



CHAPTER IV RESULTS AND DISCUSSION

4.1 Ambient Titration

The sample crude oil was characterized by a series of titrations at 25 °C, 45 °C, and 60 °C using an automated flocculation titrimer (AFT) as stated in section 3.3.2. Precipitants (titrants) used in the experiment were *n*-pentane, *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane. The oil solubility parameter calculated from the experimental data with density and molar volume at 25 °C, 45 °C, and 60 °C for crude oil N2 are shown in Table 4.1. The oil solubility parameter (δ_o) as a function of the molar volume (v) is plotted in Figure 4.1.

Table 4.1 Oil solubility parameter, density, and molar volume at different temperatures for crude oil N2

Temperature (°C)	Oil Solubility Parameter (MPa) ^{1/2}	Molar Volume (cm ³ /mol)
25	17.51	268.62
45	17.21	271.84
60	16.87	275.10

The onset solubility parameters (δ_{onset}) at different temperatures with different precipitants are summarized in Table 4.2. The onset solubility parameter can be plotted with the square root of molar volume of the precipitant (Wang *et al.*, 2004) and found to be a straight line from *n*-pentane to *n*-hexadecane, as shown in Figure 4.2. However, the extrapolation of the onset solubility parameter for larger molar volume of precipitant is invalid because whenever the oil solubility parameter crosses the onset solubility parameter, asphaltene precipitation will occur. This is not the case in the field observation when drilling mud is in contact with a crude oil.

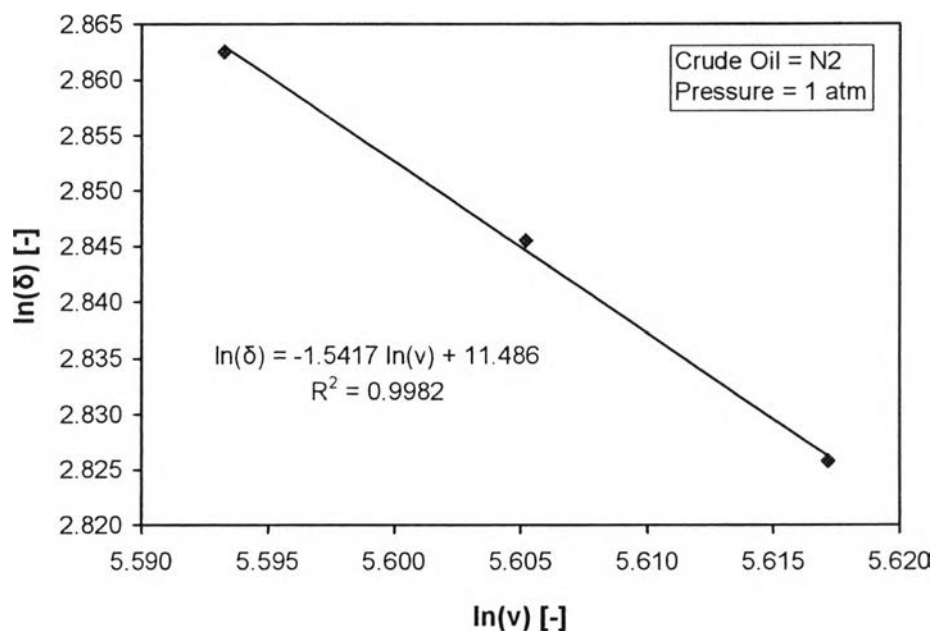


Figure 4.1 Oil solubility parameter as a function of the molar volume of crude oil N2

Table 4.2 Onset solubility parameter at different temperatures and different precipitants for crude oil N2

Temperature (°C)	Precipitant	Carbon Number	Molar Volume (cm ³ /mol)	(Mol. Vol.) ^{1/2}	δ_{onset} (MPa) ^{1/2}
25	Pentane	5	116.1	10.77	15.87
	Heptane	7	147.5	12.14	16.10
	Octane	8	163.5	12.79	16.19
	Decane	10	195.9	14.00	16.36
	Dodecane	12	228.6	15.12	16.50
	Tetradecane	14	261.3	16.16	16.67
	Hexadecane	16	291.4	17.07	16.82
45	Heptane	7	151.9	12.32	15.62
	Octane	8	168.3	12.97	15.73
	Decane	10	200.2	14.15	15.97
	Dodecane	12	233.6	15.28	16.20
	Tetradecane	14	266.5	16.32	16.36
	Hexadecane	16	299.6	17.31	16.51
60	Heptane	7	154.3	12.42	15.34
	Octane	8	171.5	13.10	15.42
	Decane	10	203.4	14.26	15.66
	Dodecane	12	237.3	15.40	15.89
	Tetradecane	14	270.5	16.45	16.08
	Hexadecane	16	303.6	17.42	16.27

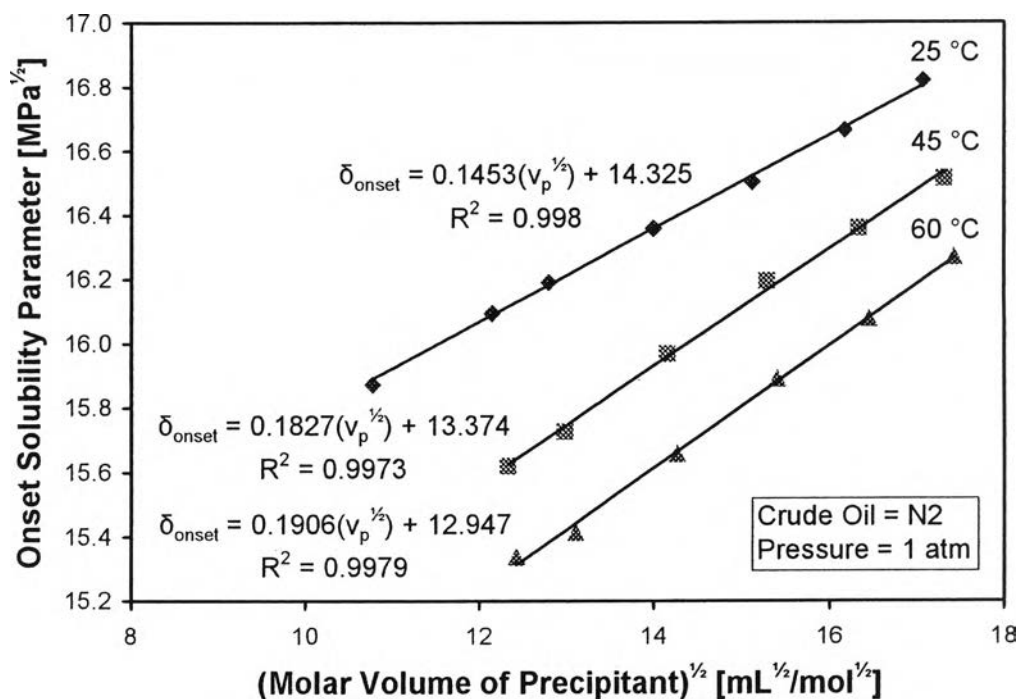


Figure 4.2 Onset solubility parameter as a function of temperature and the square root of the molar volume of the precipitant for crude oil N2

From the experimental data at 25 °C, the onset solubility parameter can also be plotted as functions of the carbon number of the precipitant (Figure 4.3), the molecular weight of the precipitant (Figure 4.4), the molar volume of the precipitant (Figure 4.5), the square root of the molar volume of the precipitant (Figure 4.6), the molar volume of the mixture (Figure 4.7), and the square root of the molar volume of the mixture (Figure 4.8). All of the plots have a very good linear fit with an R^2 value greater than 0.995 and could be used to predict the onset solubility parameter with alkanes as well. However, the extrapolation for methane, ethane, propane and *n*-butane using different correlations are not the same. Therefore, the thermodynamic theory and understanding are required in order to predict the true onset solubility parameter with lighter alkanes.

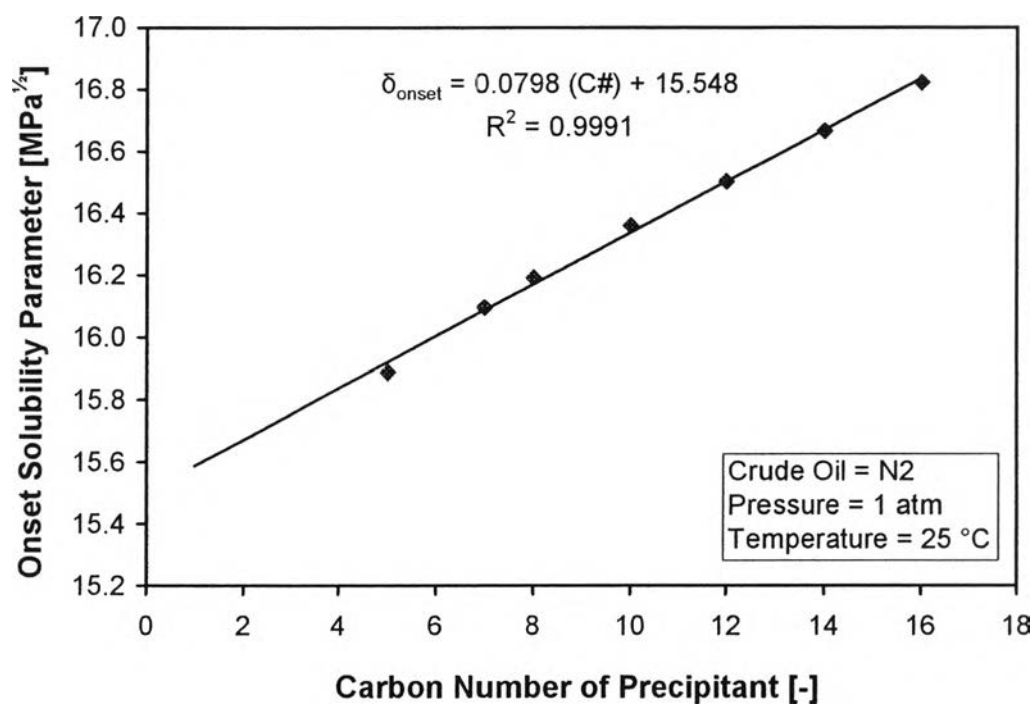


Figure 4.3 Onset solubility parameter versus the carbon number of the precipitant for crude oil N2

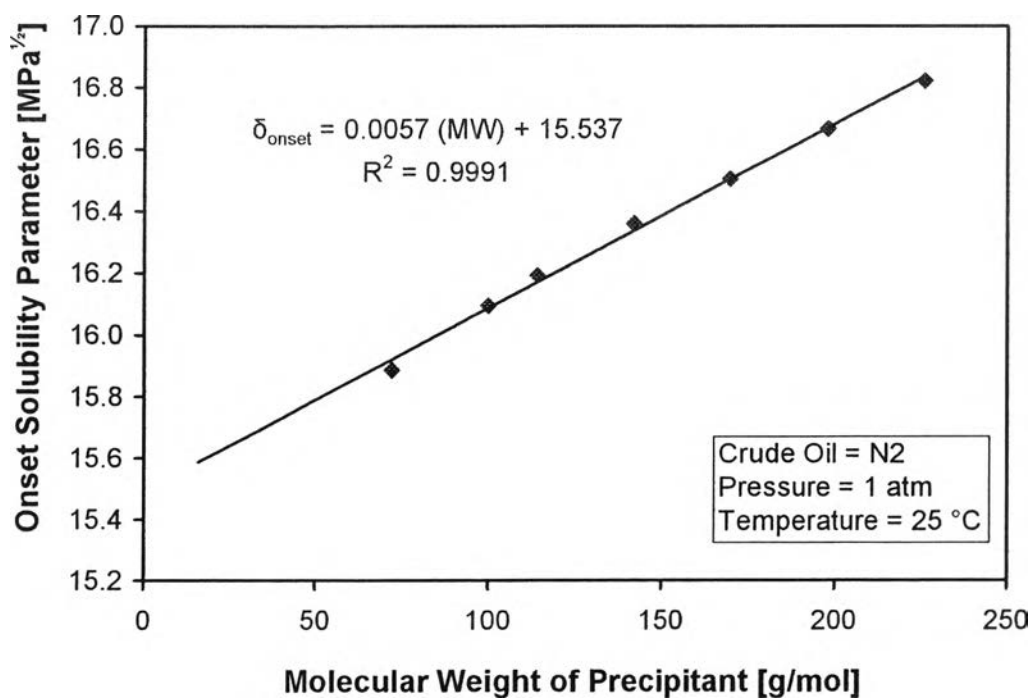


Figure 4.4 Onset solubility parameter versus the molecular weight of the precipitant for crude oil N2

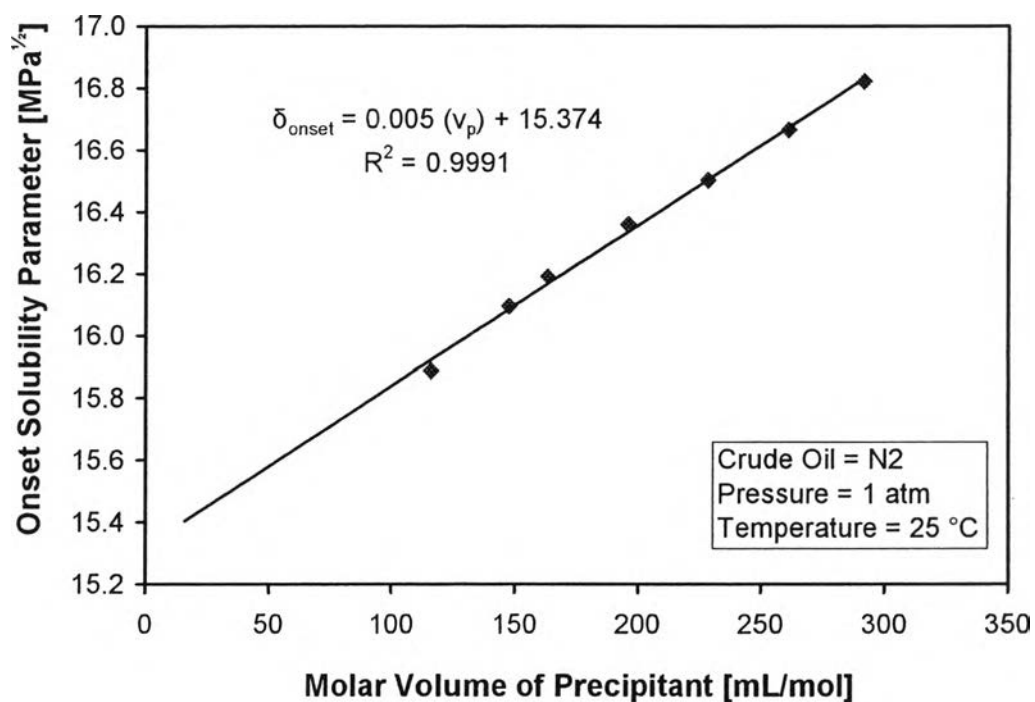


Figure 4.5 Onset solubility parameter versus the molar volume of the precipitant for crude oil N2

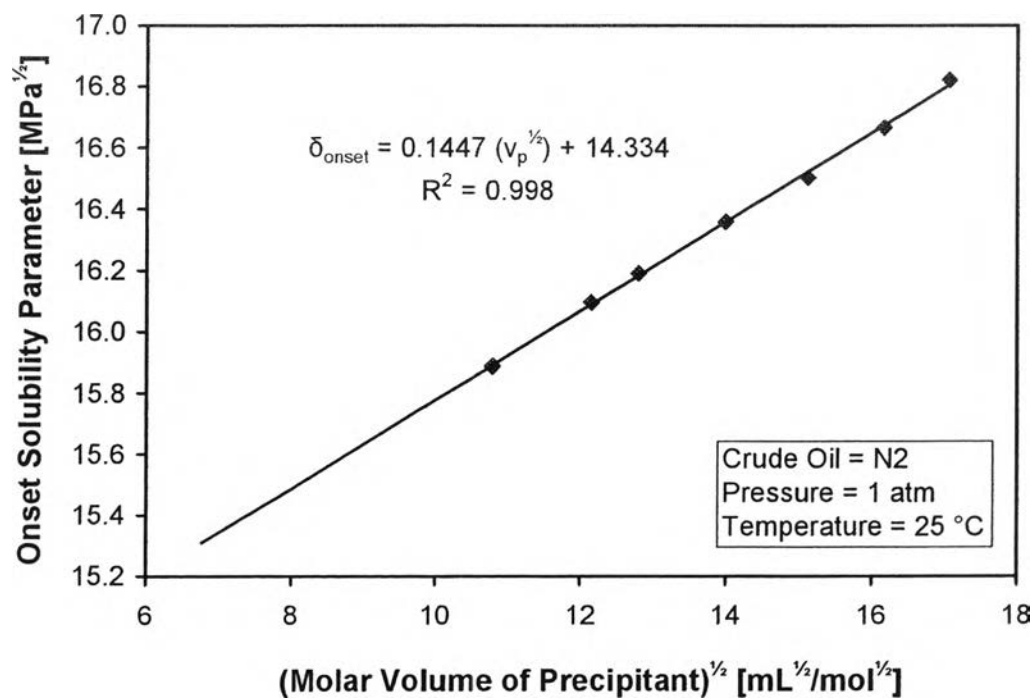


Figure 4.6 Onset solubility parameter versus the square root of the molar volume of the precipitant for crude oil N2

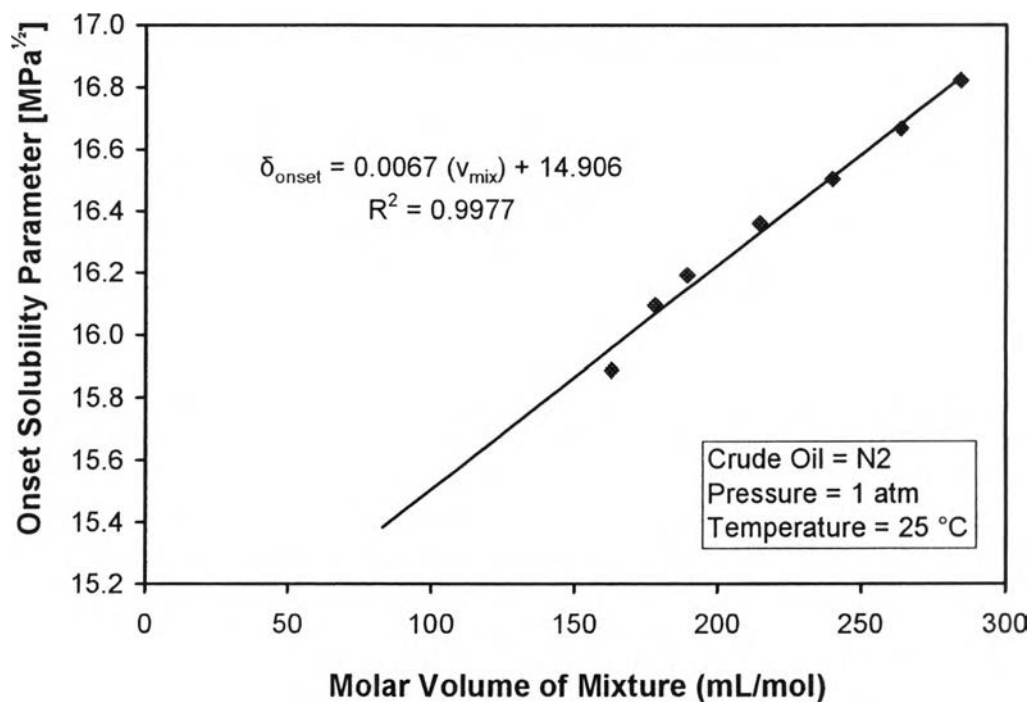


Figure 4.7 Onset solubility parameter versus the molar volume of the mixture for crude oil N2

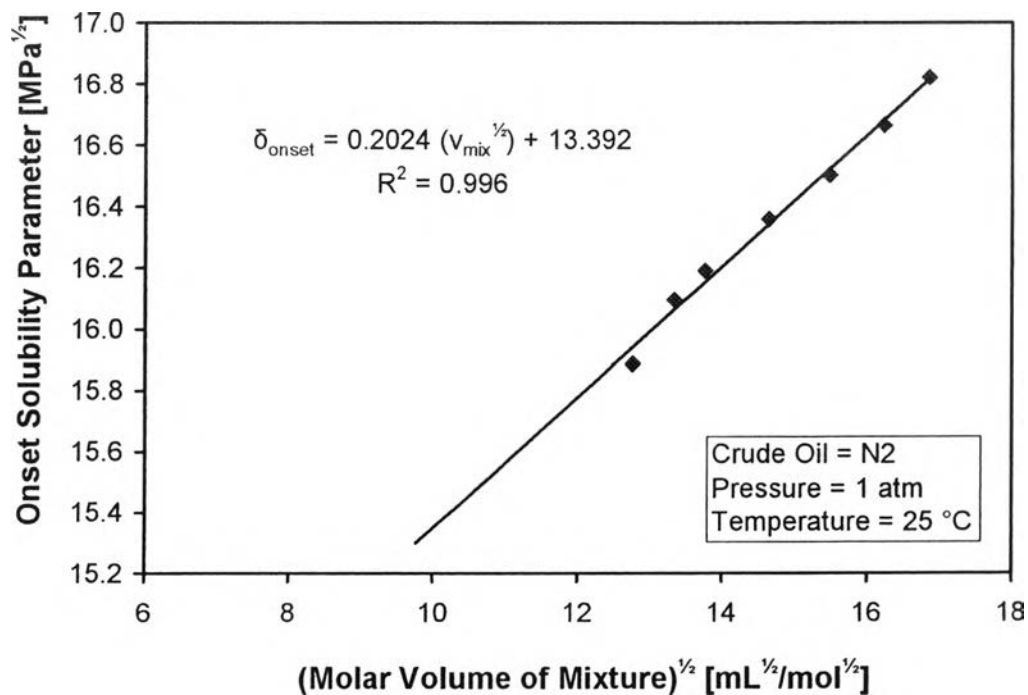


Figure 4.8 Onset solubility parameter versus the square root of the molar volume of the mixture for crude oil N2

4.2 High Pressure Titration

In order to predict the onset solubility parameter for lower carbon number alkanes, the model developed to predict the onset solubility parameter needs to be verified. Because the titrations with ethane, propane, and *n*-butane in the liquid phase are impossible under ambient conditions, these titrations must be performed under high pressure conditions where these alkanes are in the liquid phase. Because ethane has a bubble point pressure of 607.72 psi at 25 °C, all of the high pressure titrations were performed at 1000 psi.

The experimental procedure followed the standard operating procedure (SOP) described in section 3.3.4. In brief, 15-20 mL of crude oil (dead oil) was introduced to the studied vessel pressurized at 1000 psi. Then, the precipitant was added to the pressure vessel at 1000 psi with a rate of 0.5 mL/min. The laser near infrared detector (at 1550 nm) was utilized and the light transmittance was then recorded using a PC. The transmittance curve for high pressure titration with ethane, propane and *n*-butane are shown in Figure 4.9.

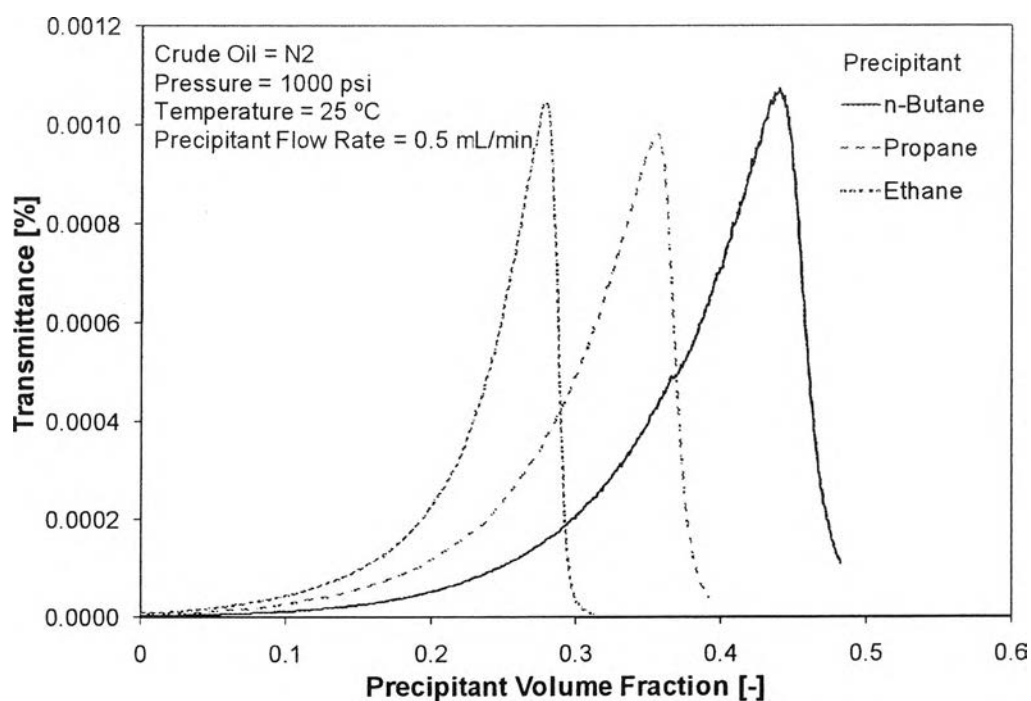


Figure 4.9 Transmittance curve for high pressure titration of crude oil N2 with ethane, propane and *n*-butane

As expected, the amount of precipitant required to initiate asphaltene precipitation for ethane is lower than propane and substantially lower than *n*-butane because ethane has a lower solubility parameter than propane and *n*-butane. When plotting the amount of precipitant needed to initiate asphaltene precipitation per amount of crude oil with carbon number of precipitant, one can obtain a typical curve, as shown in Figure 4.10. This can also be plotted with volume fraction of precipitant yielding the similar result as shown in Figure 4.11. The results on both plots show that the amount of precipitant required per amount of crude oil is at maximum between *n*-decane or *n*-dodecane due to the solubility parameter of the precipitant and the onset solubility parameter with each of the precipitant.

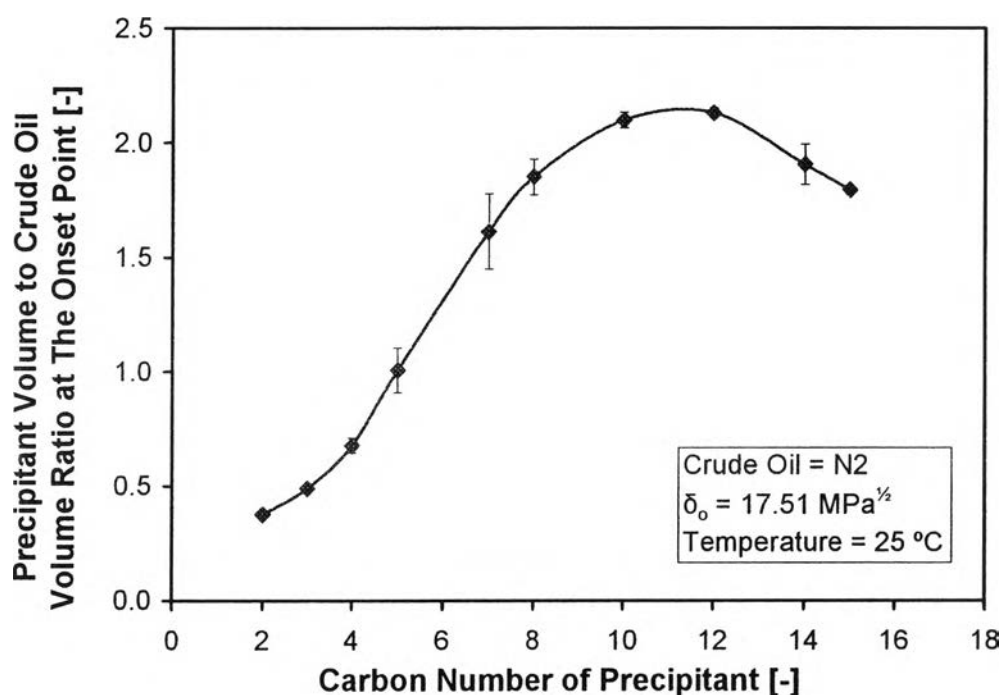


Figure 4.10 Amount of precipitant required per amount of crude oil N2 for ethane to *n*-hexadecane at the onset point

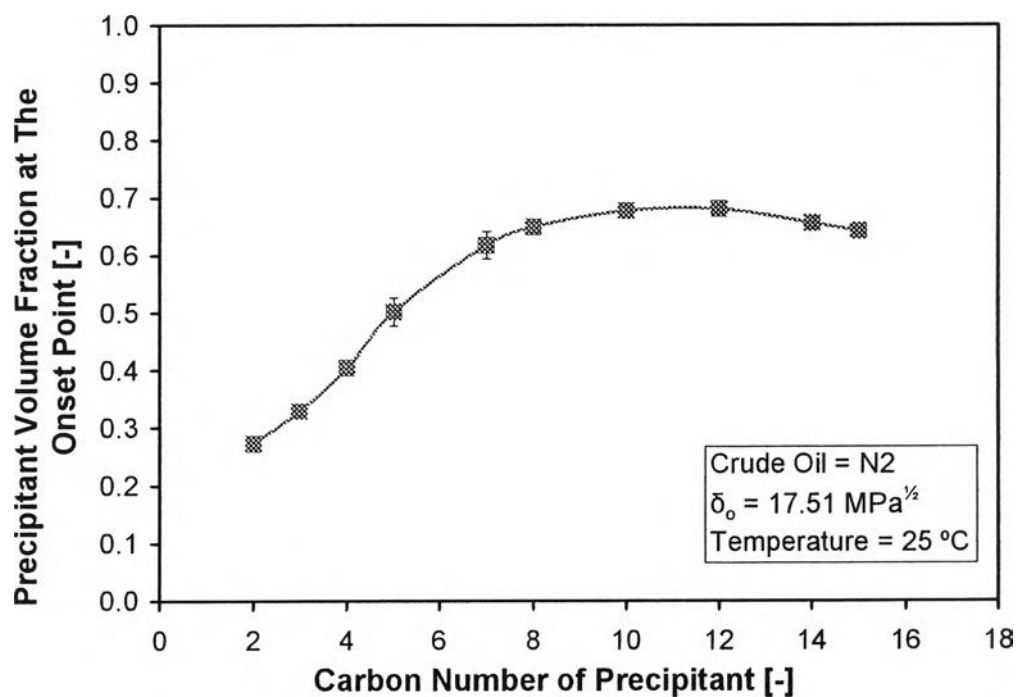


Figure 4.11 Precipitant volume fraction for ethane to *n*-hexadecane at the onset point for crude oil N2

The onset solubility parameter for ethane, propane and *n*-butane have been calculated based on the high pressure titration results and are summarized with the previous ambient titration data and shown in Table 4.3.

Table 4.3 Onset solubility parameter at 25 °C with ethane to *n*-hexadecane

Precipitant	Carbon Number	Molar Volume (cm ³ /mol)	(Mol. Vol.) ^½	δ_{onset} (MPa) ^½
Ethane	2	69	8.31	15.90
Propane	3	85	9.22	15.93
Butane	4	101.4	10.07	15.89
Pentane	5	116.1	10.77	15.87
Heptane	7	147.5	12.14	16.10
Octane	8	163.5	12.79	16.19
Decane	10	195.9	14.00	16.36
Dodecane	12	228.6	15.12	16.50
Tetradecane	14	261.3	16.16	16.67
Hexadecane	16	291.4	17.07	16.82

The onset solubility parameters are plotted with different models (Wang et al., 2004; Cimino et al., 1995; Hischberg et al., 1984 and our model with $V_{mix}^{1/2}$), as shown in Figure 4.12.

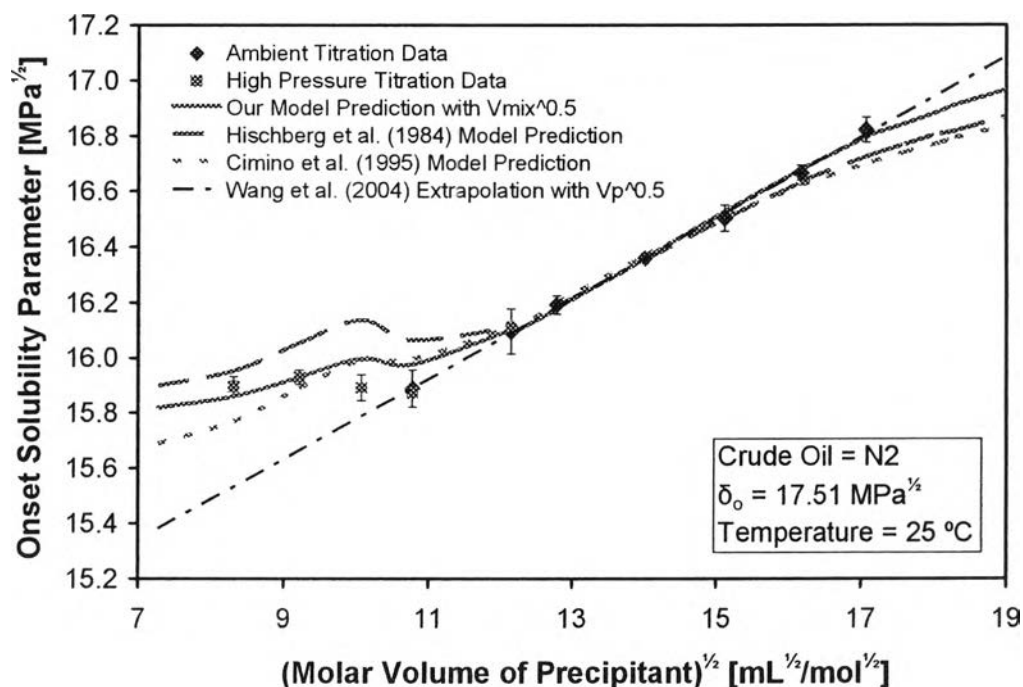


Figure 4.12 Onset solubility parameter of crude oil N₂ versus square root of the molar volume of the precipitant using different models

Figure 4.12 confirms that the onset solubility parameter does not change linearly with the square root of molar volume of precipitant for lower carbon number precipitant. However, it does agree with the Hischberg model, the Cimino model and our model, which predict that the onset solubility parameter varies with the square root of molar volume of the mixture. Therefore, our model prediction is further used for the prediction of the asphaltene instability of the live oil.

High pressure titrations at elevated temperatures with all normal alkanes from ethane to *n*-hexadecane were also performed. The onset solubility parameter was plotted with the square root of the molar volume of the mixture as in Figure 4.13 for our model prediction and the results also confirm that the onset solubility parameter does not change linearly with the square root of the molar volume of the mixture as shown in Figure 4.14.

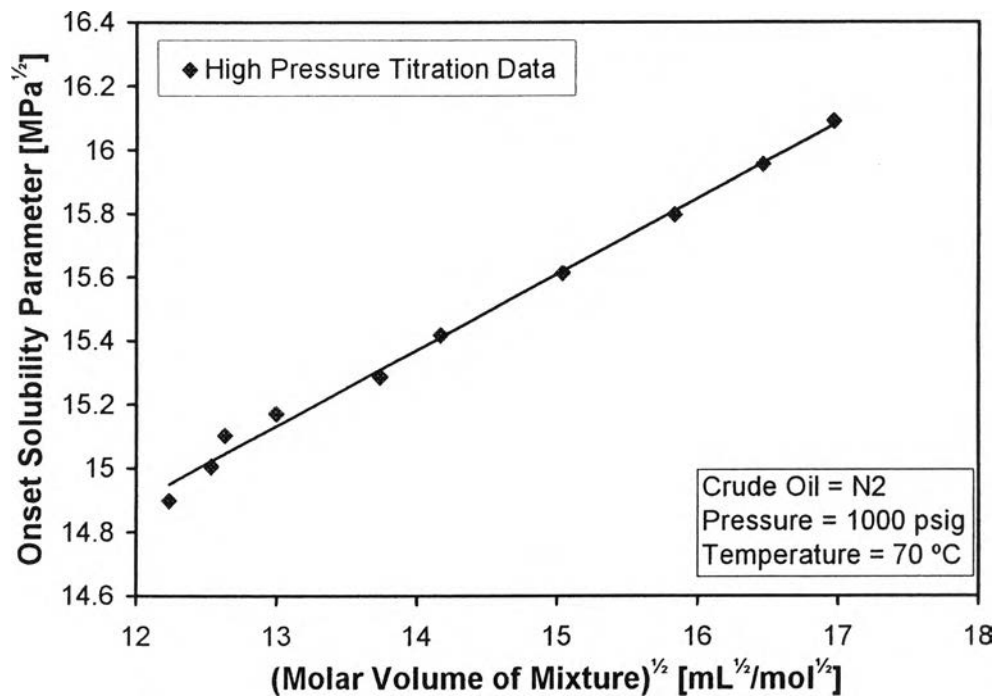


Figure 4.13 Onset solubility parameter of crude oil N2 versus square root of the molar volume of the mixture from high pressure titration

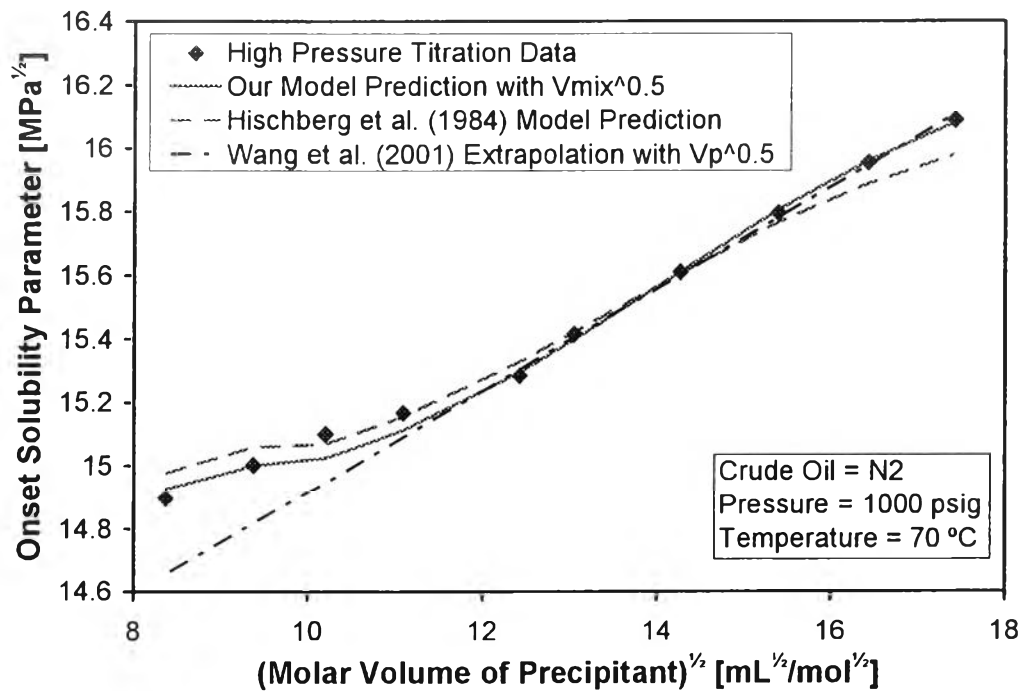


Figure 4.14 Onset solubility parameter of crude oil N2 versus square root of the molar volume of the precipitant from high pressure titration using different models

4.3 Model Prediction

The prediction of asphaltene stability consists of two parts. The first one is the calculation of the live oil solubility parameter ($\delta_{LiveOil}$) and the second one is the onset solubility parameter (δ_{onset}). If the live oil solubility parameter is greater than the onset solubility parameter at all feasible pressure, then the live oil is considered to be stable. Otherwise, asphaltene precipitation will occur.

The composition and its properties of live oil N2 are summarized in Table 4.4. The Peng-Robinson equation of state with Peneloux molar volume correction (C_{pen}) was used to estimate the molar volume and the composition of the live oil under different conditions.

Table 4.4 Live oil composition and other properties of crude oil N2

Component	Mol (%)	MW (g/mol)	T _c (°C)	P _c (psig)	Acentric Factor (-)	V _c (cm ³ /mol)	C _{pen} (cm ³ /mol)
N2	0.411	28.014	-146.95	478.14	0.037	90.1	-4.03
CO2	0.32	44.01	30.972	1054.81	0.225	94.07	5.10E-02
C1	36.474	16.043	-82.589	652.33	0.011	98.6	-4.02
C2	4.386	30.07	32.172	691.92	0.099	145.51	-2.55
C3	5.691	44.097	96.678	601.42	0.152	200.01	-3.59
C4	4.538	58.123	147.378	529.84	0.1963	257.06	-4.06
C5	3.212	72.15	193.172	474.7	0.2436	310.02	-3.5
C6	3.749	83.328	243.222	504.44	0.2227	327.8	-4.39
C7-C8	7.497	105.036	292.428	463.69	0.2661	411.83	-8.61
C9-C10	5.889	131.552	339.622	414.69	0.3224	515.52	-13.09
C11-C13	6.414	166.101	394.6	352.65	0.4081	703.56	-11.95
C14-C17	6.613	213.752	447.406	304.97	0.4983	930.61	-19.7
C18-C24	6.296	286.368	514.572	248.28	0.6424	1236.67	-22.74
C25+	8.511	606.143	671.283	167.9	1.0509	2135.37	-123.61

4.3.1 Calculation of the Live Oil Solubility Parameter

The live oil is basically composed of two main pseudo-components: stock tank oil (STO) and dissolved gases (DG) under reservoir conditions, as shown in Figure 4.15. The live oil solubility parameter can be calculated by combining the stock tank oil solubility parameter under reservoir conditions (δ_{STO}^{RC}) and the

dissolved gas solubility parameter under reservoir conditions (δ_{DG}^{RC}) using the volume average mixing rule of solubility parameter as follows:

$$\delta_{LiveOil} = \phi_{STO}^{RC} \delta_{STO}^{RC} + \phi_{DG}^{RC} \delta_{DG}^{RC} \quad (4.1)$$

Where ϕ_{STO}^{RC} = volume fraction of stock tank oil under reservoir conditions (-)

ϕ_{DG}^{RC} = volume fraction of dissolved gas under reservoir condition (-)

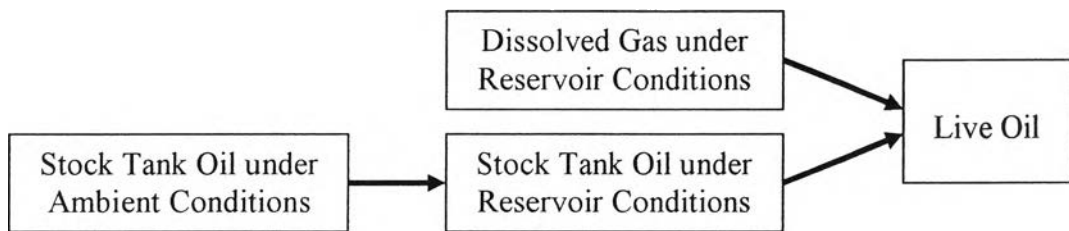


Figure 4.15 Combination diagram of live oil

With this combination concept of the live oil, Equation (4.1) can be rewritten as detailed in the Appendix A:

$$\delta_{LiveOil} = \frac{1}{D} \delta_{STO}^{RC} + \frac{r}{D} \delta_{DG}^M \quad (4.2)$$

Where D = ratio of live oil volume to stock tank oil volume under reservoir conditions (-)

r = moles of the dissolved gas per volume of stock tank oil under reservoir conditions (mol/mL)

δ_{DG}^M = molar solubility parameter of the dissolved gas ($\text{MPa}^{1/2} \text{mL/mol}$)

The stock tank oil solubility parameter under reservoir conditions (δ_{STO}^{RC}) is calculated from the stock tank oil solubility parameter under any conditions (δ_{STO}) with the molar volume (v) correction as shown in Equation (4.3) (Hildebrand and Scott, 1964).

$$\delta_{STO}^{RC} = \delta_{STO} \left(\frac{v_{STO}^{RC}}{v_{STO}} \right)^{-1.25} \quad (4.3)$$

Where v_{STO}^{RC} = molar volume of stock tank oil under reservoir conditions (mL/mol)

v_{STO} = molar volume of stock tank oil under ambient conditions (mL/mol)

For the dissolved gas, the molar solubility parameter (δ^M) is the product of the molar volume and the solubility parameter under particular conditions. The molar solubility parameter is independent of temperature and pressure just like molar refractivity. The relationship between the molar solubility parameter and the molar refractivity of normal alkanes is shown in Figure 4.16. The molar solubility parameter of the mixture can be calculated using mole average as shown in Equation (4.4).

$$\delta_{mix}^M = \sum x_i \delta_i^M \quad (4.4)$$

Where δ_{mix}^M = molar solubility parameter of the mixture (MPa^{1/2}mL/mol)

x_i = mole fraction of ith component (-)

δ_i^M = molar solubility parameter of ith component (MPa^{1/2}mL/mol)

The molar solubility parameter of light normal alkanes and the sample calculation of molar solubility parameter of dissolved gas are shown in Table 4.5. The parameters D and r are obtained from EOS predictions (flash calculations) under particular conditions. Plots of D and r as a function of pressure are shown in Figure 4.17.

Table 4.5 Sample calculation of the molar solubility parameters of dissolved gases

Component	δ^M	x_i	$\delta^M * x_i$
C1	529	0.70	369.99
C2	800	0.15	120.06
C3	1107	0.08	88.59
C4	1445	0.05	72.23
C5	1719	0.02	38.75
		$\bar{\delta}_{DG}^M$	689.62

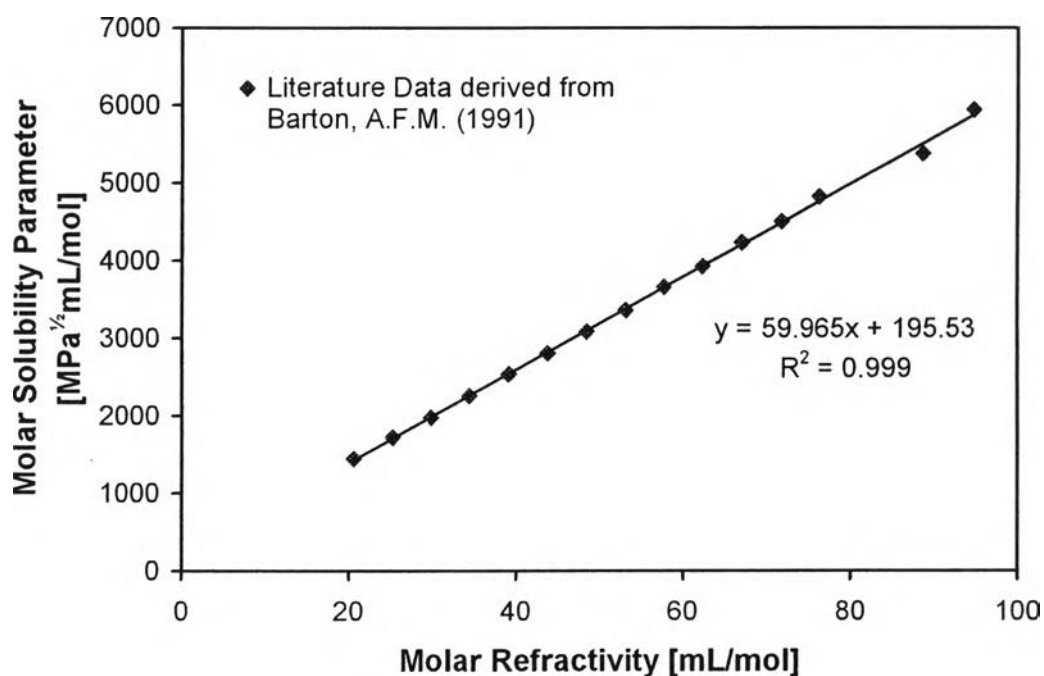


Figure 4.16 Molar solubility parameter of normal alkanes as a function of the molar refractivity

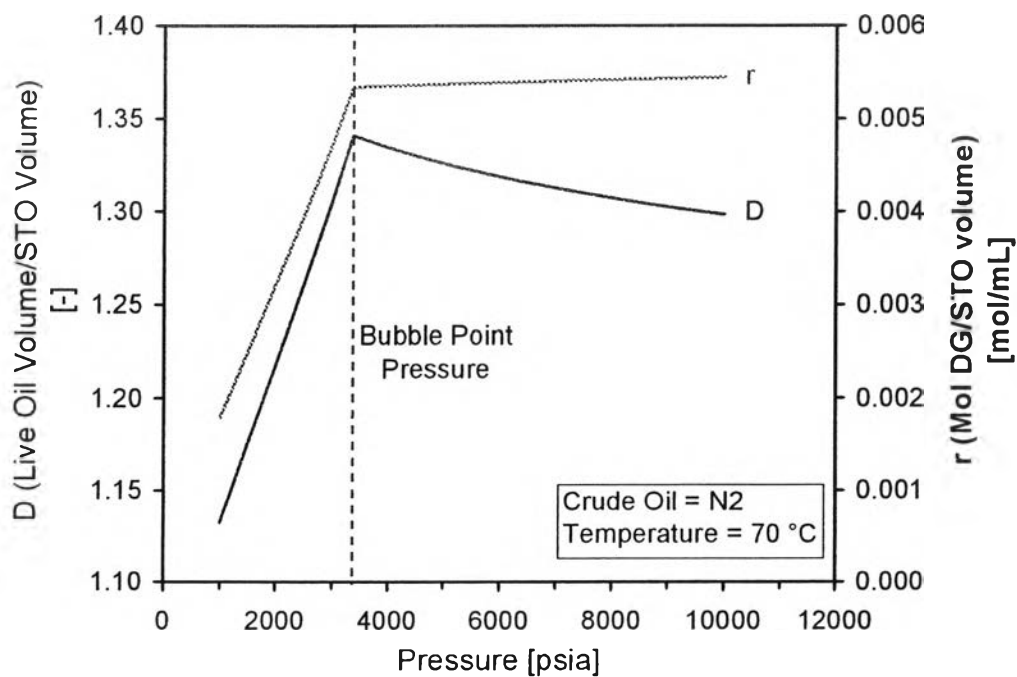


Figure 4.17 Graph of D and r as a function of pressure for crude oil N2

The calculated live oil solubility parameter is plotted as a function of pressure as shown in Figure 4.18. From the reservoir pressure to the bubble point pressure, the live oil solubility parameter decreases because the dissolved gas fraction, which has a lower solubility parameter than the stock tank oil fraction, expands more than the stock tank oil fraction lowering the live oil solubility parameter due to the volume average mixing rule of the solubility parameter. After the bubble point has been reached, dissolved gas starts evaporating out of the liquid phase and thus contributes less to the average solubility parameter, causing the live oil solubility parameter to be higher.

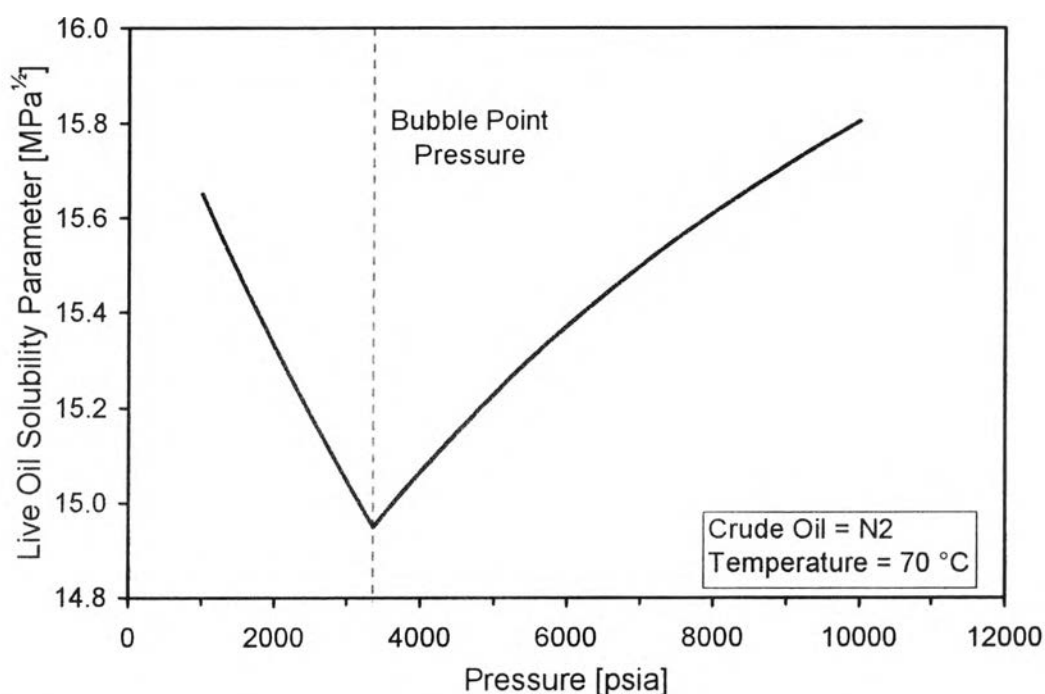


Figure 4.18 Live oil solubility parameter as a function of pressure for crude oil N2

4.3.2 Prediction of the Onset Solubility Parameter

Many researchers have tried to establish a model to predict the onset of asphaltene precipitation at reservoir conditions from the experimental data at ambient or near ambient conditions. As described earlier, Wang and Buckley (2001) developed an empirical correlation between the onset solubility parameter and square root of molar volume of precipitant. However, as in section 4.1, the onset solubility

parameter can be plotted in many different ways regarding to the precipitants (titrants) or the mixture. In the ambient titration, the precipitants ranged from *n*-pentane to *n*-hexadecane. Dissolved gases in the reservoir behave like precipitants with a molar volume outside that range of *n*-pentane to *n*-hexadecane. The empirical correlations are useful in interpolating the onset solubility parameter titrating with normal pentane (*n*-C5) to normal hexadecane (*n*-C16). But in order to extrapolate, a thermodynamic understanding of the Gibbs free energy of mixing of two pseudo components (asphaltenes and maltenes) to validate the extrapolation. The solubility models including the Hirschberg model (assuming a separated pure asphaltene phase), the Cimino model (assuming a separated pure solvent phase), and our model prediction with the square root of the molar volume of the mixture are in good agreement with the high pressure titration data as described in section 4.2. Therefore, our model prediction with the square root of the molar volume of the mixture is used to predict the onset solubility parameter for the onset solubility parameter for the live oil.

Using the correlation between the onset solubility parameter with square root of the molar volume of the mixture coupled with the molar volume of the mixture obtained from the equation of state, one can calculate the onset solubility parameter as a function of pressure as plotted in Figure 4.19. The onset solubility parameter prediction using the square root of molar volume of precipitant approach is also plotted in the same figure.

When plotting both the live oil solubility parameter and the onset solubility parameter as in Figure 4.20, it can be predicted shows that no asphaltene precipitation will occur at any pressure because the live oil solubility parameter curve does not cross or fall below the onset solubility parameter prediction.

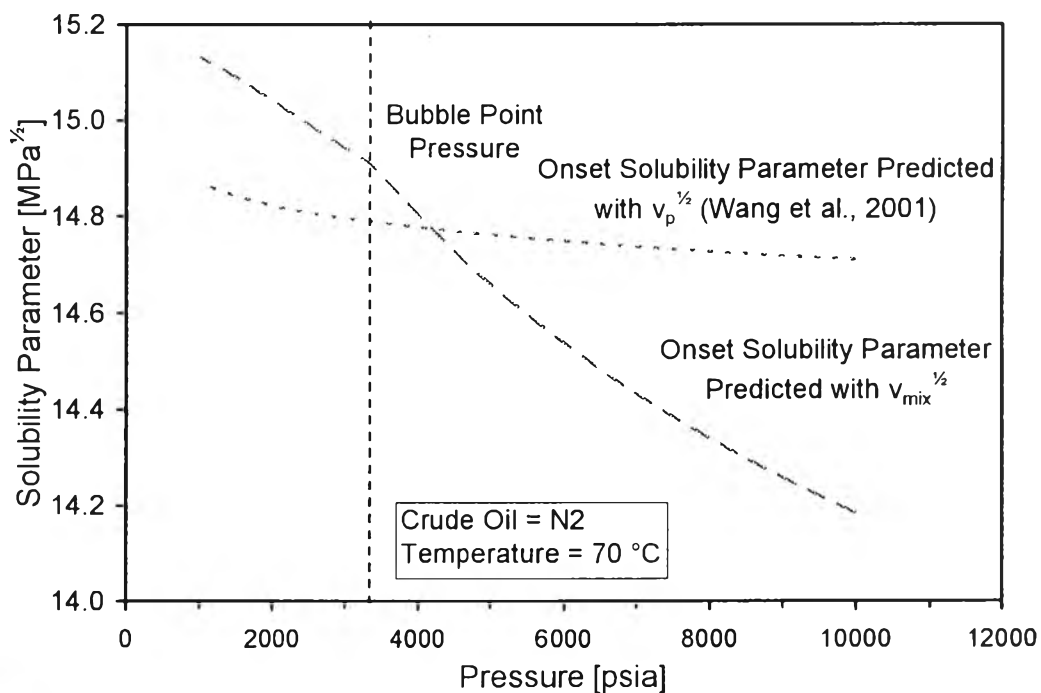


Figure 4.19 Onset solubility parameter as a function of pressure for crude oil N2

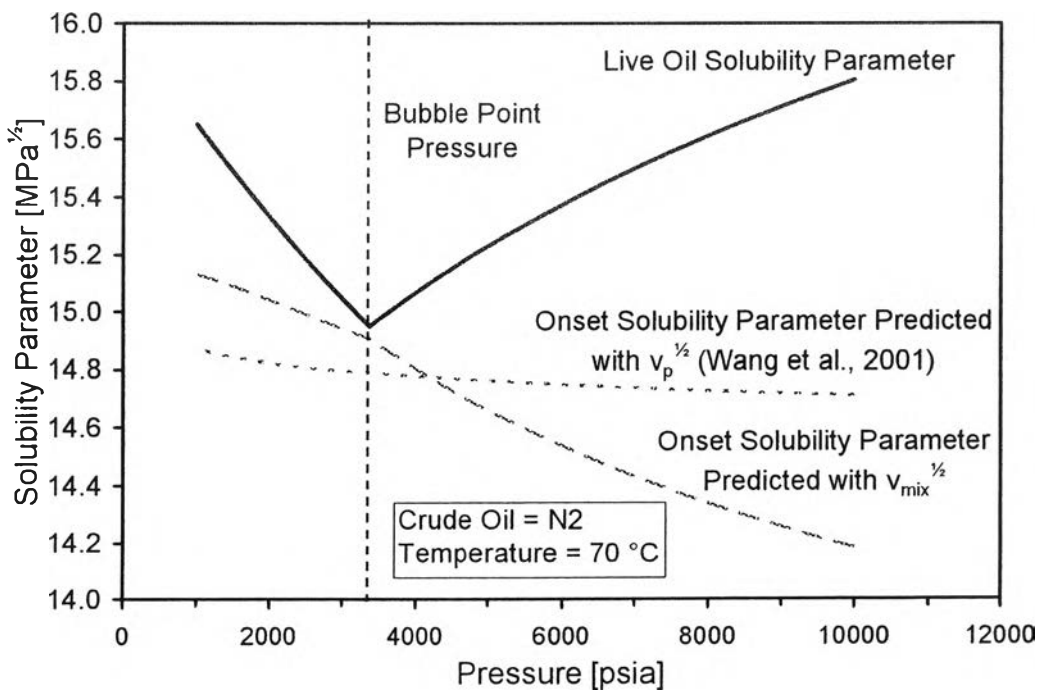


Figure 4.20 Live oil solubility parameter and the onset solubility parameter as a function of pressure for crude oil N2

4.3.3 Prediction of the effect of miscible injectant on the onset solubility parameter

When added to the live oil, the miscible injectant will lower the total solubility parameter because of the low solubility parameter that the miscible injectant has. In this specific case, the miscible injectant is very similar in composition with the separator gases which are considered as the precipitant when combining with the stock tank oil. Therefore, the onset solubility parameter will only change due to the molar volume of the total mixture. The prediction of the live oil with 50 mol % miscible injectant is shown in Figure 4.21.

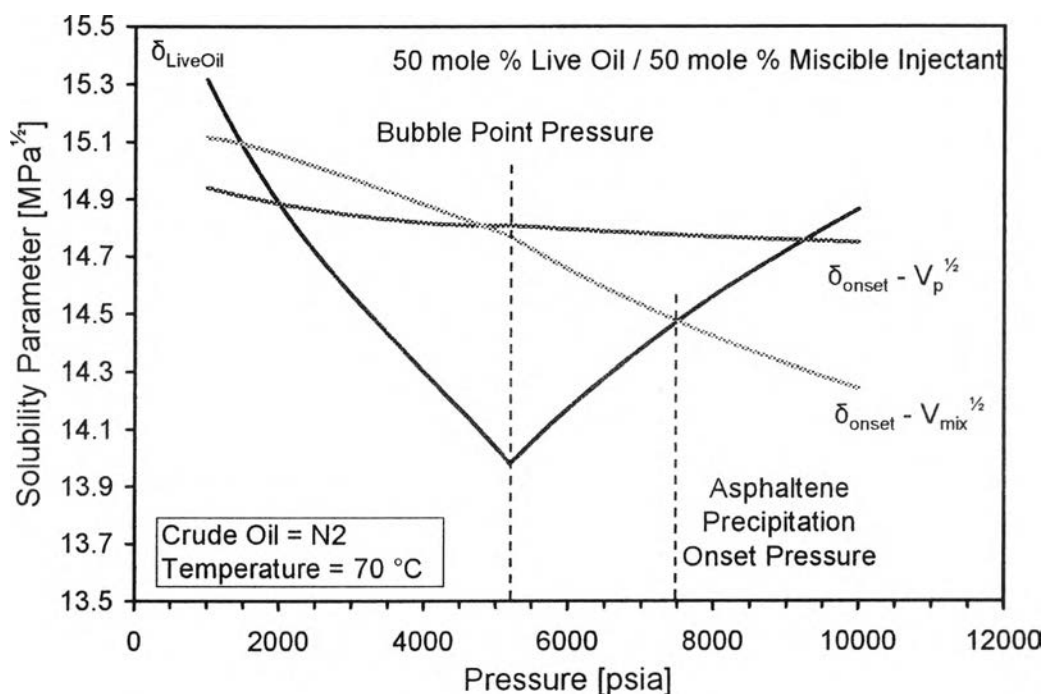


Figure 4.21 Live oil solubility parameter and the onset solubility parameter as a function of pressure for crude oil N2 with 50 mol % miscible injectant

4.4 Thermodynamic Validation

The model prediction in section 4.3 for the 50 mol % recombined live oil with 50 mol % miscible injectant was validated using pressure depletion experiment as described in section 3.3.5. At the beginning of the test, several technical

difficulties were found as described in Appendix B. After these difficulties were overcome, the experimental results show the asphaltene precipitation onset pressure as in Figure 4.22.

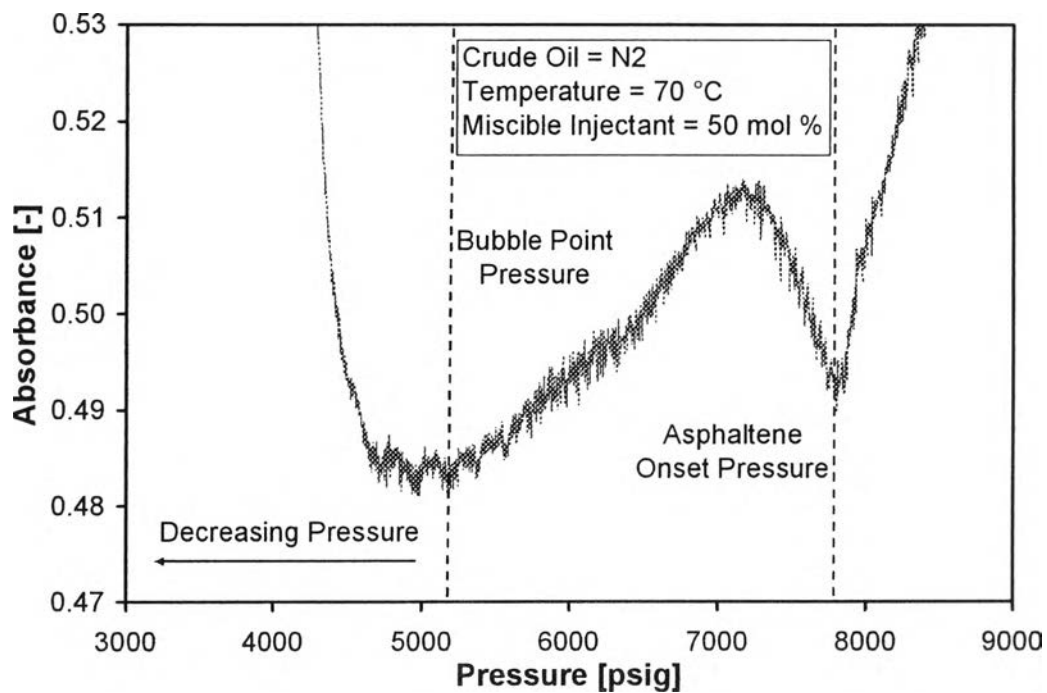


Figure 4.22 Absorbance curve from pressure depletion experiment for 50 mol % live oil N2 and 50 mol % miscible injectant

At the beginning of the pressure depletion test, the pressure was stabilized at 9000 psi and 70 °C for 40 minutes. Then, the pressure was set to decrease 20 psi per minute. When pressure decreased, density of the live oil with miscible injectant also decreased leading to lower absorbance. When it reached the asphaltene precipitation onset pressure, asphaltene precipitated out and blocked the light which led to higher absorbance until all asphaltenes dropped out. After that, absorbance decreased again due to the expansion of the live oil with miscible injectant. Once reached the bubble point pressure, bubbles scattered the light and absorbance started to deviate from a straight line.

Predicted bubble point pressure was at 5192.5 psia (5177.8 psig) and the experiment showed a bubble point pressure of about 5175 psia (about 5160 psig).

The bubble point pressure from the experiment shows good agreement with the prediction. For the asphaltene precipitation onset pressure, the prediction gave the onset pressure of 7500 psia and the experiment showed the asphaltene precipitation onset pressure of about 7765 psia (about 7750 psig). The comparison between a predicted onset pressure and experimental onset pressure shows only 265 psi different. This pressure depletion confirmed the model prediction of the onset solubility parameter with the square root of the molar volume of the mixture.

4.5 Prevention

When asphaltene precipitation could not be avoided in crude oil production, asphaltene dispersants (also called asphaltene inhibitors) can be used to prevent asphaltenes from agglomerating into large particles and depositing to the pipe wall. In this section both the measurement techniques and the asphaltene dispersants were investigated and was divided into four parts in accordance to the equipment used in the study; an automatic titration system, an optical microscope, a dynamic turbidity measurement device, and a particle size distribution measurement device.

4.5.1 Automatic Titration

The neat (untreated) crude oil N2 and the crude oil N2 treated with DR, DP, DBSA and 11 proprietary blends were titrated with *n*-heptane. The titrations were conducted to study the effect of different asphaltene chemicals on the precipitation onset of asphaltenes. Figure 4.23 shows the volume of *n*-heptane consumed per volume of crude oil at the onset point for the different chemicals studied. It is clearly seen that the using 500 ppm of the chemical additives to the crude oil N2 delays (i.e., requires more titrant to reach the onset) the precipitation of asphaltenes. The onset of the neat crude oil N2 occurred after 1.73 mL of *n*-heptane was added per 1 mL of crude oil while for the treated oil the onset point ranges between 1.89 and 2.07 mL of *n*-heptane added per 1 mL of crude oil. The data are summarized in Table 4.6. At a concentration of 500 ppm, it is difficult to differentiate the effectiveness of the different chemical inhibitors.

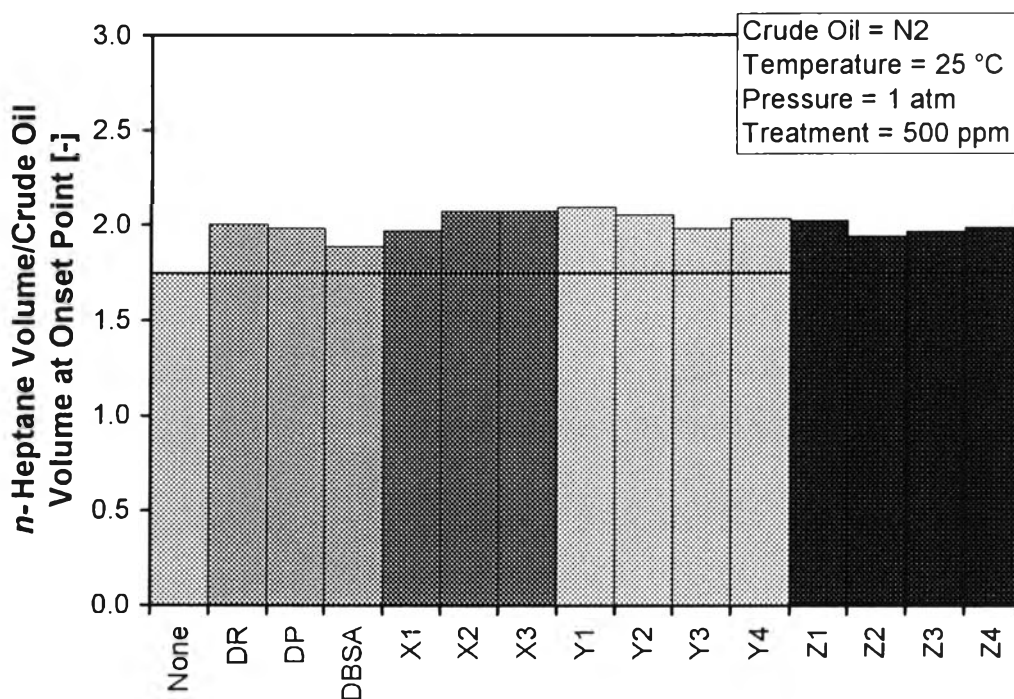


Figure 4.23 Titration results of the neat and treated crude oil N2 with 500 ppm

To study the effect of the chemical dosage on the asphaltene onset point, the neat crude oil N2 and treated samples with 25 ppm of the different chemicals (DR, DP, DBSA and 11 proprietary blends) were titrated with *n*-heptane. The titration results giving the amounts of *n*-heptane required at the onset point can be seen in Figure 4.24. For the neat crude oil, 1.73 mL of *n*-heptane were required per 1 mL of crude oil which corresponds to a volume fraction of *n*-heptane of 0.63. Upon treatment with 25 ppm, no difference was observed among the neat and treated crude oil N2 with chemical inhibitors. The results also summarized in Table 4.6.

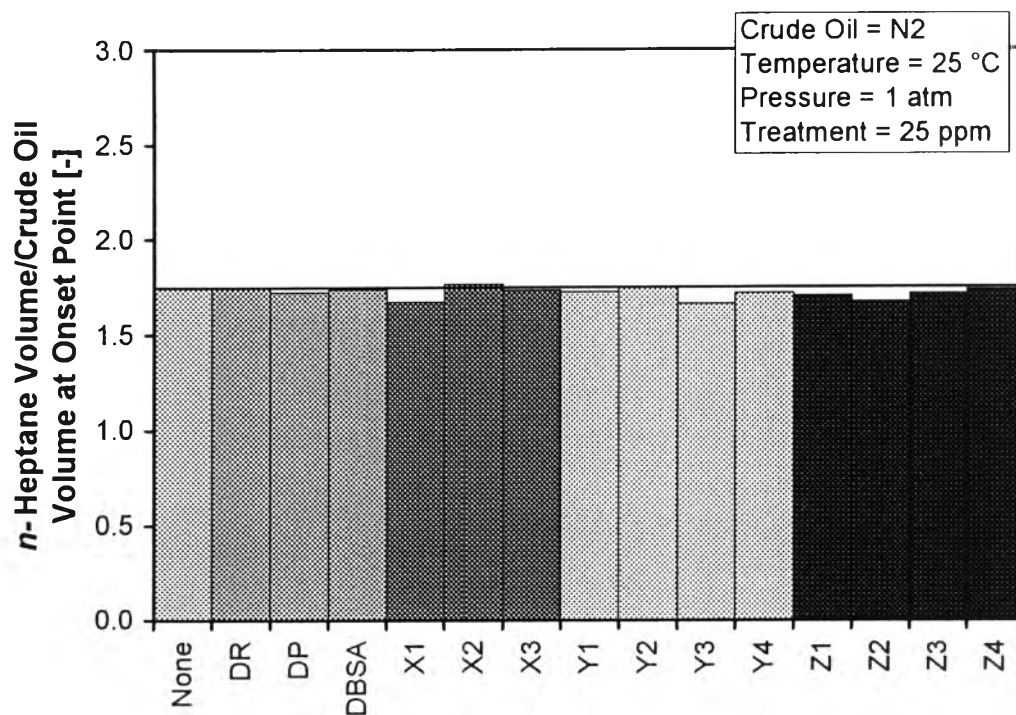


Figure 4.24 Titration results of the neat and treated crude oil N2 with 25 ppm

Table 4.6 Titration result of the neat and treated crude oil N2

Chemical	<i>n</i> -Heptane Volume per Oil Volume (500 ppm)	<i>n</i> -Heptane Volume per Oil Volume (25ppm)
None	1.75	1.75
DR	2.00	1.75
DP	1.98	1.72
DBSA	1.89	1.73
X1	1.97	1.67
X2	2.07	1.76
X3	2.07	1.73
Y1	2.09	1.72
Y2	2.05	1.74
Y3	1.98	1.66
Y4	2.03	1.71
Z1	2.02	1.70
Z2	1.94	1.67
Z3	1.96	1.71
Z4	1.98	1.73

4.5.2 Optical Microscope

Optical microscopy experiments were carried out with the crude oil N2 treated with 500 ppm of the chosen chemicals. Asphaltene particles of 1-10 μm were detected for selected additives at when the *n*-heptane to crude oil ratio was above 1.73. This result suggests that the asphaltene chemical additives at concentration of 500 ppm are unable to stop the formation of particle sizes of 1-10 μm . Consequently, at these concentrations the asphaltene chemicals are not true inhibitors as they do not stop the formation of asphaltene particles and they do not completely stop the flocculation and growth of small asphaltene particles. We will discuss this issue further in the section of particle size distribution measurement.

4.5.3 Turbidity Measurement

The neat and the crude oil N2 samples treated with 500 ppm of different chemicals (DR, DP, DBSA and 11 proprietary blends) were tested using a dynamic turbidity instrument. An aliquot of 150 μL of the crude oil sample was added to 7.5 mL of *n*-heptane in a test tube and scanned every minute for a period of one hour at 40 μm increments along the test tube height. The mean transmittance (average transmittance along the tube height) was recorded as a function of time as the particles settle. Particle in the size range of 1-10 μm will settle 5 cm between 19 hours and 0.19 hour respectively and all particles above 4.4 μm will settle 5 cm in 1 hour. If the chemical additives were effective, they would keep the asphaltenes dispersed in the solution and prevent them from settling and as a result the mean transmittance will remain unchanged. If the asphaltene chemical additives are ineffective dispersants, the asphaltene particles will agglomerate and settle out resulting in an increase in the mean transmittance. The results from the dynamic turbidity measurements on crude oil N2 are shown in Figure 4.25.

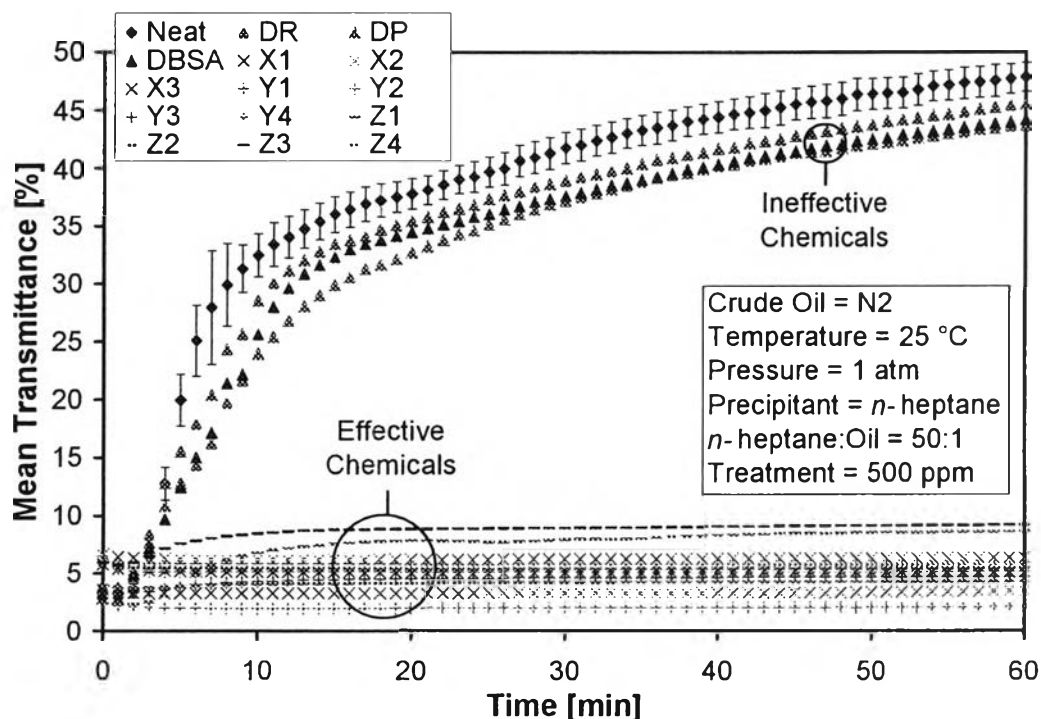


Figure 4.25 Turbidity measurement results of the neat and treated crude oil N2 with 500 ppm

Figure 4.25 shows that by treating the crude oil N2 with DR, DP and DBSA even at 500 ppm, these chemicals can not keep asphaltene in solution, thus they are called “ineffective chemical inhibitors”. However, by treating the crude oil N2 with 500 ppm of the proprietary blends, the results show that the mean transmittance remained essentially the same (below 10 % mean transmittance at 60 minutes) because the asphaltene particles remained dispersed in solution. Most of the proprietary chemicals kept the asphaltenes dispersed in solution, and as such they are called “effective chemicals”. This test required at least 10 minutes to be able to distinguish between ineffective and effective chemicals.

The samples treated with 500-ppm of the effective chemicals (X1-X3, Y1-Y4, and Z1-Z4) were diluted with the neat crude oil N2 to obtain a chemical additive concentration of 25 ppm. The dynamic turbidity of these samples was then measured and the results are shown in Figure 4.26.

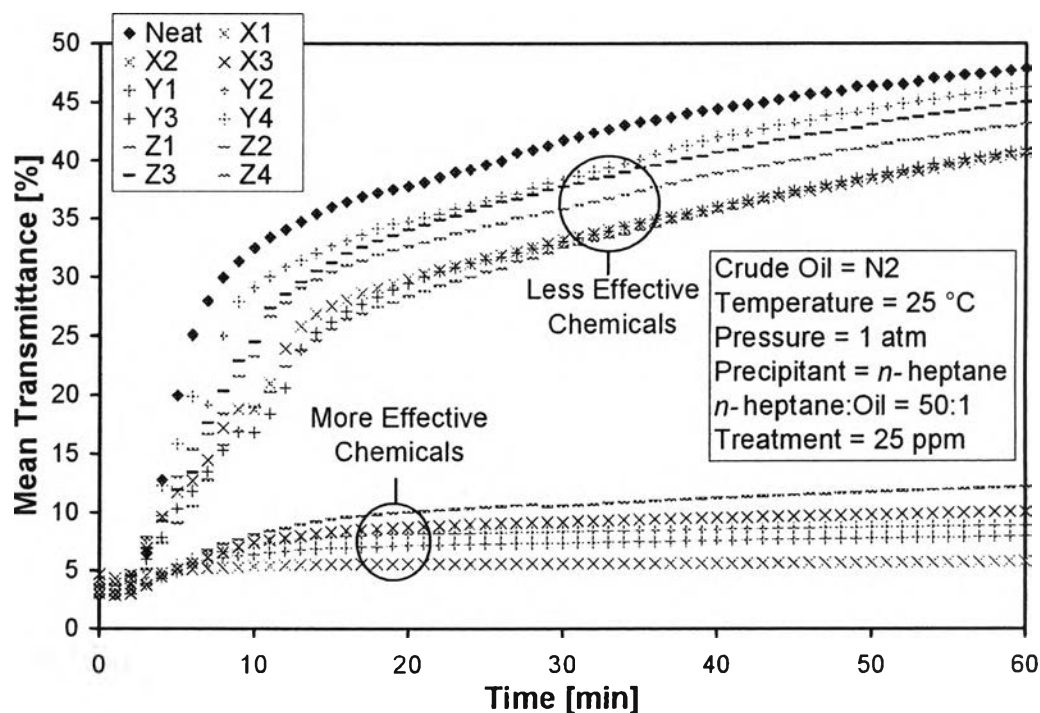


Figure 4.26 Turbidity measurement results of the neat and treated crude oil N2 with 25 ppm

Figure 4.26 shows that while the chemicals X1, Y3, Y4, Z2, Z3, and Z4 were effective at concentrations of 500 ppm, but at a 25 ppm dosage they were unable to keep asphaltenes dispersed in the solution throughout a one hour period of testing. These chemicals are classified as “less effective chemicals”. On the other hand, the chemicals X2, X3, Y1, Y2, and Z1 were effective in keeping asphaltenes dispersed in the solution of 25 ppm over the one-hour period of testing even at 25 ppm concentrations and thus these chemicals are classified as “more effective chemicals”.

In order to study the effect of inhibitor concentration, some ineffective chemicals, less effective chemicals, and more effective chemicals were tested with crude oil N2 at different concentrations. The mean transmittance at 1 hour has been recorded for each sample. The mean transmittance at 1 hour is plotted as a function of the chemical concentration in Figure 4.27. For the ineffective chemicals, there is no concentration up to 500 ppm that will prevent the asphaltenes from agglomerating and settling as can be seen by the high transmittance. For the effective chemicals,

there is a critical concentration of dispersant that will keep asphaltenes in the solution as can be seen by the fact that the mean transmittance at 1 hour is below 5 %. The results in Figure 4.27 show that the more effective chemicals require a concentration of above 50 ppm to keep asphaltenes in solution, while the less effective chemicals require about 200 ppm. From an industrial point of view, selecting the more effective chemicals can be very cost effective.

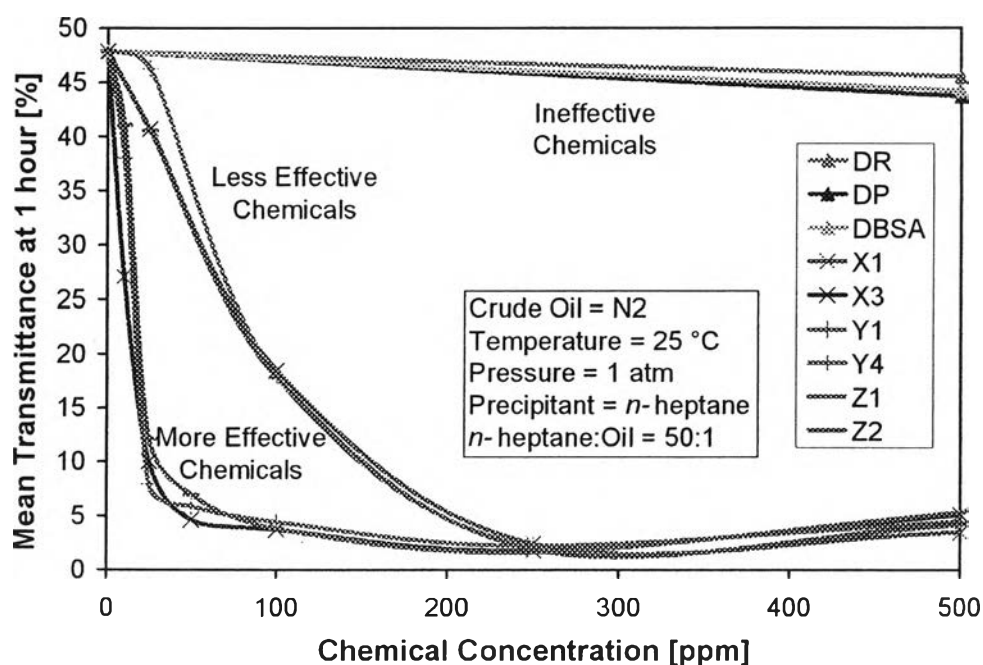


Figure 4.27 Mean transmittance at one-hour period of crude oil N2 treated with different chemical concentrations

Some of the effective chemicals were used at a concentration of 25 ppm to test with crude oils Q1 and K2. The results show that the effectiveness of these chemicals is independent of the crude oil properties (i.e., API gravity and asphaltene content) as mentioned in section 3.1.1. The turbidity measurement results (mean transmittance with time) for crude oils Q1 and K2 are shown in Figure 4.28 and Figure 4.29, respectively. The effectiveness of all chemical inhibitors based on performance at concentrations of 500 ppm and 25 ppm for crude oil N2 and the performance at 25 ppm concentration for crude oils Q1 and K2 are summarized in Table 4.7. The effective chemicals for all three crude oils were the same proprietary chemical additives X2, X3, Y1, Y2 and Z1.

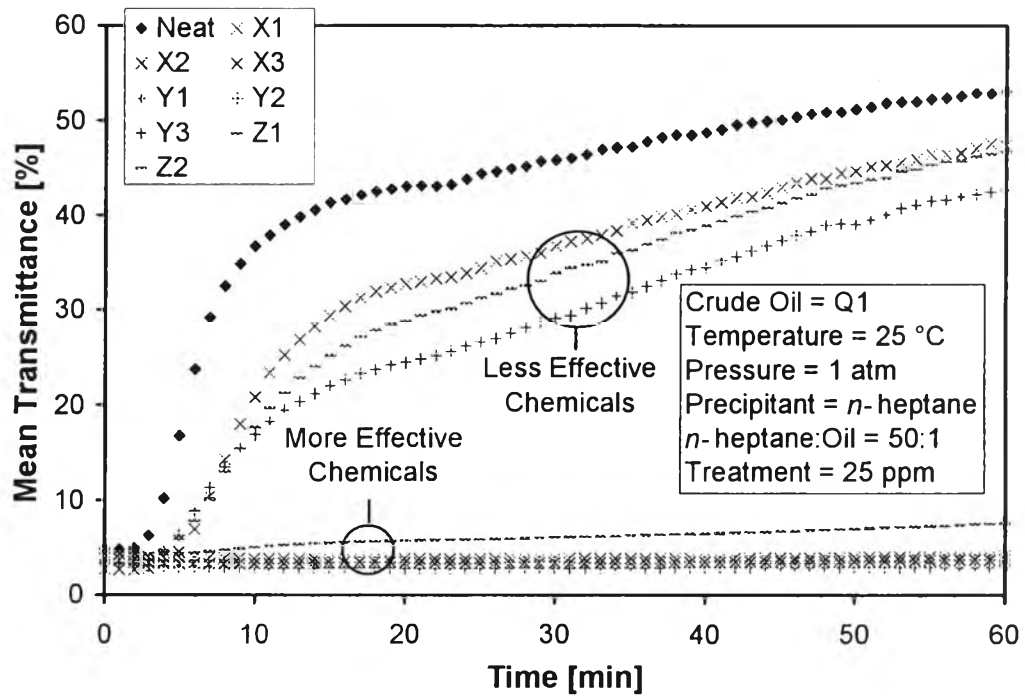


Figure 4.28 Turbidity measurement results of the neat and treated crude oil Q1 with 25 ppm

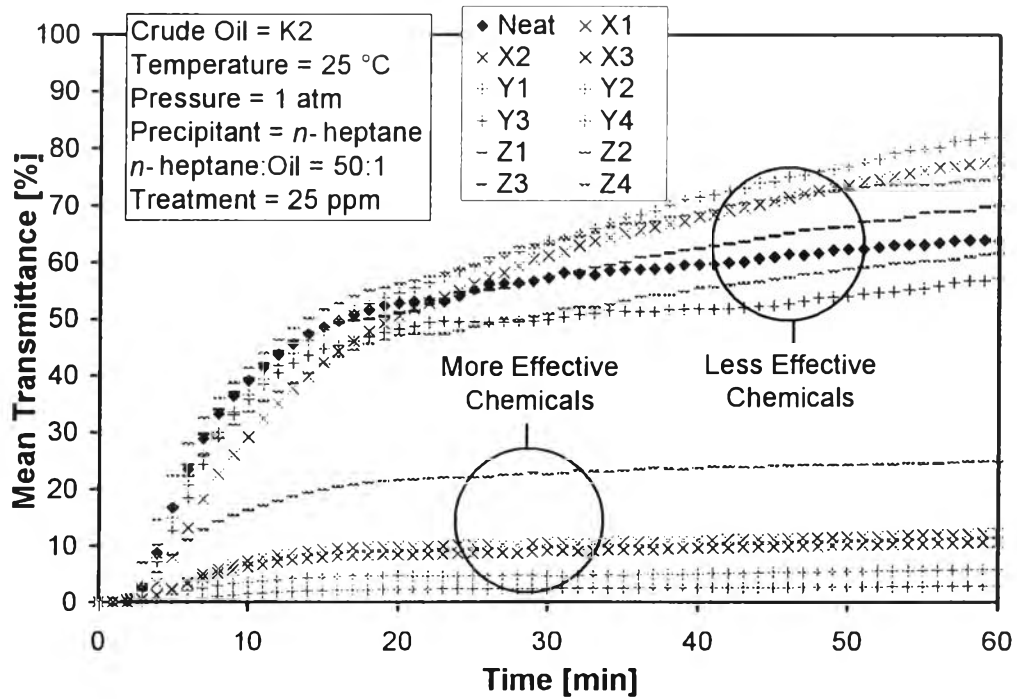


Figure 4.29 Turbidity measurement results of the neat and treated crude oil K2 with 25 ppm

Table 4.7 Effectiveness of asphaltene chemicals

Chemical	Effectiveness with crude oil N2	Effectiveness with crude oil Q1	Effectiveness with crude oil K2
DR	Ineffective	-	-
DP	Ineffective	-	-
DBSA	Ineffective	-	-
X1	Less effective	Less effective	Less effective
X2	More effective	More effective	More effective
X3	More effective	More effective	More effective
Y1	More effective	More effective	More effective
Y2	More effective	More effective	More effective
Y3	Less effective	Less effective	Less effective
Y4	Less effective	-	Less effective
Z1	More effective	More effective	More effective
Z2	Less effective	Less effective	Less effective
Z3	Less effective	-	Less effective
Z4	Less effective	-	Less effective

Comparing the titration and turbidity measurement results for crude oil N2, at concentrations of 25 ppm chemical, the titration result show no improvement indicating these chemicals can not inhibit or prevent the precipitation of asphaltenes. However, turbidity measurement demonstrated that theses chemicals could disperse asphaltenes in the solution. Consequently, turbidity measurements are a better method to evaluate dispersion and settling of asphaltenes in the solution.

4.5.4 Particle Size Distribution Measurement

The neat crude oil and the samples treated with asphaltene chemical additives were tested by adding 800 μL of the crude oil sample to 400 mL of precipitant (i.e., *n*-heptane) to yield a 1 to 500 crude oil to precipitant ratio. This high dilution is needed due to opacity of the sample, cell path length and sensitivity required.

The particle size distribution (PSD) of asphaltenes was first studied in solutions with a solubility parameter larger than the onset solubility parameter, which are considered to be stable solutions. Cyclohexane was the first solution selected because cyclohexane has a solubility parameter of $16.6 \text{ MPa}^{1/2}$, which is larger than the onset solubility parameter with *n*-heptane of $16.1 \text{ MPa}^{1/2}$, and behaves as a solvent for asphaltenes. As expected, the results from Figure 4.30 show that no asphaltenes precipitated and that the size of asphaltene particles in the crude oil are less than $0.1 \text{ }\mu\text{m}$, and are therefore called “stable asphaltenes”. Also shown in this figure is the PSD for the neat crude oil N2 in a mixture of 70 % *n*-heptane and 30 % toluene by volume. This 70/30 mixture corresponds to the solubility parameter of $16.17 \text{ MPa}^{1/2}$. Because this solution approached the onset solubility parameter, a very small amount of asphaltenes flocculated with sizes in the range of $1\text{-}20 \text{ }\mu\text{m}$. Finally, the neat crude oil N2 PSD and stability was studied in *n*-heptane. The result shows bimodal distribution indicating that two types of asphaltenes exist. The asphaltenes in the size range of $0.1\text{-}1 \text{ }\mu\text{m}$ were stabilized or dispersed perhaps by natural surfactants and are called “colloidal asphaltenes” or “stabilized asphaltenes”. The asphaltenes in the size range of $1\text{-}30 \text{ }\mu\text{m}$ are called “flocculated asphaltenes”. The particle size distributions of these solutions are shown in Figure 4.30.

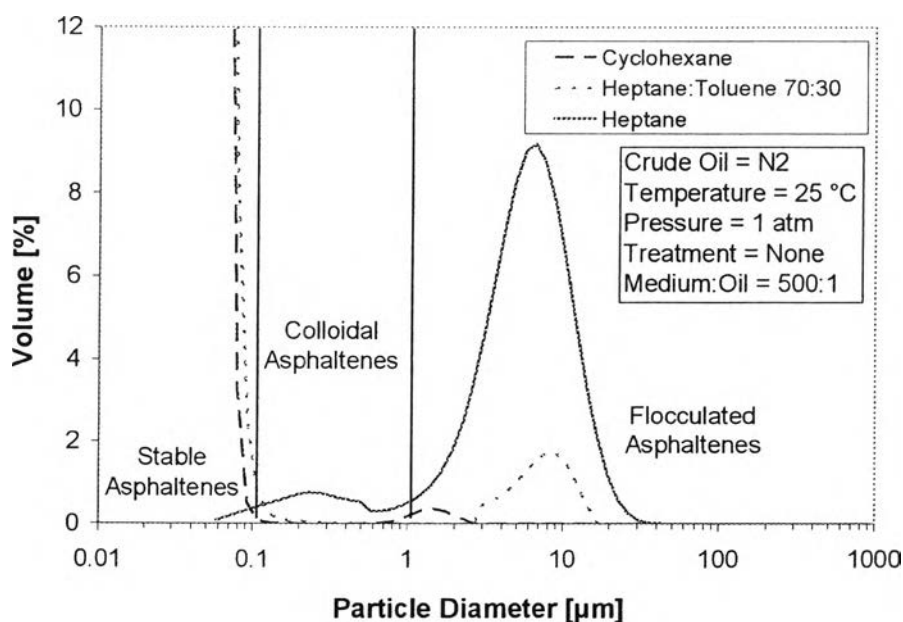


Figure 4.30 Asphaltene particle size distributions of the untreated crude oil N2 in different solutions

The effectiveness of several chemicals was investigated using the Mastersizer by treating crude oil with different concentrations of the chemical additives. The results in Figure 4.31 show that at low dosages (25 ppm to 250 ppm) of chemical X1, the PSD of asphaltenes remained relatively the same. However in Figure 4.32, one observed that at the higher dosages (500 ppm to 10000 ppm) of the chemical additive, asphaltenes remain dispersed as colloidal asphaltenes. These results are in good agreement with turbidity measurement results (Figure 4.27), which suggest the effective chemical concentration of X1 at 200 – 250 ppm.

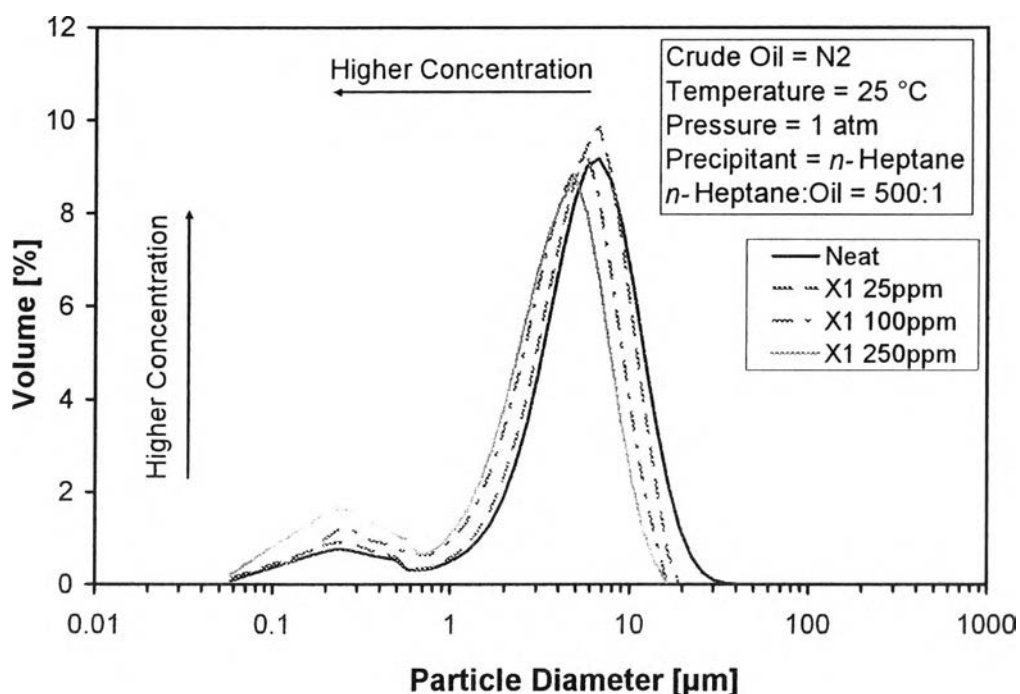


Figure 4.31 Asphaltene particle size distributions of the crude oil N2 treated at low concentrations of chemical X1

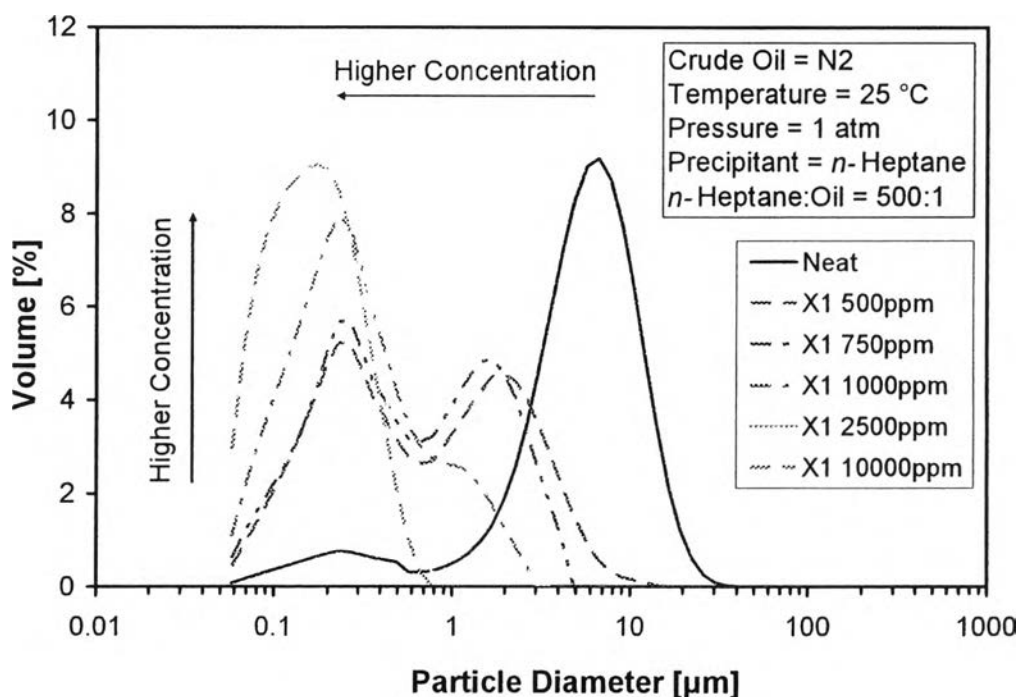


Figure 4.32 Asphaltene particle size distributions of the crude oil N2 treated at high concentrations of chemical X1

Furthermore, one can plot the percentage of the colloidal asphaltenes and flocculated asphaltenes as a function of chemical concentration and select the optimum chemical additive dosage. Figure 4.33 clearly shows that the colloidal asphaltenes formed is directly proportional to the concentration of chemical X1. The expanded logarithmic scale of the percentage of the colloidal asphaltenes and flocculated asphaltenes as a function of chemical concentration is also shown in Figure 4.34. The shape of the curve is very similar to sigmoid function.

The PSD measurements were performed using crude oil N2 with different asphaltene chemical additives to investigate the effectiveness of these chemicals as dispersity. The results (Figure 4.35) show the same trend for the more effective chemical additives, asphaltenes remain dispersed with sizes of less than 1 μm (colloidal asphaltenes) in solution and reduced flocculation.

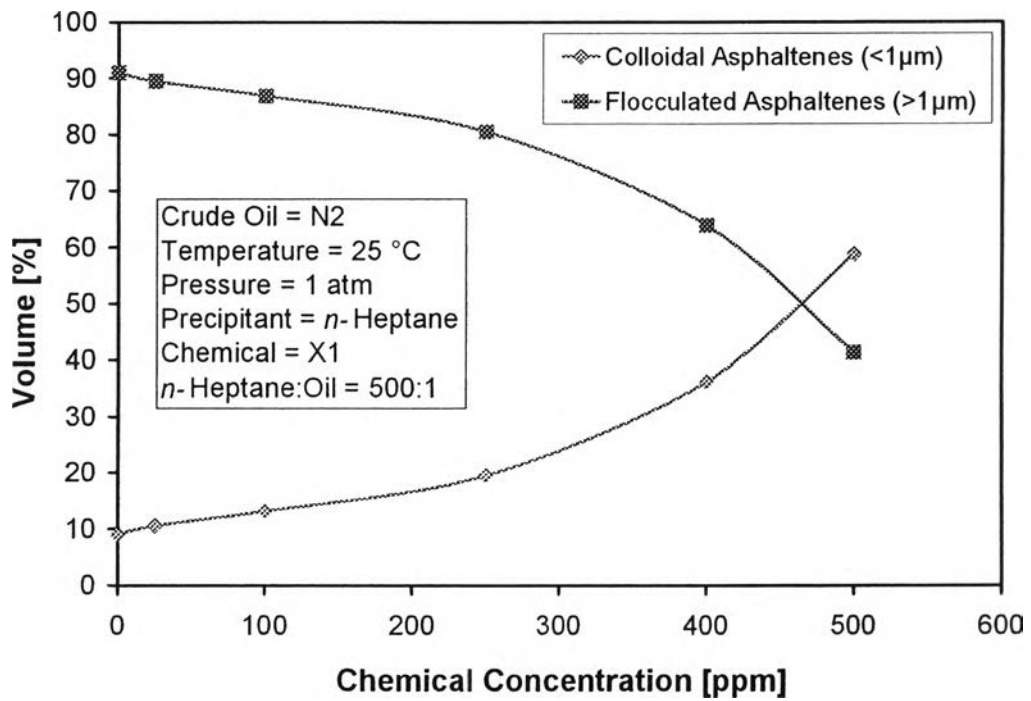


Figure 4.33 Volume percentage of colloidal asphaltenes and flocculated asphaltenes with different chemical concentrations of chemical X1

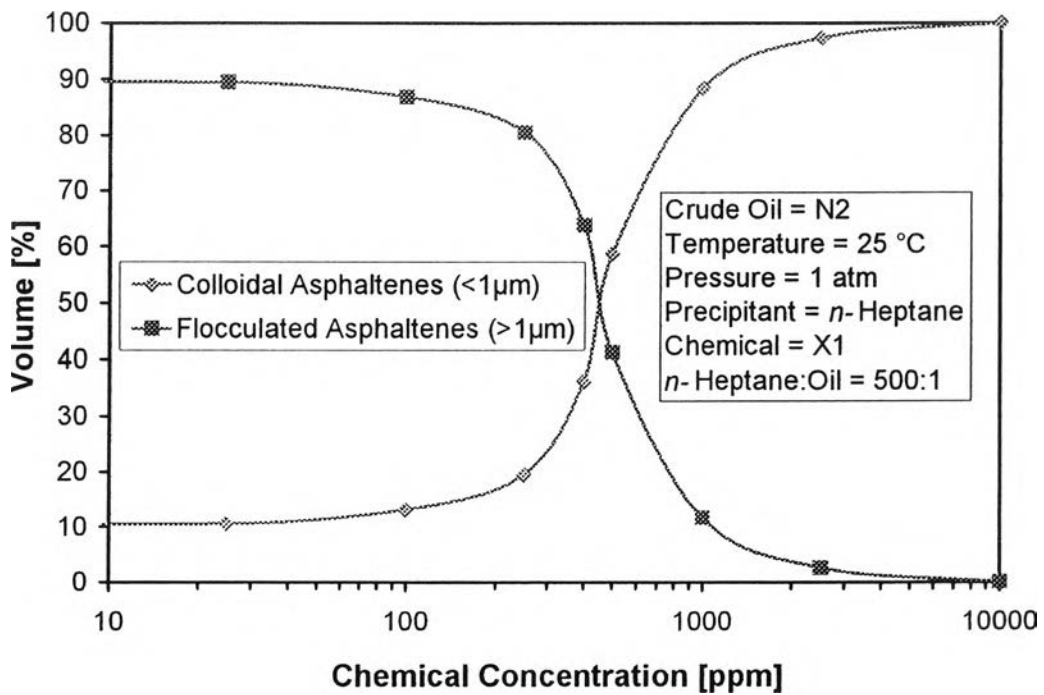


Figure 4.34 Volume percentage of colloidal asphaltenes and flocculated asphaltenes with different chemical concentrations of chemical X1 up to 10000 ppm

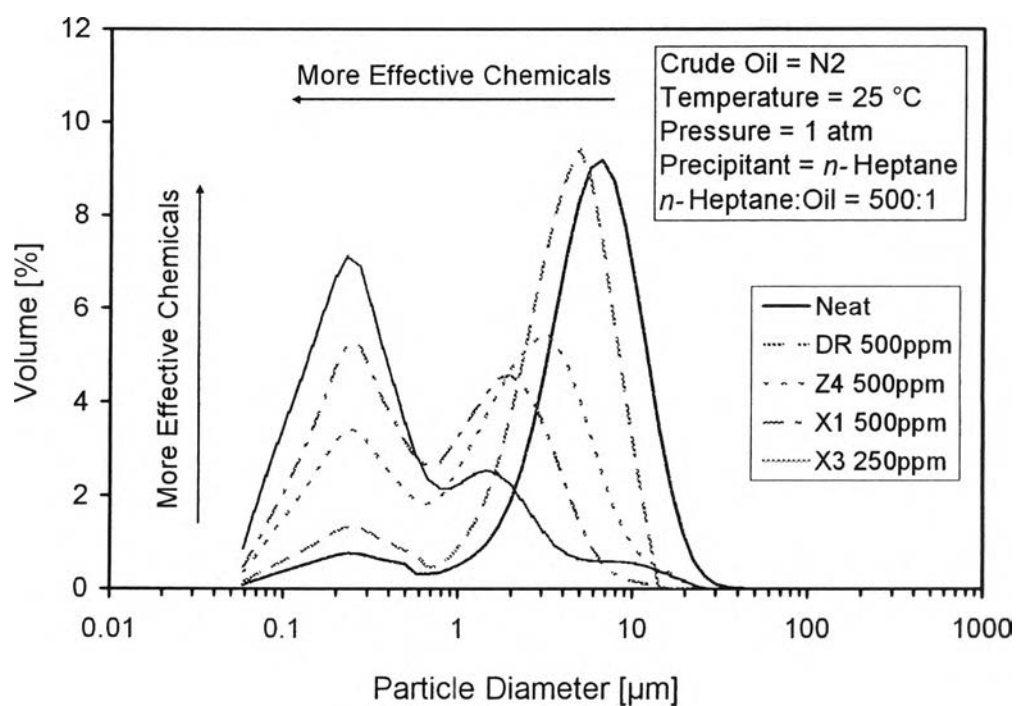


Figure 4.35 Asphaltene particle size distributions of the crude oil N2 treated with different asphaltene chemicals