

Factors Affecting the Stability of Crude Oil Emulsions

Manar El-Sayed Abdel-Raouf
Petroleum Application Department
Egyptian Petroleum Research Institute
Egypt

1. Introduction

Crude oils are typically water in crude oil (w/o) emulsions, which are often very stable. Among the indigenous natural surfactants contained in the crude oils, asphaltenes and resins are known to play an important role in the formation and stability of w/o emulsions. Asphaltenes are defined as the fraction of the crude oil precipitating in pentane, hexane, or heptane, but soluble in toluene or benzene. Asphaltenes are the most polar and heaviest compounds in the crude oil. They are composed of several poly nuclear aromatic sheets surrounded by hydrocarbon tails, and form particles whose molar masses are included between 500 and 20,000 g mol⁻¹. They contain many functional groups, including some acids and bases. Resins are molecules defined as being soluble in light alkanes (pentane, hexane, or heptane), but insoluble in liquid propane. They consist mainly of naphthenic aromatic hydrocarbons; generally aromatic ring systems with alicyclic chains. Resins are effective as dispersants of asphaltenes in crude oil. It was postulated that asphaltenes stabilize w/o emulsions in two steps. First, disk-like asphaltene molecules aggregate into particles or micelles, which are interfacially active. Then, these entities upon adsorbing at the w/o interface aggregate through physical interactions and form an interfacial network.

The introduced chapter deals with different factors that affecting the stability of crude oil emulsions and also those factors causing asphaltenes precipitation.

1.1 Types of emulsions

Emulsions have long been of great practical interest due to their widespread occurrence in everyday life. They may be found in important areas such as food, cosmetics, pulp and paper, pharmaceutical and agricultural industry (1, 2). Petroleum emulsions may not be as familiar but have a similar long-standing, widespread, and important occurrence in industry, where they are typically undesirable and can result in high pumping costs, pipeline corrosions, reduced throughput and special handling equipment. Emulsions may be encountered at all stages in the petroleum recovery and processing industry (drilling fluid, production, process plant, and transportation emulsions (3, 4).

Emulsions are defined as the colloidal systems in which fine droplets of one liquid are dispersed in another liquid where the two liquids otherwise being mutually immiscible. Oil

and water produce emulsion by stirring; however, the emulsion starts to break down immediately after stirring is stopped.

Depending upon the nature of the dispersed phase, the emulsions are classified as, O/W emulsion or oil droplets in water and W/O emulsion or water droplets in oil. Recently, developments of W/O/W type emulsion or water dispersed within oil droplets of O/W type emulsion and O/W/O type, Figure 1.

- i. **Oil-in-water emulsions (O/W):** The emulsion in which oil is present as the dispersed phase and water as the dispersion medium (continuous phase) is called an oil-in-water emulsion.
- ii. **Water-in-oil emulsion (W/O):** The emulsion in which water forms the dispersed phase, and the oil acts as the dispersion medium is called a water-in-oil emulsion.

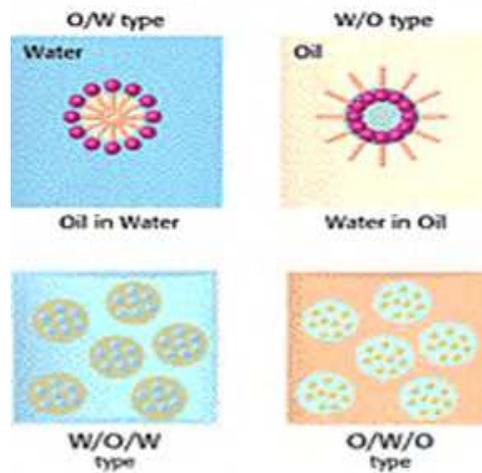


Fig. 1. Types of emulsions.

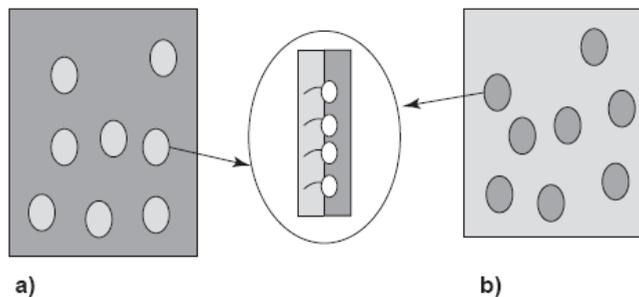


Fig. 2. (6) Schematic representation of emulsion structures. a) O/W emulsion; b) W/O emulsion. Encircled: enlarged view of a surfactant monolayer sitting at the oil-water interface.

1.2 Properties of emulsions ⁽⁵⁻⁷⁾

The emulsions satisfy the following criteria:

- i. Emulsions show all the characteristic properties of colloidal solution such as Brownian movement, Tyndall effect, electrophoresis etc.
- ii. These are coagulated by the addition of electrolytes containing polyvalent metal ions indicating the negative charge on the globules.
- iii. The size of the dispersed particles in emulsions is larger than those in the sols. It ranges from 1000 Å to 10,000 Å. However, the size is smaller than the particles in suspensions.
- iv. Emulsions can be converted into two separate liquids by heating, centrifuging, freezing etc. This process is also known as demulsification.

Many advances have been made in the field of emulsions in recent years. Emulsion stability depends on presence of adsorbed structures on the interface between the two liquid phases. Emulsion behavior is largely controlled by the properties of the adsorbed layers that stabilize the oil-water surfaces ⁽⁷⁻⁹⁾. The knowledge of surface tension alone is not sufficient to understand emulsion properties, and surface rheology plays an important role in a variety of dynamic processes. When a surface active substance is added to water or oil, it spontaneously adsorbs at the surface, and decreases the surface tension γ ⁽⁷⁾. In the case of small surfactant molecules, a monolayer is formed, with the polar parts of the surface-active molecules in contact with water, and the hydrophobic parts in contact with oil (Fig. 2). The complexity of petroleum emulsions comes from the oil composition in terms of surface-active molecules contained in the crude, such as low molecular weight fatty acids, naphthenic acids and asphaltenes. These molecules can interact and reorganize at oil/water interfaces. These effects are very important in the case of heavy oils because this type of crude contains a large amount of asphaltenes and surface-active compounds ⁽¹⁰⁻¹⁴⁾. In petroleum industry, water-in-oil (w/o) or oil-in-water (o/w) emulsions can lead to enormous financial losses if not treated correctly. Knowing the particular system and the possible stability mechanisms is thus a necessity for proper processing and flow assurance. Thus, there are desirable or undesirable emulsions as shown in Table (1).

1.3 Emulsion formation

There are three main criteria that are necessary for formation of crude oil emulsion ⁽¹⁶⁾:

1. Two immiscible liquids must be brought in contact;
2. Surface active component must present as the emulsifying agent;
3. Sufficient mixing or agitating effect must be provided in order to disperse one liquid into another as droplets.

During emulsion formation, the deformation of droplet is opposed by the pressure gradient between the external (convex) and the internal (concave) side of an interface. The pressure gradient or velocity gradient required for emulsion formation is mostly supplied by agitation. The large excess of energy required to produce emulsion of small droplets can only be supplied by very intense agitation, which needs much energy ⁽¹⁷⁻²¹⁾.

Occurrence	Usual type ^a
Undesirable emulsions	
Well-head emulsions	W/O
Fuel oil emulsions (marine)	W/O
Oil Sand Flootation process	W/O or O/W
Oil spill mousse emulsions	W/O
Tanker bilge emulsions	O/W
Desirable emulsions	
Heavy oil pipe line emulsions	O/W
Oil sand floatation process slurry	O/W
Emulsion drilling fluid, oil-emulsion mud	O/W
Emulsion drilling fluid, oil-base mud	W/O
Asphalt emulsion	O/W
Enhance oil recovery in situ emulsions	O/W

Table 1. Desirable and Undesirable petroleum emulsions ⁽¹⁰⁾.

A suitable surface active component or surfactant can be added to the system in order to reduce the agitation energy needed to produce a certain droplet size. The formation of surfactant film around the droplet facilitates the process of emulsification and a reduction in agitation energy by factor of 10 or more can be achieved. A method requiring much less mechanical energy uses phase inversion. For instance, if ultimately a W/O emulsion is desired, then an O/W emulsion is first prepared by the addition of mechanical energy. Then the oil content is progressively increased. At some volume fraction above 60-70%, the emulsion will suddenly invert and produce a W/O emulsion of smaller water droplet sizes than were the oil droplets in the original O/W emulsions ⁽²²⁾.

Emulsions of crude oil and water can be encountered at many stages during drilling, producing, transporting and processing of crude oils and in many locations such as in hydrocarbon reservoirs, well bores, surface facilities, transportation systems and refineries ^(23, 24).

1.4 Emulsion breakdown

In general there are three coupled sub-processes that will influence the rate of breakdown processes in emulsions. These are aggregation (Flocculation), coalescence and phase separation ⁽¹⁵⁾, Figure 3. They will be discussed in some details.

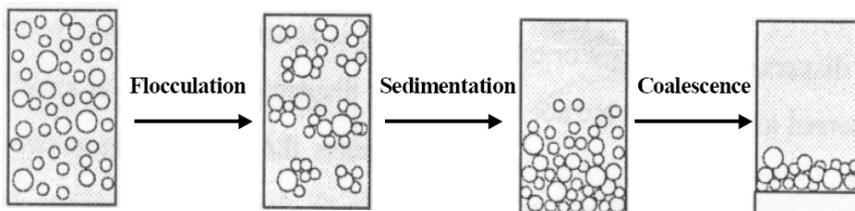


Fig. 3. Emulsion breakdown ⁽¹⁵⁾.

Flocculation ⁽¹⁵⁾

It is the process in which emulsion drops aggregate, without rupture of the stabilizing layer at the interface. Flocculation of emulsions may occur under conditions when the van der Waals attractive energy exceeds the repulsive energy and can be weak or strong, depending on the strength of inter-drop forces.

The driving forces for flocculation can be:

1. Body forces, such as gravity and centrifugation causing creaming or sedimentation, depending on whether the mass density of the drops is smaller or greater than that of the continuous phase.
2. Brownian forces or
3. Thermo-capillary migration (temperature gradients) may dominate the gravitational body force for very small droplets, less than 1 μm .

Coalescence ⁽¹⁵⁾:

It is an irreversible process in which two or more emulsion drops fuse together to form a single larger drop where the interface is ruptured. As already mentioned, for large drops approaching each other (no background electric field), the interfaces interact and begin to deform. A plane parallel thin film is formed, which rate of thinning may be the main factor determining the overall stability of the emulsion. The film thinning mechanism is strongly dependent on bulk properties (etc. viscosity) in addition to surface forces. The interaction of the two drops across the film leads to the appearance of an additional disjoining pressure inside the film, Figure 4.

Phase separation

The processes of flocculation and coalescence are followed by phase separation, i.e. emulsion breakdown.

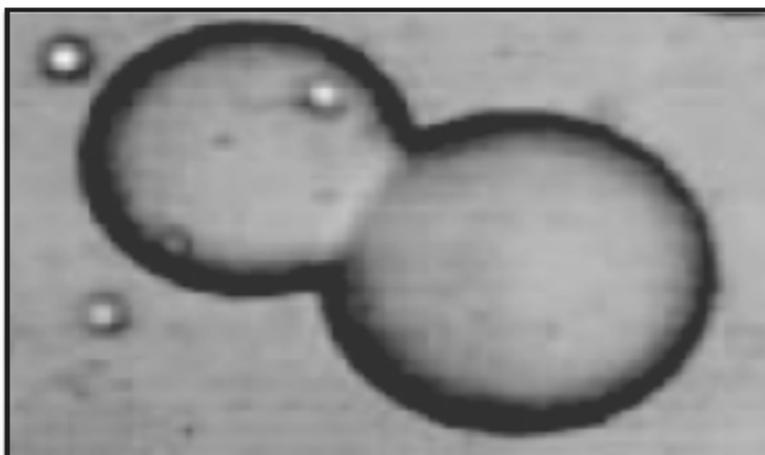


Fig. 4. Adhesion between two emulsion droplets ⁽¹⁰⁾.

1.5 Stabilization of the emulsion

There are many factors that usually favour emulsion stability such as low interfacial tension, high viscosity of the bulk phase and relatively small volumes of dispersed phase. A narrow droplet distribution of droplets with small sizes is also advantageous, since polydisperse dispersions will result in a growth of large droplets on the expense of smaller ones. The potent stabilization of the emulsion is achieved by stabilization of the interface (25-27).

1.5.1 Steric stabilization of the interface

The presence of solids at interfaces may give rise to repulsive surface forces which *thermodynamically* stabilize the emulsion. As concluded (28-30), many of the properties of solids in stabilizing emulsion interfaces can be attributed to the very large free energy of adsorption for particles of intermediate wettability (partially wetted by both oil and water phases). This irreversible adsorption leads to extreme stability for certain emulsions and is in contrast to the behavior of surfactant molecules which are usually in rapid dynamic equilibrium between the oil: water interface and the bulk phases. According to the asphaltene stabilization mechanism, coalescence requires the solid particles to be removed from the drop-drop contact region. Free energy considerations suggest that lateral displacement of the particles is most likely, since forcing droplets into either phase from the interface require extreme energies (31-38). The asphaltene stabilization effect for water droplets has already been pictured in Figure 5 where droplet contact is prevented by a physical barrier around the particles.

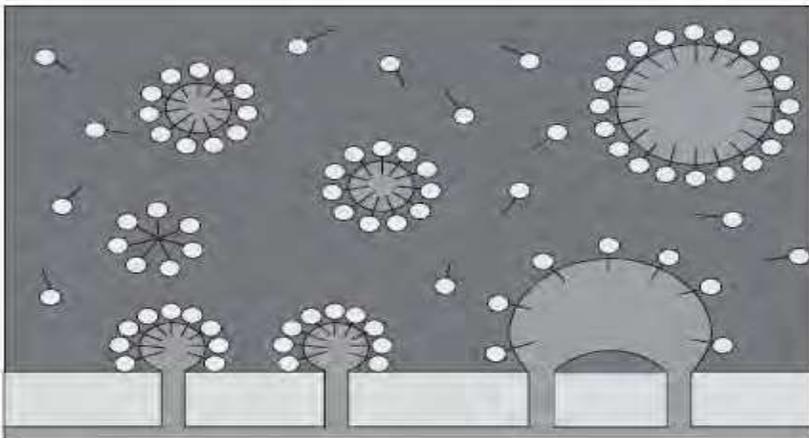


Fig. 5. Steric stabilization of the interfaces (40).

As the stability of w/o emulsions appeared clearly related to the presence of an interfacial network surrounding the water droplets (40-43), many rheological studies of water/asphalted oil interfaces have been made to clarify the mechanisms involved (44-46). The rheological properties of these interfaces have been found to be strongly dependent on the nature of solvent used for dilution, the oil concentration, the asphaltene and resin concentrations, the resin to asphaltene ratio, and so on (47-51).

1.5.2 Electric stabilization of the interface

Electrical double layer repulsion or charge stabilization by polymers and surfactants with protruding molecular chains may prevent the droplets to come into contact with each other (52-54). Also, polymers, surfactants or adsorbed particles can create a mechanically strong and elastic interfacial film that act as a barrier against aggregation and coalescence. A film of closed packed particles has considerable mechanical strength, and the most stable emulsions occur when the contact angle is close to 90°, so that the particles will collect at the interface. Particles, which are oil-wet, tend to stabilize w/o emulsions while those that are water-wet tend to stabilize o/w emulsions. In order to stabilize the emulsions the particles should be least one order of magnitude smaller in size than the emulsion droplets and in sufficiently high concentration. Nevertheless, stable w/o emulsions have been generally found to exhibit high interfacial viscosity and/or elasticity modulus. It has been attributed to physical cross-links between the naturally occurring surfactants in crude oil (i.e. asphaltenes particles) adsorbed at the water-oil interface (55, 56).

1.5.3 Composition of crude oil

A good knowledge of petroleum emulsions is necessary for controlling and improving processes at all stages of petroleum production and processing. Many studies have been carried out in the last 40 years and have led to a better understanding of these complex systems (57-60). However there are still many unsolved questions related to the peculiar behavior of these emulsions. The complexity comes mostly from the oil composition, in particular from the surface-active molecules contained in the crude. These molecules cover a large range of chemical structures, molecular weights, and HLB (Hydrophilic-Lipophilic Balance) values; they can interact between themselves and/or reorganize at the water/oil interface. Oil-water emulsions are fine dispersions of oil in water (O/W) or of water in oil (W/O), with drop sizes usually in the micron range (61, 62). In general, emulsions are stabilized by surfactants. In some cases multiple emulsions such as water in oil in water (W/O/W) or oil in water in oil (O/W/O) can be found. Emulsions can be stabilized by other species, provided that they adsorb at the oil-water interface and prevent drop growth and phase separation into the original oil and water phases. After adsorption, the surfaces become visco-elastic and the surface layers provide stability to the emulsion (63- 65). Crude oils contain asphaltenes (high molecular weight polar components) that act as natural emulsifiers. Other crude oil components are also surface active: resins, fatty acids such as naphthenic acids, porphyrins, wax crystals, etc, but most of the time they cannot alone produce stable emulsions (65). However, they can associate to asphaltenes and affect emulsion stability. Resins solubilize asphaltenes in oil, and remove them from the interface, therefore lowering emulsion stability. Waxes co-adsorb at the interface and enhance the stability. Naphthenic and other naturally occurring fatty acids also do not seem able to stabilize emulsions alone. However, they are probably partly responsible for the important dependence of emulsion stability upon water pH. The composition of crude oil is given in Figure 6 and examples of these structures are given in Figure 7 a & b (66).

These components can be separated by simple technique known as SARA analysis (Saturated, Aromatic, Resin and Asphaltenes). Some examples of the resin and asphaltenes that can be separated by using SARA analysis of are given in Figure 7a& b. The SARA analysis process is shown in Figure 8. Particles such as silica, clay, iron oxides, etc. can be

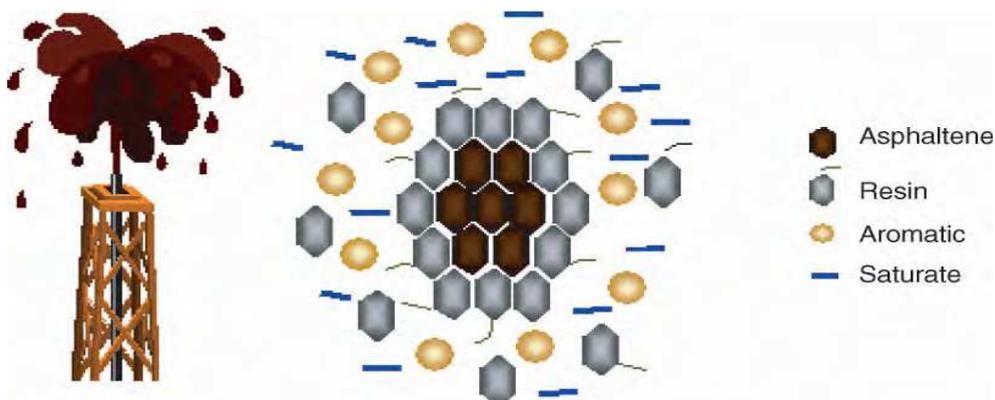


Fig. 6. Composition of crude oil.

present in crude oils. These particles are naturally hydrophilic, but can become oil-wet (hydrophobic) due to long term exposure to the crude in the absence of water. Emulsions with particles and asphaltenes combined can be much more stable than those stabilized by asphaltenes alone, provided that enough asphaltenes are present: all the adsorption sites on the particle surface need to be saturated by asphaltenes (67, 68). These species will be mentioned in some details in the next section.

1.5.4 Asphaltenes

There are many definitions of asphaltenes. Strictly speaking, asphaltenes are the crude oil components that meet some procedural definition (69). A common definition is that asphaltenes are the material that is:

Insoluble in n-pentane (or n-heptane) at a dilution ratio of 40 parts alkane to 1 part crude oil and (2) Re-dissolves in toluene.

Chemically, asphaltenes are polycyclic molecules that are disc shaped, and have a tendency to form stacked aggregates. The tendency of asphaltenes to self-aggregate distinguishes them from other oil constituents. Asphaltene aggregation is the cause of complex non-linear effects in such phenomena as adsorption at solid surfaces, precipitation, fluid's rheology, emulsion stability, etc (70, 71). Asphaltenes are regarded to be polar species, formed by condensed poly aromatic structures, containing alkyl chains, hetero atoms (such as O, S and N) and some metals.

They contain also polar groups (ester, ether, carbonyl) and acidic and basic groups (carboxylic and pyridine functional groups) that can be ionized in a certain range of pH by accepting or donating protons. Typical composition of asphaltenes is provided in Table 2. Asphaltenes average molecular weights range from approximately 800 to 3000 g mol⁻¹. They are molecularly dispersed in aromatic solvents such as toluene, and precipitate in alkanes (ASTM D2007-93, IP 143).

The procedure should also specify the temperature at which the mixing and separation takes place, the amount of time that must elapse before asphaltenes are separated from the oil/alkane mixture, and even the method used to accomplish the separation (filter size,

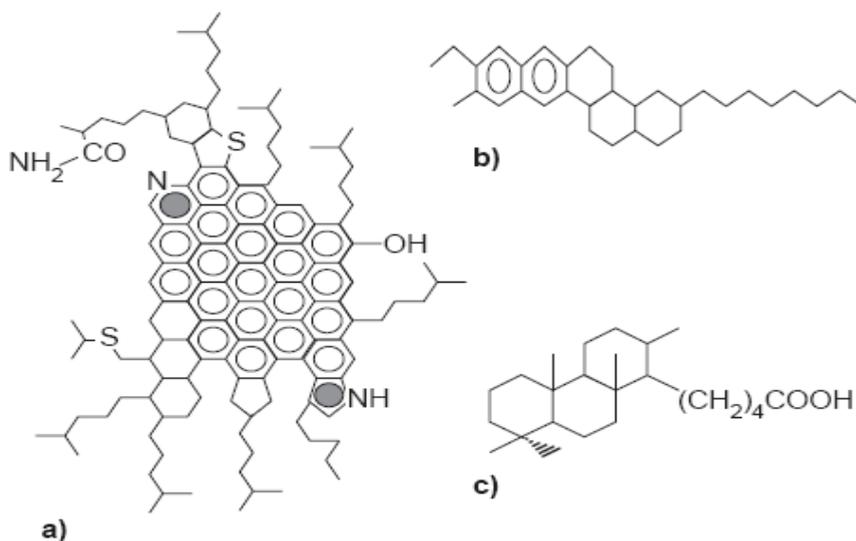


Fig. 7a. Examples of molecular structures in crude oil. a- Asphaltenes, b- Resins, c- naphthenic acids.

filtration rate), since all of these factors can affect the final result. Although there are several standardized procedures, but in reality every lab uses its own procedure. These may vary a little or a lot from the standards. They differ in color and in texture ⁽⁷²⁾.

Material separated with still lower molecular weight alkanes (e.g., propane) would be sticky and more liquid-like than those separated by n-heptane as shown in Figure 9.

Some authors point out that the precipitation techniques may provide an excessively strong interference into the delicate molecular organization of asphaltene associates (Figure 10), leading to their irreversible transformation, so that the supra-molecular architecture in solutions of the precipitated material may be different from that in native crude. Consequently, studies of aggregation in crude oil solutions may supply valuable information regarding the manner of asphaltene–asphaltene interactions in the presence of other crude oil components.

Element (in wt. %)	Range	Typical
Carbon	78-90	82-84
Hydrogen	6.1-10.3	6.5-7.5
Nitrogen	0.5-3.0	1.0-2.0
Sulfur	1.9-10.8	2.0-6.0
Oxygen	0.7-6.6	0.8-2.0
Vanadium(ppm)	0-1200	100-300
H/C	0.8-1.5	1.0-1.2

Table 2. Range and Typical Values of Elemental Composition of Asphaltenes.

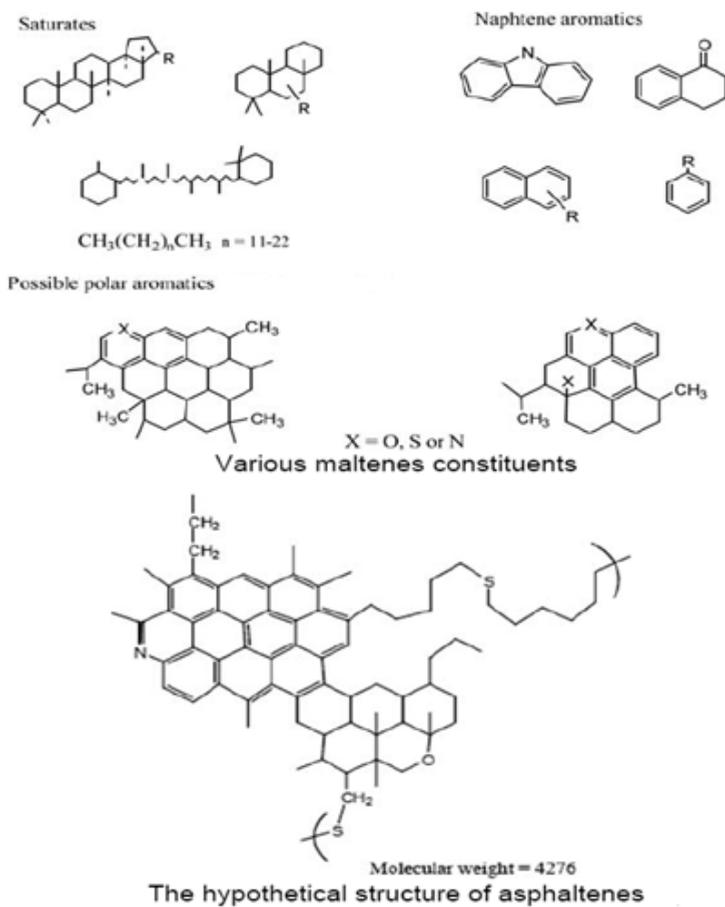


Fig. 7b. Other examples of molecular structures in crude oil.

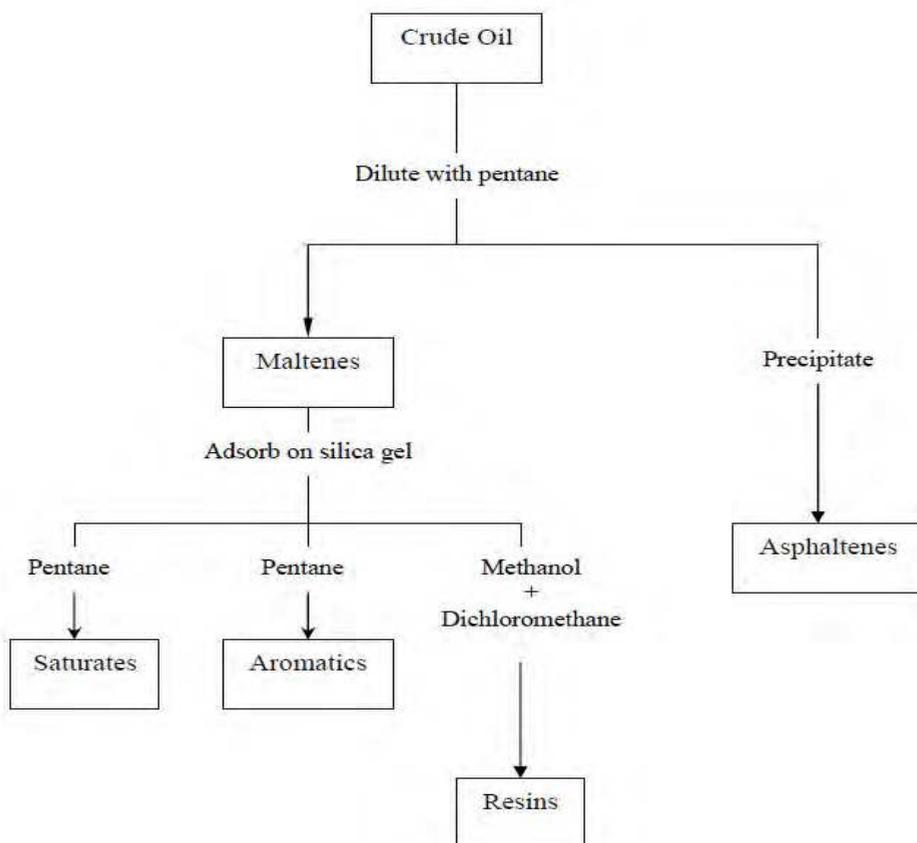


Fig. 8. SARA analysis for separation of crude oil components.



n-C5 asphaltene



n-C7 asphaltene

Fig. 9. asphaltenes separated by different alkanes.

Asphaltenes stabilize the crude oil emulsion by different modes of action. When asphaltene disperse on the interface, the film formed at a water/ crude oil interface behaves as a skin whose rigidity can be shown by the formation of crinkles at interface when contracting the droplet to a smaller drop size ⁽⁷⁸⁾. They can also aggregate with resin molecules on the interfaces and prevent droplet coalescence by steric interaction (Figure 11). Some authors suggest that asphaltene stabilize the emulsion by formation of hydrogen bonding between asphaltene and water molecules ⁽⁷⁹⁻⁸⁰⁾.

Singh et al. ⁽⁸¹⁾ postulated that asphaltene stabilize w/o emulsions in two steps. First, disk-like asphaltene molecules aggregate into particles or micelles, which are interfacially active. Then, these entities upon adsorbing at the w/o interface aggregate through physical interactions and form an interfacial network. Different modes of action of asphaltene are represented in Figure 12.

1.5.5 Resins

Just as the asphaltene have only a procedural definition, resins also are procedurally defined. There are at least two approaches to defining resins. In one approach the material that precipitates with addition of propane, but not with n-heptane, is considered to constitute the resins.

There is no universal agreement about the propane/n-heptane pair, but the general idea is that resins are soluble in higher molecular weight normal alkanes, but are insoluble in lower molecular weight alkanes. A standard method exists to quantify resins by a completely SARA analysis. Resins can be also defined as the most polar and aromatic species present in

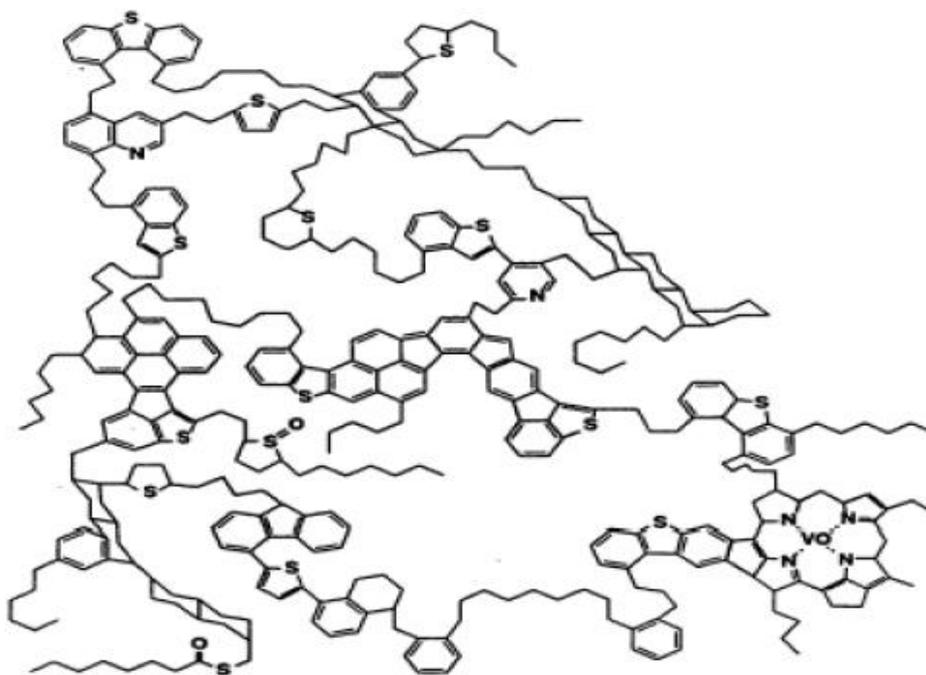


Fig. 10. Asphaltene associates (77).

deasphalted oil and, it has been suggested, contribute to the enhanced solubility of asphaltenes in crude oil by solvating the polar and aromatic portions of the Asphaltenic molecules and aggregates (82-85). The solubility of asphaltenes in crude oil is mediated largely by resin solvation and thus resins play a critical role in precipitation, and emulsion stabilization phenomena (86-88).

Resins are thought to be molecular precursors of the asphaltenes. The polar heads of the resins surround the asphaltenes, while the aliphatic tails extend into the oil, Figure 13. Resins may act to stabilize the dispersion of asphaltene particles and can be converted to asphaltenes by oxidation. Unlike asphaltenes, however, resins are assumed soluble in the petroleum fluid. Pure resins are heavy liquids or sticky (amorphous) solids and are as volatile as the hydrocarbons of the same size. Petroleum fluids with high-resin content are relatively stable. Resins, although quite surface-active, have not been found to stabilize significantly water-in-oil emulsions by themselves in model systems. However, the presence of resins in solution can destabilize emulsions via asphaltenes solvation and/or replacement at the oil/water interface (89-96), Figure 13.

1.5.6 Saturates (97-100)

Saturates are nonpolar and consist of normal alkanes (*n*-paraffins), branched alkanes (iso-paraffins) and cyclo-alkanes (also known as naphthenes). Saturates are the largest single source of hydrocarbon or petroleum waxes, which are generally classified as paraffin wax,

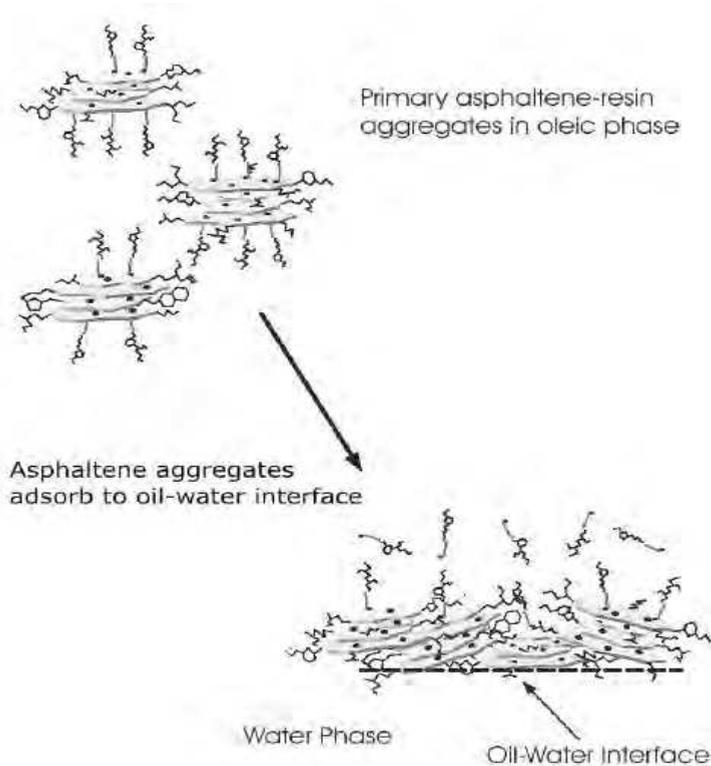


Fig. 11. Proposed stabilizing mechanism for asphaltenes in petroleum by resin molecules ⁽⁸²⁾.

microcrystalline wax, and/or petrolatum (Figure 7b). Of these, the paraffin wax is the major constituent of most solid deposits from crude oils.

1.5.7 Aromatics ⁽¹⁰¹⁻¹⁰⁶⁾

Aromatics are hydrocarbons, which are chemically and physically very different from the paraffins and naphthenes. They contain one or more ring structures similar to benzene. The atoms are connected by aromatic double bonds (Figure 7b).

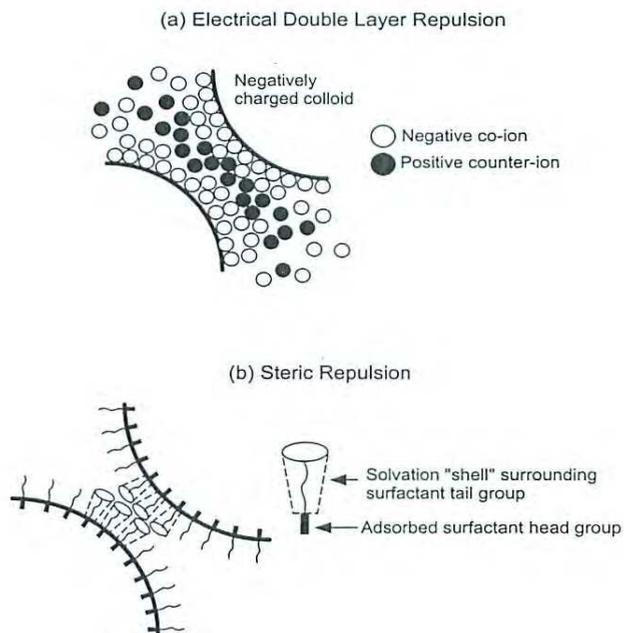


Fig. 12. Different modes of action of asphaltenes in stabilizing crude oil emulsions.

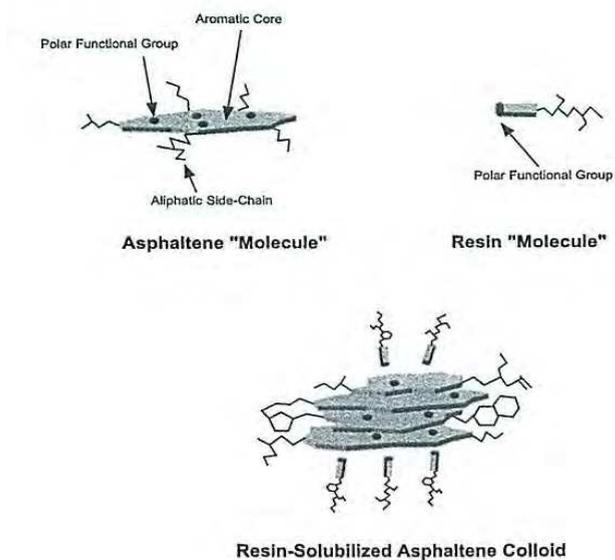


Fig. 13. Solubilization of asphaltenes by resin molecules.

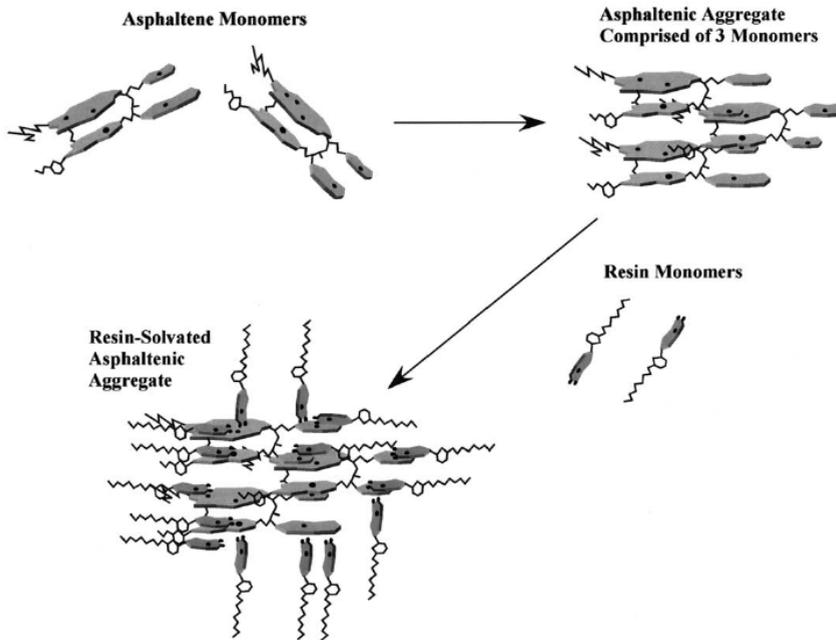


Fig. 14. Schematic illustration of asphaltene aggregates in absence and in presence of resins (82).

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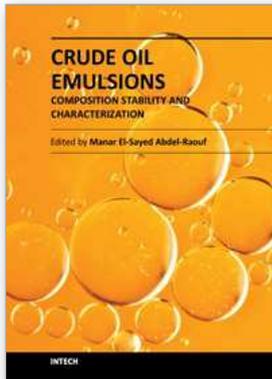
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Edited by Prof. Manar El-Sayed Abdul-Raouf

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Petroleum "black gold" is the most important nonrenewable source of energy. It is a complex mixture of different phases and components. Refining it provides a vast number of organic compounds, all of them of which are used to produce petroleum based products for numerous applications, from industry to medicine, from clothing to food industries. We can find petroleum based products all around us. This book deals with some important topics related to petroleum such as its chemical composition and stability. It is well-known that the chemical composition of crude oil differs according to the site of production, and its grade varies from waxy to asphaltenic crude. Both of them are refined to produce different products. The stability of crude oil on aging and transportation is governed by several factors and these factors are included within this book. Some new technologies for petroleum characterization are also introduced. This book is aimed at researchers, chemical engineers and people working within the petroleum industry.

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Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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Unit 405, Office Block, Hotel Equatorial Shanghai
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中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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