CHAPTER II
LITERATURE SURVEY

2.1 Definition of Asphaltene

Asphaltenes are component of petroleum liquids defined operationally. It represents the most refractory (or the heaviest) fraction. A generally accepted definition of asphaltenes is by their solvent solubility. Asphaltenes are the fraction that is insoluble in n-alkane (heptane or pentane) but soluble in toluene (Sheu and Mullins, 1995). Asphaltenes sometimes are regarded as friable solids that have no definite melting point and usually intumesce on heating with decomposition to leave a carbonaceous residue. Theses fractions usually have the high apparent molecular weight. The asphaltic constituents of petroleum usually appear as a dark brown to black, sticky and semisolid fraction. Asphaltenes, from different sources, have different elemental composition, that includes carbon (C), hydrogen (H), nitrogen (N) and some of heteroatoms such as oxygen (O), sulfur (S) and heavy metals (i.e. nickel, vanadium) (Speight, 1991). The structure of asphaltene consists of condense aromatic nuclei that carry alkyl and alicyclic systems with hetero elements (i.e. N, O and S) scattered throughout in various position, including heterocyclic location (Yen, 1970, 1971: Koot and Speight, 1975).

2.2 Stabilization of Asphaltene in Crude Oil

Asphaltenes remain dispersed in the oil medium has been a great interested until now. Asphaltenes are, in fact, insoluble in the oil fraction (Koot and Speight, 1975), but it is now clear that the asphaltene dispersion is mainly attributed to the resins. In fact, it is possible to bring about dispersion of asphaltenes in their corresponding oil fraction only by the addition of resins. The general indications are that the degree of aromaticity of and the proportion of hetero elements in asphaltene and amount of resins appear to play an important part in the ability of these materials to bring about solubility of asphaltenes in oil (Speight, 1991).

Petroleum is a complex system with each fraction dependent upon other systems for complete mobility and solubility (Koot and Speight, 1975). It is presumed that the resins associate with the asphaltenes in the manner of the electron donor-acceptor, and that there could 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 (Speight, 1991).

A typically, physical structure of petroleum indicated that asphaltene were center of micelles formed by adsorption or even by absorption of part of the maltenes, that is, resin material, onto the surface or into the interior of a sphaltene particles. In addition, asphaltenes exist as single entities in petroleum oil but may be peptized by one or more resin molecules. 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).

Asphaltenes and resins are considered to be the polar part of crude oil and their polarity affects the stabilization and precipitation in the petroleum fluid. The dipole moment of asphaltenes and resins were measured using Onsager formulation. The results showed that asphaltenes had a higher dipole moment than resin for a given petroleum fluid. However, resins from one petroleum fluid can have a higher dipole moment than the asphaltenes from another petroleum fluid (Goual and Firoozabadi, 2002). Moreover, it has been found that resins with a high dipole moment are more effective than the resins with a low dipole moment in terms of increasing the onset point of asphaltene precipitation. Nevertheless, the addition of resins to the crude increases the amount of asphaltene precipitated (Goual and Firoozabadi, 2002).

2.3 Asphaltene Flocculation and Deposition

The comprehensive mechanism and predictive models of flocculation and deposition of asphaltenes, wax and diamondoid have been well presented. The model is based on the macromolecular theory of polydisperse polymer and colloidal solutions, kinetics of aggregation, electrokinetic transport phenomena, and phase

behavior of multi-component mixtures. Moreover, the causes, effect mechanisms of such c ompounds a re w ell e xpressed. A n umber of p redicted a pplications f rom t he model are shown that it is possible to choose a formation damage free production scheme with proper planning (Mansoori, 1997).

The Flocculation points of complex systems of the crude oil and solvent/precipitant have been investigated both experimentally and theoretically. Experimentally, the oil solution was titrated by the precipitant (n-pentane, n-hexane, n-heptane or i-octane) to determine the precipitant volume necessary for flocculation (onset point). For theoretical aspect, the model 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. Both of maltenes and asphaltenes are assumed to obey Gaussian distribution functions with respect to the solubility parameter. The difference of aromaticity and heteroatom contents, which are essential factors for flocculation, are taken into account. The experimental result suggested that increasing asphaltene content resulted in the decrease of precipitant volume needed. The comparison of the calculated and the experimental results have been found agreement reasonable (Browarzik et al., 1999).

2.4 Asphaltene Fractionation

The separation of crude oils and bitumens into two fractions, asphaltenes and maltenes, is conveniently brought about by means of low molecular weight paraffinic hydrocarbons, which an additional of more than 40 vol% of n-pentane or n-heptane in the method is generally preferred at present. Moreover, subdivision of asphaltene fraction is possible by use of, say, benzene-pentane mixtures, which is one instance appearing to fractionate the asphaltenes in the basis of increasing aromaticity whereas a use of benzene-methanol mixtures to separate the asphaltenes is not only on t he b asis o f i ncreasing a romaticity b ut a lso o n t he b asis o f h eteroatom c ontent (Speight, 1991).

Fractionation of asphaltenes into different fractions having of different polarities provides a way to characterize asphaltenes since asphaltenes are known to

be composed of different functional groups and heteroatoms. Separation of an asphaltene sample into several fractions having different polarities provides a methodical way to study asphaltene structure. Dissolving asphaltenes in the binary solvent of methylene chloride and pentane, by increasing the ratio of methylene chloride to pentane step by step, asphaltene fractions are obtained. It is clear that the asphaltene fraction obtained at a low pentane to methylene chloride ratio are less polar as compared to the one obtained at a higher ratio. The physical appearance of the most polar fraction indicates a more ordered structure relative to the least polar fraction that appears to be the 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 Study of Asphaltene through Fractionation

The different fractions (different polarity) of asphaltenes were characterized in terms of appearance using Scanning Electron Microscopy (SEM) and composition using elemental analysis and ICP 90 technique (Kaminski *et al.*, 2000). It revealed that the morphology of the fractions varied from dense, shiny black particles (the most polar fraction) to porous, dull-brown powder (the least polar fraction). The result from ICP 90 suggested that heteroatom content (especially metals such as iron, nickel, vanadium, aluminum and non metals such as chlorine) played a major role in determining the high polarity of asphaltene. Moreover, the dissolution rate of different asphaltene fractions was examined. It showed that fractions of higher polarity displayed lower dissolution rate constants and dissolved to a lesser extent than the lower polarity fractions.

Tojima and coworker (1998) developed asphaltene fractionation method in order to investigate the effect of heptane-insoluble asphaltenes on residual oil stability. The peptizability of heavy fraction of C7-asphaltene defined by the Heithaus method decreased in accordance with structural condensation of fraction. On the other hand, light C7-asphaltene was considered to influence the peptizing power. The propose of new conceptual model: light asphaltene was believed to perform as peptizing material as well as resin, and heavy asphaltene to be peptized in

oil. This model could be more effective for understanding the destabilization phenomenon of residual oil.

The aggregation behaviors of C5 and C7-asphaltenes were studied by Mohamed and Ramos (1999). The surfaces and interfacial tension of different fraction asphaltenes were measured at room temperature using the ring method and employing an automatic tensiometer. From this data, it indicated that the critical micelle concentrations (CMC) of C5-asphaltene was lower that that of C7-asphaltene which resulted in higher tendency of C5-asphaltene aggregation comparing with C7-asphlatene.

2.6 Asphaltenes Solubility

Molar mass distribution and solubility modeling of asphaltene were studied by Yarrnton and Masliyah (1996). An asphaltene solubility model was developed by using Scatchard-Hildebrand theory that was hampered by uncertainty in molar volume and solubility parameter distribution of asphaltene coupling with the Flory-Huggins term for the large molecule entropy of mixing. In order to predicting dissolution performance, a solubility model with known molar mass is required. Athabasca asphaltene density was indirectly calculated by experimental asphaltene in toluene solution densities. Moreover, the molar mass of asphaltene was evaluated from interfacial tension and vapor pressure osmometry measurements together with plasma desorption mass spectrometry. By using solid-liquid equilibrium, the predicted solubilities were successful with the experimental data for both the precipitation point and the amount of precipitated asphaltene in to toluene/hexane binary solvent.

Mannistu and coworkers (1997) studied on the solubility modeling of asphaltenes in organic solvents. In this study, Athabasca asphaltenes solubilities in various organic solvents were examined and compared with the predicted solubilities obtained from the solid-liquid equilibrium model. This model was based on the Scatchard-Hildebrand theory with Flory-Huggins entropy of mixing. The result showed that, for non-polar solvents and slightly polar solvents including normal and branched alkanes, aromatics, dichloromethane, Decalin, and 1-hexene, the

solubilities were precisely predicted from both single component and three component solubility models. However, the single component solubility model was not effective for high polar solvent whereas the three component solubility parameter model was.

Rogel (1997) studied theoretical estimation of the solubility parameter distributions of asphaltenes, resins, and oils from crude oils and related materials. For asphaltene part, the theoretical result revealed that characteristic patterns which related to the stability behavior of material depended on the origin of the fractions. Furthermore, it was found that H/C ratio strongly affected the solubility behavior while heteroatom content expressed slightly influence on the solubility parameters distributions.

2.7 Solubility Parameter and Solubility Spheroid

Asphaltenes are a solubility class rather than a pure compound, and as a result, it is difficult to characterize them (Mannistu *et.al*, 1997). The most prevalent thermodynamic approach in describing asphaltene solubility has been the application of the solubility parameter (Andersen and Speight, 1999). A single-component solubility parameter model can be used with materials that have primarily dispersive interactions. A two-component solubility parameter model accounting for the dispersion and polar interaction energies has been applied to asphaltenes. More recently a three-component (Hansen) solubility parameter model, which accounts for the different contributions of interaction energies, has been used (Mannistu et al., 1997; Barton,1983: 2000).

2.7.1 Hildebrand solubility parameters (Single component solubility parameter)

The *solubility parameter* is the square root of the cohesive energy density as expressed in Equation (2.1) representing the total molecular interaction energy, which includes the dispersion, polarity, and hydrogen-bonding interaction energies. A single-component solubility parameter is expected to work well when dispersion

forces dominate, but it may not accurately represent polar molecules whose polar and hydrogen-bonding forces are of significance.

$$\delta = (CED)^{1/2} = \left(\frac{\Delta U^{vap}}{v^l}\right)^{1/2}$$
(2.1)

Where δ =   The solubility parameter ($MPa^{0.5}$)

       CED =   The cohesion energy density (MPa)

       ΔU^{vap} =   The internal energy of vaporization (kJ/mol)

       v^l =   The liquid phase molar volume (m^3/mol)

2.7.2 <u>Hansen solubility parameters</u> (Three component solubility parameters)

The Hansen three-parameter solubility model includes the effects of polar and hydrogen bonding forces in addition to the dispersive forces. Hansen *et al.* (2000), who introduced a three component solubility parameter, divided the Hildebrand solubility parameter into three components with the value of each component representing the different molecular interaction forces: dispersion forces (δ_d), polar interactions (δ_p) and hydrogen bonding forces (δ_h). The relation between Hansen solubility parameter and the former single solubility parameter is given by Equation (2.2) (Grubenmann, 1993).

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

The Hansen solubility parameters (δ_d, δ_p, δ_h) of asphaltenes can be determined experimentally and, then, they can be used as the parameters to predict the molecular weight.

The Hansen solubility parameters of asphaltene can be estimated from experimental data (Redelius, 2000). The Hansen solubility theory defines the solubility parameter space of a material as shown in Figure 2.1.
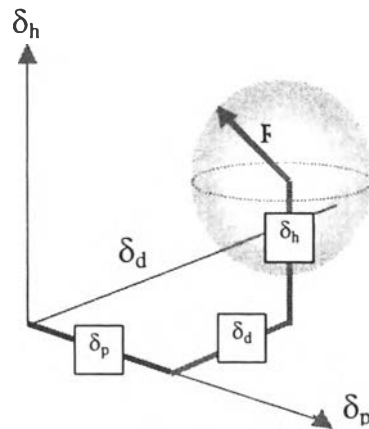
Figure 2.1 Hansen solubility space (AIC book and paper group ananual, 1984).

The solubility space divides a material into two phases. The material-soluble phase is inside the solubility space of radius R as illustrated in Figure 2.1. The external space corresponds to the material-insoluble phase. Thus, the surface of the solubility space or line separating the two phases corresponds to the point that the material just begins to flocculate and precipitate. The center point of the solubility space is the solubility parameter of the material (Hansen, 2000). From the experimental solubility curves, the flocculation points or the points that lay on the surface of the solubility space are defined as insoluble concentrations of material in the solvent.

Moreover, the solubility parameters can be determined by molar attraction constant, which are calculated by using group contribution method (Krevelen, 1976). The molar attraction constant is defined as the combination of cohesion energy and molar volume as showed in Equation (2.4). It is a useful additive quantity for low-molecular as well as for high-molecular substances. Since the molar attraction constant in dispersive component has a liner relationship with the molecular weight, it can be also predicted using molecular weight. From the definition of molar attraction constant, the dispersive solubility parameter is related to the solubility parameter as expressed in Equation (2.3) (Krevelen, 1976).

$$\delta_d = \frac{F_{d,i}}{V} \qquad (2.3)$$

$$F = \sqrt{E_{coh}V(298)} \qquad (2.4)$$

where Φ_{δ_I} =   Dispersive molar attraction constant

$E_{\chi o \eta}$ =   Cohesion energy

δ_δ =   Dispersive solubility parameter

ϖ =   Molar volume

In 1986, Shareef and coworkers determined the partial solubility parameters (Hansen solubility parameter) of inorganic pigments using the solubility data of the pigments in numerous solvents. By using a computer aided program and the characterization of spherical volume, the center p oint (solubility parameters of the pigment) and the radius of pigment solubility spheroid were calculated.

2.8 Prediction of Molecular Weight of Asphaltene using Solubility Model

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, the first step in thermodynamic modeling is the lumping of similar fractions into pseudo-components in order to simplify the calculations. The less complicated system, the easier it is to use the model. The complexity and ill-defined nature of the asphaltene fractions has, in all cases, led to the assumption that the asphaltene can be regarded as one, single, pure pseudo-component (Andersen and Speight, 1999). In both single and three-component solubility parameter models, asphaltenes in solution are assumed to be in equilibrium with their solid counterpoint, and they are 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 (Hansen, 2000):

$$K = \exp\left\{1 - \frac{v_i^l}{v_m} + \ln\left(\frac{v_i^l}{v_m}\right) + \frac{v_i^l}{RT}(\delta_i - \delta_m)^2\right\} \qquad (2.5)$$

where i denote as asphaltene

          m denote as solvent mixture

          K = Equilibrium ratio (K =X_s/X_l)

          X_s =   Solid mole fraction of asphaltene

          X_l =   Liquid mole fraction of asphaltene

          δ = Solubility parameter (MPa$^{0.5}$) = $(\Delta U_{vap}/v)^{0.5}$

    $\Delta Y_{\varpi\alpha\pi}$ =   Internal energy of vaporization (kJ/mol)

          δ_i = $\left(\Delta U^{vap}/v\right)^{0.5}$ = $(\rho A)^{0.5}$ = 22.49 MPa$^{0.5}$

          A = Slope of plot between the heat of vaporization and molecular weight of aromatic hydrocarbon (kJ/g)

                = $\Delta U^{vap}/MW$

          ρ = Density of asphaltene (kg/m^3)

          v = Liquid phase molar volume (m^3/mol) = MW/ρ

                = Molecular weight/Density

          R = Gas constant (J/mol*K) =   8.314   J/mol*K

          T = Temperature (K) = 298 K

To determine K using the (Hansen) three-component solubility parameters, Equation (2.5) is modified as follows:

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

Where δ_d = the dispersion solubility parameter (MPa$^{0.5}$)

              δ_p = the polar solubility parameter (MPa$^{0.5}$)

              δ_h = the hydrogen bonding solubility parameter (MPa$^{0.5}$)

δ_t = the total solubility parameter corresponding to the Hildebrand solubility parameter (MPa$^{0.5}$)

= $\left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5}$

b = a weighting factor, with the recommended value of 0.25 (Barton, 1983 and 2000 and Hansen, 2000)

For single component of solid asphaltene, $X_s = 1$.

Then,
$$K = \frac{1}{X_l} \qquad (2.7)$$

Where

$$X_l = \frac{\text{moles asphaltene}}{\text{moles toluene} + \text{moles heptane} + \text{moles asphaltene}} \qquad (2.8)$$

One cubic meter of the solvent mixture is taken as a basis of calculation.

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

Where $C_{A,s}$ = the solubility of asphaltene in solvent mixture (g/dm^3)

Combining Equations (2.5), (2.6), and (2.9), the solubility (g/dm^3) of asphaltene in toluene/heptane solution is:

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

where V_{total} = the total volume of solution (basis 1 m^3)

To predict the molecular weight of asphaltene, the solubility of asphaltene is measured as a function of the composition of toluene/heptane solution. The solubility parameter is determined from the heat of vaporization per unit mass (A) and density (ρ); δ_i = 22.49 MPa$^{0.5}$ for the single component parameter and from solubility spheroid center for the three component parameter model. Equations (2.5) and (2.6) are used to calculate the equilibrium ratio for single component parameter model and three component parameter model, respectively. Knowing equilibrium ratio (K) and solubility of asphaltene ($C_{A,s}$) from experimental solubility data, the molecular weight of asphaltene at certain percent solvent mixture can be determined from Equation (2.10) using analytical solving program (Maple 8).

Basically, asphaltenes are defined by solubility class that can be separated from the petroleum. Since petroleum is considered to be a continuum compounds, its properties cannot be indicated as a specific point (Speight et. al., 1981). The properties of asphaltene were always reported in terms of average value range like the predicted molecular weight in this work.