CHAPTER II
LITERATURE SURVEY

2.1 Chemistry of Asphaltenes

Asphaltenes are dark brown to black friable solids that have no definite melting point and usually intumesce on heating with decomposition to leave a carbonaceous residue. They are obtained from petroleum by the addition of a nonpolar solvent (such as a hydrocarbon) with a surface tension lower than that of 25 dyn/cm at 25°C (77°F). Liquids used for this purpose are low-boiling petroleum naphtha, petroleum ether, pentane, isopentane, hexane, and the like. Asphaltenes are soluble in liquids with a surface tension above 25 dyn/cm, such as pyridine, carbon disulfide, carbon tetrachloride and benzene. They are insoluble in liquefied petroleum gases, such as methane, ethane and propane; in fact, propane is used commercially in processing petroleum residues for asphaltenes and resins (Speight, 1991).

There are indications that asphaltenes consist of condensed aromatic nuclei that carry alkyl and alicyclic systems with hetero elements (i.e., nitrogen, oxygen and sulfur) scattered throughout in various, including heterocyclic, locations. Other basic generalizations have also been noted: with increasing molecular weight of the asphaltene fraction, both aromaticity and the proportion of hetero elements increase. However, many facets of asphaltene structure remain unknown. Asphaltenes from different sources have never before been compared with any degree of consistency. The nature of the source material and subtle regional variations in maturation conditions serve to differentiate one crude oil (and hence one asphaltene) from another (Speight, 1991).

2.2 Stabilization of Asphaltenes in Crude Oil

The mean by which asphaltenes remain disperse in the oil medium has been the subject of much speculation. Asphaltenes are, in fact, insoluble in the oil fraction, but it is now clear that the asphaltene dispersion is mainly attributable to the resins.

In fact, it is possible to bring about dispersion of asphaltene in their corresponding oil fractions only by addition of resins. The general indications are that the degree of aromaticity of, and the proportion of hetero elements in, the resins appear to play an important part in the ability of these materials to bring about solubility of the asphaltenes in oil (Speight, 1991).

Therefore, petroleum is a complex system with each fraction dependent upon other systems for complete mobility and solubility. It is presumed that the resins associate with the asphaltenes in the manner of an electron donor-acceptor and that there could well be several points of structural similarity between the asphaltenes and resins that would have an adverse effect on the ability of the resins to associate with asphaltenes from a different crude oil. It therefore appears that, when resins and asphaltenes are present together, hydrogen bonding may be one of the mechanisms by which resin-asphaltene interactions are achieved and resin-asphaltene interactions are preferred over asphaltene-asphaltene interactions (Speight, 1991).

2.3 Flocculation and Deposition of Asphaltenes

The tendency of asphaltenes to form aggregates should parallel their capacity for multilayer formation on a solid surface. A study of the solute-solid adsorption isotherms (SSA) of asphaltenes and resins on inorganic and organic surfaces were measured using the inorganic fraction (97% SiO_2) of the deposit that plugged the tubing of a production well as an inorganic adsorbent and various types of asphaltenes and the product (HA) of heating them were used as organic adsorbents in heptane. Saturation, multilayer formation and pore penetrations were apparent in the SSA experiments for the system of resin-heptane-asphaltenes. SSA results for the system of resin-heptane/toluene-HA were consistent with the steric stabilization theory of colloidal dispersion. Adsorption of aggregates or micelles of asphaltenes was apparent in both the organic and the inorganic substrates (Acevedo et al., 1995).

Chang and Fogler (1996) synthesized two types of oil-soluble polymers, dodecylphenolic resin and poly (octadecene maleic anhydride) and applied them to prevent asphaltenes from flocculating in heptane media through the acid-base interactions with asphaltenes. Their results indicated that these polymers could

associate with asphaltenes to either inhibit or delay the growth of asphaltene aggregates in alkane media.

Mansoori (1997) presented a comprehensive mechanism and predictive model for such compounds in oil wells. His model is based on the macromolecular theory of polydisperse polymer and colloidal solutions, kinetics of aggregation, electro kinetic transport phenomena and phase behavior of multicomponent mixtures. He presented the cause-and-effect mechanisms of such depositions and introduced mathematical models to be used for preventive measure in various cases of petroleum production, transportation and processing. With the application of his proposed model a number of predictive case studies were made. He showed that with proper planning in the production scheme, consideration of the characteristics of the producing petroleum, injection fluid, well casing and the reservoir it is possible to choose a formation-damage-free production scheme.

Flocculation points of complex systems of the crude oil type and solvent precipitant were experimentally and theoretically studied. The modeling of the flocculation points is based on the simple Scatchard-Hildebrand solubility theory in the framework of continuous thermodynamics. The crude oil is considered to consist of maltenes and asphaltenes. The composition of these two subsets is described by separate continuous distribution functions. The oil species are identified by their solubility parameters reflecting their degree of aromaticity and their content of heteroatom. Both maltenes and asphaltenes are assumed to obey Gaussian distribution functions with respect to the solubility parameter. In this way only the polydispersity with respect to the solubility parameter is taken into account (Browarzik *et al.*, 1999).

2.4 Study of Asphaltenes through Fractionation

Fractionation of asphaltenes into components of different polarities provides a way to characterize asphaltenes. Since asphaltenes are known to be composed of a variety of different functional groups and heteroatom, separation of the asphaltene sample into components of different polarities provides a methodical way to study asphaltene structure (Nalwaya *et al.*, 1999). Dissolving asphaltenes in binary solvent

of methylenechloride and pentane was carried out for a study of fractionation on Mobil crude. By increasing the ratio of pentane to methylenechloride step by step, asphaltene fractions are obtained. It is clear that the asphaltene fractions obtained at low pentane to methylenechloride ratio are less polar fraction and vice versa. The physical appearance of the most polar fraction indicates a more ordered structure relative to the least polar fraction that appears to be of a relatively amorphous nature. This method has been proved to be a powerful tool to characterize asphaltenes from various sources (Nalwaya *et al.*, 1999).

2.5 Dissolution of Asphaltenes

Aromatic solvents such as toluene and xylene have been used to dissolve asphaltene deposits because of its effectiveness, availability and low cost. As increasing the environmental concern, attempts have been done to find other solvents that are not hazardous to environment to remove asphaltene deposits.

Chang and Fogler (1994) studied the chemical structure of amphiphiles, the amphiphile-amphiphile interactions and the stability behavior of asphaltenes on asphaltene stabilization in aliphatic solvents using alkyl benzene- derived amphiphiles. The most effective amphiphile in their study was dodecylbenzenesulfonic acid (DBSA). According to the proposed model of asphaltene stabilization by resins, DBSA acts like resins in stabilizing asphaltenes. By attaching sulfonic head to asphaltenes, dodecyl group will create a steric hindrance around asphaltene molecules and prevent asphaltenes from aggregation.

Since the temperature in oil reservoir ranges between 60-150°C, asphaltene deposit at reservoir can change its physical and chemical properties over a period of time leading to higher degrees of difficulty in dissolving them. The effect of thermal aging of asphaltenes on their dissolution rates was studied using asphaltenes obtained from PDVSA-Intevep crude and an amphiphile/alkane system with 10 wt% dodecylbenzenesulfonic acid in heptane and aromatic solvent (toluene) in a differential reactor. The dissolution rate of the aged asphaltenes was found to be much slower than that of the unaged one. It was observed that the molecular weight of the asphaltenes increased with aging time and aging temperature. These results

suggested that there might be condensation polymerization taking place along with oxidation during the thermal aging process, which leads to higher degree of difficulty in the remediation of asphaltene deposition (Soontravanich *et al.*, 1999).

Kaminski and *coworkers* (2000) studied on the classification of asphaltenes via fractionation and the effect of heteroatom content on dissolution kinetics. They developed a fractionation technique that divides an asphaltene sample into different components based on polarity. They found that the morphology of the fractions varied from dense, shiny black particles that displayed a crystalline microstructure under SEM examination (the most polar fraction) to porous, dull-brown powders of a completely amorphous nature (the least polar fraction). Fractions of higher polarity displayed lower dissolution rate constants and dissolved to a lesser extent than the lower polarity fractions. They suggested that heteroatom content, especially metals such as iron, nickel, vanadium and nonmetals such as chlorine, plays a major role in determining the high polarity of asphaltenes and metal content may have a direct effect on dissolution rate.

2.6 Solubility of Asphaltenes

Mitchell and Speight (1973) studied on the solubility of asphaltenes in hydrocarbon solvents. The objective of their work was to provide more definite data about the ability of hydrocarbon solvents to dissolve Athabasca bitumen and thus provided some insight into the nature of the deasphalting process and the control of asphaltene precipitation. They noted that a prime requirement for a solvent to dissolve an oil or bitumen was an ability to penetrate the asphaltene micelle or the solvent must have a high solvent power (the solvent power is defined as ability of the solvent to dissolve asphaltenes).

Attempts to model asphaltene solubility with Scatchard-Hildebrand theory were hampered by uncertainly in molar volume and solubility parameter distribution within the asphaltenes. By considering asphaltenes as a series of polyaromatic hydrocarbons with randomly distributed associated functional groups, molar volume and solubility parameter distributions are calculated form experimental measurements of molar mass and density. Solid-liquid equilibrium calculations

based on solubility theory and the asphaltene property correlation successfully predict experimental data for both precipitation point and the amount of precipitated asphaltenes in toluene-hexane solvent mixtures (Yarranton and Masliyah, 1996).

Mannistu and *coworkers* (1997) studied on solubility modeling of asphaltenes in organic solvents. They measured and compared the solubility of Athabasca asphaltenes in a variety of organic solvents with predictions using a solid-liquid equilibrium calculation based on Scatchard-Hildebrand solubility theory with Flory-Huggins entropy of mixing. They found that both single solubility parameter and three-component solubility parameter models successfully predict asphaltene solubility in a variety of nonpolar and slightly polar organic solvents, including normal and branched alkanes, aromatics, dichloromethane, Decalin and 1-hexene. They also suggested that the single-component solubility parameter model cannot accurately predict asphaltene solubility in highly polar solvents and qualitative predictions, at best, are obtained from the three-component model.

Andersen and Speight (1999) investigated thermodynamic models for asphaltene solubility and precipitation. The main parameter in their model was the molecular weight of the asphaltene and only a few models take the aggregating nature of the asphaltenes into account. Even though the models are based on thermodynamic concepts, they remain empirical because of the number of parameters used in the calculations. When the solubility parameter is employed as the basis for the model, the calculation of asphaltene solubility cannot be calculated or estimated without extensive modification to the model. They concluded that the models employed for predictability of asphaltene precipitation are lacking in several respects and are not quantitative accurate.

2.7 Solubility Parameters

A solubility parameter is a kind of cohesion parameter, which describes the interactions between molecules in condensed materials. It could be expressed as the difference between the internal energy of the condensed material and that of an ideal gas of the same material at the same temperature. The solubility parameter as defined by Hildebrand is called the Hildebrand parameter and is defined by:

$$\delta = \left[\frac{\Delta U^{vap}}{V_m} \right]^{1/2}$$ (2.1)

where $\quad \delta \quad$ = the solubility parameter $(MPa)^{1/2}$

ΔU^{vap} = the internal energy of vaporization (J/mol)

V_m = the liquid phase molar volume (cm^3/mol)

The Hildebrand parameter was intended for non-polar, non-associating systems. To take other types of interactions like polar interactions and hydrogen bonding into consideration as well, solubility parameter with more than one component was introduced. An example is Hansen *et al.* (2000), who introduced a three-component solubility parameter to account for the dispersive forces, the polar interactions and hydrogen bonding. They divided the Hildebrand parameter into three components with the values of each component being determined empirically on the basis of a number of experimental observations:

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$ (2.2)

where $\quad \delta_t \quad$ = the total solubility parameter

δ_d = the dispersive component solubility parameter

δ_p = the polar component solubility parameter

δ_h = the hydrogen bonding component solubility parameter

The three components have been tabulated for a number of liquids and polymers and are called the Hansen parameter. δ_t is the total and should equal the Hildebrand parameter (Redelius, 2000).

2.8 Prediction of Asphaltene Molecular Weight from Solubility Data

The solubility of asphaltenes is of interest to the oil industry because asphaltenes can precipitate during oil production, reducing flow rates and fouling equipment. However, because asphaltenes are a solubility class rather than a pure compound, they are difficult to characterize (Mannistu et.al, 1997). The most prevalent thermodynamic approach to describe asphaltene solubility has been the

application of the solubility parameter or the concept of cohesion energy density (Andersen and Speight, 1999).

The solubility parameter is the square root of the cohesive energy density and represents the total molecular interaction energy, which includes dispersion, polar, and hydrogen-bonding interaction energies. A single-component solubility parameter is expected to work well when dispersion forces dominate but may not accurately represent polar solvents where polar and hydrogen-bonding forces are of significance. A two-component solubility parameter accounting for the dispersion and polar interaction energies has been evaluated previously for asphaltenes. More recently a three-component (Hansen) solubility parameter accounting for the different contributions of interaction energy was developed (Mannistu et al., 1997).

One of the fundamental difficulties encountered in describing the phase behavior of asphaltene-containing systems is the lack of suitable characterization parameters. For multi-component systems, such as petroleum, the first step in thermodynamic modeling is the lumping of similar fractions into pseudo-components in order to simplify the calculations. The less complicated the system is the easier is the use of the model. The complexity and ill-defined nature of the asphaltene fractions has, in all cases, lead to the assumption that the asphaltenes can be regarded as one single pure pseudo-component (Andersen and Speight, 1999). In both models, asphaltenes in solution are assumed to be in equilibrium with insoluble asphaltenes and the system is thus considered as a saturated system.

In modeling asphaltene solubility, the Scatchard-Hildebrand solubility theory coupled with Flory-Huggins entropy of mixing form the heart of the model. For asphaltene solubility, the solid-liquid equilibrium ratio is defined as follows:

$$K = \exp\left\{1 - \frac{v_i^l}{v_m} + \ln\left(\frac{v_i^l}{v_m}\right) + \frac{v_i^l}{RT}(\delta_i - \delta_m)^2\right\} \qquad (2.3)$$

The solvent mixture properties, v_m and δ_m are calculated using published values for the properties of the mixture components. For asphaltene properties, Yarranton and Masliyah (1996) developed the following correlations:

$$v^l = \frac{1000\,MW}{0.017\,MW + 1080} \tag{2.4}$$

and
$$\delta = \left(A\,(0.017MW + 1080)\right)^{1/2} \tag{2.5}$$

where K = Equilibrium ratio ($K = X_s/X_l$)

        v^l = Liquid phase molar volume of asphaltenes (cm^3/mol)

        v_m = Liquid phase molar volume of solvent (cm^3/mol)

        δ_i = Solubility parameter of asphaltene ($MPa^{1/2}$)

        δ_m = Solubility parameter of solvent ($MPa^{1/2}$)

        MW   = Molar mass of asphaltenes (g/mol)

        A   = The change of the heat of vaporization of asphaltenes per

            molar mass (kJ/g)

        R   = Gas constant (J/mol.K)

        T   = Temperature (K)

        X_s = Solid mole fraction of asphaltenes

        X_l = Liquid mole fraction of asphaltenes

To determine K using Hansen parameters, Equation (2.3) is modified as follows:

$$K = \exp\left\{1 - \frac{v^l}{v_m} + \ln\frac{v^l}{v_m} + \frac{v^l}{RT}\left[(\delta_{di} - \delta_{dm})^2 + b\left[(\delta_{pi} - \delta_{pm})^2 + (\delta_{hi} - \delta_{hm})^2\right]\right]\right\} \tag{2.6}$$

where δ_d = the dispersion solubility parameter ($MPa^{1/2}$)

        δ_p = the polar solubility parameter ($MPa^{1/2}$)

        δ_h = the hydrogen bonding solubility parameter ($MPa^{1/2}$)

        b = a weighting factor, with a recommend value of 0.25, (Hansen,

2000)

        i and m represent asphaltene and solvent mixture, respectively.

To approximate the asphaltene solubility parameters, it is assumed that all three are related to molar mass in the same manner as the single-component parameter given in Equation (2.5).

$$\delta_j = \left(A_j(0.017MW + 1080)\right)^{1/2}, j = d, p, h \tag{2.7}$$

$$\delta_d = \left(A_d\left(0.017MW + 1080\right)\right)^{1/2} \tag{2.7a}$$

$$\delta_p = \left(A_p\left(0.017MW + 1080\right)\right)^{1/2} \tag{2.7b}$$

$$\delta_h = \left(A_h\left(0.017MW + 1080\right)\right)^{1/2} \tag{2.7c}$$

Hence, the respective values of A can be related as follows (Mannistu et.al.,1997):

$$\psi_1 = \left(\frac{A_p}{A_d}\right) = \left(\frac{\delta_p}{\delta_d}\right)^2 \tag{2.8a}$$

$$\psi_2 = \left(\frac{A_h}{A_p}\right) = \left(\frac{\delta_h}{\delta_p}\right)^2 \tag{2.8b}$$

Recall the definition of equilibrium ratio:

$$K = \frac{X_s}{X_l} \; ; \; X_s = 1 \quad \text{(for single component of asphaltene)} \tag{2.9a}$$

$$X_l = \frac{\text{moles asphaltene}}{\text{moles toluene} + \text{moles heptane} + \text{moles asphaltene}} \tag{2.9b}$$

Basis: 1 liter of solvent mixture

$$\text{Moles of asphaltene in solvent mixture} = \frac{C_{A,s}}{MW_{asph}} \tag{2.9c}$$

Equation (2.10) is developed by combining Equations (2.9a), (2.9b), and (2.9c);

$$C_{A,s} = \frac{MW_{asph} * (\text{moles toluene} + \text{moles heptane})}{(K - 1)} \tag{2.10}$$

where $C_{A,s}$ = solubility of asphaltene in solvent mixture (g/l)