

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Petroleum Crude Oil

Crude oils are complex mixtures of hydrocarbons containing a variety of components with different physical and chemical properties. Often these components are divided into four major fractions; 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).

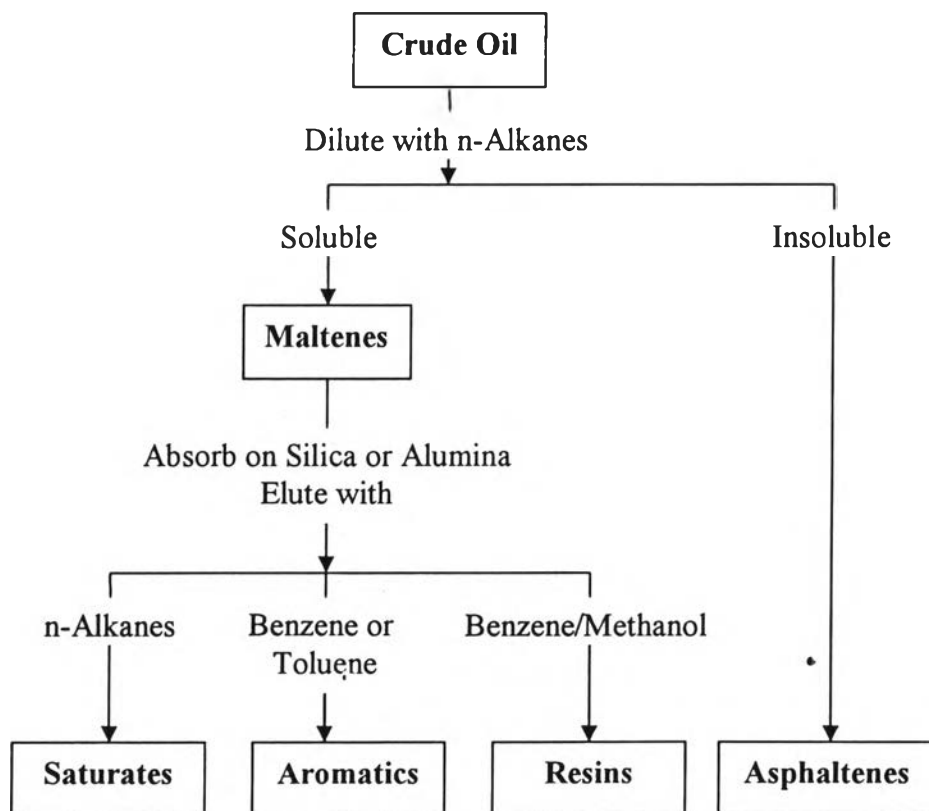


Figure 2.1 Schematic of SARA separation (Wattana, 2004).

Asphaltenes are precipitated from crude oil by the addition of normal alkanes, such as n-pentane or n-heptane with a surface tension lower than 25

dyne cm^{-1} at 25°C (77°F). The relevant parameters for asphaltene separation are both physical and chemical in nature and include: (Speight 1999):

1. Polarity
2. Aromaticity;
3. Molecular weight
4. Three-dimensional structure (the micelle) of asphaltene constituents as they exist in relationship with the other constituents of crude oil
5. Solvent power of the precipitating/extracting liquid used for separation (Figure 2.2)
6. Time required to allow the precipitating/extracting liquid to penetrate the micelle, which is dependent upon the ability of hydrocarbon liquid to penetrate the micelle, indicating that the process is diffusion controlled (Figure 2.3)
7. Ratio of the precipitating/extracting liquid to crude oil, which dictates the yield and character of the asphaltene product (Figure 2.4);
8. Temperature
9. Pressure

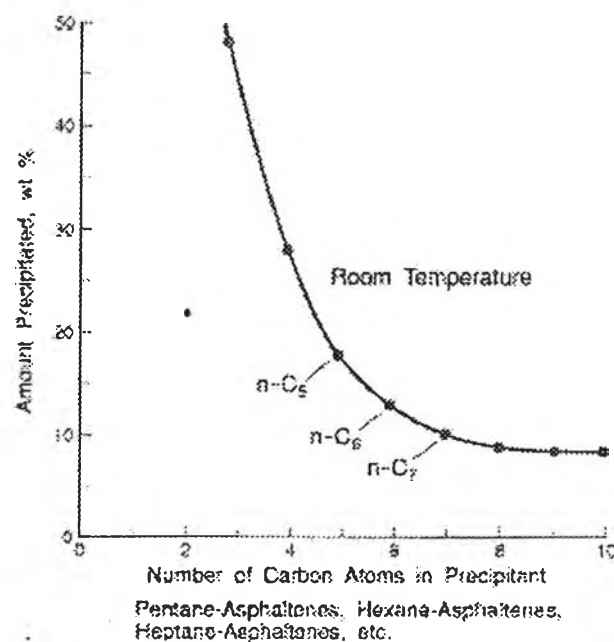


Figure 2.2 Variation of asphaltene yield with hydrocarbon used (Speight, 1999).

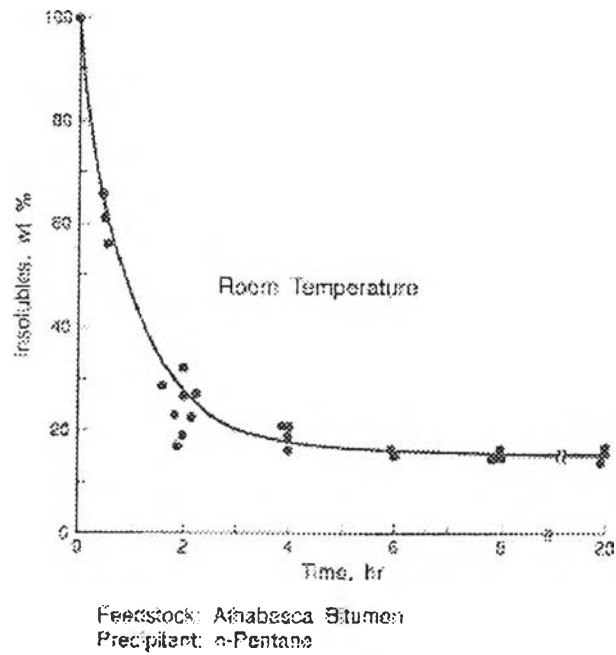


Figure 2.3 Variation of asphaltene yield with time (Speight, 1999).

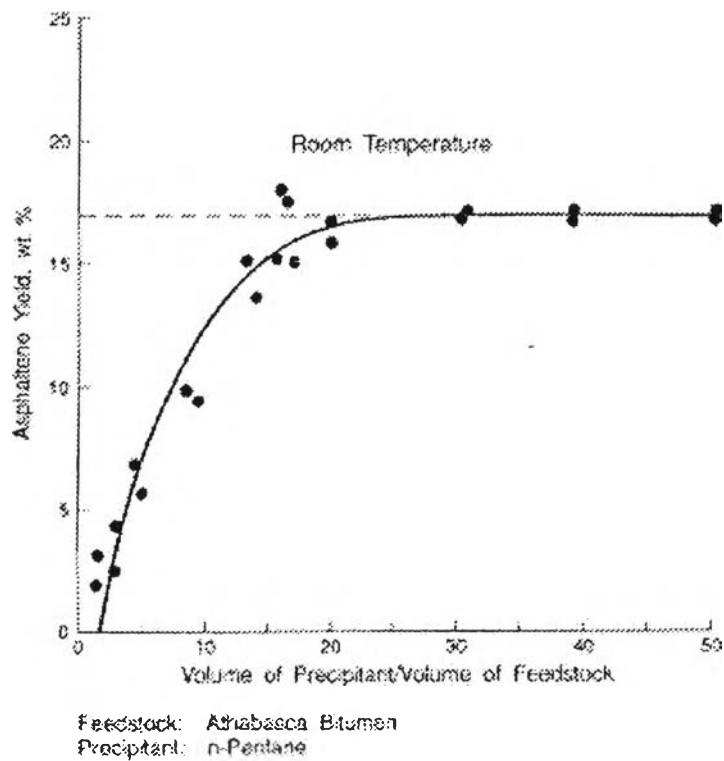


Figure 2.4 Variation of asphaltene yield with amount of hydrocarbon used (Speight, 1999).

The remaining solution, called maltenes, contains saturates, aromatics, and resins, and are separated with the use of adsorbents and elution with solvents of different polarity (Wattana, 2004).

2.2 Definition of Asphaltenes

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, 1991). 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 also 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, vanadium). In addition, asphaltenes are classified by the particular alkane used to precipitate them, such as pentane asphaltenes, hexane asphaltenes, and heptane asphaltenes.

2.3 Composition of Asphaltenes

Asphaltene composition depends on the nature of the hydrocarbon precipitant (normal alkanes) and precipitation condition. The elemental composition of asphaltenes isolated by use of excess (greater than 40) volumes of n-pentane as the precipitating medium show that asphaltenes, generally, compose 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. Although the amount of heteroatoms is small, they have a significant impact on the properties of asphaltenes; for example, solubility characteristics of asphaltenes are strongly affected by the heteroatom content, acid-base chemistry of asphaltenes is often involved heteroatomic sites (Speight, 1999).

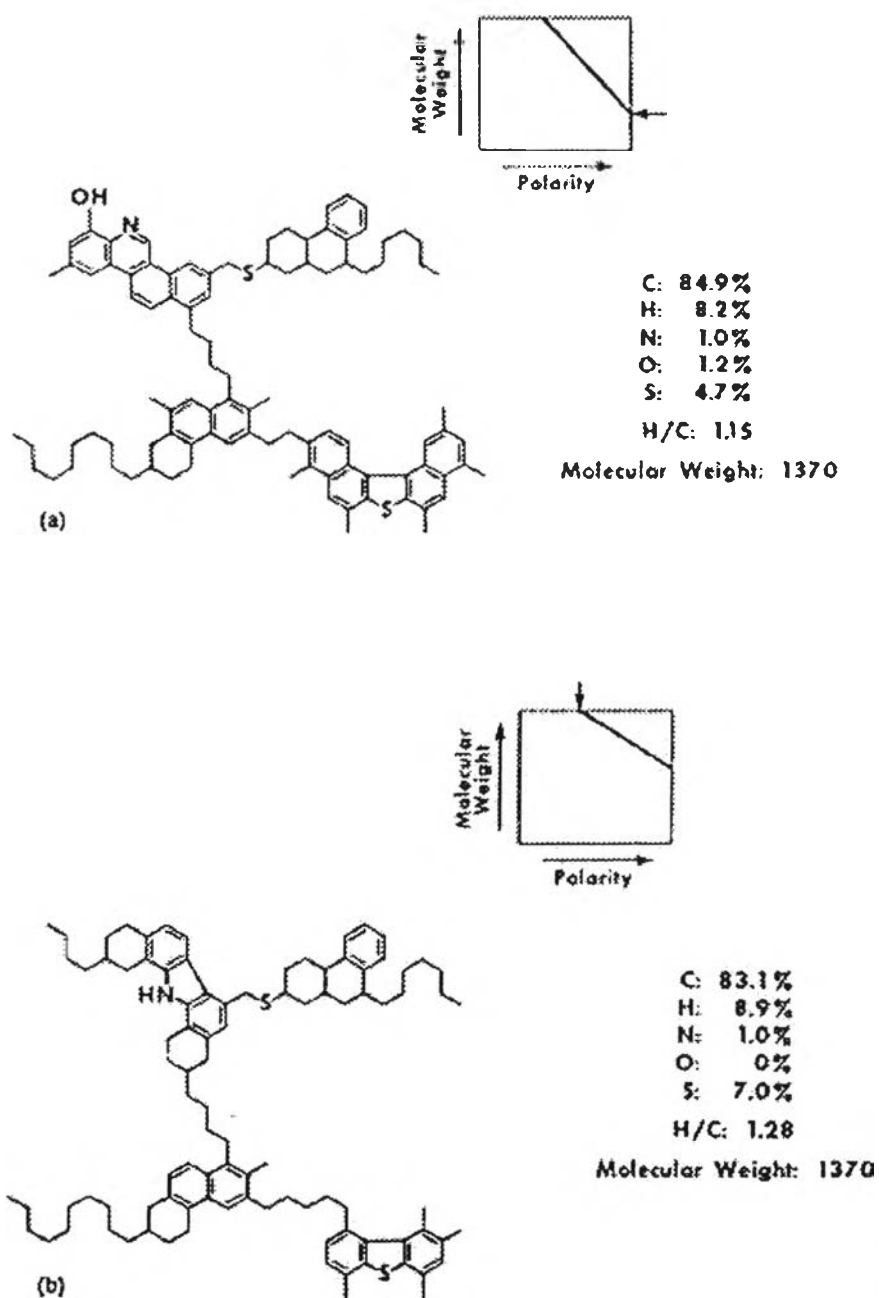


Figure 2.5 Asphaltene structure proposed by Speight (1999).

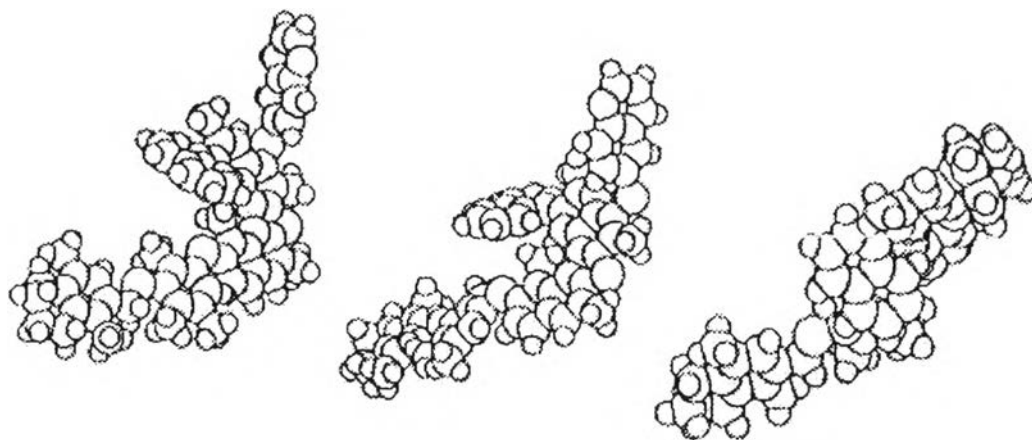


Figure 2.6 Molecular model of the structure shown in Figure 2.5a looking at the model from different angles (Speight, 1999).

2.4 Flocculation and Deposition of Asphaltenes

Asphaltene flocculation of complex systems of the type crude oil + solvent + precipitant can be modeled by simple Scatchard-Hildebrand solubility theory applying continuous thermodynamics. The crude oil is assumed to consist of maltenes and asphaltenes, whose polydispersities are both described by Gaussian distributions. These distributions are considered to depend on the solubility parameter of the oil species. Thus, the different aromaticity of the oils species and their different contents of heteroatoms are taken into account.

Unfortunately, the use of the Scatchard-Hildebrand solubility parameter is restricted to non-polar solvents and precipitants but the calculated results compared with the measured flocculation data are reasonable (Browarzik *et al.*, 1999).

Asphaltene deposition from petroleum fluids occurs due to solubility effect as well as colloidal phenomena. Asphaltene particles have the tendency to aggregate together in an irreversible fashion, grow in size, and form new and larger particles. They have an affinity to absorb resins and other charged species present in the oil and are also electrokinetically active, causing electrostatic charge generation and can also be affected by stronger electrostatic charges (Mansoori, 1997).

Among any other heavy organic depositions, asphaltene precipitation is an irreversible process, therefore, when a mixture of heavy organics containing asphaltene is precipitated out of a petroleum fluid, it will not be able to completely redissolve by reversing its conditions. This has been a major reason why equilibrium thermodynamic models have failed to predict crude oil deposition accurately (Mansoori, 1997).

2.5 Stabilization of Asphaltenes

Asphaltenes are, in fact, insoluble in the oil fraction, but it is now clear that the asphaltene dispersion is mainly attributed to the resins. In fact, the only way to bring about dispersion of asphaltenes in their corresponding oil fraction is by adding resins. The general indication is that the degree of aromaticity of, and the proportion of hetero elements in, resins appear to play an important part in the ability of these materials to bring about solubility of the asphaltenes in oil (Speight, 1991).

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 be the adverse effect on the ability of the resins to associate with asphaltenes from a different crude oil (Speight, 1991). In addition, asphaltenes exist as single entities in petroleum oil but maybe 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).

2.6 Solubility of Asphaltenes

Asphaltene solubility is of great interest to the oil industry because they 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 solubilities 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 a Flory-Huggins entropy of mixing. They found that both single-component solubility parameter and three-component solubility parameter models successfully predict asphaltene solubility in variety of nonpolar and slightly polar organic solvents, including normal and branched alkanes, aromatics, dichloromethane, Decalin, and 1-hexene.

2.7 Solubility Parameters

The solubility parameter was first described by Hildebrand and Scott in 1950. A solubility parameter is a cohesion parameter which 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 and is defined by:

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

Where δ = solubility parameter (MPa)^{1/2}

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

v^L = molar volume of the liquid (cm³/mol)

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

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

T = temperature (K)

Solubility parameters are easily calculated from the physical and chemical properties of a pure liquid. In the case of mixtures, it may also be possible to calculate the parameter based on data for the individual components by using the volume average mixing rule of solubility parameter defined by:

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

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

ϕ_i = volume fraction of ith component

δ_i = solubility parameter of component ith (MPa)^{1/2}.

For solid materials and more complex mixtures, it is usually not possible to measure or calculate solubility parameter directly. In such cases, it is necessary to obtain the solubility parameters 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.

2.8 Effect of Temperature and Pressure on the Solubility Parameter

The Hildebrand solubility parameter is dependent on both temperature and pressure as a function of molar volume as shown (Hildebrand and Scott, 1964):

$$\frac{d \ln \delta}{d \ln v} = -n \quad (2.3)$$

or
$$\delta_1 v_1^n = \delta_2 v_2^n \quad (2.4)$$

Where δ = Hildebrand solubility parameter (MPa)^{1/2}

v = molar volume of the liquid (cm³/mol)

n = constant

For many normal liquids n is about 1.25. However, a $\log \delta - \log v$ plot will provide the most accurate way to determine the value of n .

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

Hydrocarbon	Molar Volume (ml/mol)	Solubility Parameter (MPa) ^½
n-Butane	101.4	14.2
n-Pentane	116.1	14.6
n-Hexane	131.6	15.0
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

2.9 Molar Solubility Parameter of Normal Alkanes

The molar solubility parameter is a value which indicates the relative solvency behavior of normal alkanes in a given liquid phase and is independent of temperature and pressure. The molar solubility parameter is defined as:

$$\delta^M = v \cdot \delta \quad (2.5)$$

where δ^M = molar solubility parameter ((MPa)^½ml./mol)

v = molar volume (cm³/mol)

δ = Hildebrand solubility parameter

The molar solubility parameters of normal alkanes are summarized in Table 2.2.

Table 2.2 Molar solubility parameter of normal alkanes

Hydrocarbon	Molar Solubility Parameter ((MPa) ^{1/2} ml./mol)
Methane	528.6
Ethane	800.4
Propane	1107.4
n-Butane	1444.6
n-Pentane	1719.2
n-Hexane	1975.6
n-Heptane	2254.8
n-Octane	2534.3
n-Nonane	2803.3
n-Decane	3083.3
n-Undecane	3358.1
n-Dodecane	3657.6
n-Tridecane	3923.6
n-Tetradecane	4233.1
n-Pentadecane	4505.3
n-Hexadecane	4823.2
n-Octadecane	5377.5
n-Eicosane	5936.7

The molar solubility parameter, previously called the square root of cohesive energy-volume, is directly related to molar refractivity (product of molar volume, v and refractive index function, $F_{RI} = (n^2 - 1)/(n^2 + 2)$) (Scatchard, 1949) which is independent of temperature and pressure as shown in Figure 2.7.

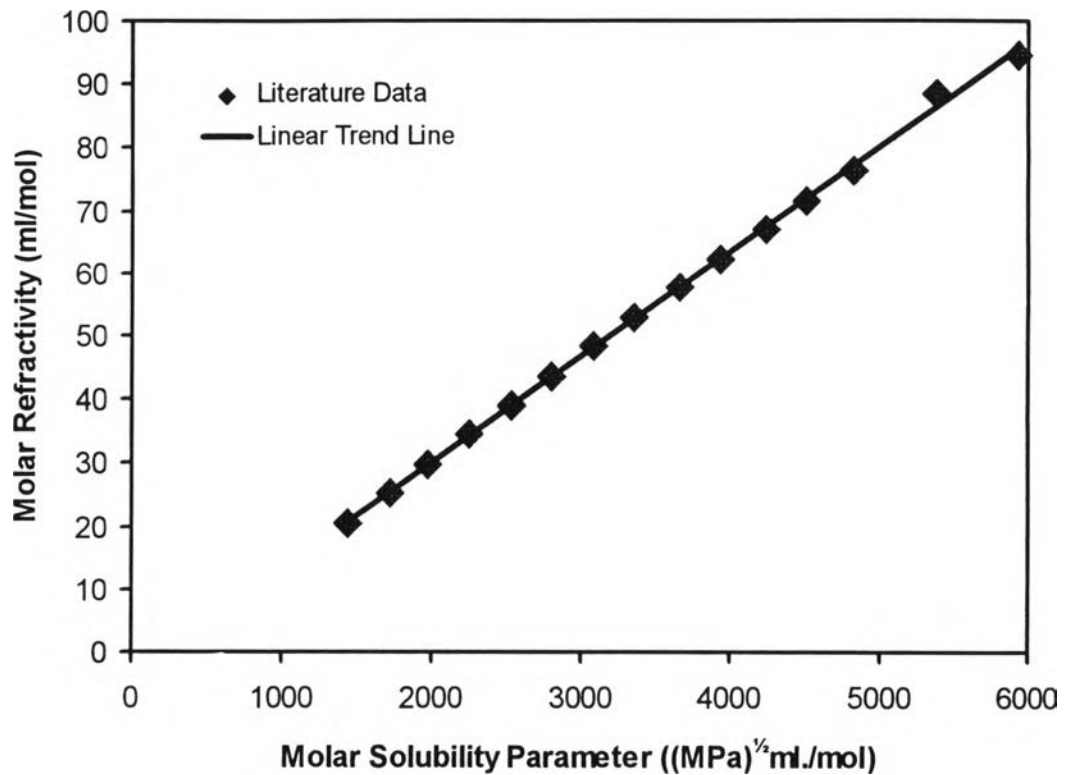


Figure 2.7 The molar solubility parameter of normal alkanes has a linear relationship with the molar refractivity which is not a function of temperature and pressure.

The molar solubility parameter of normal alkane mixtures obey the mole average mixing rule as follows:

$$\delta_{mixture}^M = \sum x_i \delta_i^M \quad (2.6)$$

where $\delta_{mixture}^M$ = molar solubility parameter of a normal alkane mixture ((MPa)^{1/2}ml./mol)

x_i = mole fraction of i^{th} component

δ_i^M = molar solubility parameter of the i^{th} component ((MPa)^{1/2}ml./mol)

2.10 Asphaltenes Precipitation Onset Tests

The asphaltene precipitation onset tests in the petroleum industry have usually been accomplished by mixing crude oil with different amounts of solvent, such as toluene, and titrating with normal alkanes, such as n-pentane or n-heptane, to initiate asphaltene precipitation. The results are often reported as a ratio of volume of normal alkane added per volume of crude oil at a given ratio of volume of solvent per volume of crude oil. From this experimental data, asphaltene precipitation onset can also be indicated as the onset solubility parameter defined by:

$$\delta_{onset} = \phi_o \delta_o + \phi_s \delta_s + \phi_p \delta_p \quad (2.7)$$

Where δ_{onset} = onset solubility parameter (MPa)^{1/2}

ϕ = volume fraction

δ = solubility parameter (MPa)^{1/2}

The subscripts o , s and p refer to crude oil, solvent, and precipitant (normal alkanes), respectively. Equation (2.7) can be rearranged in terms of the volume ratio as:

$$\frac{V_p}{V_o} = \left(\frac{\delta_s - \delta_{onset}}{\delta_{onset} - \delta_p} \right) \frac{V_s}{V_o} + \left(\frac{\delta_o - \delta_{onset}}{\delta_{onset} - \delta_p} \right) \quad (2.8)$$

where V is the volume of precipitant (p), crude oil (o), and solvent (s) respectively. By plotting V_p/V_o versus V_s/V_o , δ_o and δ_{onset} can be calculated by finding the slope and intercept of the line.