 1-Dodecene —	268
4.2.4	Concluding Remarks —	302
4.3	Pickering Emulsions —	304
4.3.1	Phase System Characterization —	304
4.3.1.1	Particle Types and Characterization —	304
4.3.1.2	Particles at the Liquid/Liquid Interface —	309
4.3.1.3	Drop Size Distributions and Stability —	310
4.3.1.4	Rheology of Pickering Emulsions —	315
4.3.1.5	Mass Transfer in Pickering Emulsions —	317
4.3.1.6	Filterability of Pickering Emulsions —	322
4.3.2	Applications —	329
4.3.3	Application Case Study —	330
4.3.3.1	Influence of the Catalyst (Rh-SX) on the Pickering Emulsion Properties —	331
4.3.3.2	Emulsions Stabilized by HNT (o/w) —	332
4.3.3.3	Reaction in and Filtration of Pickering Emulsions Using Tailored Nanospheres (w/o) —	333
4.3.3.4	Reaction in and Filtration of Pickering Emulsions Using a Commercial Particle System (w/o) —	335
4.3.4	Concluding Remarks —	336
4.4	Summary and Comparison of Phase Systems —	338
	References —	342

Sebastian Engell

5	Tools for Systems Engineering —	361
5.1	Overview —	361
5.2	Modeling and Simulation —	364
5.2.1	A Framework for Process Modeling and Simulation —	364
5.2.1.1	Requirements for Collaborative Modeling —	365
5.2.1.2	Data Model for Modeling at the Documentation Level and Hierarchical Modeling —	368
5.2.1.3	Collaborative Modeling and Web Technologies —	376

5.2.1.4	Specification of Simulation and Optimization Problems —	377
5.2.1.5	Model-Based Code Implementation of Models —	378
5.2.1.6	Examples of Models Developed and Managed in MOSAICmodeling —	380
5.2.1.7	Outlook on Model Development and Collaboration —	383
5.2.2	Fluid-Dynamic Investigations of Multiphase Processes —	383
5.2.2.1	Introduction —	383
5.2.2.2	Numerical Flow Simulations of Reactor and Settler for the MES Process —	384
5.2.2.3	Fluid-Dynamic Investigation of Gas-Liquid-Liquid Continuous Helical Flow Reactors —	392
5.2.3	Surrogate Models for Thermodynamic Equilibria of Gas-Liquid and Liquid-Liquid Systems —	400
5.3	Process Optimization —	413
5.3.1	Optimal Design of Reactors for Complex Reaction Systems —	413
5.3.1.1	Reactor-Network Synthesis —	414
5.3.1.2	Elementary Process Functions Methodology —	415
5.3.1.3	EPF Application to the Hydroformylation of Long-Chain Olefins —	421
5.3.1.4	Proof of Concept: Optimal Reactor-Design Hydroformylation of 1-Dodecene —	424
5.3.1.5	Summary —	433
5.3.2	Global Optimization for Process Design —	433
5.3.2.1	Introduction —	433
5.3.2.2	Distillation and Hybrid Separations —	437
5.3.2.3	Multi-stage Separation Networks —	443
5.3.2.4	Combined Reaction and Catalyst Recycling —	445
5.3.2.5	Liquid-Liquid Extraction —	446
5.3.2.6	Summary —	449
5.3.3	Optimization under Uncertainties in Process Development —	451
5.4	Model-Based Process Monitoring and Operation —	461
5.4.1	Online Monitoring and Online Optimization in the Development of Multiphase Processes —	461

5.4.2	Iterative Real-Time Optimization Applied to a Hydroformylation Process on Miniplant Scale —	463
5.4.2.1	Real-Time Optimization and Approaches to Handle the Plant-Model Mismatch —	463
5.4.2.2	Iterative Real-Time Optimization by Modifier Adaptation —	466
5.4.2.3	Application of Real-Time Optimization with Modifier Adaptation to the Hydroformylation of 1-Dodecene in a TMS-system on Miniplant Scale —	472
5.4.2.4	Conclusion and Outlook —	480
5.4.3	State Estimation for Reactions and Separations in a MES System in a Mini plant —	481
5.4.4	Optimal Operation of Reaction-Separation Processes in a MES Miniplant —	489
	References —	497

Kai Sundmacher

6	Integrated Process Design —	509
6.1	Introduction —	509
6.2	Selection Criteria for Liquid Multiphase Systems —	510
6.2.1	Introduction —	510
6.2.2	General Criteria for Phase System Selection —	512
6.2.3	Feasibility and Constraints for Phase Systems Application and Key Experiments —	514
6.2.3.1	Thermomorphic Multiphase System —	514
6.2.3.2	Microemulsion Systems —	516
6.2.3.3	Pickering Emulsions —	517
6.2.4	Systematic Phase System Selection and Process Design —	519
6.3	Solvent Selection for Reactions in Liquid Phases —	523
6.3.1	Standard Gibbs Energies of Chemical Reactions and Transition State Barriers —	524
6.3.2	Introducing a Three-Level Description of Chemical Reactions in Solution —	524
6.3.2.1	Taking Quantum Chemical Calculations from the Gas Phase to Infinitely Diluted Solution —	526
6.3.2.2	From Infinite Dilution to Real Solutions with Thermodynamic Activities of Reacting Species —	526

6.3.3	Solvent Selection for Chemical Equilibria and Reaction Rates —	528
6.3.3.1	Modeling Solvent Effects on Standard Gibbs Energies and Chemical Equilibria —	528
6.3.3.2	Model-Based Screening to Predict Solvent Effects on Reaction Kinetics —	530
6.3.3.3	Beyond Implicit Solvation: The Many Roles of Solvent Molecules —	532
6.3.4	Conclusions —	535
6.4	Integrated Solvent and Process Design —	535
6.4.1	Introduction to Integrated Solvent and Process Design —	536
6.4.2	Survey of Integrated Solvent and Process Design Methodologies —	538
6.4.2.1	Approaches Using Alternative Thermodynamic Models —	540
6.4.2.2	Most Recent Contributions —	541
6.4.2.3	Direct Optimization of Thermodynamic Parameters: Continuous Molecular Targeting —	541
6.4.2.4	Integrated Solvent and Process Design for the Kinetics of Chemical Reactions —	543
6.4.2.5	Genetic Optimization Approach for Complex Solvent-Process Optimization Problems —	545
6.4.3	Integrated Solvent and Process Design for Thermomorphic Multiphase Systems —	546
6.4.4	Conclusions —	551
6.5	Integrated Model-Based Process Design Methodology —	552
6.5.1	Experimental Design for Efficient and Accurate Parameter Identification —	553
6.5.2	Integrated Process Design —	555
6.5.2.1	Methodology —	556
6.5.2.2	Methods for Sensitivity Analysis in Process Synthesis —	557
6.5.2.3	Case Study I: Hydroaminomethylation of 1-Decene —	559
6.5.2.4	Case Study II: Hydroformylation of 1-Dodecene —	562
6.5.3	Advanced Integration Potential for Systematic Multiphase Process Design —	564

XII — Contents

6.5.3.1	Model-Based Solvent Selection —	565
6.5.3.2	Model-Based Optimal Reactor Design —	566
6.5.4	Summary —	568
	References —	568

Matthias Kraume

7	Résumé —	575
----------	-----------------	------------

Index —	583
----------------	------------