

Crude Oil Waxes, Emulsions, and Asphaltenes

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Introduction

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,

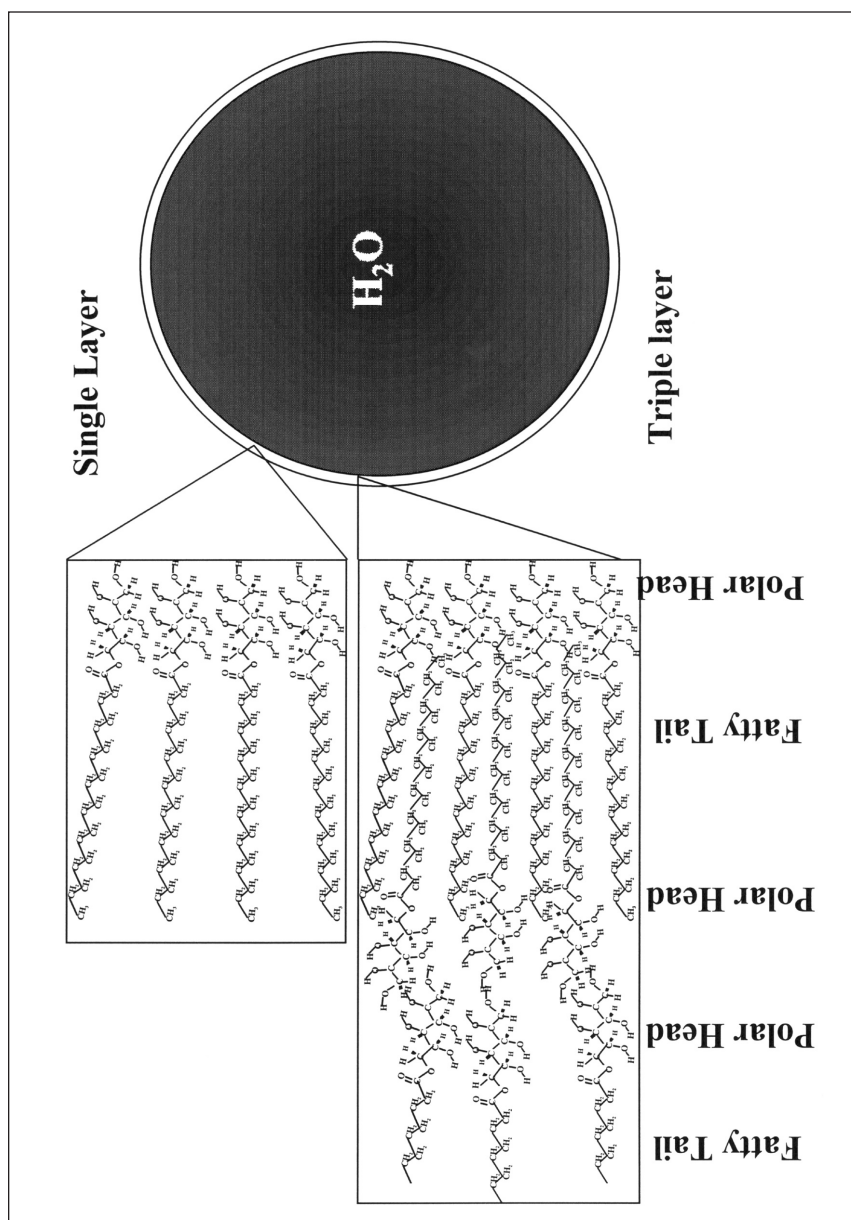


Fig. 1-9 Water-in-oil emulsion

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.

These partitioned 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

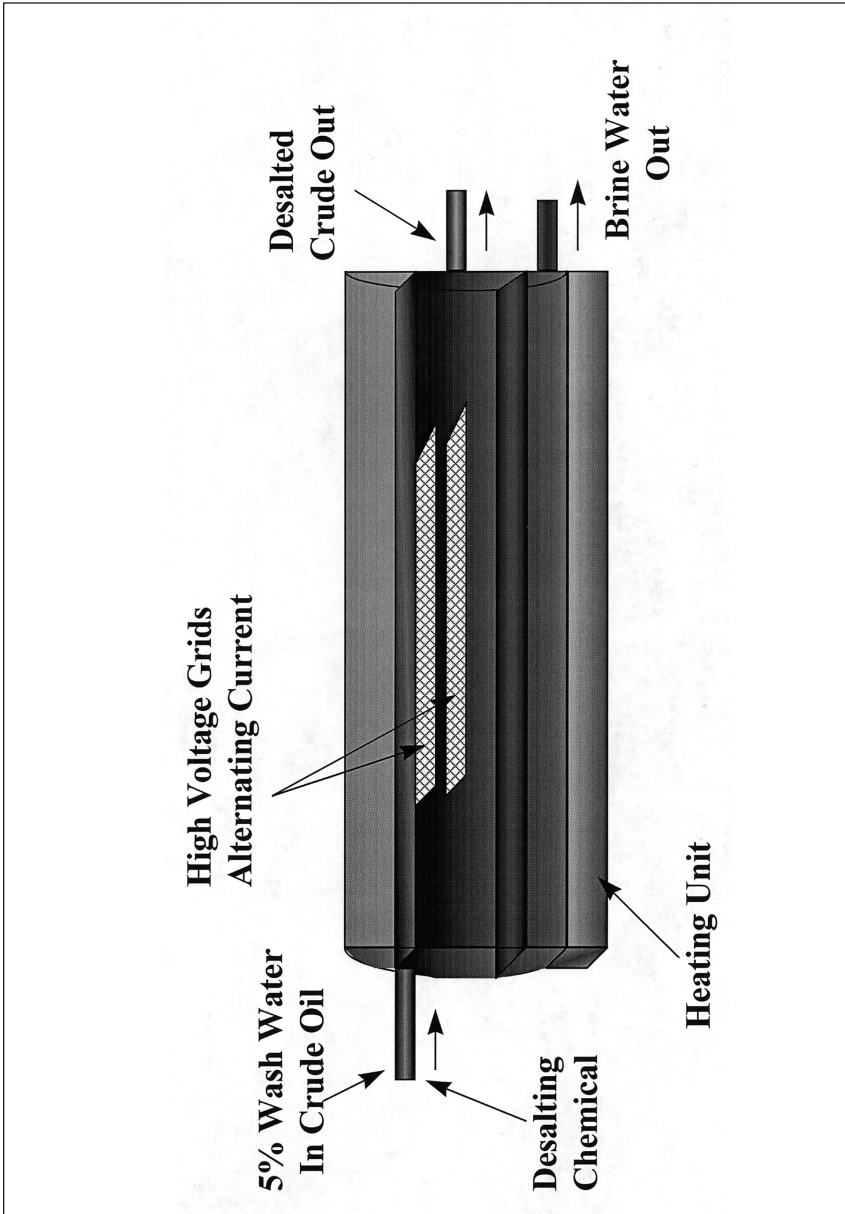


Fig. 3-9 Basic refinery unit

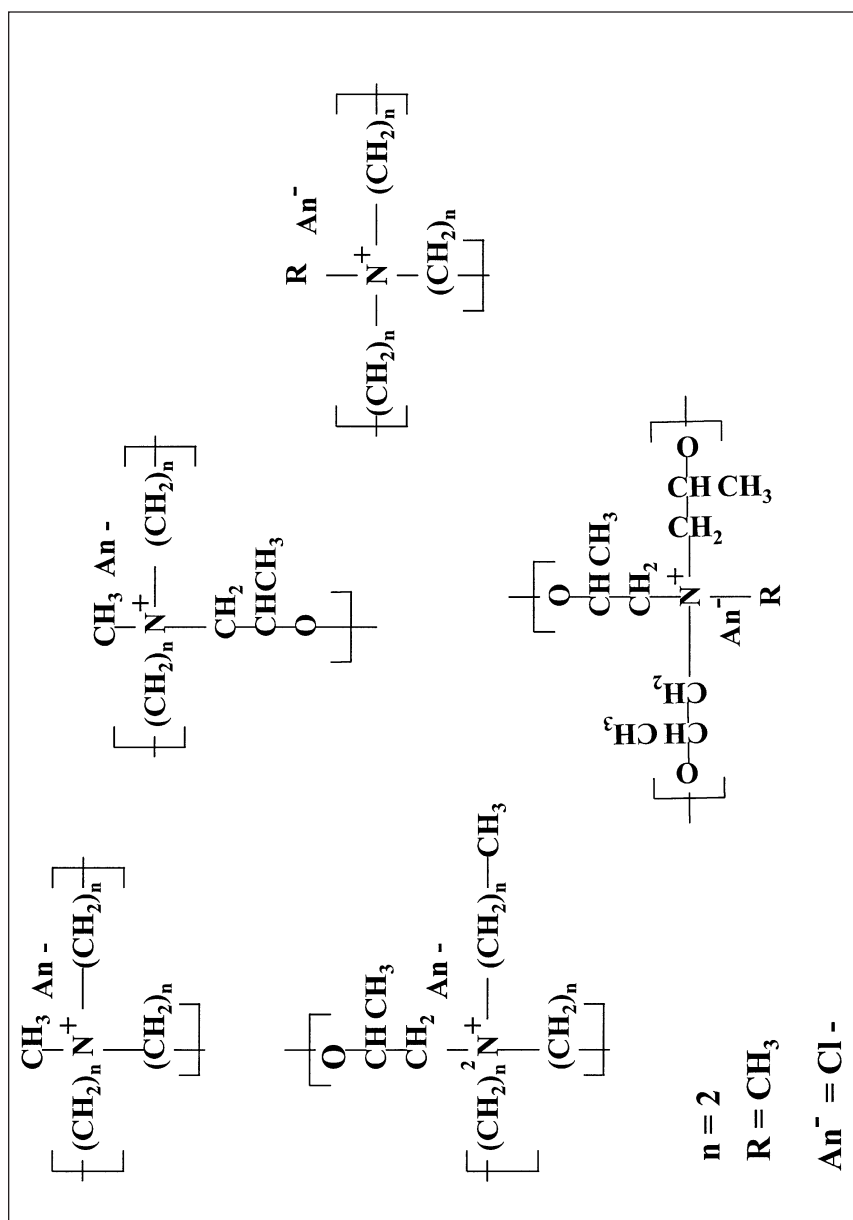


Fig. 5-2 Some idealized oil in water emulsion breakers