CHAPTER II
LITERATURE SURVEY

2.1 Asphaltene Deposition

Asphaltenes are constituents of heavier and polar fraction of crude oil. The remaining polar species are resins and aromatics. Asphaltenes, however, can form aggregates with molecular weight distribution of 10^3-10^5. These aggregates are stabilized in solution by the resins and aromatics, which act as peptizing agents (Bunger, 1981 and Briant, 1983). When these peptizing agents are removed by preferential dissolution of the resins into fluid phase (e.g., addition of an alkane), the asphaltene molecules start flocculating and aggregating into particle large enough to result in deposition. The petroleum industry defines the asphaltene content of crude oil as the n-heptane insolubles and n-pentane insolubles (IP143/84,1988). Resins can be defined as the fraction of oil not soluble in ethyacetate but soluble in n-heptane, toluene and benzene at room temperature (Hirschberg, 1984). The exact structure of asphaltenes and resins are not known. On heating, they are not molten but decompose to form carbon and volatile products above 300 to 400°C.

It is generally accepted that asphaltene flocculation may take place because of reservoir fluid temperature, pressure and composition changes or electrokinetic effects due to streaming potential generation during reservoir fluid flow (Lichaa, 1975 and Ranny et al., 1988). Usually, in the case of normal reservoir production, no significant changes in temperature are encountered. Furthermore, although a gradual pressure drop during the production life of the reservoir in most cases does occur, a drop in the pressure is generally accepted to act in a way that inhibits asphaltene flocculation. Consequently, only two dominant mechanisms of asphaltene flocculation may

be considered likely to occur in the reservoir, by composition change and/or by electronic effects (Lichaa and Herrera, 1975).

a) Problem on Downhole Safety Valves

In Nov. 1986, Ula reservoir, operated by BP Petroleum Development (Norway), the downhole safety valves became harder to open because a black material (asphaltene) deposited in the valves and interfered the opening mechanism. The deposited asphaltenes increased the friction between the flow tube and the valve housing and prevented the valves from opening with normal surface hydraulic pressures. The valves were modified on increase the opening and closing forces to overcome the extra friction.

b) Wireline Operation

The asphaltene deposition in well tubing caused a number of problems during wireline runs. Access to wireline plugs was hampered by asphaltene settling on the top of the plugs. Wireline tools were damaged by asphaltenes, interfering with their operations. These problems led to extensive delays in wireline operations, and change of running procedures was required. Equipment modifications were required to overcome these problems (Lichaa, 1997).

c) Production Restrictions

Asphaltenes were found to deposit on the well tubing wall below (in terms of depth) the crude bubble-point. This has also been observed in the Hassi-Messahoud and Ventura fields (Haskett, 1965 and Turttle, 1983). However, the downhole flowing pressures are large enough in Ula for the restriction caused by asphaltene deposition in the production tubing to have no significant effect on the oil production. Multiple phase modeling indicated only a small increase in frictional pressure drop along the tubing attributable to

asphaltenes. If the downhole flowing pressure drops significantly, then the potential for future production restrictions still exists (Lichaa, 1997).

d) Refining and Transportation Facilities

A parallel may be drawn between the asphaltene problems during production and refining because of the similarity of some processing steps and equipment. All problems were mentioned about instrumentation for the production side and refining side and provided that the crude oil is asphaltenic or asphaltene flocculation. For instance, asphaltene flocculation that would cause plugging in tower and vessel internals is a very distinct possibility. A frequent problem with pumps is plugging of cyclone separator that supplies the fluid from the discharge to the pump seals, hence, resulting in premature pump failure (Leontaritis, 1989).

e) Wettability Changes

Reservoir Wettability is often attributed to adsorption of asphaltenes onto mineral surfaces of reservoir rock (Anderson, 1986). The highly polar and heavier than water flocculation asphaltene micelle may diffuse through water and adsorb onto the rock thus making the oil wet. This should affect oil recovery, negatively, because the permeability to oil is expected to diminish and residual saturation to increase. Wettability reversal of reservoir rock is caused by asphaltene flocculation and deposition (Leontaitis, 1989)

2.2   Chemistry of Asphaltenes

Asphaltenes are black components generally presenting in the crude oils. Their molecular weights are relatively high, and they are normally polar chemicals because of the presence of functional groups (i.e., oxygen, sulfur,

nitrogen and metal ions containing functional groups) in their structures. The presence of functional groups contributes strongly to physical-chemical properties of asphaltenes (Algelt, 1994). Nitrogen-containing function groups have been shown to be both basic in nature (in the form of aliphatic and aromatic amines, particularly primary amines and pyridine derivatives) and neutral (as indoles, carbazoles and amides as well as porphyrine nitrogen) (Moschopedis et al., 1981). Sulfur, by far the predominant heteroatom, occurs principally in condensed thiophynic structure, but it also presents in aliphatic (sulfides and disulfides) and oxidized forms (Rose and Francisco, 1988). Oxygen is predominantly in the form of acidic functional groups (Rose and Francisco, 1987). The chemical moieties containing oxygen have been somewhat accessible through the use of IR. Even then, the small oxygen concentrations, the relative strong and isolated vibration bands of some oxygen-containing functional group permit their identification. Some evidence of ether group is also found. OH and NH signatures also show but not resolvable from each other (Tissot, 1984 and Chilingarian, 1978). A substantial difficulty with analysis of oxygen results from atmospheric oxidation. Organometallic compounds presenting in petroleum contain predominantly metals such as Ni, V, and Fe. These compounds are usually porphyrinic in nature and concentrated in the heavy part of crude oil.

The sulfur XANES have showed that asphaltene spectrum principally in terms of thiophene (aromatic), sulfides (saturated) and sulfoxides (Waldo et al., 1992). Generally, thiophene is present in greater quantities than sulfide (George et al., 1989). Waldo (1992) also found that, in asphaltenes, large sulfoxide fractions correlate with small sulfide fractions. The sulfur-oxygen correlation increases with decreasing sulfide. In other words, oxidation of asphaltene is associated with the consumption of sulfide and the production of sulfoxides (i.e., sulfides susceptible to oxidation are converted to sulfur oxides while thiophenes remain largely the same (Ruiz et al., 1982)).

Durand et al. (1978) found pyrrole, pyridine, pyridone (2-hydroxypyridine) and aromatic amine nitrogen XANES spectra in kerogens and bitumens. Mostly, nitrogen is present in aromatic forms; pyrrole is the most dominant nitrogen structure, with pyridine being the second most dominant structure. The pyridones and aromatic amine fractions are not too large but are always present. Also, saturated amine was found but is essentially negligible.

According to Long (1981), asphaltenes are highly polydisperse and contain a broad distribution of polar groups in their structure. Chemically, asphaltenes consist of polycyclic, condensed, aromatic ring compounds. There is significant variation in the average chemical characteristics (aromaticity, degree and nature of alkyl substitution, heteroatom, and metal content) of asphaltenes isolated from the different oils (Speight, 1992 and Long, 1989). The chemical composition of asphaltene is shown in Table 2.1, which indicates the range of compositions found from n-heptane-insoluble asphaltenes precipitated from different oils.

Table 2.1 Range of composition found for asphaltenes precipitated from crude oils with n-heptane (Speight, 1992 and Long, 1989)

| Yield of precipitate (wt.%)	up to 30
H/C ratio	0.8-1.4
S (wt.%)	0.5-10.0
N (wt.%)	0.6-2.6
O (wt.%)	0.3-4.8
fa^1	0.45-0.7
n^2	4-7

[1] Aromaticity factor (fraction of aromatic carbon) from ^{13}C-NMR.

[2] Number of alkyl carbon atoms per side chain.

The picture of asphaltenes deduced from these studies is that of aromatic polycyclic clusters variably substituted with alkyl chains that may be quite long (up to C10-C12), and connected by alkyl and heteroatom bridges. The degree of condensation of each aromatic cluster may be more or less elevated, but generally does not exceed 5-6 rings (Tissot, 1978).

Painter et al. (1981) clarified the IR absorption of heavy fraction as shown in Table 2.2.

Yen et al. (1994) studied the size distribution of asphaltenes. Figure 2.1 shows the wide ranges of molecular weights of both precipitated asphaltene and dissolved asphaltene. The average molecular weight of the precipitated asphaltene is remarkably higher than the one of the dissolved asphaltene.
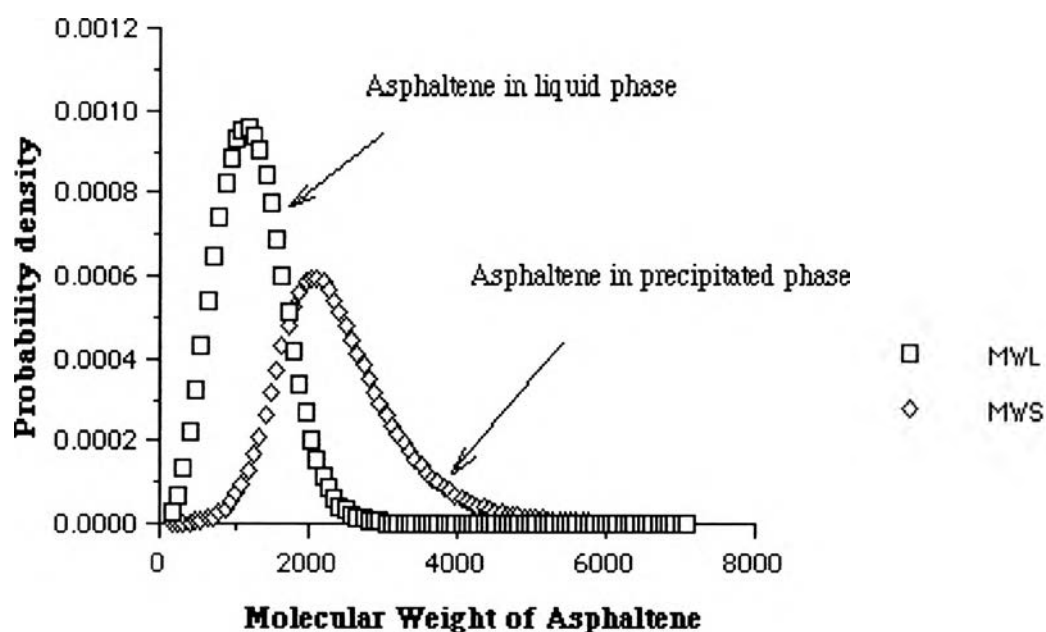
MWL = The molecular weight of asphaltene in a liquid phase

MWS = The molecular weight of asphaltene in a solid phase

Figure 2.1 Molecular size distribution of asphaltene of a California crude oil in solution and after precipitation by the addition of n-C5 (Yen, 1994).

Table 2.2 IR absorption peak of asphaltenes (Painter et al., 1981)

Wavenumber (cm^{-1}) asphaltene	Type of functional group
3500-3300	NH, OH stretching, and H-bonding
3050-3000 (shoulder)	Aromatic stretching (C-H)
2950	CH$_3$-stretching
2920, 2850	Aliphatic CH-stretching
1835	C=O, Anhydride
1775-1765	C=O, ester with electron withdrawing group attached to single bond oxygen $$\overset{\displaystyle O}{\underset{\displaystyle Ar\text{-}O\text{-}C\text{-}R}{\|}}$$
1735	C=O, ester
1720-1690	Aldehyde, ketone and acid
1650-1630	C=O highly conjucated $$\overset{\displaystyle O}{\underset{\displaystyle Ar\text{-}C\text{-}Ar}{\|}}$$
1600	Aromatic or C=C stretching
1450	CH$_2$ and CH$_3$ bending
1375	Systemetric C-CH$_3$ bending
1300-1100	C-O stretching and O-H bending in Phenoxy structures, ethers
860	Isolated aromatic H
833 (weak)	1,4 substituted aromatic groups

Mullins (1990) explored the broad light extinction profile of crude oils in the near-infrared (near-IR) spectral range. One possible mechanism to account for the extinction of transmitted light in this spectral range is electronic absorption from the asphaltene complexes. Large aromatic rings

system can undergo $\pi\pi*$ and $n\pi*$ electronic transition. Therefore, it results in producing visible and near-IR absorption. As a size of aromatic ring system increases, the band edge absorption shifts to lower energy. Ring systems with heteroatom posses $n\pi*$ transition that are appreciably red-shifted compared to $\pi\pi*$ transition but are also much weaker in intensity (Turro, 1978). However, the broad absorption spectra of asphaltene in these ranges are not distinct enough to recognize or distinguish compounds in complex mixtures.

2.3   Characteristics of Asphaltenes and Resins

The investigation of the chemical constitution of petroleum heavy fractions such as resins and asphaltenes is considerably difficult because of their complex nature. The classic definition of asphaltenes is based upon the solution properties of petroleum residues in various solvents. Marcusson in 1945 classified asphaltene and resin as follows:

(i) Neutral resins are defined as the insoluble fraction in alkali and acid. They are completely miscible with petroleum oils, including light fractions.

(ii) Asphaltenes are defined as insoluble fraction in light gasoline and petroleum ether. In contrast to resins, the asphaltenes are precipitated in the presence of excess ether.

(iii) Asphaltogenic acid is defined as the soluble fraction in an alkaline solution and in some solvents such as benzene.

There is a close relationship between asphaltenes, resins, and high molecular weight polycyclic hydrocarbons. However, the presence of oxygen and sulfur in various amounts differentiates the asphaltenes as well as resins from polycyclic hydrocarbons.

A number of investigators have attempted to postulate a model structure for asphaltenes and resins. One of representative structure of resin and

asphaltene molecule belonging to Athabacus crude (Suzuki et al., 1982) is shown in Figure 2.2. It illustrates the molecular structures of both asphaltenes and resins containing carbon, hydrogen, oxygen, nitrogen, sulfur, as well as polar and non-polar groups. The aromatic polycyclic clusters are formed by alkyl and heteroatom bridges. The alkyl chain is quite long up to C10 to C12. The degree of condensation of these aromatic clusters is commonly elevated and generally does not exceed 5-6 ring (Tissot, 1978).
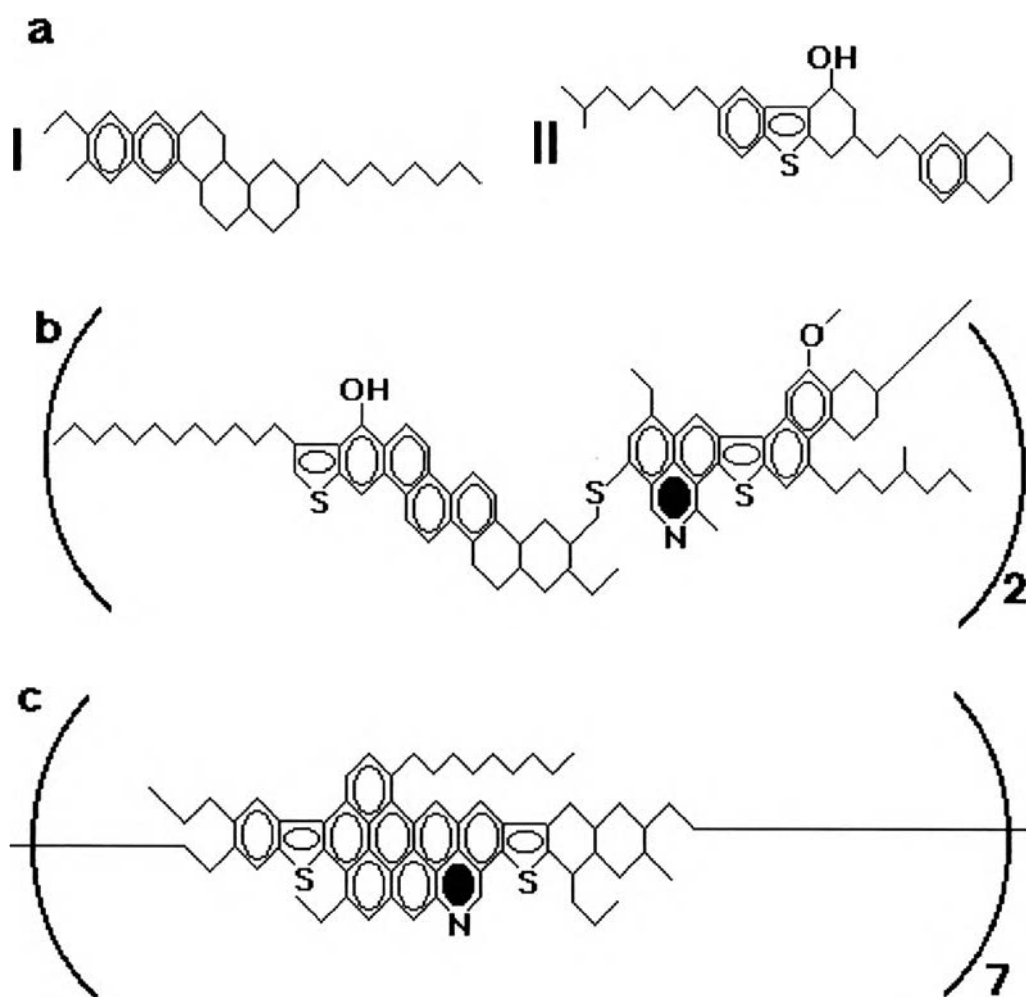
Figure 2.2 Average molecular structural models of the fractions of Athabasca tar-sand bitumen and petroleum bitumens; (a) resin fraction, (b) asphaltene fraction of tar-sand bitumen; (c) asphaltene fraction of petroleum bitumen proposed by Suzuki et al. (1982).

2.4 Flocculation of Asphaltenes

Mansoori (1997) suggested that low molecular weight or small asphaltene particles could be dissolved in a petroleum fluid. Whereas relatively large asphaltene particles may flocculate out of the solution and then be stabilized and form steric colloid under the presence of excess amount of asphaltene demonstrated in Figure 2.3.
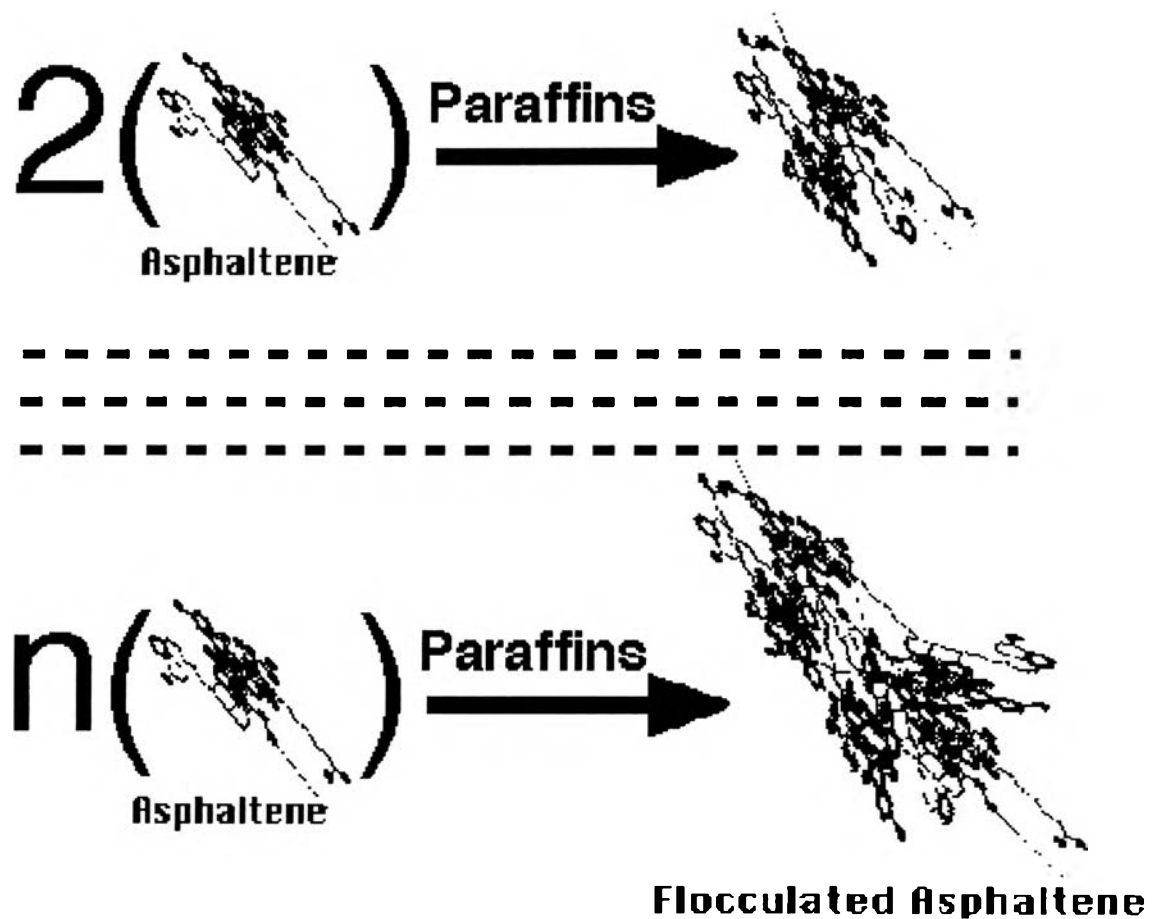

Figure 2.3 Asphaltene flocculation due to the excess amount of paraffins in the solution.

2.5 Asphaltene Steric Colloid

Although the asphaltenes themselves are known as the insoluble fraction in petroleum, they can exist as fine or coarse dispersion in the presence of the excess amount of resins. Resins are the high polarity so that they can absorb onto the asphaltenes to form steric colloid. Resins, therefore, act as a peptizing agent or colloid stabilizer by charge neutralization mechanism (Shue and Mullins, 1995). Figure 2.4 depicts the formation of asphaltene steric colloid by flocculation between asphaltenes and resins.
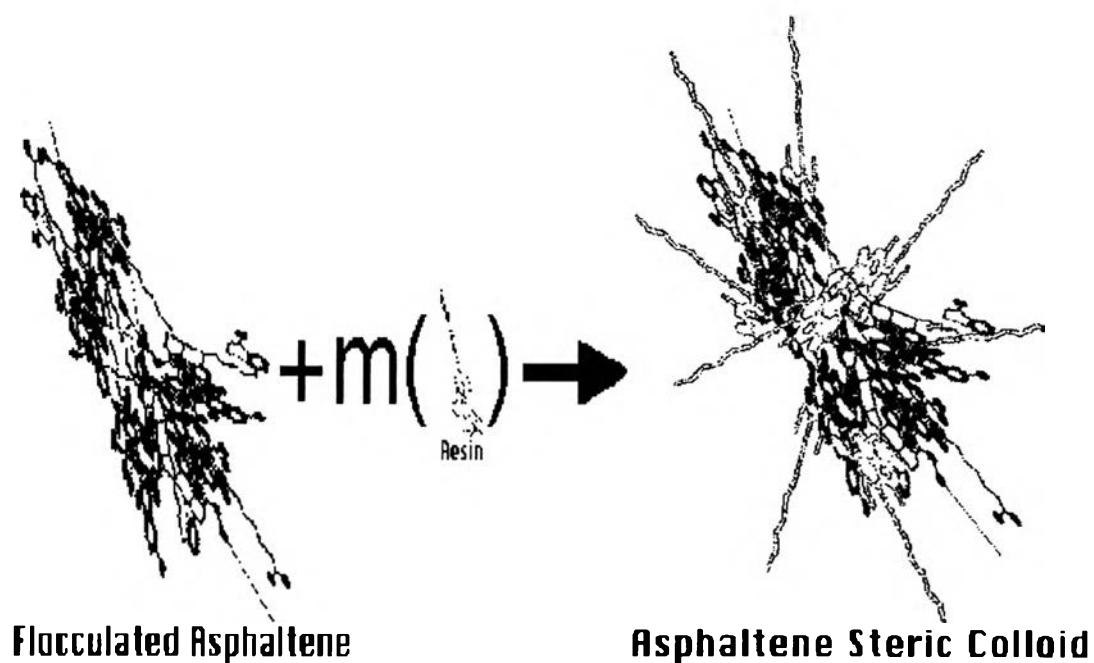

Flocculated Asphaltene   **Asphaltene Steric Colloid**

Figure 2.4 Steric-colloid formation of flocculated asphaltenes with resins (Mansoori, 1997).

2.6 Asphaltene Micelles

Several investigators have studied the critical micelle concentration of the asphaltene solution in aromatic solvents (Sheu, 1996; Andersen and Birdi,

1991; Rogacheva et al., 1980 and Ravey et al., 1988). Sheu (1996) reported that the self-association of the asphaltenes or asphaltene micelles did not grow with increasing concentration, and the sizes of the micelles formed were relatively similar. Also, he studied the physical properties of asphaltene micelles and microemulsion. He revealed that the asphaltene micelles differ from the conventional surfactant-based micellar solution because of the wide structural distribution of the asphaltene molecules.

2.7   Solubility of Asphaltenes

The solubility of asphaltenes has been studied extensively using the concept of solubility parameter. It has been found that the asphaltene stability increases linearly with the Hildebrand solubility parameter (δ) of solvents (Mitchell and Speight, 1973). The δ parameter, which is in the Flory-Huggins χ parameter, has been used to model the phase behavior of asphaltenes in both solvents and crude oil by the following expression (Hirschberg, 1984).

$$\chi = (\frac{V^m Solvent(crude)}{RT})(\delta_{Solvent\ (crude)} - \delta_{asp})^2$$

where χ is a parameter of Flory-Huggins equation and represents the difference of the intermolecular interaction between solvent molecules and asphaltene molecules

The Flowy-Huggins model has been widely used for simulating the phase behavior of asphaltenes. If the χ value exceeds 0.5, the phase separation occurs. Speight and Mitchell (1973) investigated the δ value of asphaltenes to be about 9.5 $(cal/cm^3)^{0.5}$.

2.8 Method for Solving and/or Preventing Asphaltene Deposition

A systematic approach, preventive or corrective, to handle asphaltene deposition problems depends on the stage of crude oil production. This is not by any means an easy task, and certainly asphaltenes will always be in the crude. Thus, it comes down to profitability from the different existing tools in order to cope with them.

a) Mechanical Removal Techniques

In certain circumstances, mechanical removal techniques may be an effective means of combating the heavy organic deposition (Tuttle, 1983). For example at the Hassi Messaoud field, Algeria, it was necessitated to apply frequent tubing scrapings and washings to maintain production (Haskett and Tartera, 1965). Cutting the deposits from the tubing by wireline methods is too time-consuming and sometimes impractical, so a program of washing the tubing with a solvent was established. An economical study may be beeded to indicate whether mechanical methods of cleaning are preferred over cleaning by using solvents.

b) Solvent Treatment

Solvent treatment of oil is considerably beneficial in some cases because it dilutes the crude oil and reduces the tendency of heavy organic to precipitate. Solvent treatment may not be very successful largely because solvents used are limited to costly aromatic solvents. Xylene is generally the most common solvent selected to be used in well stimulation, workover, and heavy organic inhibition and cleaning. In oil fields, which frequently need aromatic wash, it may be necessary to design an aromatic solvent with stronger washing power and better economy for a particular deposit (Garcia-Hermandez, 1989).

c) <u>Hot Oil Circulation</u>

Circulation with hot oil may be used to avoid or reduce heavy organic deposition problem. A combination of solvent treatment and reverse and normal circulation with hot oil has been tried in the past in some oil wells with mixed results (Turttle, 1983).

d) <u>Dispersants Injection</u>

Injection of dispersants or antifoulants may be effective in certain crude oils where the ratio of resin to asphaltene is not high enough to prevent asphaltene flocculation and as a result heavy organics deposition. One thing appearing to have universal acceptance is that resins in the crude act as the peptizing agents of the asphaltene particles. It is generally a good practice to analyze a crude oil for its asphaltene and resin contents and ratio. Table 2.3 shows the contents of asphaltene and resin and the ratios of asphaltene to resin of some crude oils.

d) <u>Asphaltene Inhibitors</u>

Using continuous down whole injection of asphaltene inhibitors has been done successfully (Izquierdo, 1996). A small amount of inhibitor (less than 1000 ppm) can maintain the asphaltenes in solution. The inhibitors have an active component dissolved in an aromatic solvent. These active components react with asphaltenes probably yielding a structure that is unable to associate with other asphaltene molecules. Therefore, the inhibitors prevent the development of large asphaltene insoluble unit. Dodecylbenzene sulfonic acids, alkylphenol ethoxylates, and different type of polymers have been widely applied as asphaltene inhibitors.

Table 2.3 Resins and asphaltene contents of various crude oils

Crude	o API	Resin (wt.%)	Asphaltene (wt.%)	Asph./Resin
Venezuela, Boscan	10.2	29.4	17.2	0.58
Mexico, panucon	11.7	6	12.5	0.48
Rusian, Kaluga	16.7	20	0.5	0.025
USA, TX, Hould	19.7	12	0.5	0.04
USA, CA, Huntington	26.2	19	4	0.21
USA, LA, Brookhaven	30.6	4.6	1.65	0.36
Russia, Balachany	31.7	6	0.5	0.08
Russia, Bibi-Eibat	32.1	9	0.3	0.03
Russia, Dossor	32.6	2.5	0	0
Russi, Surachany	35	4	0	0
USA, TX, Mexia	36	5	1.3	0.26
Iraq, Kirkuk	36.1	15.5	1.3	0.08
Mexico, Tecoaminocan	36.7	8.8	1.5	0.17
Mexico, Isthmus	37.8	8.1	1.3	0.16
USA, OK, Ok. City	38	5	0.1	0.02
USA, OK, Tonkava	40.8	2.5	0.2	0.08
USA, LA, Rodessa	43.8	3.5	0	0

Generally, aromatics based liquids are the most reliable and economical solvents used for removing asphaltene deposition. Due to the environmental concern, the development for the effective substitutes is needed.

In 1991, Gonzales and Middea studied the dispersion of asphaltenes in heptane by different oil soluble amphiphiles. It was found that the effectiveness of amphiphiles on the stabilization of asphaltenes was influenced by the head groups of amphiphiles and alkylphenols showed good peptizing properties. De Boer and coworkers (1995) found that alkylbenzene sulfonic
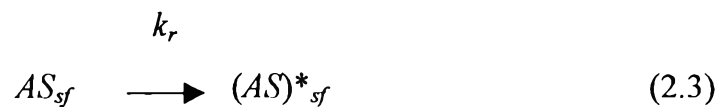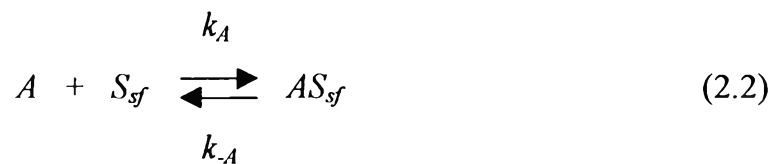
acid could effectively reduce the precipitation of asphaltenes in near-well bore regions.

2.9 The Kinetics Analysis

The dissolution of asphaltene precipitates in amphiphile/alkane solution involves both mass transfer and surface reaction processes (Fogler, 1992). The amphiphile is first transported from the bulk liquid to the asphaltene surface.

$$S_{bk} \longrightarrow S_{sf} \tag{2.1}$$

Where S_{bk} and S_{sf} are amphiphiles in the bulk fluid and at the asphaltene surfaces, respectively. Subsequently, the amphiphile near asphaltenes adsorbs on the fuctional sites (active sites) on the asphaltenes surfaces to form the amphiphile –asphaltene complex.

$$A + S_{sf} \; \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} \; AS_{sf} \tag{2.2}$$

$$AS_{sf} \; \overset{k_r}{\longrightarrow} \; (AS)^*_{sf} \tag{2.3}$$

This step is called the surface reaction step. "A" represents the functional sites on the asphaltene surface on which the amphiphile can adsorb. Afterwards, the amphiphile – asphaltene complex desorbs from the asphaltene surface,

$$(AS)^*_{sf} \; \rightleftharpoons \; (AS)_{sf} \tag{2.4}$$

and is transported to the bulk liquid

$$(AS)^*_{sf} \longrightarrow (AS)_{bk} \qquad (2.5)$$

where $(AS)^*_{sf}$ and $(AS)_{bk}$ are the asphaltene – amphiphile associated complex on the asphaltene surface and in the bulk fluid, respectively.

At equilibrium, the net rate of adsorption equals zero, hence

$$[AS_{sf}] = K_A[A][S_{sf}] \qquad (2.6)$$

where $K_A = k_A / k_{-A}$. With the first order model, the total number of functional sites on asphaltene surfaces is assumed to proportion to the mass of undissolved asphaltenes and is the sum of the bound and unbound sites. That is

$$M = [A] + [(AS)_{sf}] = [A] + K_A[A][S_{sf}]$$

Hence, $\qquad [A] = \dfrac{M}{1 + K_A[S_{sf}]}$; $\qquad (2.7)$

Then, the rate of asphaltene dissolution becomes

$$-\frac{dM}{dt} = k_r[AS_{sf}] = k_r K_A[A][S_{sf}] = k_r K_A \frac{M[S]}{1 + K_A[S_{sf}]} \qquad (2.8)$$

Chang and Fogler (1994) used a series of alkylbenzene-derived amphiphiles to investigate the asphaltene-amphiphile interaction and the stability behavior of asphaltene in amphiphile/alkane solutions. It was concluded that there were two mechanisms to explain for amphiphile molecules effective to stabilize asphaltenes in a polar media. One is the association of amphiphiles to asphaltene surfaces by the head group of amphiphiles. Another is steric-colloid formation, the establishment of the amphiphiles tail groups around asphaltene aggregate.

Permsukarome (1995) studied the major parameters affecting the kinetics of asphaltene dissolution by fluids composed of amphiphiles and alkanes. It was concluded that the rate of asphaltene dissolution generally increased with the increasing concentration of amphiphile in alkane based fluid. The relationship between the reaction rate constant and amphiphile concentration could be expressed in the Langmuir form. The rate of asphaltene dissolution by light alkane-based mecellar fluid was higher than the heavy alkane-based micellar fluid. High fluid temperature could enhance the rate molecular interaction among asphaltene particles, amphiphile molecules and solvent molecules.

In later study, Pumpaisanchai (1996) concentrated on the dissolution of asphaltene fractions with different polarities by fluids composed of amphiphiles and alkane. It was found that the dissolution rate of asphaltene fraction 1 was lower than that of asphaltene fraction 2. SEM pictures showed the different of morphology between these two factions. Asphaltene fraction 1 appeared the lower porosity than asphaltene fraction 2 did.

Determination of chemical compounds in asphaltene is emphasized in this report. Several characterization techniques differentiate asphaltenes with different properties. Differences of chemical components can correspondingly explain with the dissolution kinetics of asphaltene. Kinetic analysis is needed to determine qualitatively as well as quantitatively of the kinetic dissolution of asphaltene.

The integral method is one of methods used to determine the rate law or the kinetic expression that relates the rate of reaction to the particular concentration from experiment data. At first, the reaction order was guessed to formulate the differential equation for a batch model. If the assumed order is correct, the appropriate plot of concentration with time should be linear.