Crude Oil Waxes, Emulsions, and Asphaltenes

J. R. Becker
# Contents

## Section I  Emulsions

<table>
<thead>
<tr>
<th>Introduction</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Petroleum Companies and Emulsions</td>
<td>5</td>
</tr>
<tr>
<td>Oil and Water</td>
<td>5</td>
</tr>
<tr>
<td>Emulsions</td>
<td>6</td>
</tr>
<tr>
<td>Production Environments</td>
<td>6</td>
</tr>
<tr>
<td>Specialty Chemicals and the Environment</td>
<td>8</td>
</tr>
<tr>
<td>Oil-in-Water Emulsions and Environmental Concerns</td>
<td>8</td>
</tr>
<tr>
<td>Water-in-Oil Emulsions and Environmental Concerns</td>
<td>9</td>
</tr>
<tr>
<td>Field Application of Emulsion Breakers</td>
<td>9</td>
</tr>
<tr>
<td>Specialized Equipment</td>
<td>10</td>
</tr>
<tr>
<td>The Cost of Wet Oil</td>
<td>12</td>
</tr>
<tr>
<td>The Cost of Oily Water</td>
<td>14</td>
</tr>
<tr>
<td>Transport and Refining</td>
<td>14</td>
</tr>
<tr>
<td>Refinery Influent Streams</td>
<td>15</td>
</tr>
<tr>
<td>Emulsion Formation</td>
<td>16</td>
</tr>
<tr>
<td>Emulsion Formation Criteria</td>
<td>16</td>
</tr>
<tr>
<td>Solubility</td>
<td>16</td>
</tr>
<tr>
<td>Intermediary Agents</td>
<td>18</td>
</tr>
<tr>
<td>External and Internal Phase</td>
<td>21</td>
</tr>
<tr>
<td>Summary</td>
<td>26</td>
</tr>
</tbody>
</table>

## 2 Forces Involved in Emulsions | 31 |

| Chemical Complexities of Crude Oil Emulsions | 31 |
| Nonpolar Interactions | 33 |
| Combined Ionic and Inductive Forces | 37 |
| Aggregate Interactions | 37 |
| Bipolar Partitioning | 41 |
| Internal Phase Diffusion | 41 |
| Aggregate Number | 43 |
| Emulsion Collision Frequency | 44 |
| Emulsion Collision Energy | 46 |
| Gravitational Settling Forces | 46 |
| Summary | 47 |
## Contents

3 Macroscopic Physical Behavior of Emulsions ................. 49  
  Viscosity ................................................. 49  
  Emulsion Behavior under Shear Stress ....................... 51  
  Temperature Effects on Emulsions ......................... 53  
  Gravitational Effects on Emulsions ....................... 55  
  Electromagnetic Field Effects on Emulsions ............ 56  
  Determination of Emulsion Type ......................... 60  
  Quantifying Phases ..................................... 60  
  Quantifying Phases: Oil-in-Water Emulsions .......... 60  
  Product Screening Methods .................................. 62  
  Oil in Water Emulsion Screening ............................ 64  
  Special Test Procedures .................................. 64  
  Field Blending Practices .................................. 66  
  Summary .................................................. 69  

4 Oil Emulsion Breakers ........................................ 67  
  Water in Oil ................................................. 67  
  Nonionic Surfactants ..................................... 69  
  Nucleophiles .............................................. 77  
  Summary .................................................. 80  

5 Water Emulsion Breakers ...................................... 83  
  Oil in Water ................................................. 83  
  Organic Polysalt Emulsion Breakers ..................... 84  
  Idealized Organic Polysalts ................................ 84  
  Flocculation versus Emulsion Resolution ............... 87  
  Water in Oil Emulsion Breakers ......................... 87  
  Oil in Water Emulsion Breakers ......................... 96  
  Polyamine and Quaternium Salts ......................... 96  
  Summary .................................................. 98  

### Section II Waxes ....................................... 101  

6 Petroleum Companies and Waxes ............................... 103  
  Paraffin Wax in Crude Oil .................................. 103  
  Paraffin Wax Production Problems ....................... 104  
  Organic Deposition Control ................................ 105  
  Removal of Paraffin Wax Deposits ...................... 105  
  Wax and Work-Over ........................................ 106  
  Physical and Mechanical Wax Control ................. 106  
  Wax and Crude Oil Transport ............................. 107  
  Waxy Crude Oils and the Refinery ....................... 108  
  Treatment Problems ...................................... 108
Wax and Emulsions .................................................. 109
Solids and Waxes .................................................. 109
Waxes and Asphaltenes .......................................... 112
Some Wax Treatment Considerations ...................... 112
Testing Methodologies .......................................... 113
Summary ........................................................... 122

7 Chemical Surfaces ............................................. 125
Wax Surfaces ....................................................... 125
Surface Hierarchy .................................................. 126
Wax Defined .......................................................... 126
Wax and Viscosity .................................................. 129
The Purity Gradient ............................................... 131
Wax and Changing Surfaces .................................... 134
Surface Tension and Wax ....................................... 134
Wax Crystals .......................................................... 138
Crystal Order ........................................................ 138
Crystal Order and Surface Tension ......................... 140
Summary ........................................................... 142

8 Wax Crystal Order and Temperature ..................... 145
The Odd Relationship of Time and Temperature ........ 145
Wax Crystal Habits ............................................... 147
London Forces and van der Waals Radii ................... 147
Molecular Crystals ................................................. 147
Ternary and Higher Eutectics ................................. 150
Introduction to a Kinetic Model ............................... 154
Crystal Modifiers ..................................................... 156
A Return to a Kinetic Model ..................................... 157
Gas Chromatographic Composition Profiles
  Versus Kinetic Model ........................................... 159
Summary ........................................................... 161

9 Wax Physical Properties ..................................... 165
Melting Point and Boiling Point of Alkanes ............... 165
Bulk System Properties ......................................... 167
Molecular Contributions to Bulk System Rheology ....... 167
Quantum Considerations of Viscosity ....................... 171
Intrinsic Viscosity ............................................... 175
Pseudoplasticity and Thixotropy ............................... 176
Yield Value .......................................................... 176
Analogous Thermometry and Rheology .................... 180
Sound As a Means of Measuring Aggregate Behavior .... 180
Summary ........................................................... 183
Contents

10 Wax and Quantum Effects ........................................ 185
   Electromagnetic Effects of Aggregation ................. 185
   Waxes and Piezoelectricity .................................. 189
   Practical Applications of Electromagnetic
      Aggregation Effects .................................. 193
   Molecular Collisions ...................................... 194
   Taking Advantage of Crystallization ..................... 196
   How Crystal Modifiers Work .............................. 196
   Changes in Crystal Morphology ......................... 200
   Crystal Modifier Products ............................... 200
   Crystal Modifier Applications .......................... 202
   Crystal Modifier Synthetic Limitations ............... 202
   Some Wax Control Methods ............................. 203
   Remedial Treatment Methods .......................... 203
   Mechanical Methods .................................... 205
   Biotechnology ........................................... 205
   Supplemental Methods of Wax Control ............... 206
   Summary .................................................. 206

Section III Asphaltenes ........................................ 209

11 Asphaltenes and Crude Oil ................................. 211
   Asphaltenes Deposits ................................ 211
   Coplaner Orbital Overlap or Pi Bonding ............. 213
   Polymeric Forms Derived from Protoporphyrin ...... 213
   Solvation Sheaths ....................................... 215
   Electrostatic Behavior of Asphaltenes ................ 219
   Asphaltenes Destabiliztion ............................. 219
   Unsheathed Asphaltenes Cores ......................... 220
   Metallocenes ........................................... 220
   Magnetic Susceptibility and Streaming Potential .... 222
   External Aggregate Asphaltenes Destabiliztion ...... 222
   Summary .................................................. 224

12 Bulk Behavior of Asphaltenes ............................. 229
   Operational Definitions Versus Chemical Composition 229
   Indirect Evidence for Asphaltenes Composition ...... 230
   Field Problems with Asphaltenes ....................... 230
   Acid Effects on Asphaltenes ............................ 232
   Artificial Causes of Asphaltenes Deposition .......... 233
   Oil Field Treatment Methods ........................... 233
Contents

Production Factors Affecting Asphaltene Deposition ........... 234
Asphaltene Deposition Control by Treatment
  of Other Problems .................................................. 235
Fluid Transport Equipment ........................................ 235
Summary ................................................................. 236

13 Asphaltene Testing Methods ................................. 237
  Solvent Testing ...................................................... 237
  Core Testing Procedures ......................................... 238
  Thin-Layer Photometry ........................................... 238
  Size Exclusion Gel Permeation Chromatography ............... 240
  Proposed Microwave Tests ....................................... 240
  Proposed Ligand Replacement Method ......................... 242
  Designing Asphaltene Deposit Control Chemicals .............. 242
  Chemical Handles .................................................. 244
  Chemical Treatment Versus Reaction ............................ 246
  Radical Reactions with Sulfur .................................... 248
  Combination Product for Treatment of Asphaltenes .......... 248
  Summary ............................................................. 250

14 Physical Properties of Treating Chemicals ................. 251
  Some Physical and Chemical Testing ............................ 251
  Chemical Tests ..................................................... 252
  Physical Testing .................................................... 254
  Specialized Testing Procedures .................................. 255
  Summary ............................................................. 255

Appendix A .............................................................. 257

Appendix B .............................................................. 259

Appendix C .............................................................. 261

Index ................................................................. 267
Emulsions are among the many problems encountered in the production, transport, and refining of crude oil. Dealing with these complex structural arrangements accounts for much of the expense incurred by oil companies in their daily operations. The presence of water in oil (and oil in water) costs the producer, transporter, and refiner in several ways. When water is present in produced oil several other costly byproducts of its presence result.

Corrosion, scale, and dissolved metals are three important byproducts of the presence of emulsions in produced crude oil. Each of these individual problems must be addressed by the producers prior to the transport and refining of the crude. With increasing environmental regulations, the requirements for safe disposal of the produced water derived from the resolution of these emulsions are also increased. Thus, the cost of resolving these problems escalates, and the need for understanding their nature becomes critical to the operations of an oil company.

The information presented here is not intended to be an exhaustive discussion of the subject of emulsions, but rather a discussion directed to the particular aspects of these systems that relate to the oil industry. There is a fair amount of chemistry, physics, and mathematics involved in this subject, but efforts have been made to minimize the use of rigorous treatments of these areas. Throughout this book the approach is to develop an intuitive discussion that has practical meaning to those faced with the resolution of these problems.
Emulsion Formation

Crude oil is usually, but not always, associated with water. During the process of its retrieval from the production zone, the produced fluid undergoes a significant amount of agitation. It is this agitation combined with heat, pressure, and chemicals present in the crude that act to produce emulsions. The type of chemicals present in the crude oil are many and varied, and range from pure hydrocarbon \((C_nH_{2n+2})\) to complex hetero-atomic polycyclics. These also present a range of solubility from water-soluble to oil-soluble, and it is this range of solubilities that is responsible for the formation of emulsions. When a producing well is brought into production, the quantity of water present in the oil is determined by the content of coincident water and oil present in the formation.

Much of the crude oil produced is derived from sandstone formations. These formations consist of combinations of silicon and oxygen that tend to form as partially-charged, anionic (negatively charged) crystallites. These crystallites have a high affinity for water and are often found in close association. This close association is due to the phenomenon of hydrogen bonding, where the partially positive hydrogen of water interacts with the partially negative oxygen of the silicate \((Si_nO_{2n})\). This interaction and association results in a layer of water surrounding the crystallites, which is termed connate water.

The connate water layer tends to remain closely associated with the silicate surface, and maintains an equilibrium with the free water contained in the crude oil (see Fig. 1–4). Over time this association is established as a static condition, since no external force has acted as an agent to change this preferred state. When the reservoir is tapped, this equilibrium state is disturbed, and the pressure drives the fluid from the pore channels within the sandstone formation. The resulting increase in shearing forces combines with the equilibrium shift of free-water partial pressure in the oil phase, and emulsions begin forming.

Emulsion Formation Criteria

The criteria for the formation of emulsions can be divided into categories:

- Differences in solubility between the continuous phase and the emulsified phase must exist
- Intermediate agents having partial solubility in each of the phases must be present
- Energy sources of the appropriate magnitude to mix the phases must be available

Solubility

The first criterium requires that the phases undergoing emulsification consist of molecules that exhibit wide separations in chemical composition,
Fig. 1-9 Water-in-oil emulsion
interactions, single and multiple bipolar layering, hydrogen bonding, solvent sheathing, metal coordinate complexes, and charge sign at the interface. Additional complications arise when the physical states and interactions of the macro-aggregates are considered. Some of these interactions include partitioning of the bipolar phases, diffusion of polar phase between aggregates, aggregate number, aggregate collision frequency, collision energy, gravitational settling, and surface tension.

**Bipolar Partitioning**

The bipolar emulsifiers present in a biphased system will partition into collections of like species or molecular structure. This occurs because various molecules exhibit different behaviors under different conditions of temperature and pressure. Two of the bipolar molecules mentioned earlier (naphthoic and stearic acids) provide good examples of these different behaviors. The melting points of stearic and naphthoic acids are 71.5° C and 185.5° C, respectively. Both of these acids are found in crude oil, and therefore represent good candidates for discussion. Although the hydrogen bonding capabilities of naphthoic acid are limited, aromatic ring interactions of the unpaired electrons plus the carboxyl group interactions combine to produce its high boiling point. Solvation by the nonpolar phase is therefore less successful than it is in the case of stearic acid.

Additionally, the interactions of the carboxyl and aromatic substituents provide a much more stable aggregate than the stearic acid’s inductive alkyl and carboxyl interactions. Thus, the naphthoic and stearic acids will tend to aggregate in groups of like molecules. These aggregate groupings will collect at the interface between the nonpolar and polar phases and remain grouped at the interface (see Fig. 2–7). This explains why the emulsions formed in a mixed system tend to exhibit a partitioning of bipolar emulsifying agents.

Thesepartitioned groupings, however, do not necessarily produce smaller, stronger emulsions simply because of their intermolecular attraction forces. The strength of the intermolecular attractions must be overcome, to some degree, when the ordered emulsifier layer is formed. Thus, the geometries of the groupings, or molecular positions, are altered in going from one orientation to another, and mixed-phase emulsifier systems tend to produce emulsions with sizes that reflect the various bipolar phases present in the system.

**Internal Phase Diffusion**

Emulsions can be thought of as containers for chemically dissimilar materials occupying space inside a continuous phase of opposite polarity. These containers are semipermeable and allow interchanges of similar and appropriately sized fractions. In this way a dynamic equilibrium is set up between containers (emulsion aggregates) that maintains a balanced concentration of internal phase solutions within similarly composed aggregates. Thus, an emulsion formed from a highly concentrated ionic water
Macroscopic Physical Behavior of Emulsions

Fig. 3–9 Basic refinery unit
Fig. 5-2 Some idealized oil in water emulsion breakers