

CHAPTER II LITERATURE SURVEY

2.1 General Definition of Asphaltenes

The asphaltenes usually appear as dark brown to black friable solids and have no definite melting point. Generally, the highest molecular weight, the most highly polar fraction is often referred to asphaltene which is, by definition, a solubility class that is precipitated from petroleum by the addition of an excess of the liquid hydrocarbon. The asphaltenes, viewed structurally, contain condensed polynuclear aromatic ring systems bearing alkyl side chains having molecular weights ranging from several hundred to several thousand. These molecules normally contain significant quantities of oxygen, nitrogen, and sulfur. The asphaltic materials are generally thought to be colloiddally dispersed in solution (Schechter, 1992). In aromatic solvents, asphaltenes can form micelle-like aggregates above a certain concentration of asphaltenes, the critical micelle concentration (CMC).

2.2 Asphaltene Flocculation and Deposition

In general, asphaltene flocculation depends on the thermodynamics of the system, for example, temperature, pressure and composition. The secondary oil recovery during oil production can cause the flocculation due to the composition changes. Empirical observations indicate that the resins play an important role in stabilizing asphaltenes in crude oil and under unfavorable solvent conditions, the asphaltene species are prone to further aggregation clusters that are unstable and precipitate from crude oil (Scharbron and Speight, 1998).

When asphaltenes are precipitated from crude oil or sediment extract using n-pentane, there is a tendency for non-asphaltic, n-pentane-soluble material to be co-precipitated. The results from Py-GC/MS and ^{13}C -NMR showed that the n-pentane – soluble materials which co-precipitate with the asphaltenes from the crude oil, consisted mainly of compounds with structural similarities to asphaltenes and resins (Myhr *et al.*, 1990).

A novel method for determination of the onset of asphaltene flocculation is developed (Escobedo and Mansoori, 1993). Due to the fact that viscosity of suspensions are affected by aggregation of suspended particles, viscosities of oil solvent mixtures are used as the criteria for the determination of onset of asphaltenes. A marked deviation in viscosity was observed at the onset of asphaltene flocculation.

Asphaltene solutions in toluene/heptane mixtures are a popular system for investigating the stability and the precipitation process of asphaltenes. At a certain threshold value of the ratio heptane/toluene, the asphaltene solution becomes unstable and asphaltene particles start to aggregate. The threshold amount of toluene/heptane mixtures needed for asphaltene aggregation was found to depend on the original and concentration of the asphaltene, and varied from 45 to 55% volume (Yudin *et al.*, 1998b).

Flocculation points of complex system of the type of crude oil, solvent and precipitant were experimentally and theoretically studied. The modeling of the flocculation point is based on the simple Scatchard-Hildebrand solubility theory in the framework of continuous thermodynamics. In this, the crude oil is assumed to consist of maltenes and asphaltenes describing the polydispersity by Gaussian distributions. However, the use of the Scatchard-Hildebrand solubility parameter the model is restricted to non-polar solvents and precipitants (Browarzik *et al.*, 1999).

2.3 Asphaltene Dissolution and Stability

Kaminski and co-workers (2000) studied the characterization of asphaltenes via fractionation and the effect of heteroatom contents on dissolution kinetics. A fractionation technique that divides an asphaltene sample into different polar components showed various morphology of each fraction. The most polar fraction was dense and shiny black particles that displays a crystalline microstructure under SEM examination. On the other hand, the least polar fraction was porous and dull-brown powder of completely amorphous nature. Extensive studies using gel permeation chromatography, FTIR spectroscopy, and elemental analysis revealed no apparent structural differences between various fractions. However, substantially different dissolution characteristics were displayed by the fractions in a differential reactor. Fractions of higher polarity displayed lower dissolution rates and dissolved to a less extent than the lower polar fractions. Further analysis of the fractions using ICP-90 suggests that the heteroatom content played a major role in determining the high polarity of asphaltenes.

Tojima and co-workers (1998) developed an asphaltene fractionation method in order to investigate the effect of heptane insoluble asphaltene (C-7 asphaltene) on residual oil stability. C-7 asphaltene was separated into heavy and light fractions using a binary solvent system of toluene and heptane. It was found that the heavy fraction of C-7 asphaltene extracted by this method consisted of highly condensed polynuclear aromatics. On the other hand, light fraction of C-7 asphaltene was considered to influence the peptizing power. They proposed a new conceptual model : light asphaltenes would perform as peptizing material as well as resin, and heavy asphaltene would be peptized in oil.

Lian *et al.* (1994) reported that the nature of resin served as a good peptizing agent (interfacial agent) since the polar fractions of resin also

contain surfactants (amphiphiles). Due to this peptizing function, resins can be applied to enhance oil recovery. It was found that aromatic hydrocarbons were good dispersed mediums for peptization test. The partial precipitation of asphaltenes in a fixed amount of aromatic hydrocarbon system (such as toluene), with gradual additions of paraffinic hydrocarbon (such as pentane), in the presence of various surfactants was studied. These surfactants affected the asphaltene precipitation, either by acceleration or by retardation, depending on the structures, types and quantities of the surfactants.

It is common practice to determine the solubility of asphaltene deposits from experiments in which a fixed mass of asphaltene is placed in contact with a fixed volume of solvent. The solubility of asphaltene is calculated from the amount of sample dissolved in the volume of solvent used. Implicitly, this method assumes that the asphaltene sample is uniform with respect to its solubility.

Aromatic solvents such as toluene and xylene are normally used in the petroleum industry to remove asphaltene deposits. The effectiveness of such solvent treatment depends strongly on both the chemical characteristics of the solvent and on the specific nature of the petroleum deposits.

2.4 Asphaltene Solubility

The most prevalent thermodynamic approach to describe asphaltene solubility has been applied to the solubility parameter or the concept of cohesion energy density. The application of solubility parameter data to correlate asphaltene precipitation, and hence asphaltene – solvent interaction, has been used on prior occasions (Mitchell and Speight, 1973).

The solubility parameter, introduced by Hildebrand and Scott, is the square root of the energy of the heat of vaporization over the molar volume. The solubility parameter decreases with an increase in polarity, dipole

interaction due to aromatic ring and heteroatoms and molecular weight (Altgelt and Boduszynski, 1994).

Yarranton and Masliyah (1996) studied the asphaltene modeled solubility using a solid – liquid equilibrium calculation with K-values derived from Scatchard-Hildebrand solubility theory incorporating the Flory – Huggins entropy of mixing. The resulting multicomponent equilibrium calculation was tested on solutions of toluene and hexane. In this case, the rate of asphaltene enthalpy of vaporization changes with molar mass was one estimated parameter.

The tendency of asphaltenes to precipitate from crude oil on a variation in the solubility parameter (δ) value of the precipitating solvent mixture is more closely related to the aromaticity and polarity of the asphaltene than to their dimension. It can be concluded that molecular weight, together with aromaticity and polarity, affected asphaltene solubility in hydrocarbon media. The great difference of solubility parameters between asphaltene and solvent resulted in a phase separation. The solubility of asphaltenes decreased as the difference between the asphaltenes and solvent solubility parameters increased. Both polarity and molecular weight of asphaltenes in a solvent define the solubility boundaries. It is also evident that as the molecular weight of a particular solute decreased, there was an increased tolerance of polarity difference between solute and solvent under miscible conditions (Anderson and Speight, 1999).

In order to assure efficient interaction between two substrates, not only must the solubility parameters of the solute and solvent be similar, but the single components contributing to solubility parameter must be similar as well.

The use of mixtures of a polar and a nonpolar solvent in order to fractionate an asphaltene sample by increasing the solubility parameter of the solvent mixture has been performed. Solubility parameters are broken into

dispersion, polar, and hydrogen bonding components. This approach will tend to direct the fractionation by introducing polar force and hydrogen bonding, as well dispersion forces, as factors determining which component of the asphaltene sample are soluble in the mixture (Mannistu *et al.*,1997).

2.5 Asphaltene Molecular Weight and Aggregation

Molecular structure of asphaltenes varies significantly depending on their original, method of recovery, and history of extraction. Numerous attempts to find correlations between extensive data on asphaltene structure and their colloid properties were not successful.

The apparent molecular weights of asphaltenes span a wide range from a few hundred to several million leading to the speculation about asphaltene self-association. The tendency of the asphaltenes to form aggregates in hydrocarbon solution is one of their most characteristic features resulting in complicating the determination of asphaltene molecular weight. Scharbron and Speight (1998) found that the molecular weights measured by means of vapor pressure osmometry (VOP) or size exclusion chromatography (SEC) were significantly influenced by the condition of the analysis (temperature, asphaltene concentration, and solvent polarity).

Molecular weight measurements can be applied in monitoring aggregate size and extension of association of asphaltene components. However, it was evident from the previous work that small molecules were dissolved before large molecules, leading to an increase in weight fraction of heavy molecules in the insolubles (Andersen, 1994). The simultaneous increases in heteroatom content and molecular weight on the insolubles will lead to an increase in polarity and hence the observed increased association of molecules. These molecules should also be expected to be the least soluble asphaltene constituents due to the higher molecular weight and polarity, which

also leads to an increased melting point compared to compounds of similar molecular weight.

Yudin and coworkers (1998a) studied the kinetics of asphaltene aggregation in toluene/n-heptane mixtures with a dynamics light scattering. Two types of aggregation kinetics have been observed: diffusion-limited aggregation and reaction-limited aggregation. At the asphaltene concentrations in toluene below the critical micelle concentration of about 3 g/l, the aggregation kinetics appeared to be solely limited by diffusion. Far above the critical micelle concentration, reaction limited aggregation took place at least in the initial stage of particle growth. At a concentration of asphaltenes in toluene above the critical micelle concentration, a crossover between these two types of aggregation kinetics was observed.

It is well recognized that asphaltenes are dispersed in the crude oil due to resins. The degree of dispersion depends on the aromaticity and the chemical composition of oil. In highly aromatic oils, asphaltenes are dispersed colloidally, but the presence of excess paraffinic hydrocarbons, they are coagulated and precipitated. These precipitated asphaltenes can be re-precipitated by the addition of aromatics. This re-precipitation of adsorbed resins is the basis of the thermodynamic colloidal model proposed earlier by Leontatits (1989) as shown in Figure 2.1

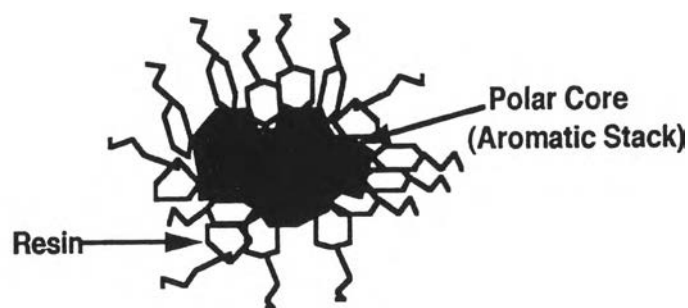


Figure 2.1 Structure of asphaltenes.

2.6 Analysis of Asphaltene Dissolution Kinetics

In order to analyze the kinetics of asphaltene dissolution, the rate of asphaltene dissolution, r_D , is assumed to be the first order with respect to the undissolved asphaltene mass as proposed in the earlier work by corresponding author (Permkukarome *et al.*, 1997):

$$-r_D = \frac{dM}{dt} = -kM \quad (2.1)$$

Integrating Equation (2.1) gives

$$\ln \frac{M}{M_0} = -kt \quad (2.2)$$

Where k is the pseudo reaction rate constant for asphaltene dissolution (min^{-1}). M_0 and M are the mass of asphaltene precipitates initially placed and that remaining undissolved at time t , respectively. The value of k can be obtained from the slope of the plot of t versus $\ln (M/M_0)$. It is important to note here that the parameter, k , represents the pseudo reaction rate constant for the mass transfer limited dissolution process. The reaction rate followed Langmuir-Hinshelwood kinetics.

In mass transfer – dominated reactions, the surface reaction is so rapid that the rate of transfer of substance from the surface to the bulk liquid phase limits the overall rate of reaction. Therefore, the concentration of asphaltenes at the surface can be assumed equal to the solubility of asphaltene in the solvent. For reaction at steady state, the mass flux of dissolved asphaltene to the bulk fluid, W_{AS} ($\text{g/cm}^2 \times \text{s}$), is equal to the rate of disappearance of asphaltene on the surface $-r_A''$ ($\text{g/cm}^2 \times \text{s}$); i.e.,

$$-r_A'' = W_{AS} = \frac{1}{\text{area}} \times \frac{dM}{dt} \quad (2.3)$$

$$\frac{dM}{dt} = k_c A (C_{A,S} - C_{A,B}) \quad (2.4)$$

where $C_{A,S}$ and $C_{A,B}$ are the concentrations of asphaltenes at the surface and in bulk fluid (g/cm^3), respectively, A is the surface area of asphaltene and k_c is convective mass transfer coefficient (cm/s). The value of k_c can be determined from the slope of the plot of dM/dt against solubility of asphaltenes in different percentage of toluene in solvent mixtures ($C_{A,S}$) (Fogler, 1992).

2.7 Prediction of Unfractionated Asphaltene Solubility from Polar Fractions

The accurate predictions of the unfractionated rate constant were made using summation of the average dissolution rates of each fraction along with the fraction yields (Kaminski *et al.*, 2000). To investigate whether an unfractionated asphaltene sample behaves as a sum of its fractions, the average fraction solubility of was multiplied by the fraction yield of each fraction. Assuming that the solubilities of each polar fractions fractionated using the same method are the same for different asphaltenes, the following equation can be established:

$$C_{S,NM5} = \sum (X_{i,NM5} \times C_{si,NMI}) \quad (2.5)$$

where $C_{s,NM5}$ = predicted solubility of unfractionated NM5(g/l)
 $X_{i,NM5}$ = mass fraction of each polar fraction
 $C_{si,NM1}$ = solubility of polar fraction NM1(g/l)

2.8 Prediction of Asphaltene Molecular Weight from Solubility Data

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 approach the dispersion forces in significance. In modeling asphaltene solubility Scatchard-Hildebrand solubility theory with a Flory-Huggins entropy of mixing term form the heart of the model. For asphaltene solubility calculation, the solid –liquid equilibria and the appropriate equilibrium ratio is defined as follows :

$$K = \exp \left[1 - \frac{V_l}{V_m} + \ln \frac{V_l}{V_m} + \frac{V_l}{RT} \times (\delta_l - \delta_m)^2 \right] \quad (2.6)$$

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 correlation:

$$V_l = \frac{1000 \times MW}{0.017 \times MW + 1080} \quad (2.7)$$

and
$$\delta_l = (A \times (0.017 \times MW + 1080))^{0.5} \quad (2.8)$$

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

V_l = Liquid phase molar volume of asphaltene (cm^3/mol)

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

δ_l = Solubility parameter of asphaltene ($\text{Mpa}^{1/2}$)

δ_m = Solubility parameter of solvent ($\text{Mpa}^{1/2}$)

MW = Molar mass of asphaltene (g/mole)

A = The change of the heat of vaporization of asphaltene with a change in molar mass (kJ/g)

R = Gas constant ($\text{J}/\text{mol}\times\text{K}$)

T = Temperature (K)

Consider the definition of equilibrium ratio :

$$K = \frac{X_s}{X_l} \quad (2.9)$$

where X_s = Solid mole fraction = 1 (for single component of asphaltene)

X_l = Liquid mole fraction of asphaltene

$$= \frac{\text{mole of asphaltene}}{\text{mole of toluene} + \text{mole of heptane} + \text{mole of asphaltene}}$$

Basis : 1 litre of solvent mixture

$$\text{Mole of asphaltene} = \frac{C_{A,S}}{\text{MW}}$$

$$C_{A,S} = \frac{\text{MW} \times (\text{mole of toluene} + \text{mole of heptane})}{(K - 1)} \quad (2.10)$$

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