CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Definition of Asphaltenes

Asphaltenes are usually defined as the heaviest and most polar component of crude oil that is insoluble in a light normal alkane but soluble in an aromatic solvent. Speight (1999) referred to asphaltenes as the dark brown to black friable solids that have no definite melting point and usually foam and swell on heating to leave a carbonaceous residue. The author also compiled the relevant parameters for asphaltene separation which are physical and chemical in nature including polarity, aromaticity, molecular weight, three dimensional structure of asphaltenes, solvent power of the precipitating/extracting liquid used for separation, time required to allow the precipitating /extracting liquid to penetrate the micelle, ratio of precipitating liquid to crude oil, temperature and pressure.

2.2 Composition and Structure of Asphaltenes

The ratio of hydrogen to carbon of asphaltenes usually varies over only a narrow range of 1.15±0.5 % whereas large variations occur in the proportions of the hetero elements. Oxygen content varies from 0.3 to 4.9 % and sulfur content varies from 0.3 to 10.3%. Nitrogen content of asphaltenes shows lesser degree of variation in the range of 0.6-3.3 %. From fractionation studies, on the basis of aromaticity and polarity, the more aromatic species contains higher amount of nitrogen indicating that the nitrogen species locates predominately in aromatic system (Speight, 1999).

Oxygen has been identified in carboxylic, phenolic, and ketonic location but it is not usually regarded as located in heteroaromatic ring systems. The results obtained from infrared spectroscopy show the evidence for the location of oxygen within asphaltene molecule. The band at 3,585 cm^{-1} represents the presence of free nonhydrogen-bonded phenolic hydroxyl groups while the bands at 1,680 and 1,760 cm^{-1} indicate a nonhydrogen-bonded carbonyl of ketone. The band falls within range 1,725-1,760 cm^{-1} indicating esters of polyfunctional phenols (Speight, 1999).

Sulfurs occur in the forms of benzothiophenes, dibenzothiophenes, and naphthene. Other forms occuring in asphaltene molecule are the alkyl-alkyl sulfides, alkyl-aryl sulfides, and aryl-aryl sulfides (Speight, 1999).

Even though the exact structure of asphaltenes are extremely complicated, many researchers have tried to propose the structural model by compiling all information.

Asphaltene models proposed by Speight (1999), which is compatible with the other constituents of petroleum and is able to represent the thermal chemistry and other process operations, are represented in Figure 2.1.

2.3 Stabilization of Asphaltenes in Crude Oil

The basic concept proposed by Leontarittis (1989) is that asphaltenes exist in the oil in colloidal suspension, stabilized by resins adsorbed on their surface. Since resins are highly polar, and attacked by the charged asphaltene kernels, they concentrate around the surface of the asphaltene particle forming a protective layer. Asphaltenes, together with resins, are called micelles. The destruction of micelles can occur due to the addition of flocculent paraffin like n-pentane.

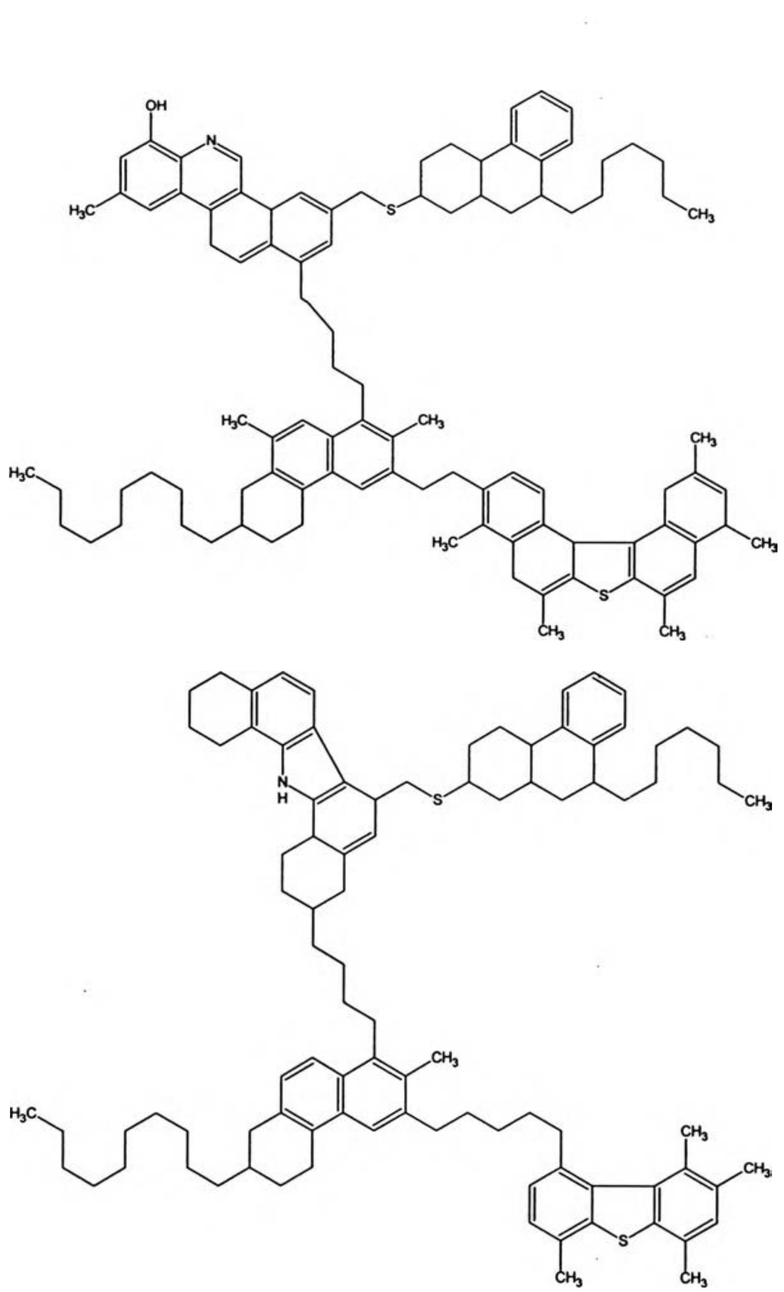

Figure 2.1 Asphaltene structures proposed by Speight (1999)

2.4 Potentiometric Titration

Dubey (1991) developed a new potentiometric titration in order to quantity the base content of crude oils, which is related to wettability. This new method is modified the method obtained from ASTM D664-81 by changing the titration solvent from the mixture of toluene, isopropanol and water to metyl isobutyl ketone (MIBK) and from alcoholic hydrochloric acid to perchloric acid in glacial acetic acid. The electrode used in this study was an Orion Sure-flow Ross combination pH electrode. A series of oils that were already known their base contents were used to test this method. In most cases, an end point was easily detected but for some crudes which did not give the detectable inflection, a known amount of quinoline in decane was added to the crude to force a good inflection. After comparing the base number obtained from spiked and unspiked titrations of oils which gave good inflections, the base numbers agree within experimental error. With this new method, comparison of base numbers for four crude oils with the old method, base numbers were at least 4.5 times those obtained previously.

The principle of potentiometric titration is to measure the potential as a function of titrant volume by using a suitable indictor electrode. The data obtained from the potentiometric titration are more reliable than data from titration using chemical indicator and are particularly useful with colored or turbid solutions in detecting the unsuspected species (Skoog,1990).

Figure 2.2 represents the apparatus for performing a manual potentiometric titration. It consists of four important units, saturated calomel electrode, indicator electrode, pH meter with mV scale and buret. The procedure of potentiometric titration begins in a large increment of titrant at the outset and in a smaller and smaller increment as the end point is approached.

Several methods can be used to determine the end point of a potentiometric titration. The most straightforward is a direct plot of potential as a function of titrant volume. The midpoint of the steeply rising portion is taken as the end point. The second approach is to plot the change in potential per unit volume of titrant as a function of average volume. The end point is the maximum point of that curve (Skoog,1990).

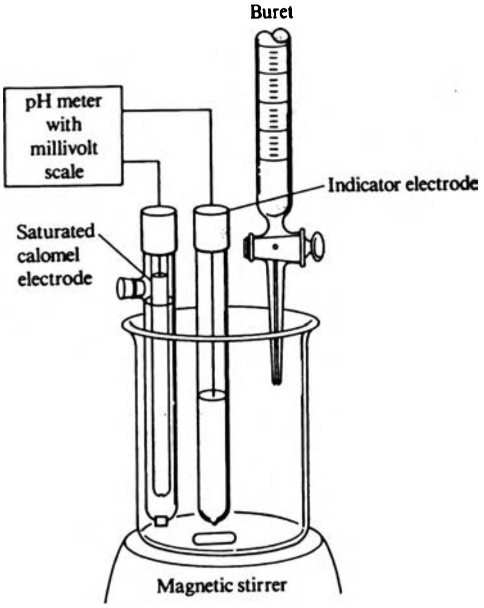

Figure 2.2 Apparatus for potentiometric titration

2.5 Dissolution Study of Asphaltenes

Chang and Fogler (1994a, 1994b) studied the stabilization of asphaltene in aliphatic solvents using alkylbenzene-derived amphiphiles. The experiment was divided into two parts. For the first part, a series of alkylbenzene-derived amphiphiles were used to study the influence of chemical structure of these amphiphiles on the effectiveness of asphaltene solubilization and the strength of asphaltene-amphiphile interaction. It was explained that there was the adsorption of amphiphiles to asphaltene surfaces and the establishment of a stable steric layer around asphaltene molecules. The results showed that increasing polarity of amphiphile's head group strengthened the attraction of amphiphiles to asphaltene through acid-base interaction resulting in increasing the effectiveness of amphiphile. Increasing the tail length of amphiphile could also increase its effectiveness by forming a steric –stabilization layer with asphaltenes. The effectiveness could be improved by adding extra polar group such as hydroxyl group and selecting the appropriated alkane solvent.

For the second part, authors studied the asphaltene-amphiphile interactions and structures using FT-IR and SAXS techniques. Two types of amphiphiles were used in this study, p-alkylphenol and p-alkylbenzene sulfonic acid. The results from FT-IR spectra confirmed that asphaltenes could from acid-base interaction with both amphiphiles. The SAXS results showed that the association of asphaltene itself and with p-nonylphenol was similar. On the other hand, the SAXS' profiles changed when adding DBSA to asphaltenes. It demonstrated the strong association between DBSA and asphaltene.

A year later, Permsukarome (1996) studied parameters affecting the kinetics of asphaltene dissolution by amphiphile/alkane solution using a differential reactor. With the first-order reaction assumption, the specific dissolution rate constant, k, varied with amphiphile concentration, types of alkane solvents, reaction temperature and fluid flow rate. The variation of k with respect to amphiphile concentration can be described by Langmuir-Hinshelwood kinetics. Increasing reaction temperature and fluid flow also enhanced the rate of asphaltene dissolution when lighter alkanes were used.

Pumpaisanchai (1997) investigated the dissolution of different polarity asphaltenes by amphiphile/alkane solution. The dissolution rate was found lower in higher polarity asphaltenes. SEM pictures showed the difference in morphology of asphaltenes. The high polarity asphatene had lower porosity than the low polarity one.

Komesvarakul (1998) correlated the chemical structure of asphaltenes with the dissolution kinetics. The most polar asphaltene by fractionation using dichloromethane and n-pentane had the most crytalline-like structure, the highest degree of aromaticity and the highest ion contents resulting in the lowest specific rate constant (min^{-1}) but the highest reaction rate constant (g/m^2-min)

In the same year, Tangtayakom (1998) characterized asphaltenes with different polarity by many techniques. The DSC results exhibited the morphology of different polarity asphaltene in the same way as obtained by Pumpaisarnkul (1998), It was concluded that the more polarity of asphaltene had the lower porosity. The lower polarity asphaltene having higher specific surface area was also observed. From the results of the dissolution study using 10wt. % DBSA/heptane in a differential reactor, it was concluded that more polarity asphaltenes were more difficult to be dissolved and sometimes could not be dissolved at a low reaction temperature. In this work, there was no difference observed from FT-IR and GPC results.

In recent work, Soontravanich (1999) studied the effects of aging time and aging temperature on the dissolution of asphaltenes when asphaltenes were aged in air at the pressure of 15 in Hg vacuum. The results showed that dissolution rate decreased with increasing aging time and/or aging temperature. The morphology of aged asphaltenes from SEM picture changed to more amorphous when aging time increased. Two reactions occurring during aging process were oxidation reaction and condensation polymerization reaction. An emergence of absorbance peak at 1,680 cm^{-1} from FT-IR spectra supported the oxidation reaction while the increase of molecular weight supported the polymerization reaction.