

Microemulsions

Background, New Concepts,
Applications, Perspectives

Edited by

Cosima Stubenrauch

School of Chemical and Bioprocess Engineering,
University College Dublin, Ireland

WILEY

A John Wiley and Sons, Ltd, Publication

Contents

<i>List of Contributors</i>	xi
<i>Preface</i>	xiii
<i>Some Thoughts about Microemulsions</i>	
<i>Bjorn Lindman</i>	xv
1 Phase Behaviour, Interfacial Tension and Microstructure of Microemulsions	
<i>Thomas Sottmann and Cosima Stubenrauch</i>	<i>1</i>
1.1 Introduction	1
1.2 Phase behaviour	2
1.2.1 Microemulsions with alkyl polyglycolethers	3
1.2.2 Microemulsions with technical-grade non-ionic surfactants	13
1.2.3 Microemulsions with alkylpolyglucosides	14
1.2.4 Microemulsions with ionic surfactants	17
1.2.5 Microemulsions with non-ionic and ionic surfactants	22
1.3 Interfacial tension	23
1.3.1 Adsorption of the surfactant	24
1.3.2 Interfacial tension and phase behaviour	25
1.3.3 Tuning parameters for the interfacial tension	27
1.3.4 & Scaling of the interfacial tension	30
1.4 Microstructure	31
1.4.1 Mean curvature of the amphiphilic film	32
1.4.2 - Transmission electron microscopy	34
1.4.3 Estimation of length scales and overview of microstructure	38
1.5 Conclusion	40
Acknowledgement	42
Notes	42
References	42

2	Scattering Techniques to Study the Microstructure of Microemulsions	48
	<i>Thomas Hellweg</i>	
2.1	Introduction	48
2.2	Scattering from droplet microemulsions	50
2.2.1	General outline	50
2.2.2	Quasi-elastic scattering from droplets: theory	50
2.2.3	Small angle neutron scattering from droplets	53
2.2.4	Examples	55
2.3	Scattering from bicontinuous microemulsions	58
2.3.1	Small angle scattering from bicontinuous microemulsions	59
2.3.2	Neutron spin-echo studies of bicontinuous microemulsions	61
2.3.3	Examples	62
2.4	Summary	65
2.5	Appendix	65
2.5.1	General remarks	65
2.5.2	Space and time correlation functions	66
	References	78
3	Formulation of Microemulsions	
	<i>Jean-Louis Salager, Raquel Anton, Ana Forgiarini and Laura Marquez</i>	84
3.1	Basic concepts	84
3.1.1	Microemulsions	84
3.1.2	Why is formulation important?	86
3.2	Representation of formulation effects	87
3.2.1	Unidimensional formulation scan representation	88
3.2.2	Bidimensional map representation	89
3.2.3	Other representations	91
3.3	Physico-chemical formulation yardsticks	92
3.3.1	Early formulation concepts	92
3.3.2	Correlations for the attainment of optimum formulation	94
3.3.3	Generalised formulation as SAD and HLD	101
3.4	Quality of formulation	104
3.4.1	Winsor's basic premise	104
3.4.2	Alcohol conventional effects	105
3.4.3	Linker effects	106
3.4.4	Extended surfactants	108
3.4.5	Quality and transparency	109
3.5	Formulations for special purposes	110
3.5.1	Surfactant mixing rules	110
3.5.2	Reduction in hydrophilicity with ionic-non-ionic surfactant mixtures	112
3.5.3	Synergy with anionic-cationic surfactant mixtures	112
3.5.4	Temperature-insensitivity with anionic-non-ionic surfactant mixtures	113
3.5.5	Effect of composition variables and fractionation problems	116

3.6	Final comment	117
	Acknowledgements	117
	Notes	117
	References	117
4	Effects of Polymers on the Properties of Microemulsions	
	<i>Jurgen Allgaier and Henrich Frielinghaus</i>	122
4.1	Introduction	122
4.2	Amphiphilic polymers	123
4.2.1	Phase behaviour and structure formation	123
4.2.2	Dynamic phenomena and network formation	131
4.3	Non-amphiphilic polymers	135
4.3.1	Repulsive interactions of polymers	136
4.3.2	Transition to adsorbing polymers and two adsorption cases	139
4.3.3	Cluster formation and polymer-colloid interactions	143
	References	144
5	Reactions in Organised Surfactant Systems	
	<i>Reinhard Schomacker and Krister Holmberg</i>	148
5.1	Introduction	148
5.2	Motivation for surfactant systems as reaction media	149
5.3	Selected reactions	155
5.3.1	Nucleophilic substitution reactions	155
5.3.2	Regioselective synthesis	160
5.3.3	Hydrogenation and hydroformylation reactions	163
5.4	Engineering aspects	166
5.4.1	Selection and tuning of surfactant systems	167
5.4.2	Type of organised surfactant system	169
5.4.3	Work-up procedures for product isolation	171
5.5	Conclusion	176
	References	177
6	Microemulsions as Templates for Nanomaterials	
	<i>Satya P. Moulik, Animesh K. Rakshit and Ignac Capek</i>	180
6.1	Introduction	180
6.1.1	Basics of microemulsions	180
6.1.2	Synthesis of nanoparticles	183
6.1.3	Characterisation and properties of nanoparticles	183
6.2	Preparation of nanocompounds	185
6.2.1	Sulphides	186
6.2.2	Sulphates	187
6.2.3	Hydroxides	188
6.2.4	Oxides	188

6.2.5	Core-shell products	190
6.2.6	Miscellaneous	192
6.3	Metal and metal/polymer nanoparticles	193
6.3.1	General concepts	193
6.3.2	Anisotropic metal nanoparticles	194
6.3.3	Core-shell metal nanoparticles	195
6.3.4	Core-shell metal/polymer nanoparticles	197
6.4	Outlook	200
	Acknowledgements	202
	References	202
7	Non-Aqueous Microemulsions	
	<i>Feng Gao and Carlos C. Co</i>	211
7.1	Introduction	211
7.2	Self-assembly in polymer blends	211
7.3	Self-assembly in room temperature ionic liquids	215
7.4	Self-assembly in supercritical CO ₂	217
7.5	Self-assembly in non-aqueous polar solvents	219
7.6	Self-assembly in sugar glasses	221
7.7	Conclusions	224
	References	224
8	Microemulsions in Cosmetics and Detergents	
	<i>Wolfgang von Rybinski, Matthias Hloucha and Ingegard Johansson</i>	230
8.1	Introduction	230
8.2	Microemulsions in cosmetics	230
8.2.1	Cleanser, bath oils, sunscreens, hair treatment	231
8.2.2	Improved skin and bio-compatibility	236
8.2.3	Carrier for skin actives	237
8.2.4	Perfume	238
8.2.5	The phase inversion temperature method	239
8.3	Microemulsions in detergency	242
8.3.1	Introduction	242
8.3.2	In situ formation of microemulsions	246
8.3.3	Direct use of microemulsions	248
	References	254
9	Microemulsions: Pharmaceutical Applications	
	<i>Vandana B. Patravale and Abhijit A. Date</i>	259
9.1	Introduction	259
9.2	Microemulsions	260
9.2.1	Overview of general advantages of microemulsions	260
9.2.2	Formulation considerations	261
9.2.3	Effect of temperature on microemulsions	267

9.2.4	Microemulsion characterisation and evaluation	267
9.3	Applications in transdermal and dermal delivery	268
9.3.1	Potential mechanisms for improved dermal/transdermal transport	269
9.3.2	Microemulsions as smart dermal/transdermal delivery vehicles	269
9.4	Applications in oral drug delivery	275
9.4.1	Self-microemulsifying drug delivery systems	276
9.4.2	Oral delivery of peptides	279
9.5	Applications in parenteral drug delivery	281
9.5.1	Advantages of microemulsions in parenteral delivery	282
9.5.2	Formulation considerations	282
9.5.3	Potential explored	283
9.6	Applications in ocular drug delivery	285
9.6.1	Formulation considerations	285
9.6.2	Potential explored	286
9.7	Mucosal drug delivery	287
9.7.1	Potential explored	288
9.8	Microemulsions as templates for the synthesis of pharmaceutical nanocarriers	289
9.8.1	Synthesis of solid lipid nanoparticles	289
9.8.2	Synthesis of nanosuspensions	289
9.8.3	Engineering of nano-complexes	290
9.8.4	Microemulsion polymerisation	291
9.9	Application in pharmaceutical analysis	291
9.10	Future perspectives	292
	References	293
10	Microemulsions in Large-Scale Applications	
	<i>Franz-Hubert Haegel, Juan Carlos Lopez, Jean-Louis Salager and Sandra Engelskirchen</i>	302
10.1	Introduction	302
10.1.1	General considerations	302
10.1.2	Products and processes	303
10.1.3	Requirements for large-scale applications	304
10.2	Soil decontamination	305
10.2.1	Requirements	305
10.2.2	Non-aqueous phase liquids	306
10.2.3	Microemulsion-forming systems	307
10.2.4	Use of preformed microemulsions	310
10.2.5	Challenges	311
10.3	Microemulsions in enhanced oil recovery	312
10.3.1	Why enhanced oil recovery and not alternative fuels?	312
10.3.2	Why microemulsions?	313
10.3.3	Basic scientific and technical problems	315

10.3.4	Current state-of-the-art in enhanced oil recovery	321
10.3.5	Future 'GUESSTIMATES'	324
10.4	Degreasing of leather	325
10.4.1	Washing processes	325
10.4.2	Leather degreasing via microemulsions	325
10.4.3	The degreasing mechanism	334
	Acknowledgement	335
	References	335
11	Future Challenges	
	<i>Cosima Stubenrauch and Reinhard Strey</i>	345
11.1	Introduction	345
11.2	Bicontinuous microemulsions as templates	345
11.2.1	Why use bicontinuous microemulsions as templates?	345
11.2.2	What are the challenges?	347
11.2.3	What route is the most promising?	348
11.3	Nanofoams	351
11.3.1	Why synthesise nanofoams?	351
11.3.2	What are the challenges?	351
11.3.3	What route is the most promising?	351
11.4	Clean combustion of microemulsions	354
11.4.1	Why use microemulsions for fuel combustion?	354
11.4.2	What are the challenges?	355
11.4.3	What route is the most promising?	357
11.5	Solubilisation of triglycerides	358
11.5.1	Road map to the solubilisation of triglycerides	358
11.5.2	The linker concept	362
	Acknowledgement	364
	References	364
	<i>Index</i>	367