

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Crude Oil

Two Alaska crude oil samples (Oil A and Oil B) and one Canadian heavy oil sample (Oil C) were used in this study. The existing particles in the oil samples such as sand or clay were centrifuged out prior to experimentation. Properties of the crude oil samples are presented in Table 3.1.

**Table 3.1** Properties of crude oil samples

	Oil A	Oil B	Oil C
Density at 25°C (g/ml)	0.9044	0.8835	1.0122
Molecular Weight* (g/mol)	278	236	624
n-Heptane Asphaltene (wt%)	2.23	6.34	21.4

\*Molecular weight of each crude oil is acquired from PVTsim EOS data.

#### 3.1.2 Asphaltene Precipitants and Solvent

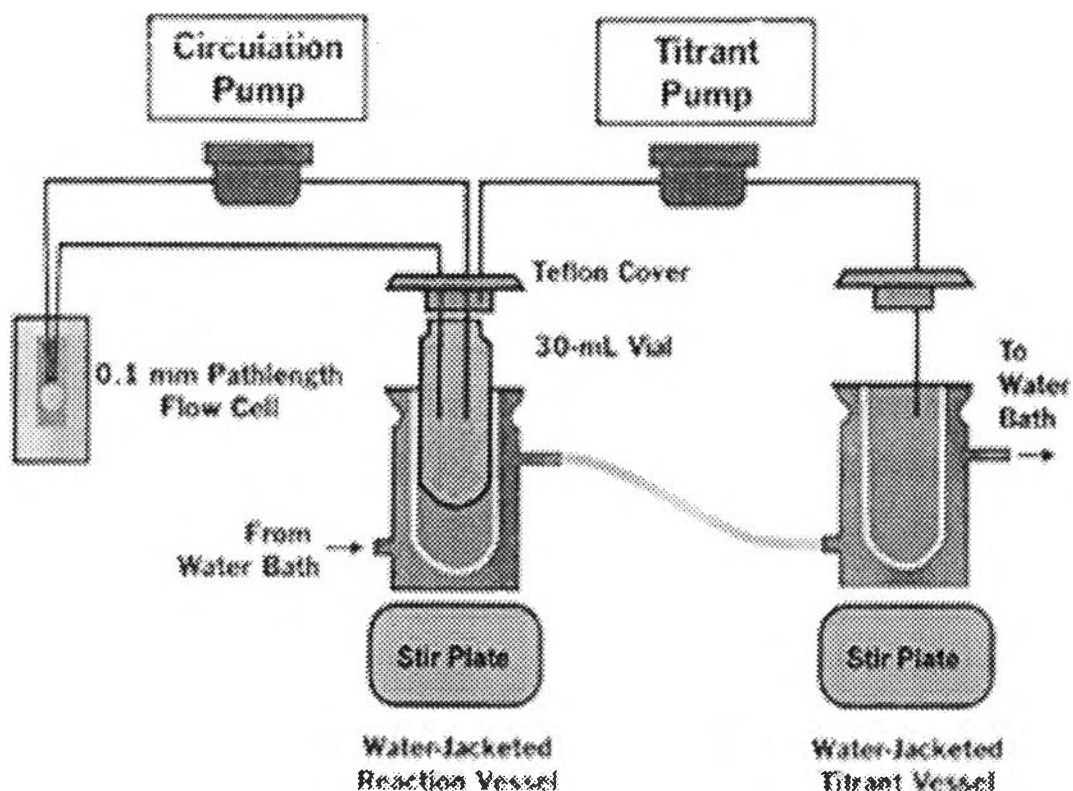
Normal alkanes from n-Pentane to n-Hexadecane were used to titrate with crude oil samples to precipitate the asphaltenes. Toluene was used in the test as a solvent. Properties of asphaltene precipitants and solvent at 25°C are in Table 2.1.

### 3.2 Experimental Equipment

#### 3.2.1 Asphaltene Precipitation System

The asphaltene precipitation onset was determined using an Automated Flocculation Titrimeter (AFT) by Western Research Institute with LS-1 Tungsten Halogen Light Source, USB2000 Miniature Fiber Optic Spectrometer by Ocean Optics, Inc. and 0.1mm path length quartz flow cell by Starna Cells, Inc. to measure the light transmittance at 740nm. The temperature was controlled to  $\pm 0.01^\circ\text{C}$  with a

circulating water bath. Sample crude oil or crude oil/toluene mixtures of about 3 g were titrated with normal alkanes at the rate of 0.5 ml/min. The online data acquisition and system control was performed using a PC. The titration system is illustrated in Figure 3.1.



**Figure 3.1** Schematic of precipitation system.

### 3.2.2 Density Measurement

The density of the crude oil at different temperatures was measured based on standard procedure ASTM D 4052-96 using a DMA 48 Density/Specific Gravity/Concentration Meter by Anton PAAR with accuracy of  $\pm 0.0001 \text{ g/cm}^3$ .

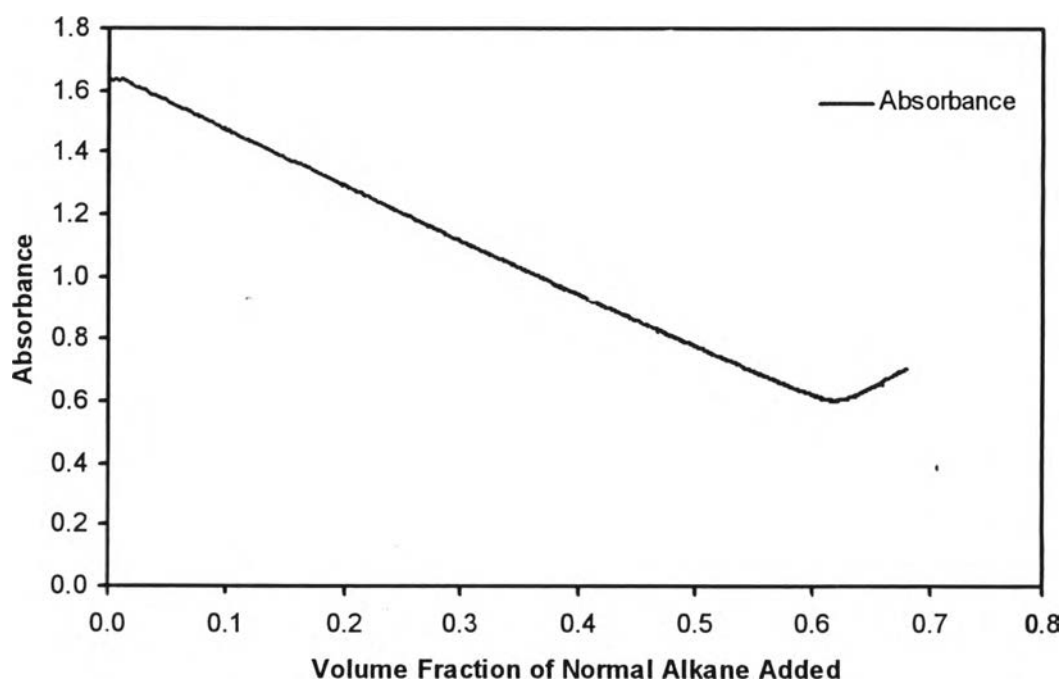
### 3.2.3 Asphaltene Content Measurement

Asphaltene content in crude oil was based on standard procedure ASTM D 893-85 method with n-heptane as a precipitant.

### 3.3 Experimental Methods

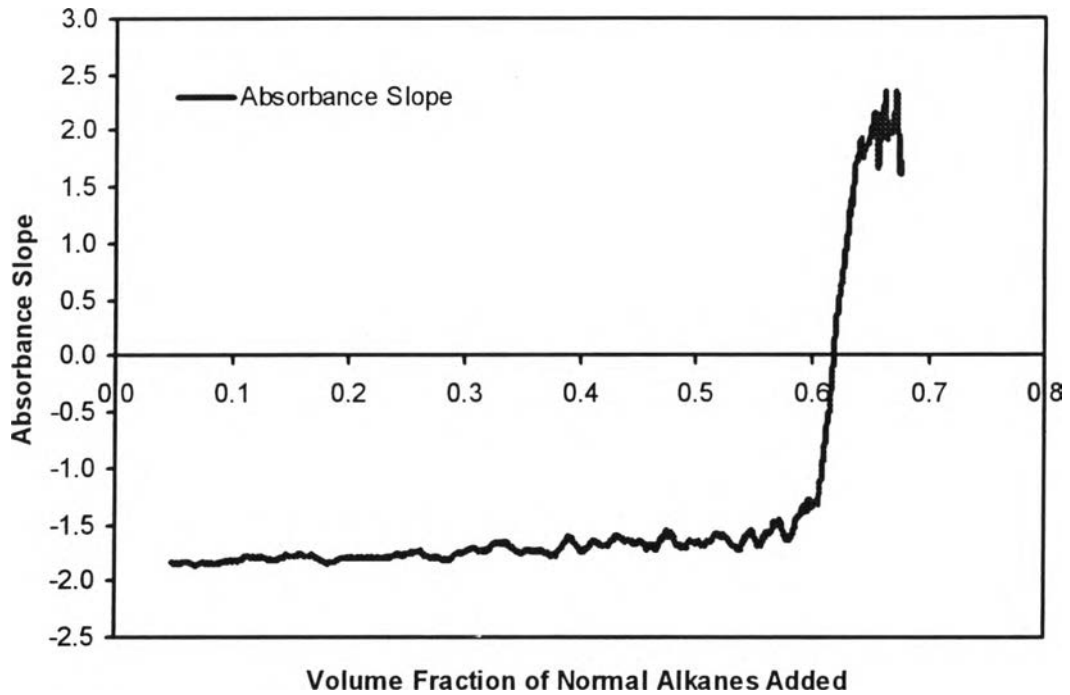
#### 3.3.1 Onset Point Determination

The precipitation onset of asphaltene during titration with normal alkanes (asphaltene precipitants) is usually identified by the point of minimum light absorbance or maximum light transmittance (Browarzik *et al.*, 1999; Yang *et al.*, 1999; Andersen, 1999) which actually is not correct. The first part of the titration curve shows a decrease in absorbance due to the dilution effect by normal alkanes. The curve continues to decrease until the point of minimum light absorbance. At this point, there are sufficient asphaltene particles to counteract the dilution effect. Therefore, the actual precipitation onset point should be located before the point of minimum light absorbance, where the deviation from the dilution takes place. Figure 3.2 shows the light absorbance as a function of volume fraction of normal alkane added.



**Figure 3.2** Absorbance as a function of volume fraction of normal alkane added.

In order to identify the deviation point, the absorbance slope was plotted as a function of volume fraction of normal alkane added as shown in Figure 3.3.



**Figure 3.3** Absorbance slope as a function of volume fraction of normal alkane added.

According to Beer's Law (Blaedel and Meloche, 1963), the light absorbance is a linear function of concentration:

$$A = abc \quad (3.1)$$

where  $A$  = absorbance,  
 $a$  = absorptivity  
 $b$  = path length  
 $c$  = concentration.

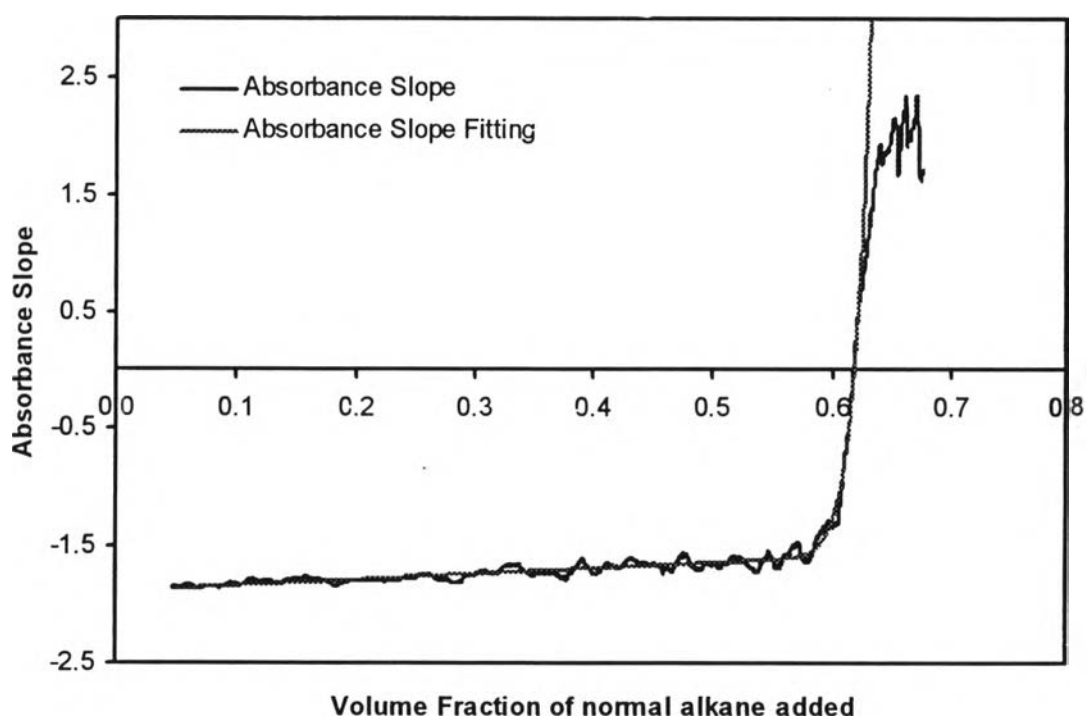
Or the derivative of light absorbance should be a constant. The mathematical equation to fit the experimental data can be derived by utilizing Beer's Law.

$$\frac{dA}{dc} = (c - \alpha)\beta^{(c-\alpha)} + \gamma + ab \quad (3.2)$$

where  $c$  = volume fraction of normal alkane added

$\alpha, \beta, \gamma = \text{constant}$

The  $ab$  term represents the derivative of Beer's law, the  $\gamma c$  term represents the non-ideality of Beer's law that the derivative changes with concentration, and the  $(c - \alpha)\beta^{(c - \alpha)}$  term represents the effect of asphaltene precipitation. The constant,  $\beta$  is a fitting parameter and its value is very high ( $10^5 - 10^{10}$ ) whenever  $c - \alpha \leq 0$  this term is negligible but after  $c - \alpha > 0$  this term dominates the asphaltene precipitation effect that results in increasing of derivative of absorbance. Parameter  $\alpha$  can be considered to be the volume fraction of normal alkane added at the true onset point. The fitting of equation (3.2) to the absorbance slope is shown in Figure 3.4.



**Figure 3.4** The absorbance slope as a function of volume fraction of normal alkane added with the fitting curve.

### 3.3.2 Typical Precipitation Results

Precipitation results are usually reported as mixtures of crude oil, solvent and asphaltene precipitant as shown in Figure 3.5 and Figure 3.6.

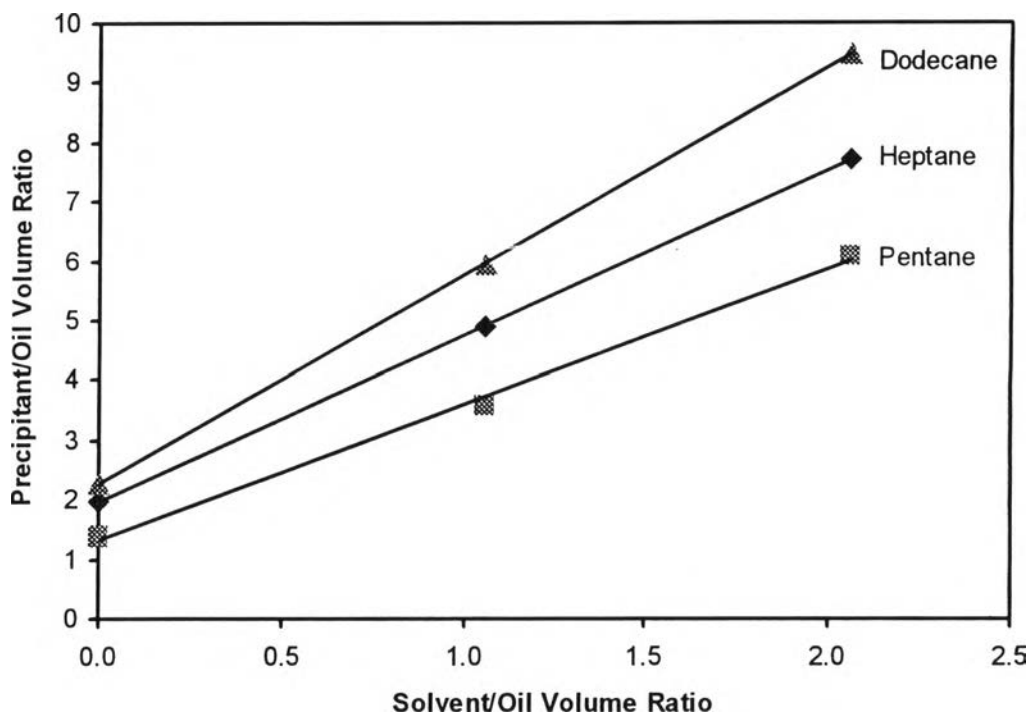


Figure 3.5 Typical precipitation results with different asphaltene precipitants.

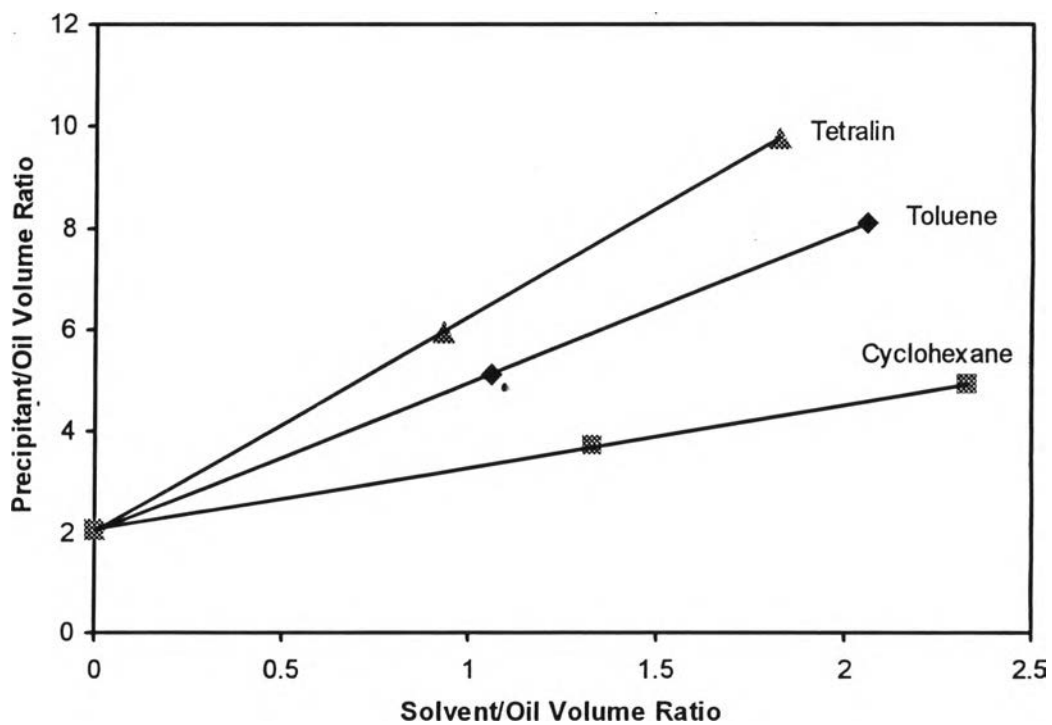
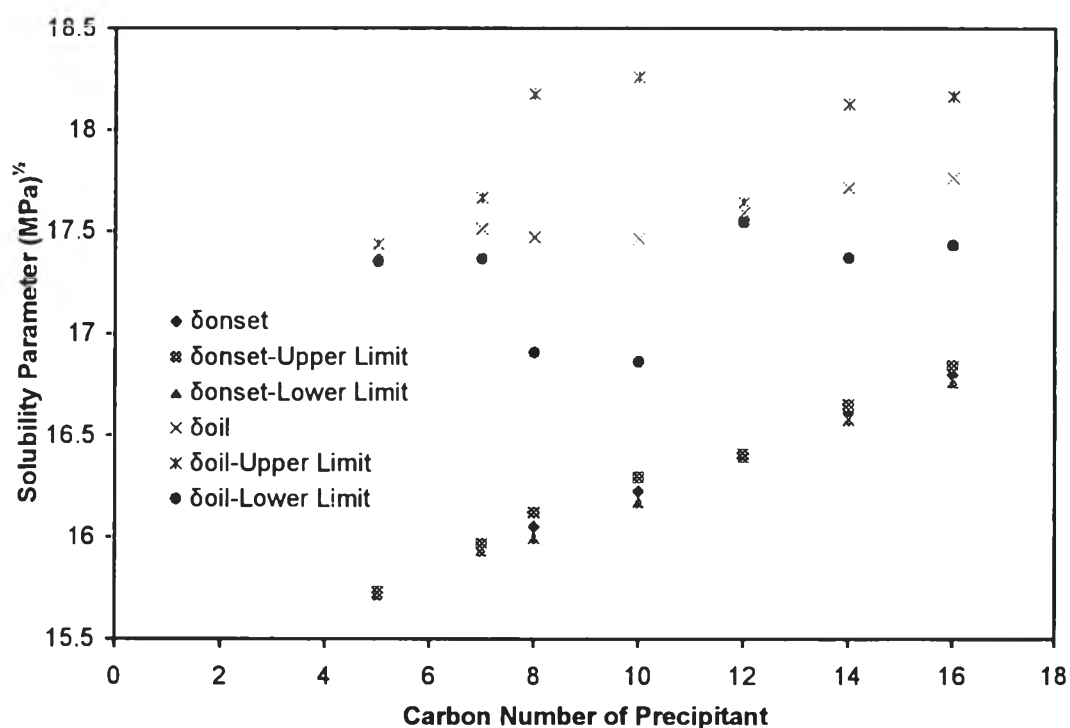


Figure 3.6 Typical precipitation results with different solvents.

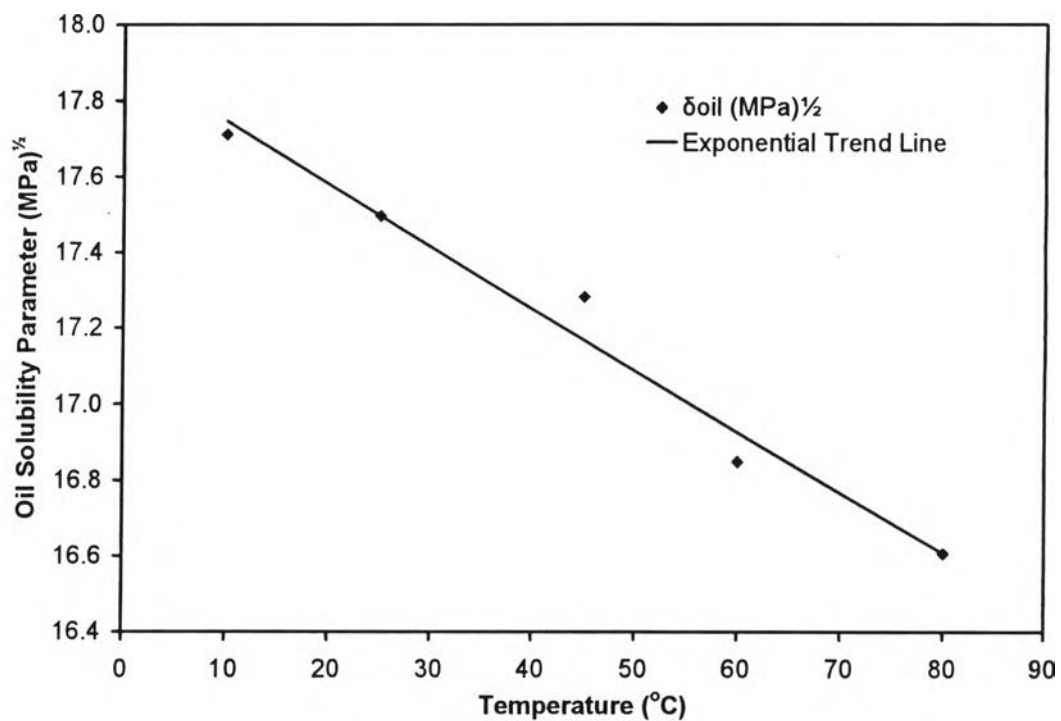
From Figure 3.6, mixing crude oil with different solvents (cyclohexane, toluene, and tetralin) and titrating with n-heptane gives the same intercept. From equation (2.8), the intercept is dependent on the oil solubility parameter and the onset solubility parameter. Therefore, it appears that the oil solubility parameter and the onset solubility parameter are independent of the solvent.

For the effect of asphaltene precipitant on the oil solubility parameter and the onset solubility parameter, Figure 3.7 shows that the oil solubility parameter is statistically (95 percent confidence) the same with different asphaltene precipitants, but the onset solubility parameter changes with different asphaltene precipitants.

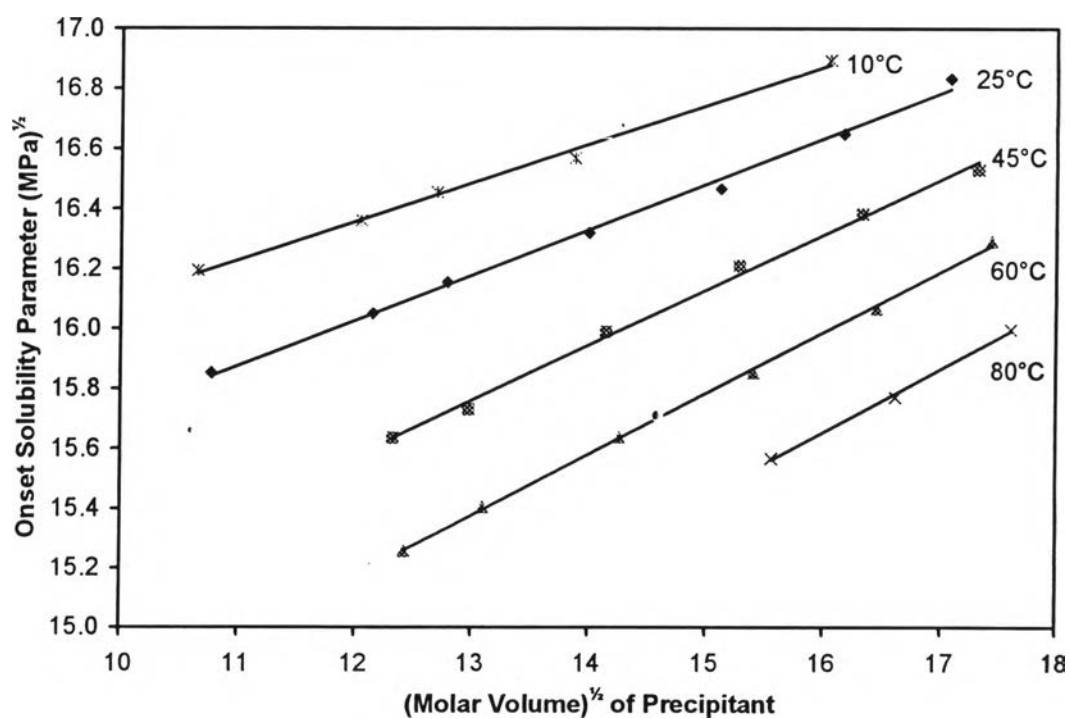


**Figure 3.7** The 95 percent confidence on the oil solubility parameter and the onset solubility parameter.

From equation (2.8), the oil solubility parameter and the onset solubility parameter can be calculated, which shows that the oil solubility parameter is only a function of temperature as shown in Figure 3.8 and the onset solubility parameter is a function of temperature and type of asphaltene precipitant as shown in Figure 3.9.

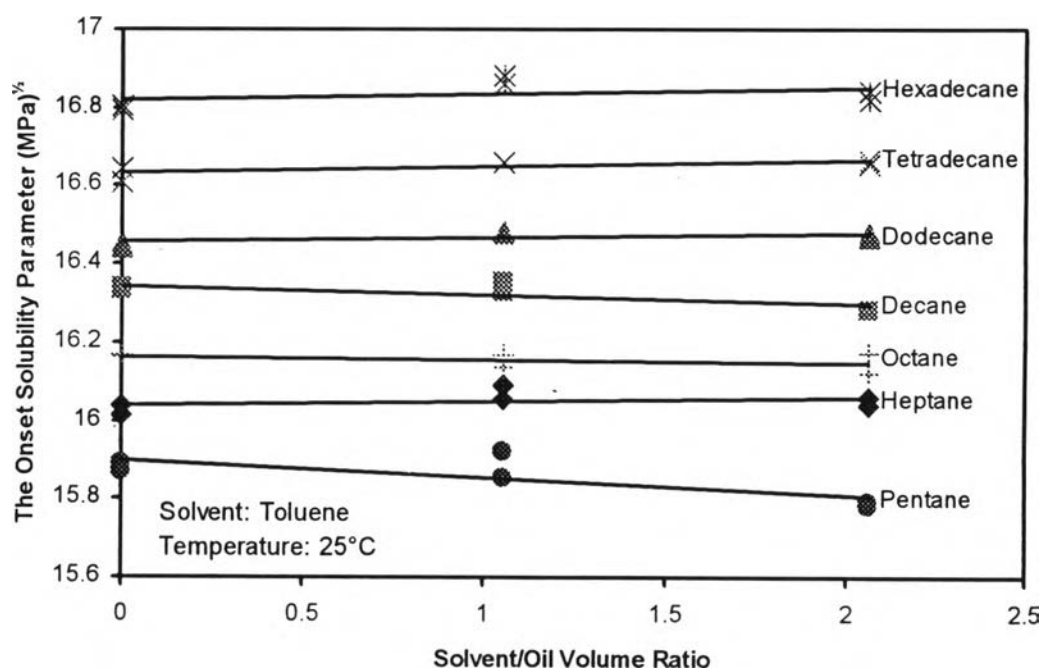


**Figure 3.8** The oil solubility parameter is only a function of temperature.



**Figure 3.9** The onset solubility parameter is a function of temperature and the type of asphaltene precipitant.





**Figure 3.10** The effect of the solvent on the onset solubility parameter.

As stated earlier, Figure 3.10 shows that the onset solubility parameter is independent of the solvent.