CHAPTER II
LITERATURE SURVEY

2.1 Crude Oil Composition

Crude oils are complex mixtures of hydrocarbons containing a variety of components with different physical and chemical properties. These components are often divided into four major classes/hydrocarbon types: saturates, aromatics, resins, and asphaltenes (SARA). The SARA separation is based on the difference in solubility and polarity of each fraction as demonstrated in Figure 2.1 (Wattana, 2004).
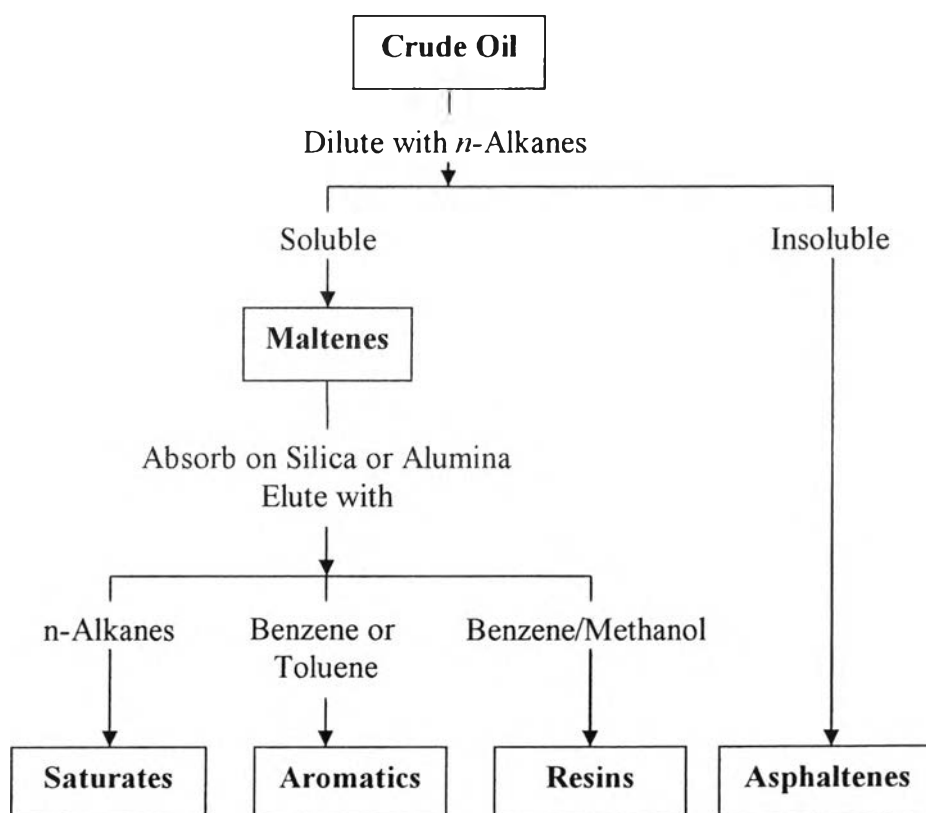

Figure 2.1 Schematic of SARA separation (Wattana, 2004)

Hydrocarbon types or SARA analysis was improved and described by Gharfeh *et al.* (2006). An improved method for SARA analysis was proposed to reduce the loss of light ends (light hydrocarbons) in the separation process. A weighed portion of the oil is distilled at 450 °F using ASTM method D 86 (ASTM, 2005a). The distillate is captured and analyzed by supercritical fluid chromatography (SFC) to determine both the saturate and aromatic content. The SFC analytical procedure is based on ASTM method D 5186 (ASTM, 2003b). The residue is analyzed using ASTM method D 893 (ASTM, 2005b) to determine asphaltene content by pentane precipitation and the filtrate is analyzed for additional saturates, aromatics and polars/resins by open column chromatography using ASTM method D 2007 (ASTM, 2003a). The schematic diagram for the SARA analysis procedure is shown in Figure 2.2.
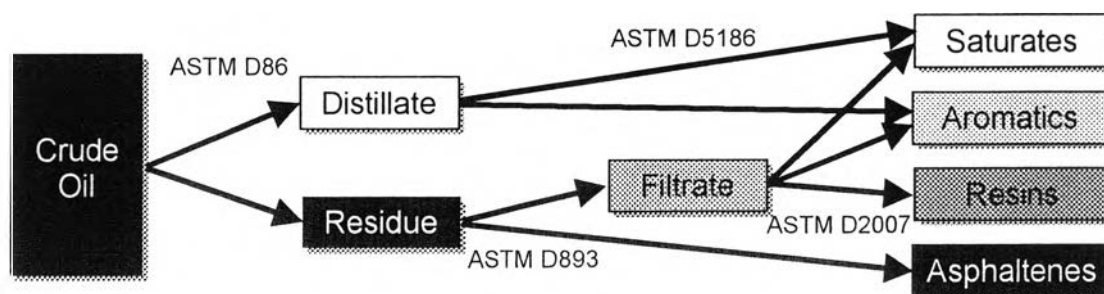

Figure 2.2 Schematic diagram of SARA analysis procedure

2.2 Asphaltene Definition and Composition

Asphaltenes are the heaviest and most polar fraction in crude oils and are defined as the fraction that is soluble in aromatic solvents, such as benzene or toluene and insoluble in light normal alkanes, such as *n*-pentane or *n*-heptane (Speight, 1999; Sheu and Mullins, 1995). They are dark brown to black friable solids with no definite melting point and usually intumesce on heating with decomposition to leave a carbonaceous residue. Furthermore, asphaltenes have different elemental compositions, that include carbon (C), hydrogen (H), and some heteroatoms, such as oxygen (O), nitrogen (N), sulfur (S), and heavy metals (i.e. nickel (Ni) and vanadium (V)).

Asphaltene composition is dependent on the nature of the hydrocarbon precipitant (normal alkanes) and precipitation conditions. The elemental composition of asphaltenes isolated by a use of excess (greater than 40) volumes of n-pentane as the precipitating medium show that asphaltenes are generally composed of 82 ± 3 wt.% carbon, 8.1 ± 0.7 wt.% hydrogen, corresponding to H/C molar ratios of 1.15 ± 0.05. Asphaltenes also contain heteroatoms of 0.3 to 4.9 wt.% oxygen, 0.3 to 10.3 wt.% sulfur, and 0.6 to 3.3 wt.% nitrogen and trace amounts of other heteroatoms (Speight, 1999).

2.3 Asphaltene Molecular Weight, Size and Structure

Another significant property of asphaltenes is the molecular weight. Two decades ago, Boduszynski (1987, 1988) used field-ionization mass spectroscopy (FIMS) to determine the molecular weight of different distillation cuts and non-distillable residue which includes asphaltenes. The molecular weight of asphaltenes obtained from FIMS is about 700 amu. (atomic mass unit) with roughly a full-width-half-maximum (FWHM) of 500 to 1000 amu. (Boduszynski, 1987; Boduszynski, 1988; Mullins, 2005). Later, asphaltene molecular weight was measured using time-resolved fluorescence depolarization (TRFD) and found to be about 750 amu. with a full-width-half-maximum of 500-1000 amu. (Groenzin and Mullins, 1999; Groenzin and Mullins, 2000; Buch *et al.*, 2003; Mullins, 2005; Badre *et al.*, 2006). This result was found to be consistent with the value obtained from FIMS. In the most recent work, asphaltenes molecular weight were analyzed by electronspray ionization – Fourier transform ion cyclotron resonance mass spectroscopy (ESI-FT-ICR-MS, the world's highest resolution mass spectrometer) and the results showed excellent agreement with the above results (Hughey *et al.*, 2002; Marshall and Rodgers, 2004; Mullins, 2005).

The molecular size and structure of asphaltenes are of interest to researchers and different molecular structures and models were proposed. Direct imaging of asphaltenes using scanning tunneling microscopy (STM) (Zajac *et al.*, 1994) and high-resolution transmission electron microscopy (HRTEM) (Sharma *et al.*, 2002) yields the size of the ring systems of approximately 10 Angstroms, corresponding to

roughly 6 fused rings, but can range from 4-10 fused rings (Mullins, 2005). Asphaltene molecular structures proposed by Mullins (2005) are shown in Figure 2.3.
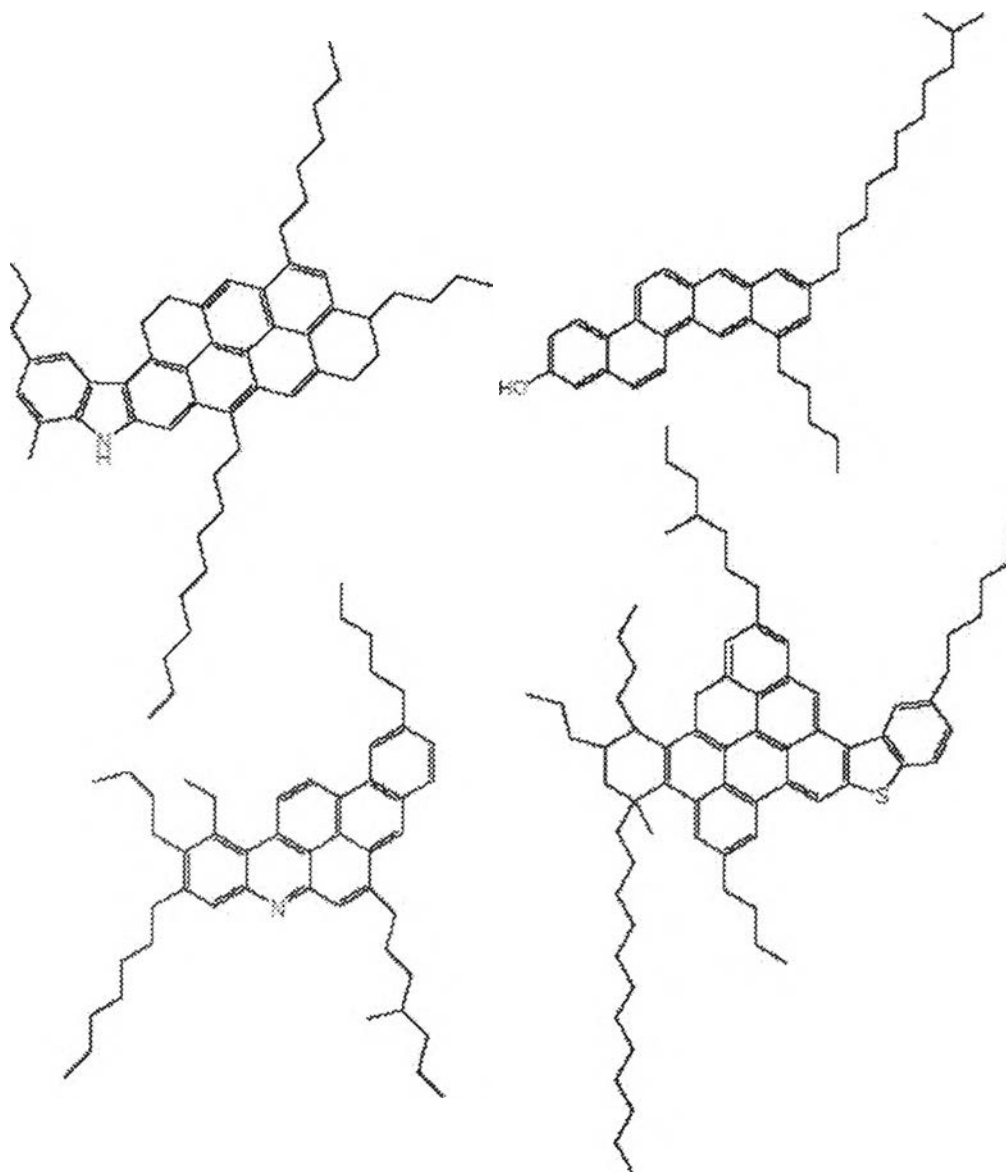

Figure 2.3 Asphaltene molecular structures proposed by Mullins (2005)

2.4 Solubility of Asphaltenes

Asphaltene solubility is of great 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

component, they are difficult to characterize, and asphaltene solubility has proven difficult to predict (Mannistu *et al.*, 1997).

Mannistu and coworkers (1997) measured the solubility of Athabasca asphaltenes in a variety of organic solvents and compared them to predictions using a solid-liquid equilibrium calculation based on Scatchard-Hildebrand solubility theory with the Flory-Huggins entropy of mixing. They found that both the single-component solubility parameter and the 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.

2.5 Precipitation of Asphaltenes

Asphaltene precipitation is usually performed using a mixture of crude oil, solvent (i.e. toluene) and precipitant (i.e. *n*-pentane or *n*-heptane). The precipitant is gradually added to the crude oil and solvent (if any) mixture to induce precipitation. The asphaltene precipitation onset point is usually determined using microscopy (i.e. optical microscope) and spectroscopy (i.e. UV-Vis spectroscope, laser NIR detector or refractometer). The automatic titration system (ASTM, 2001) has advantages over manual mixing because it takes less time and less crude oil sample to determine the asphaltene precipitation onset. However, one needs to be careful on the interpretation of the titration data because the actual onset point is prior to the maximum light transmittance (minimum absorbance) due to the dilution effect by precipitant overwhelm the precipitation of asphaltenes (Kraiwattanawong, 2005).

Asphaltene precipitation of the crude oil / solvent / precipitant mixture can be modeled using the simple Scatchard-Hildebrand solubility theory applying continuous thermodynamics (Hilderbrand and Scott, 1964). The system is assumed to consist of two pseudo-components: asphaltenes and maltenes (the rest of the mixture). The Gibbs free energy of mixing for asphaltenes and maltenes can be estimated from the solubility parameter (Hilderbrand and Scott, 1964).

2.6 Solubility Parameters

The solubility parameter was first described by Hildebrand and Scott in 1950 (so called Hilderbrand solubility parameter). A solubility parameter is a numerical value that describes the interaction between molecules in condensed materials. It can 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 (Redelius, 2000). The Hildebrand solubility parameter is defined by:

$$\delta = \sqrt{\frac{\Delta U^{vap}}{v}} \cong \sqrt{\frac{\Delta H^{vap} - RT}{v}} \qquad (2.1)$$

Where δ = solubility parameter (MPa$^{\frac{1}{2}}$)

ΔU^{vap} = energy of vaporization to the gas at zero pressure (J/mol)

v = molar volume of the liquid (cm^3/mol)

ΔH^{vap} = heat of vaporization of the liquid (J/mol)

R = ideal gas constant (8.314 J/mol/K)

T = temperature (K)

A solubility parameter of a pure liquid can be easily calculated from physical and chemical properties. In the case of mixtures, a solubility parameter can be calculated based on data for the individual components by using the volume average mixing rule of solubility parameter defined by:

$$\delta_{mixture} = \sum_{i=1}^{n} \phi_i \delta_i \qquad (2.2)$$

Where $\delta_{mixture}$ = solubility parameter of a mixture (MPa$^{\frac{1}{2}}$)

ϕ_i = volume fraction of ith component (-)

δ_i = solubility parameter of component ith (MPa$^{\frac{1}{2}}$)

For solid materials and more complex mixtures, it is usually not possible to measure or calculate the solubility parameter directly because it is very difficult to obtain energy of vaporization. In such cases, it is necessary to obtain the solubility parameter by indirect methods. The principle is to mix a material with known

solubility parameters, and measure the interaction. An example of the latter is to dissolve a material in different solvents with known solubility parameters and record the solubility (Redelius, 2000). The molar volumes and solubility parameters of some hydrocarbons at 25°C are summarized in Table 2.1.

Table 2.1 Molar volumes and solubility parameters of various hydrocarbons at 25°C (Barton, 1991)

Hydrocarbon	Molar Volume (mL/mol)	Solubility Parameter (MPa$^{\frac{1}{2}}$)
Methane	53*	9.6*
Butane	69*	11.6*
Propane	85*	12.7*
n-Butane	101.4	13.5
n-Pentane	116.1	14.3
n-Hexane	131.6	14.8
n-Heptane	147.5	15.3
n-Octane	163.5	15.5
n-Nonane	179.7	15.6
n-Decane	195.9	15.8
n-Undecane	211.2	15.9
n-Dodecane	228.6	16.0
n-Tridecane	243.7	16.1
n-Tetradecane	261.3	16.2
n-Pentadecane	276.4	16.3
n-Hexadecane	291.4	16.4
n-Octadecane	326.9	16.45
n-Eicosane	359.8	16.5
Cyclohexane	108.7	16.8
Toluene	106.9	18.2
Benzene	89.4	18.8

* Estimated from gas solubility data (Blanks and Prausnitz, 1964)

## 2.7 Asphaltene Precipitation Models

Precipitation of asphaltenes occurs in a wide range of situations. The major factors that drive the asphaltene precipitation are composition, pressure and temperature. Therefore, a successful model should be able to capture the changes in the thermodynamics of the system. There are four groups of model proposed in the literature which include the following:

- Colloidal models
- Micellization models
- Solid phase models
- Solubility models

2.7.1 Colloidal Models

This model is based on the assumption that asphaltenes exist in the oil as suspended solid particles or colloids stabilized by resin molecules, as shown in Figure 2.4. Another assumption is that the short range intermolecular repulsive forces between resin molecules prevent asphaltenes from flocculation (Leontaritis and Mansoori, 1987). These repulsive forces can be overcome by replacing resin molecules with less repulsive molecules (i.e. normal alkanes). Therefore, in this model, resins play an important role in keeping the colloidal asphaltenes in the solution.

The Flory-Huggins statistical thermodynamics theory was used to calculate the chemical potential of resin molecules. The critical resin concentration $(C_R)_{crit}$ is defined for a particular oil mixture that if the resin concentration (C_R) is less than $(C_R)_{crit}$, flocculation is possible. The critical resin concentration can be determined by adsorption experiments or titration experiments (Leontaritis and Mansoori, 1987).
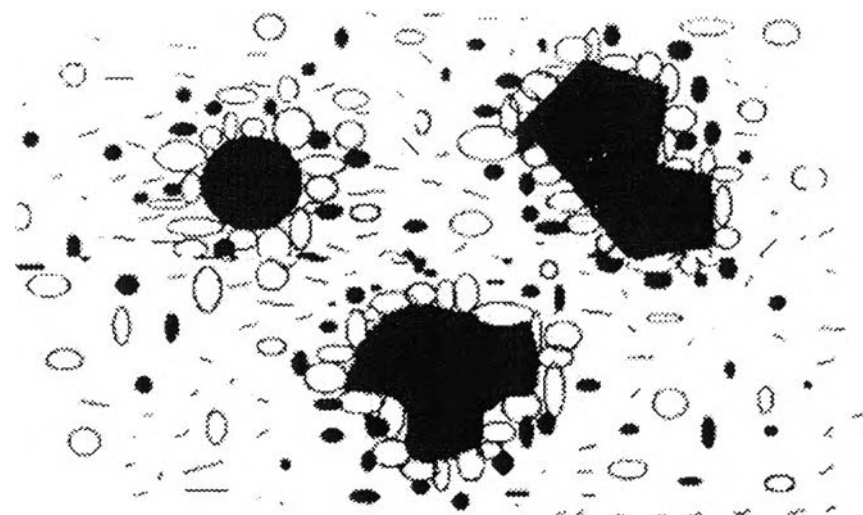
NOTES

1 0 ◯ represents resin molecules

2 0 ◆ represents aromatic molecules

3 0 ～ represents oil molecules of different size and paraffinic nature

4 0 ⬤ represents asphaltene particles of different sizes and shapes

Figure 2.4 Schematic of colloidal model (Leontaritis and Mansoori, 1987)

2.7.2 Micellization Models

This model was proposed by Victorov and Firoozabadi (1996) and by Pan and Firoozabadi (1996, 1997, and 2000). This model assumes that an asphaltene colloidal particle has a core that is formed by aggregated asphaltene molecules surrounding by resin molecules (so called micelles), as shown in Figure 2.5. All the specific features of the micellization models are calculated by minimizing the Gibbs free energy of micellization. An equation of state can be used to incorporate the effect of pressure, temperature and composition.
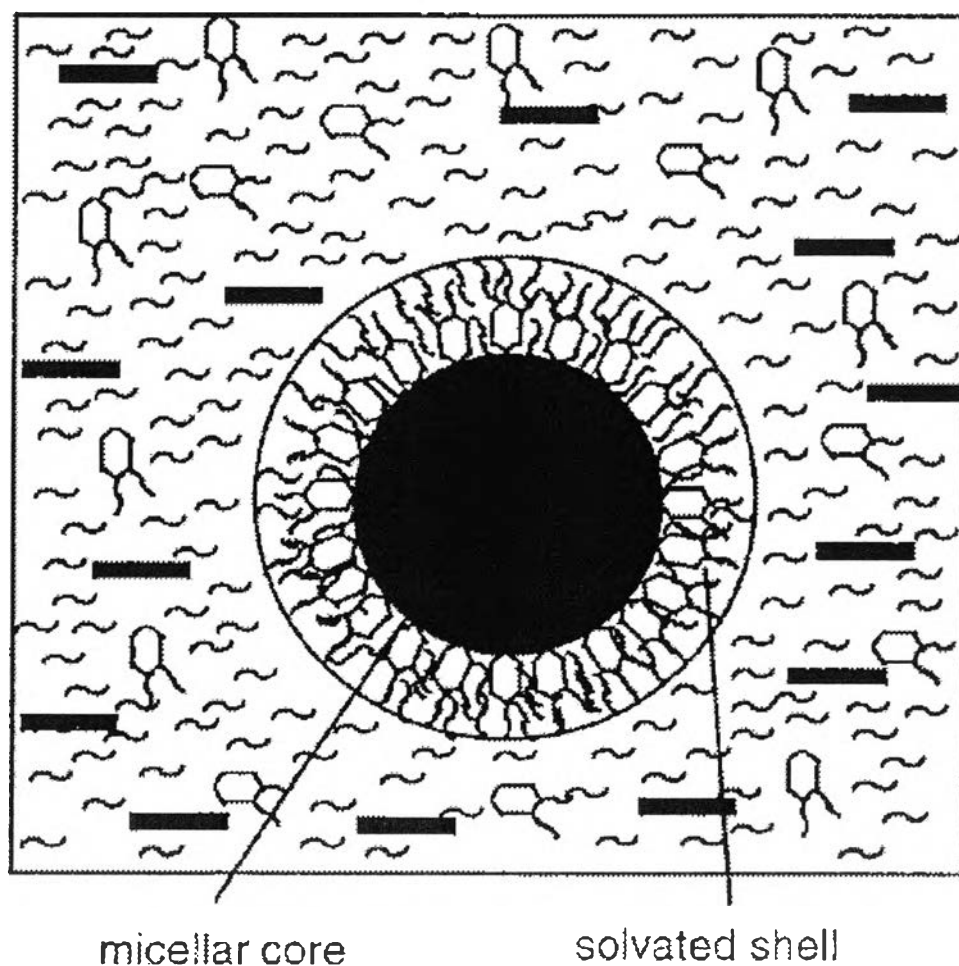
micellar core   solvated shell

Figure 2.5 Schematic of micellization model (Pan and Firoozabadi, 1996)

2.7.3 Solid Phase Models

Nghiem *et al.* (1993) proposed that precipitated asphaltenes are a pure dense phase. The three-phase vapor/liquid/asphaltenes flash calculation using a cubic equation of state was used. The amount of precipitated asphaltenes can be obtained by equating the fugacities of asphaltenes in both the liquid and solid phases. This model is easy to implement and gives reasonable results in matching the experimental data (Qin *et al.*, 2000). As in the other models, experimental data is required.

2.7.4 Solubility Models

This approach was first proposed by Fussel (1979) to calculate multiphase equilibria of liquid/liquid/vapor using the Redlich-Kwong equation of state (EOS). Then Hischberg et al. (1984) developed a thermodynamic liquid model to describe the behavior of asphalt and asphaltenes in reservoir crude oils upon changes in pressure, temperature and composition. This thermodynamic model (assuming reversibility) uses a combination of vapor/liquid model and a liquid/liquid model instead of a three phase model for simplicity. The modified Flory-Huggins theory (Prausnitz et al., 1986) with the Soave equation of state was used to calculate the amount of precipitated asphaltenes assuming that precipitation does not change the vapor/liquid equilibrium (VLE) (Hischberg et al., 1984). Hischberg et al. (1984) simplified the equation by assuming that the separated phase consists of pure asphaltenes and obtained the following equation:

$$(\phi_a)_{max} = \exp\left\{\frac{v_a}{v_L}\left[1-\frac{v_L}{v_a}-\frac{v_L}{RT}(\delta_a-\delta_L)^2\right]\right\} \qquad (2.3)$$

Where $(\phi_a)_{max}$ = maximum volume fraction of asphaltenes soluble in crude oil (-)

v_a = molar volumes of asphaltenes (cm^3/mol)

v_L = molar volumes of crude oil (cm^3/mol)

δ_a = solubility parameters of asphaltenes ($MPa^{1/2}$)

δ_L = solubility parameters of crude oil ($MPa^{1/2}$)

Kawanaka et al. (1991) proposed a model considering a polydispersity of asphaltenes. The Flory-Huggins model was replaced by the Scott and Magat model (Scott and Magat, 1945; Scott, 1945) which is the heterogeneous polymer solution theory, to take into account heterogeneity of asphaltenes.

In 1995, Cimino et al. (1995a and 1995b) developed a modeling approach based on the polymer solution thermodynamics using the experimental phase behavior data from the laboratory tests. They assumed that a pure solvent phase separates upon phase separation, implying that all asphaltenes are separated at the precipitation onset point and obtained the following equation:

$$\ln\!\left(1-\phi_a^*\right)+\left(1-\frac{v_s}{v_a}\right)\phi_a^* + \frac{v_s}{RT}\left(\delta_a - \delta_s\right)^2 \phi_a^{*2} \tag{2.4}$$

Where ϕ_a^* = volume fraction of asphaltenes in the nucleating phase at the onset point (-)

v_a = molar volumes of asphaltenes (cm^3/mol)

v_s = molar volumes of solvent (cm^3/mol)

δ_a = solubility parameters of asphaltenes ($MPa^{\frac{1}{2}}$)

δ_s = solubility parameters of solvent ($MPa^{\frac{1}{2}}$)

Wang and Buckley (2001a) proposed a new two-component asphaltene solubility model (ASM) to predict the phase behavior of asphaltenes in crude oils without any simplifying assumptions. This model is based on the changes of the Gibbs free energy of mixing using the Flory-Huggins polymer theory (Huggins, 1941; Flory, 1942) coupled with the solubility parameter estimation. From the Flory-Huggins theory, the Gibbs free energy of mixing of asphaltenes and maltenes (the rest of the mixture) at a particular pressure can be defined as

$$\Delta G_{mix} = RT\left[n_m \ln\phi_m + n_a \ln\phi_a + n_m\phi_a \frac{v_m}{RT}\left(\delta_a - \delta_m\right)^2 \right] \tag{2.5}$$

Where ΔG_{mix} = Gibbs free energy of mixing (J)

R = ideal gas constant (8.314 J/mol/K)

T = temperature (K)

v_m = molar volumes of maltenes (cm^3/mol)

δ_a = solubility parameters of asphaltenes ($MPa^{\frac{1}{2}}$)

δ_m = solubility parameters of maltenes ($MPa^{\frac{1}{2}}$)

This model matches the experimental data under ambient conditions with precipitants ranging from n-pentane to n-pentadecane. Further investigation is needed to be performed for better understanding of the role of smaller (lighter) precipitants (including methane to n-butane) on the asphaltene precipitation onset. Furthermore, a comprehensive model is needed to incorporate the effects of pressure and temperature on the asphaltene precipitation onset. Finally, one should be able to

predict the asphaltene precipitation onset of the live oil from a few ambient experimental data.

2.8 Live Oil

Live oil or reservoir fluid can be considered to have two major fractions: stock tank oil (STO) and dissolved gas (DG) (Gharfeh *et al.*, 2006). Any parameters of the live oil (i.e. refractive index and solubility parameter) can be obtained experimentally or mathematically by combining these parameters of stock tank oil and dissolved gas. A schematic diagram is shown in Figure 2.6.
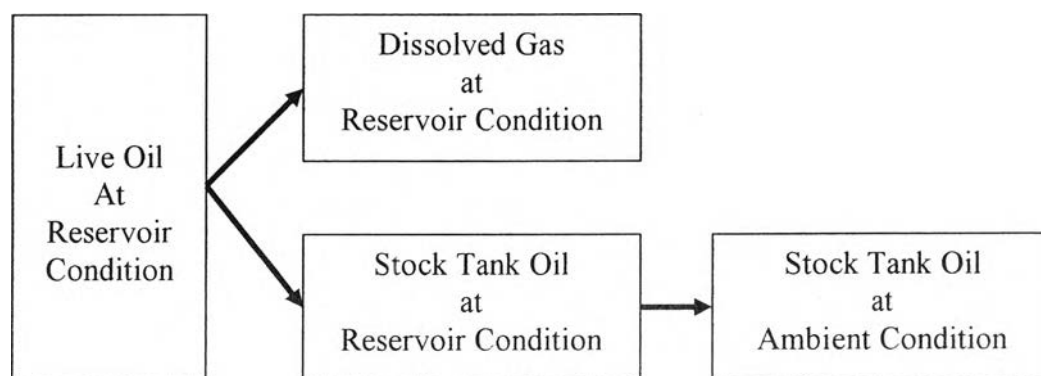

Figure 2.6 Schematic of live oil

2.9 Miscible Injection

In oil production, the injection of water, carbon dioxide, hydrocarbon solvents or hydrocarbon gases are widely used to enhance oil recovery. These injections not only maintain or increase the reservoir pressure, but also decrease the viscosity of reservoir fluid for better transportation. In some cases, the produced gases are reinjected to the reservoir and these reinjected gases are called miscible injectant (MI). Miscible injectants usually contain 60-80% of methane, which is considered to be the precipitant for asphaltenes. Therefore, the effect of miscible injection the precipitation of asphaltenes should be investigated.

2.10 Previous Work on Modeling

Kraiwattanawong (2005) developed a mathematical method to determine the actual precipitation onset point from the automatic titration data and was found to be consistent with a visual observation. The experimental and mathematical methods were developed to determine the oil solubility parameter and the onset solubility parameter. The oil solubility parameter is found to be independent of precipitant and solvent type because it is a property of the crude oil itself. The onset solubility parameter is found to be independent of solvent type, but strongly dependent on the precipitant type.

The Hischberg model (Hischberg, 1984) was found to be very good in predicting the onset solubility parameter in the experimental range. This model was simplified by correlating the onset solubility parameter with the square root of the molar volume of the mixture. The extrapolation with the square root of molar volume of precipitant (Wang and Buckley, 2001; Wang et al., 2003; Wang et al., 2004) was also investigated. The three extrapolation methods above were compared and the prediction with the Hischberg model and the simplified model with the square root of molar volume of mixture are in good agreement. The onset solubility parameter of the live oil was predicted with the square root of the molar volume of the mixture. The effect of miscible injectant (MI) was also investigated and incorporated into the model prediction. The results of the model were compared with the high pressure experimental data and found to be in excellent agreement.

2.11 Asphaltene Dispersants

Asphaltene dispersants (often called asphaltene inhibitors) are chemicals or blend of chemicals which can be used to prevent asphaltene precipitation, delay asphaltene precipitation, and/or stabilize precipitated asphaltene particles. These chemicals are surfactant-like chemicals with polar head and non-polar tail. The examples of these chemicals are 4-Dodecyl Resorcinol (DR), 4-Dodecyl Phenol (DP), and 4-Dodecyl Benzene Sulfonic Acid (DBSA). The molecular structures of these known chemical compounds are shown in Figure 2.7.
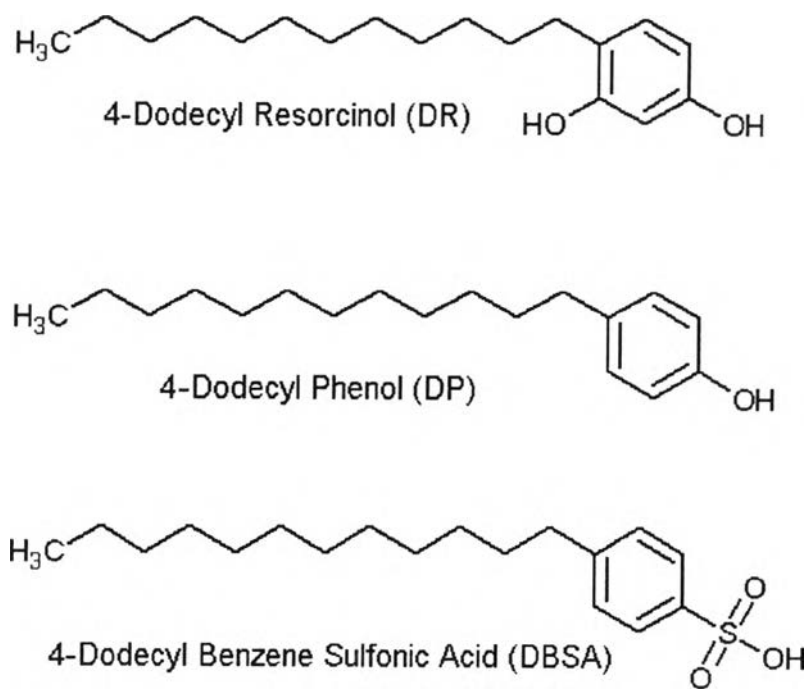
4-Dodecyl Resorcinol (DR)

4-Dodecyl Phenol (DP)

4-Dodecyl Benzene Sulfonic Acid (DBSA)

Figure 2.7 Molecular structure of DR, DP, and DBSA