

1.1 Definition of Crude Oil:

Crude oil, meaning literally rock oil, is the term used to describe a myriad of hydrocarbon-rich fluids that has accumulated in subterranean reservoirs. Crude oil varies dramatically in color, odor, and flow properties that reflect the diversity of its origin (Speight, 2001).

Crude oil is a naturally occurring mixture of hydrocarbons, generally in a liquid state, that may also include compounds of sulfur, nitrogen, oxygen, metals, and other elements (Speight, 2001; William, 1996). Many Geologists believe that crude oil is the result of the breakdown of organic matter-plant and animals- by some unknown process (the organic theory). Some, however, think that living things had nothing to do with it (the inorganic theory) (Kate, 1997).

The organic theory holds that oil and gas formed from the remains of plants and animals. (The term organic refers to living things, or organisms). Most geologists think that the plant and animals that gave rise to oil and gas were very small, even microscopic in size. In theory these tiny organisms lived in ancient rivers and seas, as they do today. The rivers carried the plants and animals to the sea, along with silts and muds. The same kinds of organisms lived in shallow seas and the marginal waters of the warmer oceans, where they fell in a slow, steady rain to the bottom as they died. Most were eaten or oxidized before reaching bottom, but some escaped destruction and were entombed in the ooze and mud on the seafloor. As a result, a rich mixture of sediment (grains of silt, sand, and mud) and organic material formed that was cut off from any oxygen dissolved in the water. Without oxygen, the organic material could not decay normally. In time, after thousands and thousands of years, a thick body of sediment and organic remains built up on the bottom of the sea. Eventually more sediment were deposited on top of the organic mixture until the great weight of the overlying sediment pushed the lower sediments deep into the earth, where the bottom beds became rock. Geologists

believe that high heat and pressure, bacteria, chemical reactions, and other forces worked on the organic remains and transformed them into oil and gas (Kate, 1997; API, 1996).

The inorganic theory, first put forth in the early 1800, holds that crude oil is either left over from the formation of the solar system or was formed later deep within the earth. This theory has the advantage of explaining why crude oil deposits are often very deep, in patterns that relate more to large-scale structural features of the crust than to smaller-scale sedimentary rocks. Geologists that support the inorganic theory also believe that it explains why crude oil taken from a large area is often chemically similar even though the formations where it was found are made of different geological ages (Kate, 1997).

1.1.1 Physical Properties of Crude Oil:

Historically, physical properties such as boiling point, density (gravity), odor, and viscosity have been used to describe oils (Speight, 2001).

1.1.1.1 Density, Specific gravity and API:

In the early days of the petroleum refining industry, density and specific gravity data were used to indicate crude oil quality, and Correlate with aromatic character, naphthenic character, and paraffinic character.

The specific gravity is highest for aromatics and lowest for paraffins. The API gravity reverses this relationship. The density and specific gravity of crude oil are two properties that have found wide use in the industry for preliminary assessment of the character of the crude oil (Speight, 2001).

Density is defined as the mass of a unit volume of material at a specified temperature and has the dimensions of grams per cubic centimeter. Density is measured at a standard temperature, mostly 15.6 or 20°C (60 or 68°F). Density and specific gravity (thence the API gravity) can be determined relatively easily but are

no longer the means of a preliminary assay of the sample and are no longer the guide that they used to be in terms of determining (or estimating) the product slate. Specific gravity is the ratio of the mass of a volume of a substance to the mass of the same volume of water and is dependent on two temperatures, those at which the masses of the sample and the water are measured. The standard temperatures for a specific gravity in the petroleum industry in North America are 60/600F (15.6/315.6°C). The specific gravity values of petroleum samples are close to those of density and range from about 0.80 for light paraffinic crude oils to about 0.98 for heavy oil and about 1.00-1.03 for bitumen (Speight, 2001).

The use of density or specific gravity has largely been replaced by the API (American Petroleum Institute) gravity as the preferred property. It is one criterion that is used in setting prices for petroleum. In the United States, the API gravity has been used for the classification of a reservoir and the accompanying tax and royalty consequences. The specific gravity of petroleum usually ranges from about 0.8 (45.3° API) for the lighter crude oils to over 1.0 (10° API) for heavy crude oils and bitumen (Speight, 2001). The densities of most iso-compounds are slightly (but not always) greater than those of the normal hydrocarbons. Ring compounds and heteroatom compounds have a significantly higher density than that of the paraffins. Density, and thus specific gravity, is influenced by the chemical composition of petroleum, but quantitative correlation is difficult to establish, especially when complex mixtures such as petroleum, heavy oil, and bitumen are concerned. However, an interesting aspect of density is its change with temperature, an effect that plays an important role in the recovery of bitumen from tar sand by the hot water process. Thus increased amounts of aromatic compounds result in an increase in density, whereas an increase in saturated compounds results in a decrease in density. Indeed, it is also possible to recognize certain preferred trends between the density of petroleum and one or another of the physical

properties. For example, an approximate correlation exists between the density (API gravity) and sulfur content, Conradson carbon residue, viscosity, asphaltenes plus resins, and nitrogen content (Speight, 2001).

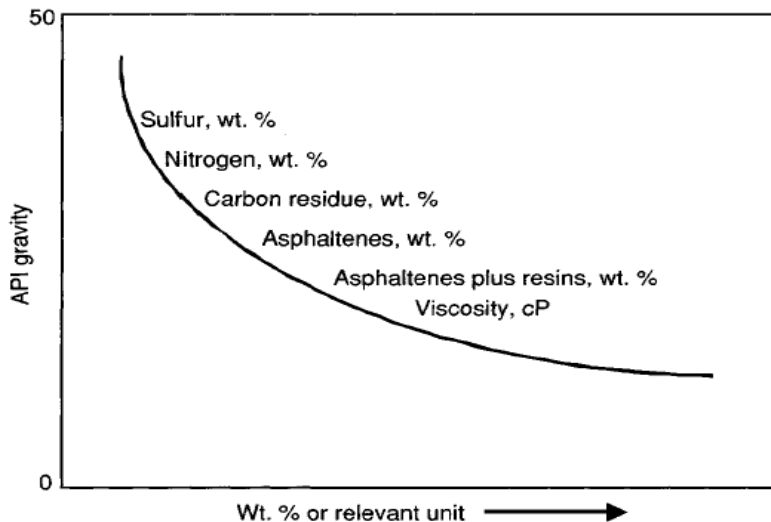


Fig. 1.1 Inter-property relationships of various samples

1.1.1.2 Pour Point:

Pour point is the temperature at which the oil stops flowing and becomes semi-solid or plastic. The pour point temperature is high in the oils if their wax or asphaltene content is high. Lighter oils with low viscosity and density have lower pour points (Shweta, 2005).

1.1.1.3 Volatility:

It is the ease by which the components of the oil are lost to the atmosphere due to evaporation. It is represented as the percentage of the total oil evaporated at different temperature ranges. The rate and extent of loss of volatiles depends upon surface to volume ratio and thus, the loss of volatiles increases for thin layers of oil as compared to the situation with oil in bulk. The presence of volatile components in the early stages of the oil spill incident can increase the risk of oil combustion (Speight, 2001; Shweta, 2005).

1.1.1.4 Flash Point:

The temperature at which the vapor of the oil will ignite, when exposed to an ignition source is called flash point of the oil. Light oils can ignite under most ambient conditions, however bunker and other heavy fuel oils do not cause a serious fire hazard when spilled on the seawater surface (Shweta, 2005).

1.1.1.5 Viscosity:

Viscosity is the force in dynes required to move a plane of 1cm^2 area at a distance of 1 cm from another plane of 1cm^2 areas through a distance of 1 cm in 1 second. In the centimeter-gram-second (cgs) system the unit of viscosity is the poise (P) or centipoise ($\text{cP} = 0.01 \text{ P}$). Two other terms in common use are kinematic viscosity and fluidity. The kinematic viscosity is the viscosity in centipoises divided by the specific gravity, and the unit is the stokes ($\text{St}, \text{cm}^2/\text{s}$), although centistokes ($\text{cSt} = 0.01 \text{ St}$) is in more common usage; fluidity is simply the reciprocal of viscosity (Speight, 2001).

The measurement of the viscosity of petroleum has been regarded by the petroleum industry to have particular importance because of the role it plays in the assessment of petroleum properties and, hence, the producibility of a reservoir. In addition, the viscosity of oil must also be considered when determining the amount of diluents that will permit pipeline transportation of the oil. The changes in viscosity with temperature, pressure, and rate of shear are pertinent not only in lubrication but also for such engineering concepts as heat transfer. The viscosity and relative viscosity of different phases, such as gas, liquid oil, and water, are determining influences in producing the flow of reservoir fluids through porous oil-bearing formations.

The rate and amount of oil production from a reservoir are often governed by these properties. Viscosity data are also needed to determine reliable energy requirements for transportation of the produced oils through pipelines. As with the

density, the viscosity of petroleum is also related to the asphaltene content and increases on the application of pressure. The pressure coefficient of viscosity correlates with the temperature coefficient, even when oil samples of widely different types are compared. At higher pressures the viscosity decreases with increasing temperature, as at atmospheric pressure; in fact, viscosity changes of small magnitude are usually proportional to density changes, whether these are caused by pressure or by temperature. In summary, an increase in total pressure results in an increase in viscosity of heavy oil and bitumen at any given temperature. This increase is, however, small compared to viscosity at atmospheric condition (Speight, 2001).

Finally, as the crude oil weathers, its viscosity increases due to the progressive loss of the light volatile (lower molecular weight) fractions. Viscosity increases with decrease in temperature. Evaporation and emulsification increases the viscosity of the fresh spilled oil (Shweta, 2005).

1.1.1.6 Surface and Interfacial Tension:

Surface tension is a measure of the force acting at a boundary between two phases. If the boundary is between a liquid and a solid or between a liquid and a gas (air) the attractive forces are referred to as surface tension, but the attractive forces between two immiscible liquids are referred to as interfacial tension. The surface and interfacial tensions of petroleum are important because they are indicative of the ease of formation and stability of emulsions and foams, that is, they indicate the relative detergent properties of a crude oil. Thus surface and interfacial tension data can also be used to indicate the potential for oil recovery from a reservoir. The surface and interfacial tensions are determined by measuring the force necessary to detach a planar ring of platinum-iridium wire from the surface of the liquid. For interfacial tension, the ring is detached from the liquid of higher surface tension. The force is measured by a direct-reading torsion-type balance. This reading is

corrected by a factor that depends on the force applied, the density of the solutions, and the dimensions of the ring. Surface and interfacial tensions provide information pertaining to the presence and concentration of surface active agents. These compounds play an important role in the performance of flotation and emulsion systems (Speight, 2001).

1.1.2 Classification of Crude Oil:

Crude oil may be called light or heavy in reference to the amount of low boiling constituents and the relative density (specific gravity). Likewise, odor is used to distinguish between sweet (low sulfur) and sour (high sulfur) crude oil. Viscosity indicates the ease of (or more correctly the resistance to) flow. Although not directly derived from composition, the terms light or heavy or sweet and sour provide convenient terms for use in descriptions. For example, light crude oil (often referred to as conventional crude oil) is usually rich in low boiling constituents and waxy molecules whereas heavy crude oil contains greater proportions of higher boiling, more aromatic, and heteroatom containing (N-, O-, S-, and metal-containing) constituents. Heavy oil is more viscous than conventional crude oil. Bitumen is solid or near solid (Speight, 2001).

Conventional (light) crude oil is composed of hydrocarbons together with smaller amounts of organic compounds of nitrogen, oxygen, and sulfur and still smaller amounts of compounds containing metallic constituents, particularly vanadium, nickel, iron, and copper (Speight, 2001; William, 1996).

The purely hydrocarbon content may be higher than 90% by weight for paraffinic petroleum and 50% by weight for heavy crude oil and much lower for tar sand bitumen. The nonhydrocarbon constituents are usually concentrated in the higher boiling portions of the crude oil. The carbon and hydrogen content is approximately constant from crude oil to crude oil even though the amounts of the

various hydrocarbon types and of the individual isomers may vary widely (Speight, 2001).

1.1.3 Chemical Composition of Crude Oil:

Crude oils are a continuum of tens of thousands of different hydrocarbon molecules. However, the proportions of the elements in crude oils vary over fairly narrow limits despite the wide variation found in properties from the lightest crude oils to highly asphaltenic crudes. The carbon content normally is in the range 83–87% and the hydrogen content varies between 10 and 14%. In addition, varying small amounts of nitrogen (0.1-2.0%), oxygen (0.05-1.5%), sulfur (0.05-6.0%) and metals (Ni and V), are found in crude oils (Speight, 2001; Sjoblom *et al.*, 2003).

Due to the complex composition of crude oils, characterization by the individual molecular types is not possible, and elemental analysis is unattractive because it gives only limited information about the constitution of petroleum due to the constancy of elemental composition. Instead, hydrocarbon group type analysis is commonly employed. Knowledge of the distribution of major structural classes of hydrocarbons in crude oils is needed in various fields in the petroleum industry. Examples are studies related to reservoir evaluation, migration and maturity, degradation processes, processing, and environmental effects (Aske, 2002). The SARA separation is an example of such group type analysis, separating the crude oils in four main chemical classes based on differences in solubility and polarity. The four SARA fractions are the saturates (S), aromatics (A), resins (R), and the asphaltenes (A) (Fig. 1.2). Instead of molecules or atoms, certain structures are here considered the components of the crude oil, and the SARA separation can be seen to give information somewhat between that obtained by elemental analysis and analysis for individual molecules (Sjoblom *et al.*, 2003).

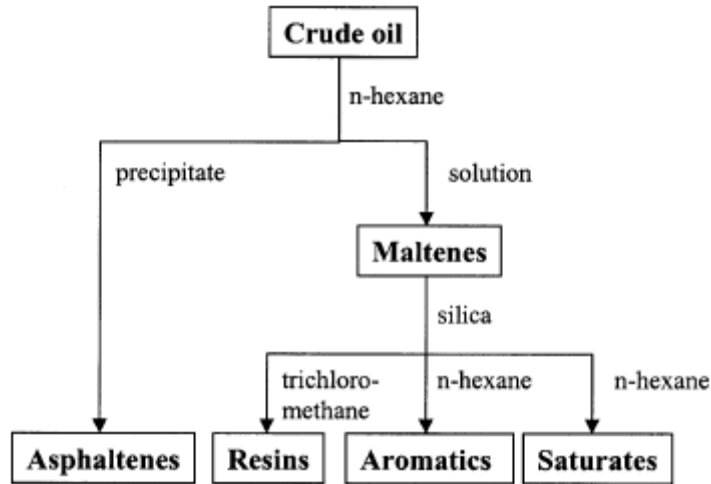


Fig. 1.2 SARA separation scheme (Sjoblom *et al.*, 2003)

1.1.3.1 Saturates:

The saturates (aliphatics) are non polar hydrocarbons, without double bonds, but including straight chain and branched alkanes, as well as cycloalkanes (naphtenes) (Sjoblom *et al.*, 2003). Cycloalkanes contain one or more rings, which may have several alkyl side chains. The proportion of saturates in a crude oil normally decreases with increasing molecular weight fractions, thus the saturates generally are the lightest fraction of the crude oil. Wax is a sub class of the saturates, consisting primarily of straight chain alkanes, mainly ranging from C₂₀ to C₃₀. Wax precipitates as a particulate solid at low temperatures, and is known to effect emulsion stability properties of crude oil systems (Speight, 2001; Aske, 2002).

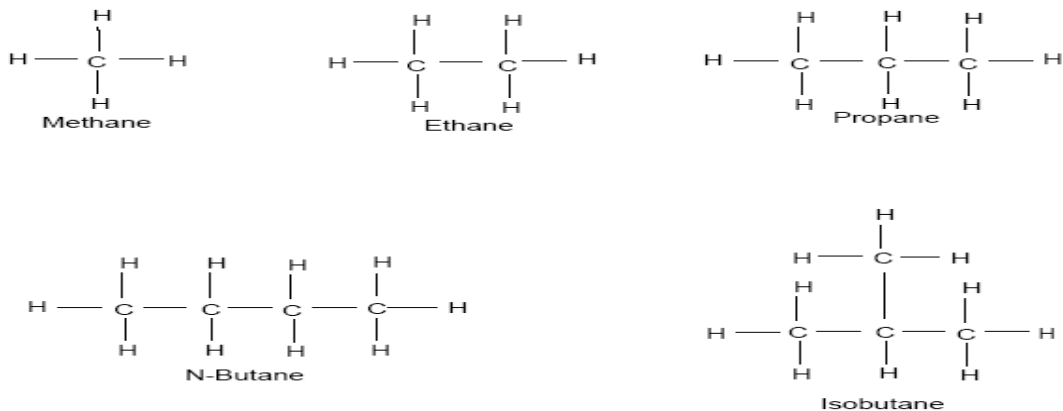


Fig. 1.3 Examples of Paraffins found in crude oil (Stark, 1998)

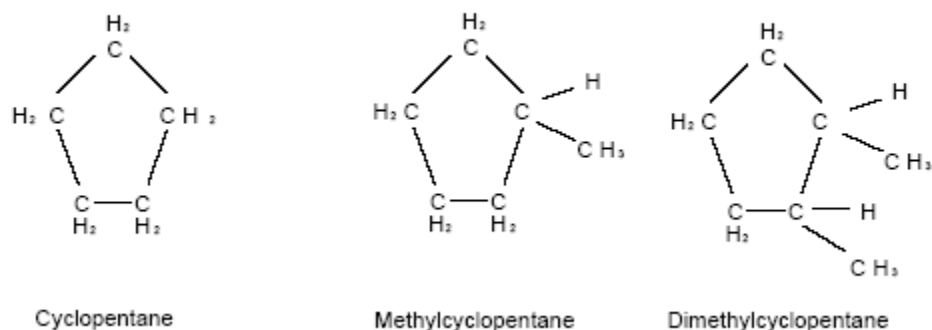


Fig. 1.4 Examples of Naphthenes found in crude oil (Stark, 1998)

1.1.3.2. Aromatics:

The term aromatics refer to benzene and its structural derivatives. Aromatics are common to all petroleum, and by far the majority of the aromatics contain alkyl chains and cycloalkane rings, along with additional aromatic rings. Aromatics are often classified as mono-, di-, and tri-aromatics depending on the number of aromatic rings present in the molecule. Polar, higher molecular weight aromatics may fall in the resin or asphaltene fraction (Speight, 2001; Aske, 2002; William, 1996).

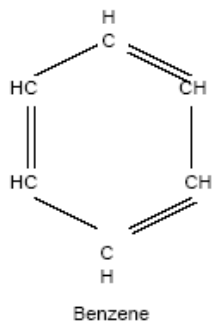


Fig. 1.5 Example of an aromatic hydrocarbon found in crude oil (Stark, 1998)

1.1.3.3 Resins:

This fraction is comprised of polar molecules often containing heteroatoms such as nitrogen, oxygen or sulfur. The resin fraction is operationally defined, and one common definition of resins is as the fraction soluble in light alkanes such as pentane and heptane, but insoluble in liquid propane. Naphthenic acids are

commonly regarded as a part of the resin fraction (Sjoblom *et al.*, 2003). Resins have a higher H/C ratio than asphaltenes, 1.2-1.7 compared to 0.9-1.2 for the asphaltenes. Resins are structurally similar to asphaltenes, but smaller in molecular weight (< 1000 g/mole) (Aske, 2002).

1.1.3.4 Asphaltenes:

The asphaltene fraction, like the resins, is defined as a solubility class, namely the fraction of the crude oil precipitating in light alkanes like pentane, hexane or heptane. This precipitate is soluble in aromatic solvents like toluene and benzene. The asphaltene fraction contains the largest percentage of heteroatoms (O, S, and N) and organometallic constituents (Ni, V, and Fe) in the crude oil. The structure of the asphaltenes has been the subject of several investigations, but is now believed to consist of polycyclic aromatic clusters, substituted with varying alkyl side chains (Sjoblom *et al.*, 2003). The molecular weight of asphaltenes molecules has been difficult to measure due to the asphaltenes tendency to self aggregate, but molecular weights in the range 500-2000 g/mole are believed to be reasonable (Aske, 2002).

The higher content of asphaltene, together with the presence of sulfur and metals, makes oil recovery difficult both by affecting the rheological properties of the material from the oil well or by increasing environmental pollution hazards (Lucinda, 1992).

In addition to SARA fractions, crude oil contains Nitrogen, Sulfur and Oxygen Compounds. These are usually abbreviated as NSO compounds and sometimes referred to as asphaltics. Although present in small amounts, the N, S, and O atoms contribute greatly to the nonhydrocarbon fraction of a crude oil by their incorporation into hydrocarbon molecules. The residuum contains a high percentage of NSO compounds (William, 1996).

1.1.3.5 Nitrogen Compounds:

Most crude oils contain nitrogen; a large proportion of it occurs in the high boiling fractions and in the residuum. Examples of the nitrogen compounds present in petroleum include mono-, di-, and tri alkylpyridines, quinoline and alkyl substituted quinolines, tetrahydroquinolines and dialkylbenz[h]quinolines. Carbazole and methyl- through decyl- substituted carbazoles have also been identified. The high boiling fractions from one crude oil contained a variety of nitrogen compound types (in excess of 0.1 wt% concentrations) that included indoles, carbazoles, benzcarbazoles, pyridines, quinolines, and phenanthridines. N/O compounds such as amides, hydroxypyridines and hydroxyquinolines, as well as compounds containing two nitrogens such as azaindoles and azacarbazoles, were also found. Other molecular types including pyrroles, isoquinolines, benzoquinolines, and benzologues of acridine may be present in crude oil. Porphyrins are observed in the residuum, usually in association with metals. Certain aromatic, nitrogen compounds (e.g., pyridines and quinolines) are basic and can cause coking on acid catalysts during petroleum processing (Speight, 2001; William, 1996).

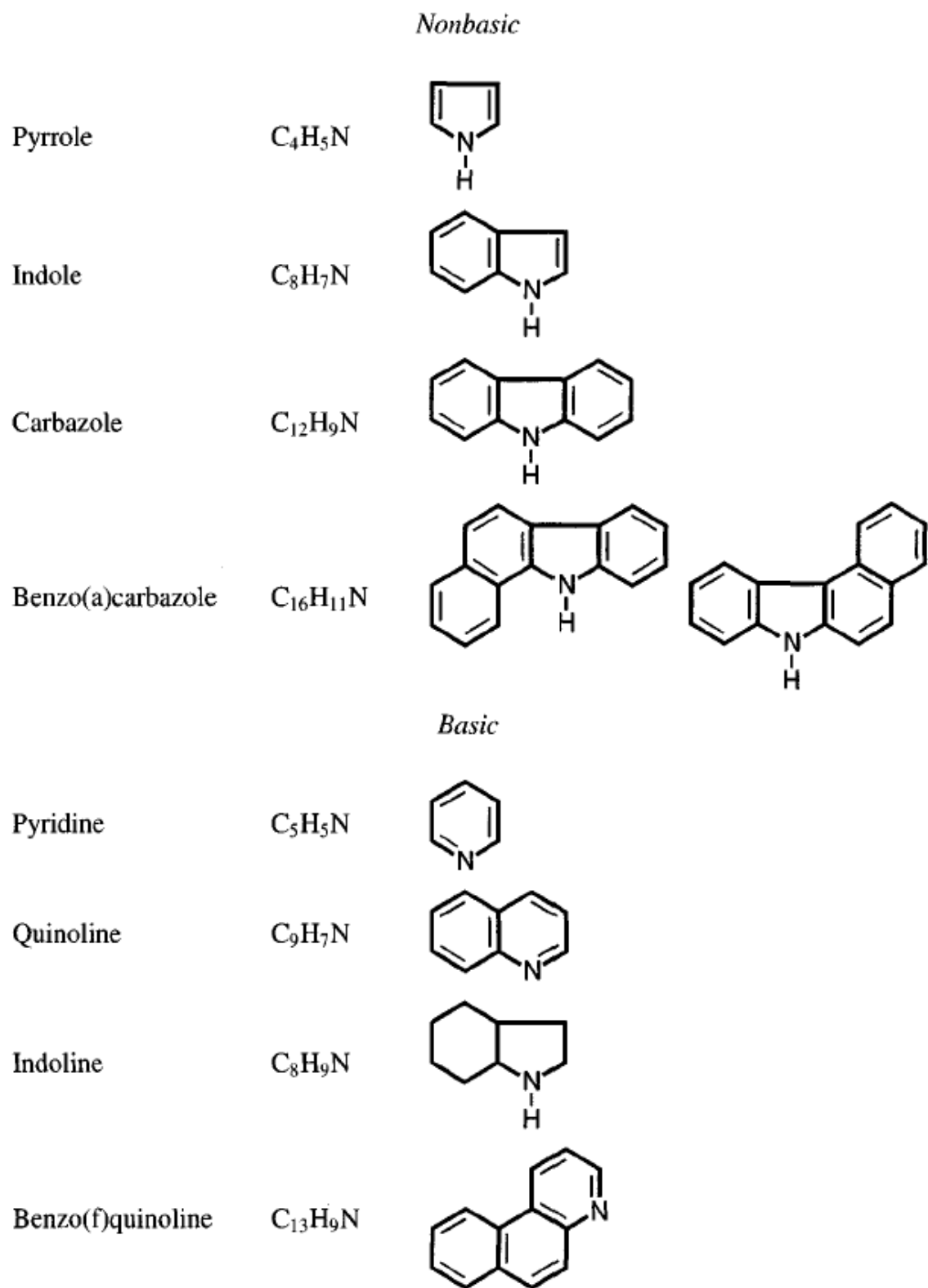


Fig. 1.6 Types and nomenclature of organic nitrogen compounds found in crude oil (Speight, 2001)

1.1.3.6 Sulfur Compounds:

All crude oils contain sulfur in one of several forms including elemental sulfur, hydrogen sulfide, and carbonyl sulfide (COS), and in aliphatic and aromatic compounds. The amount of sulfur containing compounds increases progressively with an increase in the boiling point of the fraction. A majority of these compounds have one sulfur atom per molecule, but certain aromatic and polynuclear aromatic molecules found in low concentrations in crude oil contain two and even three sulfur atoms. Identification of the individual sulfur compounds in the heavy fractions poses a considerable challenge to the analytical chemist. Alkyl thiols (mercaptans) with normal or branched alkyl groups and with the thiol group in a primary, secondary, or tertiary location have been found in petroleum, together with cycloalkyl thiols, having rings of five or six carbon atoms. Continuous chain or branched alkyl sulfides and cyclic sulfides with four or five carbon atoms in their rings have been detected. Mixed alkyl cycloalkyl sulfides have also been found. Alkyl polycyclic sulfides containing one to eight cycloparaffin rings were identified in certain crudes. Aromatic compounds of sulfur include thiophenes, their benzo- and dibenzo- derivatives, and benzonaphthothiophenes. Thioindans and alkylaryl sulfides are also present. In general, mercaptans are more malodorous than sulfides and hydrogen sulfide. The presence of significant amounts of sulfur can induce catalyst poisoning during the refining of crude oil (Speight, 2001; William, 1996).

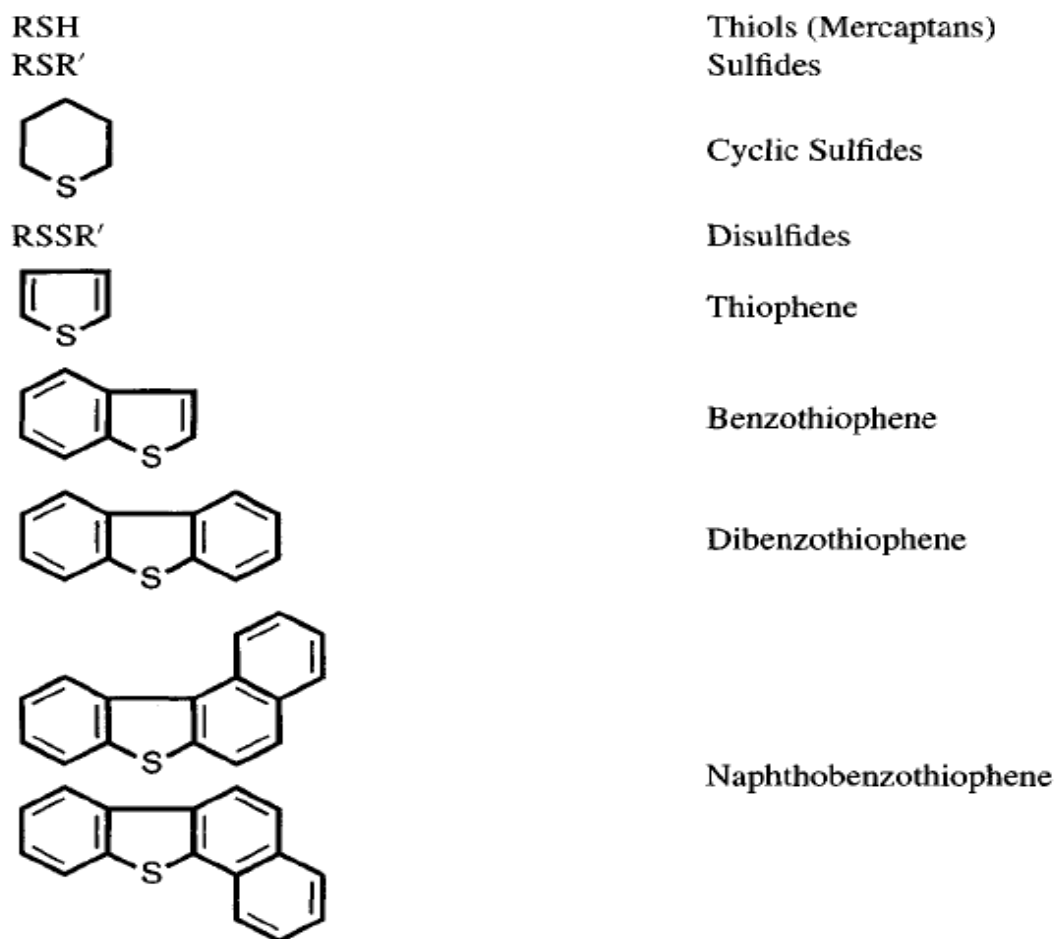


Fig. 1.7 Types and nomenclature of organic sulfur compounds found in crude oil (Speight, 2001)

1.1.3.7 Oxygen Compounds:

Most crude oils contain only small amounts of oxygen. Oxygen compounds are mainly carboxylic acids, including straight chain fatty acids, branched chain acids, naphthenic acids, and dicarboxylic acids. Other molecular types observed in the higher boiling fractions include furans and their benzo-, dibenzo-, and benzonaphtho- derivatives. Oxygen may also be present in the form of phenols, alcohols, esters, and ketones and in combination with nitrogen (Speight, 2001; William, 1996).

Alcohols	
Methyl alcohol	CH_3OH
Phenol	$\text{C}_6\text{H}_5\text{OH}$
Ethers	
Dimethyl ether	CH_3OCH_3
Diphenyl ether	$\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$
Carboxylic acids	
Acetic acid	$\text{CH}_3\text{CO}_2\text{H}$
Benzoic acid	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$
Esters	
Ethyl acetate	$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$
Ketones	
Acetone	CH_3COCH_3
Furans	
Furan	$\overline{\text{CH}=\text{CHOCH}=\text{CH}}$

Fig. 1.8 Types and nomenclature of organic oxygen compounds found in crude oil (Speight, 2001)

1.1.3.8 Metals:

The metals present in crude oils usually exist as complexes of cyclic organic molecules called porphyrins. The parent structure of the porphyrins is tetramethenetetrapyrrole ($\text{C}_{20}\text{H}_4\text{N}_4$), also known as porphin.

In a metalloporphyrin, the transition metal atom is held at the center of the porphyrin ring by coordination with the four pyrrole N atoms. Inorganic compounds of metals are probably not related to the genesis of petroleum. Nickel and vanadium are present in petroleum in concentrations of less than 1 ppb to 1000 ppm, in combined form with porphyrins. Some of the lighter metalloporphyrins are volatile, while the high molecular weight porphyrins appear in the nonvolatile residuum (William, 1996).

1.2 Oilfield Produced Water Definition and Properties:

Produced water is the water trapped in underground reservoir rocks and is brought to surface along with crude oil and gas. Besides elevated concentration of heavy metals such as barium, uranium, cadmium, chromium, strontium and lead, produced water contains dispersed oil droplets and dissolved organic compounds

and significant amount of anion such as carbonate, bromide sulfate, in some cases the water can be a useful by-product or even a salable commodity. Produced water is most often considered a waste, but the industry is beginning to consider this material as a potential profit stream (Ayad *et al.*, 2010).

1.2.1 Physical Properties of Oilfield Produced Water:

1.2.1.1 pH:

The pH is extremely important for several reasons. The solubility of CaCO_3 and iron compounds is highly depended on pH. The higher the pH, the greater the tendency for precipitation. As the pH decreases the scaling tendency of the water is decreased, but its corrosivity is increased. Most oilfield waters have a pH between 4 and 8 (Patton, 1986).

1.2.1.2 Suspended Solids:

The quantity of suspended solids which can be filtered from a given volume of water using a membrane is one basis for estimating the plugging tendency of water. Determination of the composition of the suspended solids makes it possible to ascertain their origin (corrosion products, scale particles, formation sand, etc) so that proper remedial action can be taken (Patton, 1986).

1.2.1.3. Dissolved Salts:

The total dissolved solids are simply the total amount of matter dissolved in a given volume of water. The resistance to electrical current flow is a function of the number of ions dissolved in the water. The lower the resistance the higher the concentration of ions dissolved in the water (Patton, 1986).

1.2.1.4 Turbidity:

Turbidity simply means that the water is not clear and that it contains undissolved matter such as suspended solids, dispersed oil or gas bubbles.

Turbidity indicates the possibility of formation plugging in injection operations (Patton, 1986).

1.2.1.5. Temperature:

The temperature of the water affects the scaling tendency, the pH and solubility of gases in water. The specific gravity of water is also a function of temperature (Patton, 1986).

1.2.1.6 Specific Gravity:

$$\text{Specific Gravity} = \frac{\text{Density of Water Sample}}{\text{Density of Pure Water}}$$

Density is simply weight per volume. Pure water weighs 1 g/mL thus, a specific gravity greater than 1.0 means that the water of interest is more dense, or weighs more than an equal volume of pure water. Since the waters we are interested in contain dissolved solids, they are always more dense than pure water and therefore have a specific gravity greater than 1.0. The magnitude of the specific gravity is a direct indicator of the total amount of solids dissolved in the water (Patton, 1986).

1.2.2 Chemical Composition of Oilfield Produced Water:

1.2.2.1 Cations:

***Sodium** is a major constituent in oilfield waters, and it is precipitate as NaCl from extremely salty brine.

***Calcium** ion is a major constituent of oilfield brines, and it is of major importance because it readily combines with bicarbonate, carbonate or sulfate ions and precipitates to form adherent scales or suspended solids.

***Magnesium** ions are usually present in much lower concentrations than calcium. They tend to add to CaCO₃ scaling problems by co-precipitating with the calcium ion.

*The natural **iron** content of formation waters normally is quite low and its presence is usually indicative of corrosion. The presence of precipitated iron compounds is one of the major causes of formation plugging.

***Barium** is of importance primarily because of its ability to combine with the sulfate ion to form barium sulfate, which is extremely insoluble.

***Strontium** can combine with the sulfate ion to form insoluble strontium sulfate. It is often found in scales mixed with barium sulfate (Patton, 1986).

1.2.2.2 Anions:

***Chloride** ion is nearly always the major anion in produced brines and is usually present as a major constituent in fresh waters. The major source of chloride ion is NaCl, the primary problem associated with the chloride ion is that the corrosivity of the water increases as it gets saltier.

***Sulfate** ion is a problem because of its ability to react with calcium, barium or strontium to form insoluble scales. It also serves as a food substance for sulfate reducing bacteria.

***Bicarbonate** ion can react with calcium, magnesium, iron, barium and strontium ions to form insoluble scales.

***Carbonate** ion can also react with calcium, magnesium, iron, barium and strontium ions to form insoluble scales. Carbonate ions are rarely present in produced water because the pH is usually too low.

*The presence of **sulfides** in water increases its corrosivity. Dissolved sulfides exist in water as a mixture of HS^- ions and dissolved H_2S gas. It may be present naturally in the water or it may be generated by sulfate-reducing bacteria. In addition, iron sulfide will be generated as a corrosion product, and it is a very efficient plugging agent (Patton, 1986).

1.2.2.3 Dissolved Oxygen:

Contributes significantly to the corrosivity of water. If dissolved iron is present in water, the entry of oxygen into the system can result in the precipitation of dissolved iron as insoluble iron oxide which may result in plugging. Oxygen also facilitates the growth of aerobic bacteria, the presence of bacteria may result in corrosion and/or plugging (Patton, 1986).

1.2.2.4 Dissolved Carbon Dioxide:

Influences the pH, corrosivity and CaCO₃ scaling tendency of water (Patton, 1995).

1.2.2.5 Dissolved Oil in Water:

The presence of dispersed oil in water can cause decreased injectivity in several ways, it can cause emulsion blocks in the formation. It serves as an excellent glue for certain solids, such as iron sulfide, thereby increasing their plugging efficiency. Also when produced water is disposed into surface waters, the concentration of oil in water is usually limited by government regulation (Patton, 1986).

1.3 Process of Crude Oil Production in FPF:

The FPF consists of oil treating facilities and utilities systems, and can be divided into the following major sections, Crude oil receiving system, Crude oil processing system, Crude oil storage / exporting system, Gas flare system, Produced water system, and Various utility systems.

The FPF will lower the water content (<10%) in oil prior of sending to the CPF. An inlet manifold will collect all the trunk lines from the surrounding OGMs, individual Oil Gathering Lines from the wellheads if necessary. The inlet manifold will be provided with additional production header for full capacity to keep it as standby when the normal header is used for wax cleaning. A testing facility is available at the facility to test any well directly coming to the FPF.

The crude oil coming from the OGMs or directly from the wells will be sent to the First Stage Separators through a common header where water and associated gas

are separated from the fluid by gravity separation. The oil is then heated to 105° C by Crude-Crude exchangers and Crude Oil Heaters and is sent to the Second Stage Separator(s) for final bulk water separation. The de-watered Crude Oil from the FPF will be degassed at the gas boot and then sent to the crude oil storage tanks. Booster pumps will pump the de-watered crude oil to the crude oil pipeline pumps, and is sent to the CPF for final dehydration.

De-emulsifier chemical will be added to the crude oil to enhance the water separation efficiency. A provision will be made to inject above chemical at Well site, OGM and in FPF. The evolved gases will be sent to the flare.

The produced water from First and second stage separators will be treated in the water treatment facility located in the facility.

YO-YO operation facilities (between CPF and FPF) are provided to avoid gelling of crude oil in the pipeline. This operation is envisaged during shutdown periods (PDOG, 2006).

1.4 Surfactants, General Characterization:

During the production of crude oil, water co-produced with the crude oil can coexist in reservoir with the crude oil in the so-called aquifer layer, which lies beneath the crude oil zone which may be naturally occurred or may injected as a second stage recovery to maintain the reservoir operating pressure and fluid flow profile. The water produced with the crude oil may be as a discrete phase as it flows up the well riser, but it is mixed into the crude oil at the wellhead chokes and valves where there is significant mixing, turbulence and pressure drops. The co-production of water with crude-oil can give rise to a variety of problems, such;

- The expense of pumping or transporting the water via pipeline or tanker.
- The corrosion of pipe work pumps production, equipment and downstream overhead distillation columns.
- The additional production equipment required to give export quality crude oil.

- The poisoning of downstream refinery catalysts.
- The problems associated with increased oil viscosity as a consequence of finely dispersed water within crude oil.

Thus, there are a number of commercial and operational reasons for removing the demulsified water from the crude oil. Consequently, those factors, which either enhance or reduce oil emulsion stability, are of considerable importance in the oil industry. One of the readily used methods for breaking the emulsion is chemical demulsification by surfactants.

The studies of chemical reactivity at interfaces occupy an important place in chemical sciences (Benjamin, 1996). The domain of surface science is perhaps one of the most interdisciplinary areas of modern science and technology. During the last few decades, rapid advances in the understanding of surface phenomenon have taken place. However, the importance of surface science has been recognized for more than a century. A class of compounds called surface-active compounds (or surfactants) that decrease prominently the interfacial tension or interfacial free energy of the interfaces (Preston, 1948). Surfactant molecules are amphiphilic in character, i.e., they possess hydrophilic and hydrophobic regions (Stein, 1992) having a long hydrocarbon tail and a relatively small ionic or polar head group. Amphiphiles can be ionic (cationic, anionic) zwitterionic or nonionic depending on the nature of their head groups.

The surfactants have a tendency to accumulate at the interface of immiscible fluids with a marked influence resulting in decrease in free energy which is reflected in a corresponding lowering of interfacial tension that facilitates emulsification of the immiscible fluids and hence such compounds are also known as emulsifiers. A schematic diagram of a typical surfactant is shown in Fig. 1.9.

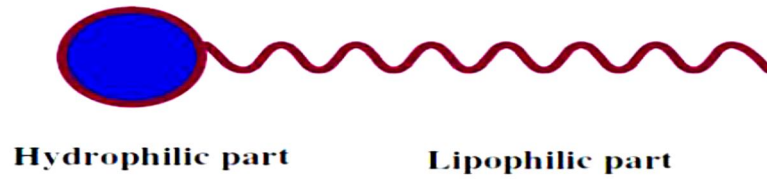


Fig. 1.9 Schematic diagram of surface-active molecule

Research on surfactants is a rapidly developing field due to their booming applications in many important practical and fundamental sciences like petroleum oil recovery, corrosion inhibition, water and environmental pollutions, understanding the mysterious role of biological membranes, biotechnology and other systems. The behavior of surfactants in solution were the subject of considerable interest because of its wide applications, in different industries, medical sciences, life sciences, analytical chemistry, pollution control and even in the fields of physics and engineering (Tahany, 2013).

1.4.1 Classification of surfactants:

Depending on the charge of head groups, the surfactants are classified as:

***Anionic:** the surface – active portion of the molecule bears a negative charge like carboxylate, sulfate, sulfonate and phosphate

*As the polar groups. $\text{RC}_6\text{H}_4\text{SO}_3^- \text{Na}^+$ (alkyl benzene sulfonate) is a common example of this class.

***Cationic:** the surface – active portion of the molecule bears a positive charge like protonated amines and quaternary ammonium based products e.g. $\text{RN}^+(\text{CH}_3)_3 \text{Cl}^-$ (quaternary ammonium chloride).

***Zwitterionic:** both negative and positive charges may be present in the surface-active portion. The positive charge is almost ammonium and the source of negative charge may vary, although carboxylate is the most common; e.g. $\text{R}^+ \text{NH}_2\text{CH}_2\text{COO}^-$ (long chain amino acid) (Tahany, 2013).

***Amphoteric surfactants:** some referred to the zwitterionic as amphoteric and this is not always correct. An amphoteric surfactant is one that, depending on pH, can be cationic, zwitterionic or anionic. Among normal organic substances, simple amino acids are well known examples of amphoteric compounds (Tahany, 2013).

***Polymeric:** these surfactants are commonly used as de-emulsifiers; such as ethoxylatedpolyalkyl phenol formaldehyde resin.

***Nonionic:** the surface – active portion of the molecule does not bear any ionic charge; e.g. $\text{RCOO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ (ethoxylated of long chain fatty acid).

1.4.2 Micelles, Micellar Structure and Properties:

In polar solvents such as water, amphiphilic surfactant monomers assemble to form a micelle in such a way that their hydrocarbon tails huddle in the core of the micelle, and the polar head groups project outwards into the polar bulk solution and locate at the micelle-water interface such that the hydrophobic tails are shielded from water. Micelles often drawn as static structures of spherical aggregates of oriented surfactant molecules. However, micelles are in dynamic equilibrium with surfactant monomers in the bulk, which are frequently being exchanged with the surfactant molecule in the micelles. The equilibrium between monomer and aggregate is established within a few milliseconds. At equilibrium, the number of micelles disintegrated in the same time. In addition, the micelles themselves have the property of constantly disintegrating and reforming. The surface layer of a micelle resembles a concentrated electrolyte solution with a dielectric constant lower than that of the bulk water. The micellar phase is less polar than water and the ionic micelles have polarity near to that of pure ethanol even at the stern layer (Abbott, 1992; Saha, 1994). A variety of properties like the number of monomers in a micelle, the aggregation number determines the size and geometry of the micelle and hence is an important quantity (Tahany, 2013). In aqueous solutions, the aggregation numbers for surfactants generally range

between 10 and 100. The significant meaning of the aggregation number as per the corrosion point of view comes from the fact that its value is inversely proportional to the minimum surface area per molecule. Surface polarity decreases with an increase in the aggregation number (Zacchariasse, 1981).

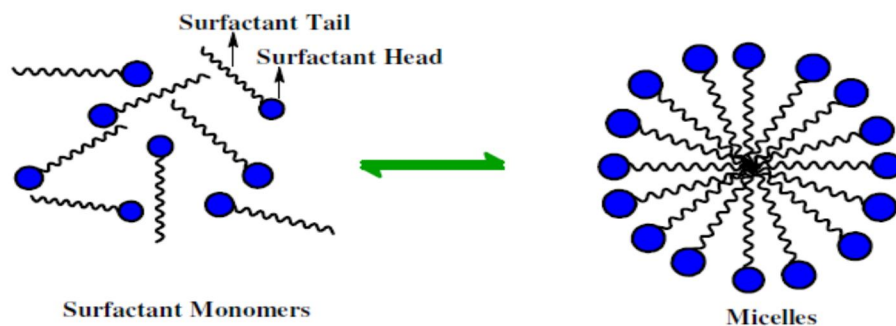


Fig. 1.10 Schematic illustration of the reversible monomer-micelle thermodynamic equilibrium

The significant physical meaning of the value of Hydrophilic-Lypophilic Balance (HLB) for the surfactant is to find out the effectiveness of the surfactant as a corrosion inhibitor or de-emulsifier. A lower value of HLB suggests that the surfactant is more oil soluble, while a high value of HLB indicates that the surfactant is more water soluble (Shinoda, 1984; Schott, 1995). Fig. 1.11 represents that, the electric charge in ionic micelles is neutralized by counter ions in the electrical double layer around it. The first layer immediately adjacent to its surface is called stern layer (Rathman, 1984). In this layer, the counter ions are adsorbed so strongly that there is no thermal agitation and they migrate simultaneously with the colloidal micelle in an electrical field. According to the most widely accepted model, head groups of surfactant molecules are also located in this layer. The rest of the double layer is called the diffuse (Gouy-Chapman) layer since the ions are diffused into the bulk solution because of the thermal motion. The core radius is about the length of the fully extended alkyl chain of the amphiphile. The core is assumed to consist of two regions, namely the inner and

outer core. The outer core contains approximately the first four methylene groups. There is also another defined region within micelles called palisade layer (mantle) which includes the head groups. Based on the Hartely model, the overall volume of a micelle is approximately twice that of the stern layer (Bunton, 1978).

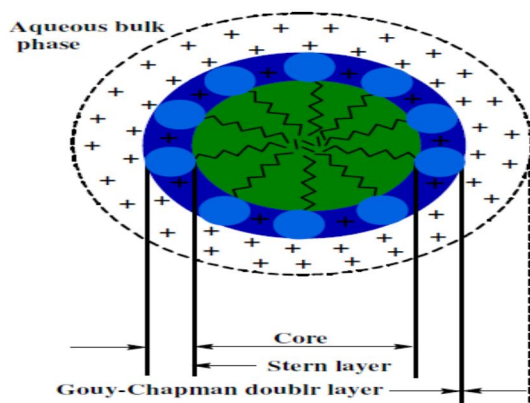


Fig. 1.11 Model of a typical ionic micelle showing the location of Head group (-) surfactant chain (\\W\\W) and counter ions (+)

The shape and size of the micelle depends on the architecture of the surfactant molecules and the charge on the head group. There are different types of aggregates of surfactants that are formed depending upon the solution concentration and the molecular structure of the surfactant molecule. These consist of spherical micelle, cylindrical micelle, bilayers, vesicles, worm like micelle, rod shaped micelle, reverse micelle (also called inverse micelle) etc. Fig. 1.12.

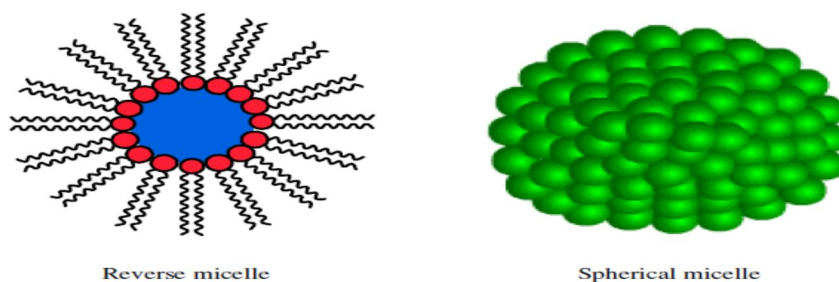


Fig. 1.12 Schematic representations of organized aggregates that may form in aqueous solution of surfactant depending on the concentration

1.4.3 Critical Micelle Concentration:

Surfactants or amphiphilic molecules contain both hydrophilic and hydrophobic parts. The hydrophilic part of the molecule prefers to interact with water while the hydrophobic part is repelled from water. Surface active molecules adsorb at the air/water interface, decreasing surface tension. As the interface becomes saturated, the molecules start to form aggregates or micelles in the bulk of the liquid, with the surface tension remaining constant.

The amphiphile molecules exist in dilute solutions as individual species in the media with ideal physical and chemical properties. As the amphiphile concentration increases, these properties deviate gradually from ideality and at the concentration where aggregation of monomers into micelles occurs; an abrupt change is observed Fig. 1.13. This concentration is called the critical micelle concentration (CMC).

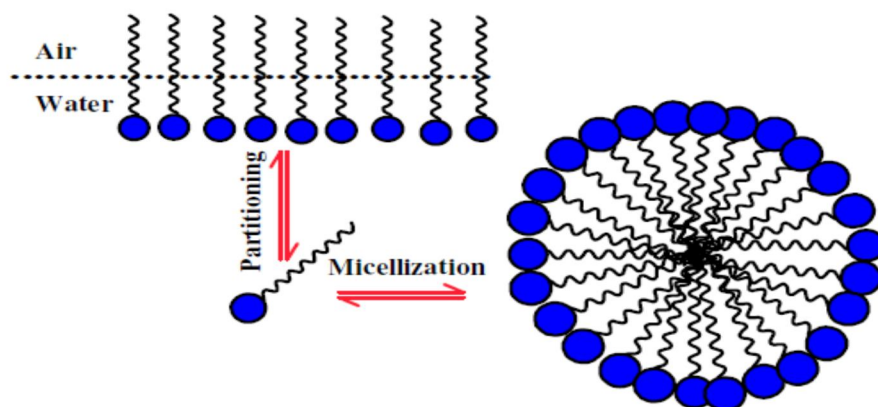


Fig. 1.13. Schematic representation of changes observed at critical micelle concentration

CMC is a key parameter for the optimization of surfactants in chemical formulations and home & beauty care products. Various factors effects the CMC values e.g., temperature, the length of the hydrocarbon tail, the nature of the counter ions and the existence of salts and organic additives; and thus amphiphile

shave characteristic CMC values under given conditions (Mandal, 1991 ; Sucheta, 1992). When micelles formation takes place, the head group repulsions are balanced by hydrophobic attractions and for ionic micelles, also by attractions between head groups and counter ions. Hydrogen bonds can also be formed between adjacent head groups (Shinitzky, 1993; Venkatesan, 1994). Nowadays, surfactants are widely used and find a very large number of applications in the petroleum industry. This is attributed to their significant capability to influence the properties of surfaces and interfaces. In this work we deal with surfactant as de-emulsifier.

1.5 Emulsion:

The co-production of water and crude oil in the form of an emulsion is highly undesirable from a process and product quality point of view.

Emulsification is the process whereby water in oil emulsions is formed (Fingas and Fieldhouse, 2003). The history of the emulsification process can start already in the reservoir where the crude oil and water are squeezed through narrow pores and the surface tension should be the driving force for spherical droplet formation. This can happen at both high pressures and temperatures. When the crude oil is processed from the well-head to the manifold, there is usually a substantial pressure reduction with a pressure gradient over chokes and valves where the mixing of oil and water can be intense. After this, the well-stream is entering the separator (usually several placed sequentially in a train), where most of the water is separated from the crude. The final treatment normally takes place in the electrocoalescer after which the level of water should be below 0.5%. The processing of oil and water offers several possibilities to vigorously mix the phases and create an emulsion (Sjoblom *et al.*, 2003).

1.5.1 Definition of Emulsion:

An emulsion is a mixture in which one liquid is uniformly distributed (usually as tiny globules) in another liquid (Kate, 1997), in other words, an emulsion is a dispersion of one immiscible liquid into another in the form of droplets, through the use of a chemical reagent that reduces the interfacial tension between the two liquids to achieve stability. Commonly this chemical reagent consists of an amphiphile molecule that contains both hydrophilic and hydrophobic groups (Canizares *et al.*, 2006). In the oil industry, oil is produced from reservoirs in association with natural formation water. This mixture in the form of oil and water emulsion (Jinxin *et al.*, 2006).

1.5.2 Types of Emulsion:

In the oilfield, the two basic types of emulsions are water in oil (w/o) or oil in water (o/w). More than 95% of the crude oil emulsions formed in the oil field are of the w/o type (Sun *et al.*, 2002; Ezzati *et al.*, 2005). An emulsion may be tight (difficult to break) or loose (easy to break).

Whether an emulsion is tight or loose depends on a number of factors, four of which are, the properties of oil and water, the amount of agitation or shear it undergoes, the percentage of oil and water found in the emulsion, and the types and amounts of emulsifying agents present (Kate, 1997; Dicharry *et al.*, 2006).

1.5.3 Stability of Emulsion:

The emulsion stability results from the presence of interfacial barrier preventing coalescence of the dispersed water droplets (Mosayebi and Abedini, 2013). The factors contributing to the stability of water in crude oil emulsions is a problem of great concern and economic importance to the oil companies in the production of oil from underground reservoirs. Several theories have been proposed to explain the effect of chemicals (emulsifying agents or surfactants), associated impurities and other variables such as viscosity of oil, specific gravity of oil, water

percentage, age of emulsion and amount of agitation (Ali and Alqam, 2000; Petroleum extension service, 1990). An oil of high viscosity requires more time for the water droplets to coalesce and settle out than does an oil of low viscosity. Heavy oil (one with high specific gravity or low API gravity) tends to keep water droplets in suspension longer than oil with low specific gravity or high API gravity. Water in oil emulsion with high water percentage tends to form less stable emulsion. Since emulsifiers are surface active, they migrate to the surface of the water droplets and begin to surround them with a skin, or film. This film becomes thicker with time and makes the emulsion more difficult to resolve. Since agitation increases the formation of small droplets, emulsions formed at high agitation, or shear rates, are more stable than those formed with less agitation (Petroleum extension service, 1990). Although the mechanism for the formation and stability of w/o emulsions has been discussed by other workers, the complex chemical nature of crude oils makes it difficult to relate the dispersion behavior to the physicochemical properties at the crude oil–water interface. Moreover, each oil well has its own characteristics and offers individual problems (Ali and Alqam, 2000).

Some compounds, like short chain fatty acids, are amphiphilic or amphipathic; they have one part that has an affinity for nonpolar media and one part that has an affinity for polar media. These molecules form oriented monolayers at interface and show surface activity (they lower the surface or interfacial tension of the medium in which they are dissolved). These compounds are termed surfactants, surface active agents, tensides, or, in the very old literature, paraffin chain salt. The term surfactant is now probably the most commonly used (Schramm, 2000). There are natural surface active fractions such as asphaltenes, resin, naphthenic acid, and porphyrin materials that can adsorb onto the interface and form a firm film at the

oil-water interface, resulting in high stability of crude oil emulsions (Sun *et al.*, 2002).

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 (Dicharry *et al.*, 2005; Langevin *et al.*, 2004). Asphaltenes are the most polar and heaviest compounds in the crude oil. They are composed of several polynuclear aromatic sheets surrounded by hydrocarbon tails, and form particles whose molar masses are included between 500 and 20,000 g. 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. 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 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 (Dicharry *et al.*, 2005).

Asphaltenes and resins have surface-active and structure-forming properties, accumulate at the interface and hence have pronounced effects on emulsion stabilization and breaking. The asphaltenes tend to form aggregates which have an adsorbed covering sheath of aromatic resins as a stabilizing layer. These proposed interactions between the resins and asphaltenes are illustrated in Fig. 1.14 (Joseph and Peter, 1997).

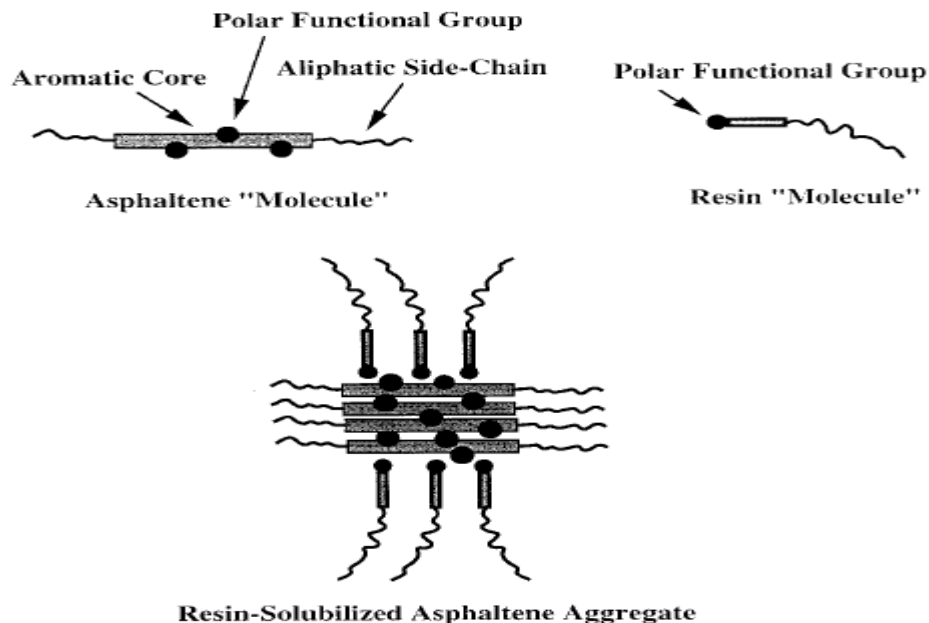


Fig. 1.14 Schematic of the proposed mechanism of interaction between resins and asphaltenes

Strong indications have been obtained that emulsions stabilized by individual asphaltene molecules, which are dissolved in the oil phase in the form of a molecular solution, are of little significance for crude oils, when compared with stabilization by colloidal dispersed asphaltenes. As a rule, asphaltenes are not soluble in the distillate part of the crude or residual oil, but they do dissolve to varying extent when associated with resins (Joseph and Peter, 1997; Fingas and Fieldhouse, 2009; Langevin *et al.*, 2004). The presence of an adsorbed layer of asphaltenes from crude oil on finely divided solids was reported to alter the wettability and other characteristics of these solids dramatically, thus enabling them to stabilize w/o emulsions (Moran and Czarnecki, 2007; Ali and Alqam, 2000; Joseph and Peter, 1997).

Recent studies show that, emulsions containing inorganic particles can be even more stable than those stabilized by asphaltenes only. Factors that have to be considered are particle-size and shape, concentration, wettability of the particles, pH and electrolyte concentration in the phase and other inter-particle interactions

(Hannisdal *et al.*, 2006). Silica particles have been studied extensively because their properties resemble those of natural inorganic colloids like clays. 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). Fine particles adsorbed at the droplet surface act as a barrier preventing droplets from coalescing (Nianxi *et al.*, 2001). This effectively 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 (Hannisdal *et al.*, 2006). Sometimes, other factors can contribute to the water in oil emulsion stability. The use of alkaline-surfactant-polymer (ASP) technique for the oil recovery from the oil bearing reservoirs shows that the ASP technique enhances the oil recovery, but some of the components in ASP form stable water in oil emulsion. Later it was found that the alkali added reacts with the acidic components (and resins and asphaltenes) in crude oil during the residence in the reservoir and form interfacially active component that accumulate at the oil-water interface and facilitates the formation of water in oil stable emulsion (Mingyuan *et al.*, 2004; Jixiang *et al.*, 2006).

In recent years an ever-increasing production of acidic crude oils with high amounts of naphthenic acids is taking place. Since the naphthenic acids and their soaps are surface/interfacially active they will accumulate at w/o interfaces where they can stabilize colloidal structures. Naphthenic acids are classified as monobasic carboxylic acids of the general formula RCOOH , where R represents a cycloaliphatic structure. The term naphthenic acid is generally used to account for all carboxylic acids present in crude oil, including acyclic and aromatic acids. These naphthenic acids show a polydispersity in size and structure. The smallest molecules are readily dissolved in the aqueous phase at pH 5, while the larger

molecules are preferably oil-soluble. Most of these homologues are dissolved in an aqueous phase at elevated pH. Crude oils with high content of naphthenic and fatty acids gave stable emulsions, and it was found that emulsions with much higher stability were observed at higher pH values for water in acidic crude emulsions. Addition of Ca^{+2} on Na^{+} ions led to destabilization of the emulsions, except in one case, where addition of Ca^{+2} at high pH gave a stabilizing effect (Trond and Johan, 2003).

1.5.4 Methods of Emulsion Breakdown (De-emulsification):

De-emulsification is defined as a process of breaking emulsions with intention to separate water from oil (Nuraini *et al.*, 2011).

There exist several techniques for enhancing the de-emulsification. The typical ones found in the literature are the addition of chemical de-emulsifier, pH adjustment, gravity or centrifugal settling, filtration, heat treatment and electrostatic de-emulsification, etc. There are advantages and disadvantages to each of these de-emulsification techniques. In processes using a chemical de-emulsifier, there are additional problems of disposing of the chemical de-emulsifier in both the aqueous phase and the recovered-oil phase. The oil phase is usually re-emulsified for the next liquid membrane process that should not contain any chemical de-emulsifier. The pH effect can sometimes be used to break oil in water emulsions, but is not effective in water in oil emulsions. Centrifugation is sometimes an efficient method for some emulsions; however, the costs to run and maintain this are fairly high. Heating has also been used in de-emulsification, but is energy-intensive. Electric field methods have been used to de-emulsify water-in-oil emulsions. It promotes an irreversible rupturing of the stabilizing emulsions and the droplets coalesce if the external field exceeds a certain critical value. However, it is ineffective for the water in oil emulsion having high water content or a swelling. It can produce a sponge phase which contains abundant internal aqueous

phase in the interface of oil and aqueous phase, so that de-emulsification efficiency is seriously affected (Sun *et al.*, 1999). The simplest method is to allow the emulsion to stand for a long time so that the water can settle out because of its greater density. This method is not always successful because the emulsions quite often do not separate even after standing a very long time. Other means must then be used to speed the process. Common methods of emulsion treating involve the use of chemicals or heat, or both. The treatment which is selected is determined by the characteristics of the emulsion and the cost of other methods (API, 1996).

1.5.4.1 Chemical Treatment:

Several theories have been proposed to explain the effect chemicals have on emulsion. One theory suggests that emulsions can be resolved by phase inversion. Thus, to break water in oil emulsion, another chemical should be added that normally produces oil in water, or reverse emulsion. By reversing the phase, complete separation can be obtained (Petroleum extension service, 1990). Another theory suggests that, chemical called de-emulsifier, weakens the emulsifying film around the water droplet in a water in oil emulsion in order to make the droplets of water merge, or coalesce. When droplets merge, they get bigger, and big, heavy water drops settle out faster than small, light once. A bottle test helps determine which chemical is the most efficient de-emulsifier for a particular emulsion. Results from a bottle test also indicate the smallest amount of the treating chemical necessary to break the quantity of emulsion being produced (Kate, 1997; Petroleum extension service, 1990).

Most de-emulsifiers used in breaking crude oil emulsion are blends of two or more de-emulsifier compounds. Those de-emulsifier types are polyglycol esters, low molecular weight resin derivatives, high molecular weight resin derivatives, sulfonates, polymerized oils and esters, alkanolamine condensates, oxyalkylated phenols, polyamine derivatives (Jinxin *et al.*, 2006), copolymers of

polyoxyethylene and polypropylene or polyester or blends of different surface-active substances (Zhiqing *et al.*, 2004). The de-emulsification ability of a de-emulsifier is mainly controlled by two factors: One is the hydrophilic–lypophilic ability. The other is the ability to destroy the interfacial film. The structure of a de-emulsifier can influence both of the above two factors. The stability of any emulsion is largely due to the nature of the formed interfacial film. The stability of this film is strongly dependent on adsorption–desorption kinetics and solubility of the surface-active fractions and its interfacial rheological properties. Rheological properties are the main characteristics of the dynamic properties of a film. There are two rheological properties of interfacial films, interfacial shear and dilational viscoelasticity. It seems that dilational viscoelastic parameters are usually much larger than the shear ones. The difference can be of several magnitudes. Interfacial dilational viscoelasticity seems to play a significant role in emulsion stability (Sun *et al.*, 2002; Dicharry *et al.*, 2006).

The de-emulsifiers molecules were adsorbed gradually on oil-water interfacial film and replaced the emulsifiers. That replacement decreased both the strength and the life of oil film and film thickness until it collapsed (Wanli *et al.*, 2006). Dendrimers are defined as macromolecules containing highly branched and dimensional structures with a large number of reactive terminal groups Fig. 1.15. Many amphiphilic dendrimer copolymers were synthesized, and it was found that dendrimer molecules consist of hydrophilic and hydrophobic groups, and at an interface, hydrophilic groups will orient toward the polar phase whereas hydrophobic groups will orient toward the oleic phase. The hydrophilic groups caught the water drops like an anchor. It appears that the modifications at the water/oil interface caused by the addition of copolymers govern the overall de-emulsification process. Such modification at the water/oil interface will result in a

sudden reduction in binding forces between water and crude oil (Zhiqing *et al.*, 2005).

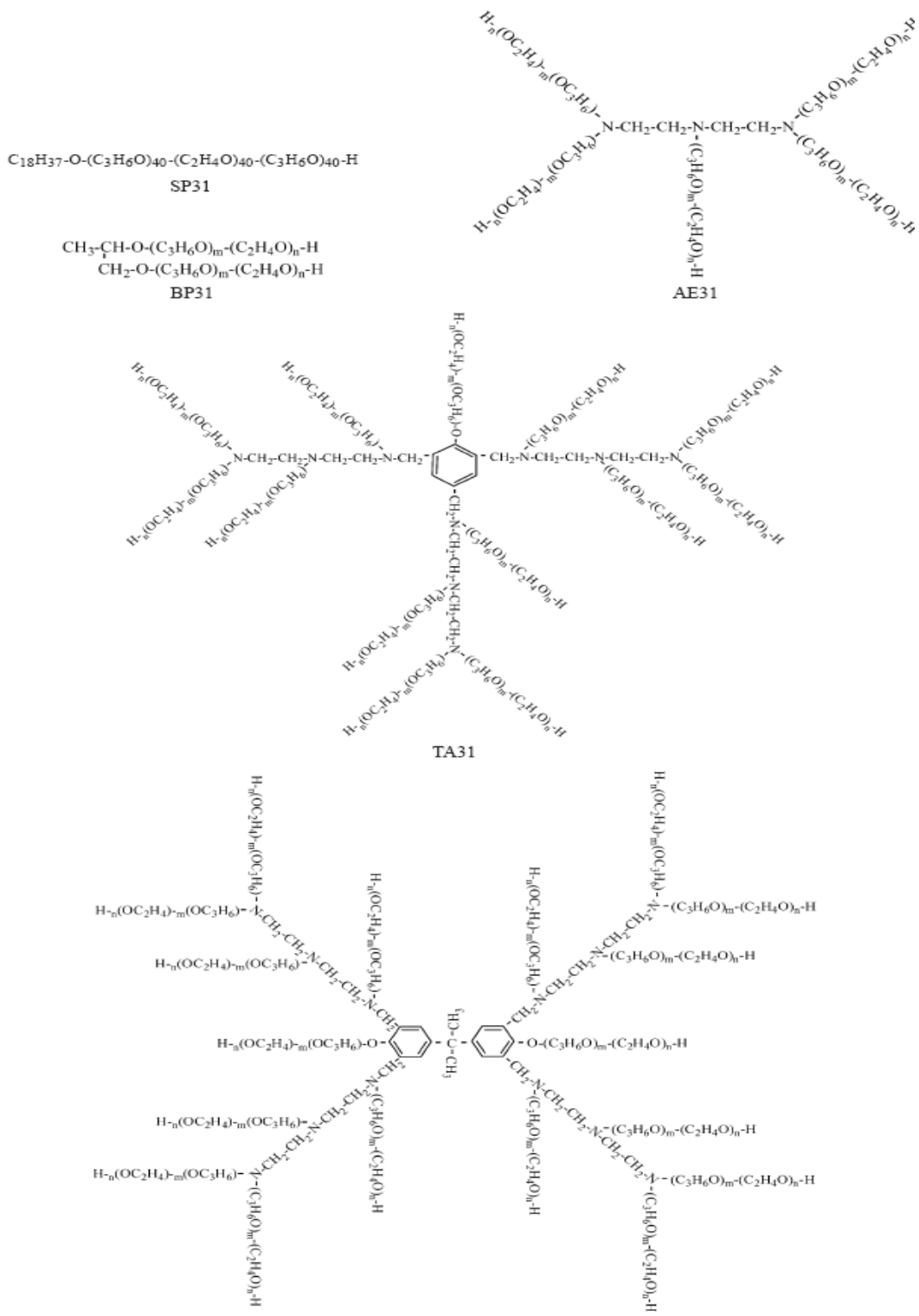


Fig. 1.15 Molecular structures of some dendrimer block copolymers

Amphiphilic block copolymers, which contain hydrophilic poly ethylene oxide (PEO) and hydrophobic poly propylene oxide (PPO) blocks, are commercially available and widely used as de-emulsifiers. These de-emulsifiers are surface-active agents and develop high surface pressures at crude oil/water interfaces. This results in replacement of rigid films of natural crude oil surfactants by a film which is conducive to coalescence of water droplets. The efficiency with which a surfactant acts as a de-emulsifier depends on many factors related to the structure of the surfactant. Such factors include the distribution of the de-emulsifier throughout the bulk volume of the emulsion, the partitioning of the de-emulsifier between the phases, and the temperature, pH, and salt content of the aqueous phase. Other factors of importance are the mode of injection of the de-emulsifier, the concentration of the de-emulsifier, the type of solvent carrier, the amount of water in the emulsion, and the age of the emulsion (Zhiqing *et al.*, 2005).

(Al-Sabagh *et al.*, 2011) synthesized nine types of de-emulsifiers based on bisphenol (bisphenol A (BA), bisphenol AC (BAC) and bisphenol (CH(BCH) having different ethylene oxide units ($n = 27, 34, 45$) namely; E (x + y) (where E represents BA, BCH or BAC and (x + y) represents the ethylene oxide units (27, 34, 45). The efficiency of these de-emulsifiers was tested on water-in-oil emulsion (w/o) at different concentrations (100, 200 and 300 ppm), 7.4% asphaltene content and 30%, 50% and 70% water content. From the obtained data, the best de-emulsifier was E(34)BA, which shows 100% de-emulsification after 58 min at 30% water content and 300 ppm of de-emulsifier.

1.5.4.2 Heat Treatment:

When an emulsion is heated, it becomes less viscous, and the water and oil molecules move about rapidly, causing the water droplets to strike each other. When the force and frequency of the collision are great enough, the film of emulsifier that surrounded each droplet breaks, and the water drops merge and

separate from the oil. Heat alone may not cause an emulsion to break down. Usually the application of heat is an auxiliary process to speed up separation. If possible, the treating process uses little or no heat because heat allows valuable lighter hydrocarbons to boil off from the oil (Kate, 1997; Petroleum extension service, 1990).

1.5.4.3 Treatment with Electricity:

Electricity is also used to treat emulsions, usually in conjunction with heat and chemicals. The film around the water droplets formed by the emulsifier is composed of molecules that have a positive and a negative end, very much like a bar magnet. When an electric current disturbs this film of polar molecules, the molecules rearrange themselves. The film is no longer stable, and adjacent water droplets coalesce freely until large drops form and settle out by gravity (Kate, 1997; Petroleum extension service, 1990).

1.6 Mechanism of De-emulsification:

It is an unfortunate fact that there exists no single coherent theory regarding the mechanism of de-emulsification. De-emulsification is believed to be accompanied by inversion followed by coagulation. It is important to note that the coagulation of the disperse phase occurs as two-stage process, flocculation and coalescence. In the second stage, termed coalescence, each aggregate combines to form a single drop. This is an irreversible process, leading to a decrease in the number of water droplets and finally to complete de-emulsification (Kim, 1995).

1.6.1 Flocculation:

The first stage, flocculation, the droplets of the dispersed phase form aggregates in which the drops have not entirely lost their identity; such aggregation is often reversible. This aggregation of droplets is due to attraction by Van der Waals forces. This process involves, in some sense, overcoming of the repulsion effect of

the double layer. To enhance the flocculation process, a common practice is to use chemical de-emulsifiers that are believed to:

- *Promote the flocculation of the droplets by weakening the repulsive forces that stabilize the emulsion.

- *Enhance the drainage of the interfacial film between the flocculated droplets.

1.6.2 Coalescence

In the coalescence step each aggregate combines to form a single drop. This is an irreversible process, leading to a decrease in the number of water droplets and finally to complete de-emulsification (Young, 1996).

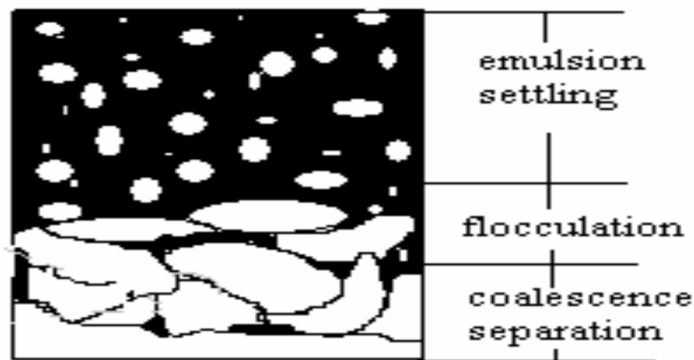


Fig. 1.16 Schematic representation of de-emulsification mechanism

(Cockbain and McRobert, 1953) have studied the rate of coalescence of individual oil drops at a water-oil interface in presence of a number of surface-active agents. The most interesting observation from this study was the fact that, for a given system, the lifetime of the droplets at the water-oil interface was not uniform, but exhibited a distribution of lifetime (Cockbain and McRobert, 1953). Subsequently, similar measurements were performed on water-oil systems in the absence of a stabilizing agent and they found that the distribution of rest times for the droplet at

the interface followed by a three-halves power dependence on the time (Tahany, 2013).

$$\ln(N/N_0) = -K(t-t_0)^{3/2}$$

Where;

K: The constant of rupture.

N: The number of stabilizing particles.

N₀: Total number of droplets examined.

t: Coalescence time.

So, when two water drops approach each other, a thin film of the continuous water phase is trapped between the drops. The behavior of the thin film determines the degree of stability (or instability) of the emulsion, and the rate of thinning determines the time required for the two drops to coalesce. When the film has thinned to a critical thickness, it ruptures, and the two drops unite into a larger drop. Examination of the cinematographic record reveals that rupture could start at different points in the interfacial film, and occasionally the film ruptured at two places simultaneously. It also suggests that, in the presence of a surface-active compound, which confers appreciable surface rigidity, the droplet may be less deformable, and the dimple is less pronounced. A possible mode of action is that the de-emulsifier replaces the natural surfactant in the expanded part of the interface formed by deformation, as two drops approaches each other. If the interfacial tension of the de-emulsifier is less than that of the natural surfactant, an interfacial tension gradient is created which enhances drainage of the intervening fluid film and leads to binary coalescence. The larger drops naturally sediment faster. If the rate of sedimentation is greater than the rate of interfacial, coalescence a dense-packed layer is formed at the disengaging interface, which may be stabilized by the presence of the de-emulsifier. The effect of de-emulsifier on the

film properties have been reported, a correlation between stability of water-in-oil emulsion and film pressure has been made. The de-emulsifiers that reduced the film pressure to greater extent were found to be most effective (Tahany, 2013).

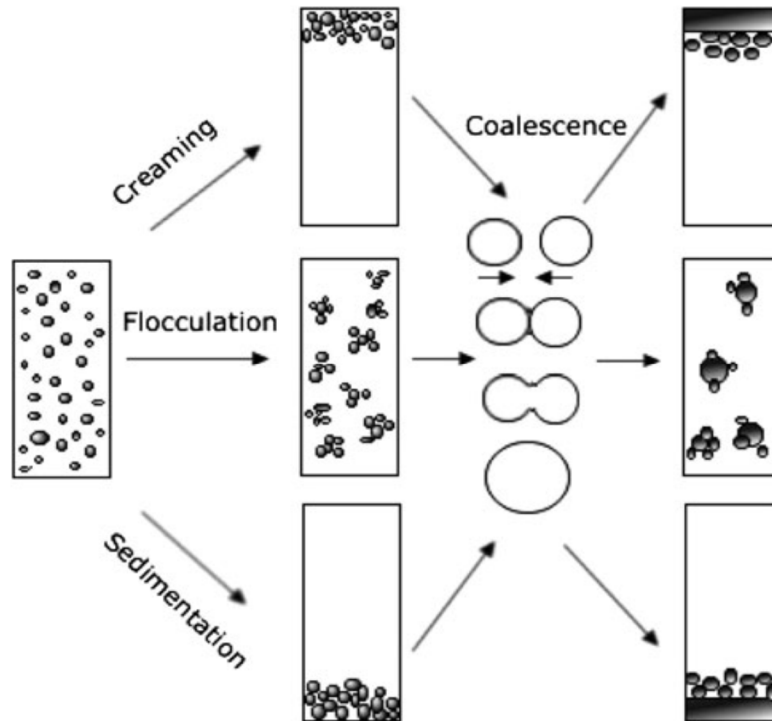


Fig. 1.17 Processes taking place in an emulsion leading to emulsion breakdown and separation

1.7 Factors influencing the De-emulsifier Efficiency:

1.7.1 Solvent:

The de-emulsifier is a viscous material and is diluted with an organic solvent. This organic solvent is seen as having a viscosity-reducing role; yet, it can also have a positive benefit to emulsion resolution if selected correctly. There is a little reason to suppose that the solvent affects the interface between the crude oil and the emulsified water droplets in an emulsion but there is strong evidence that the solvent affects the de-emulsifier molecules alone. Even if the solvents were equally soluble in the crude oil, it is possible to predict how the surface-active behavior of the de-emulsifiers can change. The highly aggregated de-emulsifier molecules will

not be as surface active as the low aggregated molecules. Xylene is more compatible with crude oil than propanol. We can therefore explain how xylene, which is more soluble in the crude oil, gives a more uniform distribution of low or unaggregated de-emulsifier molecule, which are able to adsorb readily at a crude oil-water interface. Furthermore, which is added to chemical de-emulsifiers to reduce chemical viscosity for easy handling/delivery can have a very significant effect on the final efficiency of the chemical de-emulsifier through its dispersion power in the crude oil emulsion (Tahany, 2013).

1.7.2 Hydrophilic- Lypophilic Balance (HLB):

Attempts have been made to arrive at some correlation between de-emulsifier performance and properties like molecular structure, HLB, interfacial tension, interfacial viscosity, partition coefficient, dynamic interfacial tension and relative solubility number (Sharma, 1982; Bhardwaj and Hartland, 1993). But no generalized conclusions have been arrived yet. De-emulsification still remains more of an art than science. There have been numerous attempts to formulate simple rules connecting the emulsion stability. Historically, the first one was the Bancroft's rule (Bancroft, 1913), which states that stable emulsion is formed when the surfactant is soluble in the continuous phase.

It has been found that the efficiency of the de-emulsifier may be related to HLB behavior through the de-emulsification process (Cooper, 1980).

(Shetty, *et al.*, 1992) have found that a water-soluble de-emulsifier can effectively destabilize the w/o emulsions. They studied the effects of de-emulsifiers with varying HLB's on the destabilization of water-in-oil emulsions; they concluded that a de-emulsifier could have a very good performance when it contains a high percentage of hydrophilic groups (high HLB number) (Young, 1996).

Different formulas for calculating HLB numbers are available.

For example Davis expression reads:

$$\text{HLB} = 7 + (\text{Hydrophilic group number}) - 0.475 \text{ nc}$$

Where:

nc: number of $-(\text{CH}_2)-$ groups in the lypophilic part of molecule.

HLB numbers for normal nonionic surfactants were determined by simple calculation.

A commonly used formula for nonionics:

$$\text{HLB} = 20 [\text{MH} / (\text{MH} + \text{ML})]$$

Where;

MH: molecular weight of hydrophilic portion of the molecule.

ML: molecular weight of lypophilic portion of the molecule.

For alcholethoxylates and alkyl phenol ethoxylates:

$$\text{HLB} = \text{e.o} \% / 5$$

Where; e.o, %: percent of ethylene oxide in molecules

For fatty acid esters of polyol:

$$\text{HLB} = 20 [1 - \text{Saponification number} / \text{Acid number}]$$

(Tahany, 2013).

1.8 Jatropha Curcas:

Jatropha curcas is a drought – resistant shrub/tree belonging to the family Euphorbiaceae (Merchant *et al.*, 1988; Wilson *et al.*, 2013). Cultivated in Central and South America, *Jatropha curcas* was distributed by Portuguese seafarers in Southeast Asia, India and Africa. Propagated by cuttings, is widely planted as a hedge to protect fields from browsed animals. The plant and its seeds are non edible to animal and humans; toxicity of seeds is mainly due to the presence of curcine and deterpine. The existing distribution of *Jatropha curcas* shows that introduction has been most successful in drier regions of the tropics. It grows on

well-drained soils with good aeration and is well adapted to marginal soils with low nutrient content (Merchant *et al.*, 1988; Fingas *et al.*, 1993).

Jatropha is a multipurpose plant with many attributes and considerable potential. The various parts of Jatropha plant have many useful applications. The oil extracted from the seed can be utilized as a biodiesel feed stock and in soap production. During the World War II, the Jatropha seed oil was used as a diesel substitute (Fingas *et al.*, 1993; Martin *et al.*, 2013). The leaves are used in traditional medicine against coughs or as an antiseptic (Fingas *et al.*, 1993; Aske *et al.*, 2001). It is applied locally to treat algodoncillo, lip-fire, and bad-mouth; it has been attributed abortive properties. The leaves macerated in castor oil are used in home medicine to accelerate the discharge of infected pimples. Because of its property to coagulate blood immediately, the juice flowing from the trunk (the sap) is used as a hemostatic to contain bleeding from small wounds. Apart from its coagulant effects, the latex has antibiotic properties against some bacteria; it is applied directly to wounds and cuts as antiseptic, as well as on rashes, burns, and skin infections (Khafniza, 2012).

The tree itself can be used as fire wood and as a hedge plant for protection. The latex produced from the branches can act as a haemostatic agent. The oil cake, a byproduct remaining after the extraction of oil can be used as an organic fertilizer (Fingas *et al.*, 1993). Jatropha oil is non-edible due to the presence of anti-nutritional factors such as phorbol esters, phytic acid, trypsin inhibitor and saponins [Fingas *et al.*, 1993; Azza and Ferial, 2010].

The utilization of edible food crops (com, soya, etc.) for the production of biofuels are expected to create a short supply of food for human consumption. The utilization of non-edible and renewable crops such as jatropha is expected to minimize this problem (Fingas *et al.*, 1993; Singh and Padhi, 2009). In addition to this, the increased environmental concern and the anticipated diminution of

petroleum reserves are the main reasons for the exploration of alternative non-edible crops for biodiesel production (Fingas *et al.*, 1993; Zaki *et al.*, 1996; Taylor, 1997; Anil and Stanley, 2011).

The lipid fraction of *Jatropha* oil seed were extracted and analyzed for their chemical and physical properties such as acid value, percentage free fatty acids (% FFA), iodine value, peroxide value and saponification value as well as viscosity, and density. The fatty acid and triacylglycerol (TAGs) composition of the extracted lipid was revealed using the gas chromatography (GC) and high pressure liquid chromatography (HPLC) method. Both oleic acid (44.9%) and linoleic acid (33.0%) were detected as the dominant fatty acids while palmitic acid (15.4%) and stearic acid (6.26%) were the saturated fatty acids found in the *Jatropha* oil (Fingas *et al.*, 1993; Taylor, 1997; Aske *et al.*, 2001).

Table 1.1 Chemical and Physical Properties of *Jatropha curcas* seed oil (Taylor, 1997).

Parameter	Value
% FFA as oleic acid	2.23
Iodine value	103.62
Saponification value	193.55
Peroxide value	1.93
Percentage oil content (kernel)	63.16
Density at 20° C (g/ml)	0.90317
Viscosity at room temperature (cp)	42.88
Physical state at room temperature	Liquid

Table 1.2 Fatty acid composition of *Jatropha curcas* seed oil (Fingas *et al.*, 1993).

Composition	%
Palmitic acid	15.3974
Stearic acid	6.2653
Oleic acid	44.9305
Linoleic acid	33.4068
Unsaturated Fatty Acid	75.64
Saturated Fatty Acid	24.36

1.9 Fatty Acids:

Fatty acids are carbon chains with a methyl group at one end of the molecule (designated omega, ω) and a carboxyl group at the other end. The carbon atom next to the carboxyl group is called the α carbon, and the subsequent one the β carbon. The letter n is also often used instead of the Greek ω to indicate the position of the double bond closest to the methyl end. The systematic nomenclature for fatty acids may also indicate the location of double bonds with reference to the carboxyl group (Δ) (Bhattacharyya, 1992).

1.9.1 Saturated Fatty Acids:

Saturated fatty acids are ‘filled’ (saturated) with hydrogen. Most saturated fatty acids are straight hydrocarbon chains with an even number of carbon atoms. The most common fatty acids contain 12–22 carbon atoms (Bhattacharyya, 1992).

1.9.2 Unsaturated Fatty Acids:

Monounsaturated fatty acids have one carbon–carbon double bond, which can occur in different positions. The most common monoenes have a chain length of 16–22 and a double bond with the cis configuration. This means that the hydrogen atoms on either side of the double bond are oriented in the same direction. In

polyunsaturated fatty acids (PUFAs) the first double bond may be found between the third and the fourth carbon atom from the α carbon; these are called ω -3 fatty acids. If the first double bond is between the sixth and seventh carbon atom, then they are called ω -6 fatty acids (Bhattacharyya, 1992).

1.9.3 Major Fatty Acids:

The most common saturated fatty acid in animals, plants and microorganisms is palmitic acid. Stearic acid is a major fatty acid in animals and some fungi, and a minor component in most plants. Myristic acid has a widespread occurrence, occasionally as a major component.

Shorter-chain saturated acids with 8–10 carbon atoms are found in milk and coconut triacylglycerols. Oleic acid is the most common monoenoic fatty acid in plants and animals. It is also found in microorganisms. Palmitoleic acid also occurs widely in animals, plants and microorganisms, and is a major component in some seed oils. Linoleic acid is a major fatty acid in plant lipids (Bhattacharyya, 1992).

1.9.4 Hydrolysis of Fatty Acids:

The reaction can be catalyzed by acid, base, or lipase, but it also occurs as an uncatalyzed reaction between fats and water dissolved in the fat phase at suitable temperatures and pressures. Base catalyzed hydrolysis, historically, soaps were produced by alkaline hydrolysis of oils and fats, and this process is still referred to as saponification. On a laboratory scale, alkaline hydrolysis is carried out with only a slight excess of alkali, typically 1M potassium hydroxide in 95% ethanol, refluxing for one hour, and the fatty acids recovered after acidification of the reaction mixture. This is a sufficiently mild procedure that most fatty acids, including polyunsaturates, epoxides, and cyclopropenes, are unaltered (Salimon *et al.*, 2011).

1.9.5 Esterification of Fatty Acids:

Fatty acids are converted to esters by reaction with an excess of alcohol using an acid catalyst or a lipase. For the preparation of methyl esters for GC analysis, boron trifluoride, sulfuric acid, or anhydrous hydrogen chloride in methanol are commonly used. Reaction is complete in 30 minutes at reflux. Propyl and butyl esters are prepared in a similar way with the corresponding alcohols (Earl and Tong, 2005).

1.9.6 Ester Exchange Reactions of Fatty Acids:

The fatty acid or alcohol groups present in an ester can be exchanged in a number of ways: by reaction with an excess of other fatty acids (acidolysis), alcohols (alcoholysis), or other esters (interesterification). Generally, the starting point will be a triacylglycerol, and these reactions provide routes by which the composition and properties of oils and fats can be modified.

1.10 Objectives of the Work:

In this work, a non-conventional, homologous series of de-emulsifiers derived from natural oil such as vegetable oil were synthesized to replace the conventional de-emulsifiers. These de-emulsifiers are characterized by their high tendency toward de-emulsification.

This study aimed to synthesize and characterize eighteen environmentally friendly nonionic de-emulsifiers derived from *Jatropha* non edible oil to evaluate their surface activities. In addition, using as de-emulsifier in petroleum industry for breaking water in oil emulsion.