Table of Contents

- 1 Petroleomics and Structure-Function Relations of Crude Oils and Asphaltenes Oliver C. Mullins
- 1 Introduction p. 1
- 2 Evolution of the Oil Patch p. 5
- 3 Phenomological Petroleum Analysis p. 7
- 4 Petroleomics p. 10
- 5 Building Up Petroleum Science-A Brief Outline p. 10
- 6 Asphaltenes: An Update of the Yen Model p. 13
- 7 Future Outlook in Petroleum Science p. 14
- References p. 16
- 2 Asphaltene Molecular Size and Weight by Time-Resolved Fluorescence Depolarization Henning Groenzin and Oliver C. Mullins
- 1 Introduction p. 17
- 1.1 Overview p. 17
- 1.2 Chemical Bonding of Functional Groups in Asphaltenes p. 18
- 1.3 Techniques Employed to Study the Size of Asphaltenes p. 18
- 1.4 Time-Resolved Fluorescence Depolarization (TRFD) p. 21
- 1.5 The Optical Range Relevant to Asphaltene Investigations p. 22
- 1.6 Structure Predictions from TRFD p. 26
- 2 Theory p. 27
- 2.1 The Spherical Model p. 27
- 2.2 The Anisotropic Rotator p. 30
- 3 Experimental Section p. 33
- 3.1 Optics Methods p. 33
- 3.2 Sample Preparation p. 35
- 3.3 Solvent Resonant Quenching of Fluorescence p. 37
- 4 Results and Discussion p. 39
- 4.1 Basic TRFD of Asphaltenes p. 39
- 4.2 Many Virgin Crude Oil Asphaltenes-and Sulfoxide p. 43
- 4.3 Asphaltene Solubility Subfractions p. 43
- 4.4 Asphaltenes and Resins p. 45
- 4.5 Coal Asphaltenes versus Petroleum Asphaltenes p. 45
- 4.6 Thermally Processed Feed Stock p. 50
- 4.7 Alkyl-Aromatic Melting Points p. 53
- 4.8 Asphaltene Molecular Structure 'Like your Hand' or 'Archipelago' p. 54
- 4.9 Considerations of the Fluorescence of Asphaltenes p. 56
- 4.10 Asphaltene Molecular Diffusion; TRFD vs Other Methods p. 57
- 5 Conclusions p. 59
- References p. 60
- 3 Petroleomics: Advanced Characterization of Petroleum-Derived Materials by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) Ryan P. Rodgers and Alan G. Marshall
- 1 Introduction p. 63
- 2 FT-ICR MS p. 65

- 2.1 Mass Accuracy and Mass Resolution p. 67
- 2.2 Kendrick Mass and Kendrick Plots p. 68
- 2.3 van Krevelen Diagrams p. 73
- 2.4 DBE and Z Number p. 75
- 2.5 ESI for Access to Polars p. 75
- 2.6 EI, FD, and APPI for Access to Nonpolars p. 76
- 3 Molecular Weight Determination by Mass Spectrometry p. 78
- 3.1 Low Molecular Weight for Petroleum Components p. 79
- 3.2 Mass Spectrometry Caveats p. 82
- 3.3 High Molecular Weight for Petroleum Components p. 83
- 4 Aggregation p. 84
- 5 Petroleomics p. 87
- Acknowledgments p. 88
- Glossary p. 89
- References p. 89
- 4 Molecular Orbital Calculations and Optical Transitions of PAHs and Asphaltenes Yosadara Ruiz-Morales
- 1 Introduction p. 95
- 2 Computational Details p. 100
- 3 Results and Discussion p. 102
- 3.1 Topological Characteristics of PAHs p. 103
- 3.2 The HOMO-LUMO Optical Transition p. 106
- 3.3 Aromaticity in PAHs and Asphaltenes: Application of the Y-rule p. 119
- 3.4 The FAR Region in Asphaltenes p. 124
- 3.5 Most Likely PAH Structural Candidates of the FAR Region in Asphaltenes from 5 to 10 Aromatic Rings p. 127
- 4 Conclusions p. 135
- Acknowledgments p. 135
- References p. 135
- 5 Carbon X-ray Raman Spectroscopy of PAHs and Asphaltenes Uwe Bergmann and Oliver C. Mullins
- 1 Introduction p. 139
- 2 Theory p. 142
- 3 Experiment p. 143
- 4 Results and Discussion p. 145
- 5 Conclusion and Outlook p. 152
- Acknowledgments p. 153
- References p. 153
- 6 Sulfur Chemical Moieties in Carbonaceous Materials Sudipa Mitra-Kirtley and Oliver
 C. Mullins
- 1 Introduction p. 157
- 2.5 Coal and Kerogen Macerals p. 162
- 2 Carbonaceous Materials p. 159
- 2.1 Production and Deposition of Organic Matter p. 159
- 2.2 Diagenesis p. 160
- 2.3 Sulfur in Carbonaceous Sediments p. 161

- 2.4 Kerogen Formation p. 162
- 2.6 Catagenesis p. 164
- 2.7 Asphaltene Fractions in Crude Oils p. 165
- 3 X-Ray Absorption Near Edge Structure (XANES) p. 165
- 4 Experimental Section p. 168
- 4.1 Synchrotron Beamline p. 168
- 4.2 Samples p. 169
- 4.3 Least Squares Fitting Procedure p. 171
- 5 Results and Discussions p. 172
- 5.1 Sulfur XANES on Kerogens p. 174
- 5.2 Sulfur XANES on Oil Fractions p. 175
- 5.3 Sulfur K-Edge XANES on Coals p. 176
- 5.4 Nitrogen XANES p. 178
- 6 Conclusion p. 183
- References p. 184
- 7 Micellization Stig E. Friberg
- 1 Introduction p. 189
- 2 Micelles in Aqueous Solutions p. 190
- 3 Inverse Micellization in Nonpolar Media p. 194
- 4 Asphaltene Association in Crude Oils p. 199
- 5 Conclusions p. 201
- Acknowledgments p. 202
- References p. 202
- 3 Experimental Section p. 218
- 8 Insights into Molecular and Aggregate Structures of Asphaltenes Using HRTEM Atul Sharma and Oliver C. Mullins
- 1 Introduction p. 205
- 2 Theory of HRTEM and Image Analysis p. 208
- 2.1 Basics of HRTEM p. 208
- 2.2 Quantitative Information from TEM Images p. 212
- 3.1 Samples p. 218
- 3.2 HRTEM Method p. 218
- 4 Results and Discussion p. 219
- 5 Conclusions p. 227
- Acknowledgments p. 228
- References p. 228
- 9 Ultrasonic Spectroscopy of Asphaltene Aggregation Gaelle Andreatta and Neil Bostrom and Oliver C. Mullins
- 1 Introduction p. 231
- 2 Ultrasonic Spectroscopy p. 233
- 2.1 Ultrasonic Resonances p. 234
- 2.2 Plane Wave Propagation p. 235
- 2.3 Experimental Section p. 236
- 2.4 Compressibility of Liquids and Ultrasonic Velocity p. 238
- 3 Micellar Aggregation Model p. 238
- 3.1 Theory p. 238

- 3.2 Experimental Results on Surfactants p. 241
- 4 Experimental Results on Asphaltenes p. 247
- 4.4 Differences Between Coal and Petroleum Asphaltenes p. 254
- 4.1 Background p. 247
- 4.2 Ultrasonic Determination of Various Asphaltenes Aggregation Properties p. 248
- 4.3 Comparison of Experimental Results on UG8 Asphaltenes and Maltenes p. 253
- 5 Conclusion p. 255
- References p. 255
- 10 Asphaltene Self-Association and Precipitation in Solvents-AC Conductivity Measurements Eric Sheu and Yicheng Long and Hassan Hamza
- 1 Introduction p. 259
- 2 Experimental p. 264
- 2.1 Sample p. 264
- 2.2 Instrument p. 264
- 2.3 Measurement p. 265
- 3 Theory p. 266
- 4 Results p. 269
- 5 Discussion and Conclusion p. 274
- 6 Future Perspective p. 276
- References p. 276
- 3 Experimental Method p. 282
- 11 Molecular Composition and Dynamics of Oils from Diffusion Measurements Denise E. Freed and Natalia V. Lisitza and Pabitra N. Sen and Yi-Qiao Song
- 1 Introduction p. 279
- 2 General Theory of Molecular Diffusion p. 280
- 4 Mixtures of Alkanes p. 283
- 4.1 Chain-Length Dependence p. 284
- 4.2 Dependence on Mean Chain Length and Free Volume Model p. 285
- 4.3 Comparison with Experiments p. 287
- 4.4 Viscosity p. 289
- 4.5 Discussion p. 291
- 5 Dynamics Of Asphaltenes In Solution p. 292
- 5.1 The Proton Spectrum of Asphaltene Solutions p. 292
- 5.2 The Diffusion Constant and Diffusion Spectrum p. 293
- 5.3 Discussion p. 294
- 6 Conclusions p. 296
- Acknowledgment p. 296
- References p. 296
- 12 Application of the PC-SAFT Equation of State to Asphaltene Phase Behavior P. David Ting and Doris L. Gonzalez and George J. Hirasaki and Walter G. Chapman
- 1 Introduction p. 301
- 1.1 Asphaltene Properties and Field Observations p. 302
- 1.2 The Two Views of Asphaltene Interactions p. 303
- 1.3 Our View and Approach p. 305
- 2 Introduction to SAFT p. 306
- 2.1 PC-SAFT Pure Component Parameters p. 307

- 2.2 PC-SAFT Characterization of a Recombined Oil p. 307
- 2.3 Comparison of Results and Analysis of Asphaltene Behavior p. 313
- 2.4 Effect of Asphaltene Polydispersity on Phase Behavior p. 317
- 3 Summary and Conclusions p. 323
- Acknowledgments p. 324
- References p. 325
- 3 Experimental p. 331
- 13 Application of Isothermal Titration Calorimetry in the Investigation of Asphaltene Association Daniel Merino-Garcia and Simon Ivar Andersen
- 1 Introduction p. 329
- 2 The Concept of Micellization p. 330
- 3.1 Asphaltene Separation p. 331
- 4 Application of ITC to Surfactants p. 332
- 4.1 Nonaqueous Systems p. 334
- 5 ITC Experiments with Asphaltene Solutions: Is There a CMC? p. 335
- 6 Modeling ITC Experiments p. 338
- 7 Application of ITC to Various Aspects of Asphaltene Association and Interaction with Other Substances p. 340
- 7.1 Investigation of Asphaltene Subfractions p. 341
- 7.2 Effect of Methylation of Asphaltenes p. 343
- 7.3 Interaction of Asphaltene with Other Compounds p. 345
- 8 Conclusions p. 350
- Acknowledgments p. 350
- References p. 351
- 14 Petroleomics and Characterization of Asphaltene Aggregates Using Small Angle Scattering Eric Y. Sheu
- 1 Introduction p. 353
- 2 Asphaltene Aggregation p. 355
- 3 SAXS and SANS p. 356
- 4 SAXS and SANS Instruments p. 362
- 5 SAXS and SANS Experiments and Results p. 364
- 5.1 SAXS Measurement on Ratawi Resin and Asphaltene p. 365
- 5.2 SANS Measurement on Asphaltene Aggregation, Emulsion, and Dispersant Effect p. 367
- 6 Discussion p. 371
- References p. 373
- 7 Conclusion p. 372
- 8 Future Perspectives p. 373
- Acknowledgments p. 373
- 15 Self-Assembly of Asphaltene Aggregates: Synchrotron, Simulation and Chemical Modeling Techniques Applied to Problems in the Structure and Reactivity of Asphaltenes Russell R. Chianelli and Mohammed Siadati and Apurva Mehta and John Pople and Lante Carbognani Ortega and Long Y. Chiang
- 1 Introduction p. 375
- 2 WAXS Synchrotron Studies and Sample Preparation p. 377
- 3 SAXS p. 380

- 3.1 Fractal Objects p. 381
- 3.2 Scattering from Mass Fractal Objects p. 383
- 3.3 Scattering from a Surface Fractal Object p. 383
- 4 SAXS Studies of Venezuelan and Mexican Asphaltenes p. 383
- 5 Self-Assembly of Synthetic Asphaltene Particles p. 393
- 6 Conclusions p. 399
- Acknowledgments p. 399
- References p. 400
- 16 Solubility of the Least-Soluble Asphaltenes Jill S. Buckley and Jianxin Wang and Jefferson L. Creek
- 1 Introduction p. 401
- 1.1 Importance of the Least-Soluble Asphaltenes p. 402
- 1.2 Detection of the Onset of Asphaltene Instability p. 403
- 1.3 Asphaltenes as Colloidal Dispersions p. 403
- 1.4 Asphaltenes as Lyophilic Colloids p. 405
- 1.5 Solubility of Large Molecules p. 405
- 1.6 Solubility Parameters p. 406
- 1.7 Flory-Huggins Predictions: The Asphaltene Solubility Model (ASM) p. 412
- 2 Asphaltene Instability Trends (ASIST) p. 414
- 2.1 ASIST Established by Titrations with n-Alkanes p. 414
- 2.2 Use of ASIST to Predict Onset Pressure p. 417
- 3 Asphaltene Stability in Oil Mixtures p. 420
- 4 Some Remaining Problems p. 424
- 4.1 Effect of Temperature on ASIST p. 425
- 4.2 Polydispersity and Amount of Asphaltene p. 425
- 4.3 Wetting, Deposition, and Coprecipitation p. 426
- 4.4 Model Systems and Standards p. 426
- 5 Conclusions p. 427
- Acknowledgment p. 427
- Appendix V Prediction of Live Oil Asphaltene Stability from ASIST p. 436
- References p. 428
- Appendix I Asphaltene Onset Detection by Batch Titration p. 429
- Appendix II Historical Interpretations of n-Alkane Titration Data p. 432
- Appendix III Calculation of Solubility Parameters Using PVTsim p. 432
- Appendix IV Oil and Asphaltene Properties p. 434
- 17 Dynamic Light Scattering Monitoring of Asphaltene Aggregation in Crude Oils and Hydrocarbon Solutions Igor K. Yudin and Mikhail A. Anisimov
- 1 Introduction p. 439
- 2 Dynamic Light Scattering Technique p. 441
- 3 Aggregation of Asphaltenes in Toluene-Heptane Mixtures p. 448
- 4 Aggregation of Asphaltenes in Crude Oils p. 454
- 5 Stabilization of Asphaltene Colloids p. 460
- 6 Viscosity and Microrheology of Petroleum Systems p. 462
- 7 Conclusions p. 465
- Acknowledgments p. 466
- References p. 466

- 18 Near Infrared Spectroscopy to Study Asphaltene Aggregation in Solvents Kyeongseok Oh and Milind D. Deo
- 1 Introduction p. 469
- 2 Literature p. 470
- 3 Experimental p. 472
- 4.3 Effect of the Solvent p. 479
- 4 Results and Discussion p. 473
- 4.1 Asphaltene Aggregation or Self-Association p. 473
- 4.2 Onset of Asphaltene Precipitation p. 475
- 4.4 Asphaltene Subfractions p. 485
- 5 Conclusions p. 486
- Acknowledgments p. 487
- References p. 487
- 19 Phase Behavior of Heavy Oils John M. Shaw and Xiangyang Zou
- 1 Introduction p. 489
- 2 Origin of Multiphase Behavior in Hydrocarbon Mixtures p. 490
- 3 Phase Behavior Prediction p. 493
- 3.1 Bulk Phase Behavior Prediction for Hydrocarbon Mixtures p. 493
- 3.2 Asphaltene Precipitation and Deposition Models p. 494
- 4 Experimental Methods and Limitations p. 495
- 5 Phase Behavior Observations and Issues p. 497
- 5.1 Heavy Oil p. 497
- 5.2 Heavy Oil + Solvent Mixtures p. 500
- 5.3 Phase Behavior Reversibility p. 504
- 6 Conclusions p. 506
- Acknowledgments p. 507
- References p. 507
- 20 Selective Solvent Deasphalting for Heavy Oil Emulsion Treatment Yicheng Long and Tadeusz Dabros and Hassan Hamza
- 1 Introduction p. 511
- 2 Bitumen Chemistry p. 512
- 3 Stability of Water-in-Bitumen Emulsions p. 515
- 3.1 In situ Bitumen Emulsion and Bitumen Froth p. 515
- 3.2 Size Distributions of Emulsified Water Droplets and Dispersed Solids p. 516
- 3.3 Stabilization Mechanism of Bitumen Emulsions p. 518
- 4 Effect of Solvent on Bitumen Emulsion Stability p. 519
- 5 Treatment of Bitumen Emulsions with Aliphatic Solvents p. 522
- 5.1 Behavior of Bitumen Emulsion upon Dilution p. 522
- 5.2 Settling Characteristics of Bitumen Emulsions Diluted with Aliphatic Solvent p. 524
- 5.3 Settling Curve and Settling Rate of WD/DS/PA Aggregates p. 526
- 5.4 Structural Parameters of WD/DS/PA Aggregates p. 531
- 5.5 Measuring Settling Rate of WD/DS/PA Aggregates Using In-Line Fiber-Optic Probe p. 534
- 5.6 Asphaltene Rejection p. 537
- 5.7 Product Quality-Water and Solids Contents p. 538
- 5.8 Product Quality-Micro-Carbon Residue (MCR) p. 540

- 5.9 Product Quality-Metals Contents p. 542
- 5.10 Product Quality-Sulfur and Nitrogen Contents p. 542
- 5.11 Viscosity of Bitumen p. 543
- 6 Conclusion p. 543
- Acknowledgments p. 545
- References p. 545
- 21 The Role of Asphaltenes in Stabilizing Water-in-Crude Oil Emulsions Johan Sjoblom and Pal V. Hemmingsen and Harald Kallevik
- 1 Introduction p. 549
- 2 Chemistry of Crude Oils and Asphaltenes p. 551
- 2.1 Analytical Separation of Crude Oil Components p. 551
- 2.5 Disintegration of Asphaltenes Studied by NIR Spectroscopy p. 559
- 2.2 Solubility and Aggregation of Asphaltenes p. 554
- 2.3 Characterization of Crude Oils by Near Infrared Spectroscopy p. 555
- 2.4 Asphaltene Aggregation Studied by High-Pressure NIR Spectroscopy p. 556
- 2.6 Asphaltene Aggregation Studied by NMR p. 563
- 2.7 Adsorption of Asphaltenes and Resins Studied by Dissipative Quartz Crystal Microbalance (QCM-D) p. 563
- 2.8 Interfacial Behavior and Elasticity of Asphaltenes p. 566
- 3 Chemistry of Naphthenic Acids p. 569
- 3.1 Origin and Structure p. 570
- 3.2 Phase Equilibria p. 570
- 4 Water-in-Crude Oil Emulsions p. 572
- 4.1 Stability Mechanisms p. 572
- 4.2 Characterization by Critical Electric Fields p. 573
- 4.3 Multivariate Analysis and Emulsion Stability p. 574
- 4.4 High-Pressure Performance of W/O Emulsions p. 578
- Acknowledgments p. 584
- References p. 584
- 22 Live Oil Sample Acquisition and Downhole Fluid Analysis Go Fujisawa and Oliver C. Mullins
- 1 Introduction p. 589
- 2 Wireline Fluid Sampling Tools p. 591
- 3 Downhole Fluid Analysis with Wireline Tools p. 593
- 3.1 Measurement Physics p. 593
- 3.2 DFA Implementation in Wireline Tools p. 601
- 4 Live Oil Sampling Process p. 604
- 4.1 Contamination p. 604
- 4.2 Phase Transition p. 606
- 4.3 Chain of Custody p. 607
- 5 "What Is the Nature of the Hydrocarbon Fluid?" p. 608
- 6 "What Is the Size and Structure of the Hydrocarbon-Bearing Zone?" p. 610
- 7 Conclusions p. 614
- References p. 615
- 23 Precipitation and Deposition of Asphaltenes in Production Systems: A Flow Assurance Overview Ahmed Hammami and John Ratulowski

- 1 Introduction p. 617
- 2 Chemistry of Petroleum Fluids p. 619
- 2.1 Saturates p. 621
- 2.2 Aromatics p. 621
- 2.3 Resins p. 621
- 2.4 Asphaltenes p. 622
- 3 Petroleum Precipitates and Deposits p. 622
- 3.1 Petroleum Waxes p. 622
- 4 Terminology: Precipitation vs. Deposition p. 624
- 3.2 Asphaltene Deposits p. 623
- 3.3 Diamondoids p. 623
- 3.4 Gas Hydrates p. 623
- 5 Mechanisms of Asphaltene Precipitation: What We Think We Know and Why? p. 625
- 5.1 Colloidal Model p. 626
- 5.2 Effect of Compositional Change p. 626
- 5.3 Effect of Pressure Change p. 628
- 5.4 The de Boer Plot p. 630
- 5.5 Reversibility of Asphaltene Precipitation p. 631
- 6 Sampling p. 631
- 7 Laboratory Sample Handling and Analyses p. 634
- 7.1 Sample Handling and Transfer p. 634
- 7.2 Compositional Analyses p. 635
- 7.3 Oil-Based Mud (OBM) Contamination Quantification p. 635
- 7.4 Dead Oil Characterization p. 637
- 7.5 Dead Oil Asphaltene Stability Tests p. 640
- 8 Live Oil Asphaltene Stability Techniques p. 643
- 8.1 Light Transmittance (Optical) Techniques p. 643
- 8.2 High Pressure Microscope (HPM) p. 647
- 8.3 Deposition Measurements p. 651
- 9 Asphaltene Precipitation Models p. 652
- Acknowledgment p. 656
- References p. 656
- Index p. 661