CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Crude Oils

The crude oils (stock tank oils) used in this study are crude oil N2, Q1, and K2 from different fields in the North Slop of Alaska. After the water was removed prior to experimentation, additionally any sand or clay was also removed before any testing by centrifugation. Properties of the crude oil are presented in Table 3.1.

Table 3.1 Properties of crude oils

Property	Crude Oil N2	Crude Oil Q1	Crude Oil K2
Density at 25°C (g/mL)	0.8700	0.8696	0.9081
Molecular Weight (g/mol)	233.7	N/A	252.9
Saturates (wt.%)	55.9	59.6	49.5
Aromatics (wt.%)	23.9	26.5	28.4
Resins (wt.%)	17.5	10.1	12.4
Asphaltenes (wt.%)	2.7	3.8	9.7

3.1.2 Recombined Live Oil

The recombined live oil used in this study was prepared by a third party company by combining the stock tank oil with gas mixture of a known composition that simulates separator gases under reservoir conditions. A stock tank oil/separator gas mixture was then reconditioned in a rocking cell for 3-5 days before use. The composition of the recombined live oil N2 is shown in Table 3.2. To make the recombined live oil with miscible injectants, a mixture of recombined live oil was mixed with particular molar ratio of miscible injectants and then reconditioned in a rocking cell for 3-5 days. The composition of the recombined live oil of crude oil N2

is shown in Table 3.2. Composition of the recombined live oil N2 with 50 mol% miscible injectant is shown in Table 3.3.

Table 3.2 Composition of recombined live oil N2

Component (Symbol / Name)		Molecular Weight (g/mol)	Reservoir Fluid (mole %)	Reservoir Fluid (weight %)
N_2	Nitrogen	28.01	0.569	0.138
CO_2	Carbon Dioxide	44.01	0.433	0.165
H_2S	Hydrogen Sulfide	34.08	0.000	0.000
C1	Methane	16.04	44.666	6.191
C2	Ethane	30.07	4.336	1.127
C3	Propane	44.10	4.407	1.679
iC4	i-Butane	58.12	0.957	0.481
nC4	n-Butane	58.12	2.124	1.067
iC5	i-Pentane	72.15	1.021	0.637
nC5	n-Pentane	72.15	1.283	0.800
C6	Hexanes	86.18	2.000	1.489
C7	Heptanes	94.03	3.420	2.779
C8	Octanes	107.90	4.085	3.808
C9	Nonanes	122.21	2.914	3.077
C10	Decanes	134.07	2.741	3.175
C11	Undecanes	147.00	2.292	2.911
C12	Dodecanes	161.00	2.026	2.818
C13	Tridecanes	175.00	2.096	3.169
C14	Tetradecanes	190.00	1.912	3.139
C15	Pentadecanes	206.00	1.783	3.173
C16	Hexadecanes	222.00	1.490	2.858
C17	Heptadecanes	237.00	1.308	2.679
C18	Octadecanes	251.00	1.254	2.718
C19	Nonadecanes	263.00	1.138	2.587
C20	Eicosanes	275.00	0.977	2.322
C21	Heneicosanes	291.00	0.840	2.111
C22	Docosanes	305.00	0.756	1.993
C23	Tricosanes	318.00	0.684	1.880
C24	Tetracosanes	331.00	0.636	1.818
C25	Pentacosanes	345.00	0.569	1.697
C26	Hexacosanes	359.00	0.519	1.610
C27	Heptacosanes	374.00	0.458	1.479
C28	Octacosanes	388.00	0.476	1.595
C29	Nonacosanes	402.00	0.390	1.354
C30+	Triacontanes Plus	991.96	3.440	29.479
Total	(%)		100.000	100.000
Average Molecular Weight (g/mol)			115.74	

Table 3.3 Composition of recombined live oil N2 with 50 mol% miscible injectant

Component (Symbol / Name)		Molecular Weight (g/mol)	Reservoir Fluid (mole %)	Reservoir Fluid (weight %)
N_2	Nitrogen	28.01	0.506	0.201
CO_2	Carbon Dioxide	44.01	0.480	0.300
H_2S	Hydrogen Sulfide	34.08	0.000	0.000
C1	Methane	16.04	53.464	12.174
C2	Ethane	30.07	7.418	3.166
C3	Propane	44.10	9.155	5.730
iC4	i-Butane	58.12	1.739	1.435
nC4	n-Butane	58.12	3.700	3.052
iC5	i-Pentane	72.15	1.152	1.180
nC5	n-Pentane	72.15	1.219	1.248
C6	Hexanes	86.18	1.262	1.544
C7	Heptanes	94.80	1.809	2.434
C8	Octanes	108.30	2.010	3.089
C9	Nonanes	122.57	1.479	2.573
C10	Decanes	135.12	1.366	2.620
C11	Undecanes	147.00	1.111	2.319
C12	Dodecanes	161.00	1.020	2.331
C13	Tridecanes	175.00	1.077	2.674
C14	Tetradecanes	190.00	0.946	2.552
C15	Pentadecanes	206.00	0.865	2.530
C16	Hexadecanes	222.00	0.745	2.346
C17	Heptadecanes	237.00	0.649	2.182
C18	Octadecanes	251.00	0.622	2.217
C19	Nonadecanes	263.00	0.591	2.205
C20	Eicosanes	275.00	0.469	1.831
C21	Heneicosanes	291.00	0.406	1.679
C22	Docosanes	305.00	0.374	1.619
C23	Tricosanes	318.00	0.336	1.518
C24	Tetracosanes	331.00	0.310	1.454
C25	Pentacosanes	345.00	0.282	1.383
C26	Hexacosanes	359.00	0.234	1.192
C27	Heptacosanes	374.00	0.245	1.301
C28	Octacosanes	388.00	0.224	1.236
C29	Nonacosanes	402.00	0.189	1.077
C30+	Triacontanes Plus	653.90	2.544	23.608
Total (%)			100.000	100.000
Average Molecular Weight (g/mol)			70.46	

3.1.3 Asphaltene Precipitants and Solvents

C.P. grade ethane (99.0% purity), instrument grade propane (99.5% purity), and instrument grade butane (99.5% purity) were supplied by Scott Specialty Gasses Inc. HPLC grade pentane (99.6% purity), HPLC grade heptane (99.4% purity), reagent grade octane (95% purity), certified grade decane (99.9% purity), laboratory grade dodecane (98% purity), certified grade tetradecane (99.9% purity), and certified grade hexadecane (99.9% purity) were supplied by Fisher Scientific. Certified grade toluene (99.9% purity) and certified grade cyclohexane (99% purity) were also supplied by Fisher Scientific and used as solvents. Properties of asphaltene precipitants and solvents at 25 °C are summarized in Table 2.1.

3.1.4 Asphaltene Dispersants

Known chemical compounds, namely; 4-Dodecyl Resorcinol (DR) (97% purity) and 4-Dodecyl Phenol (DP) (mixture of isomers) were obtained from Aldrich and 4-Dodecyl Benzene Sulfonic Acid (DBSA) (mixture of isomers, 90% purity) was obtained from Fluka. In addition, eleven proprietary blends (X1, X2, X3, Y1, Y2, Y3, Y4, Z1, Z2, Z3, and Z4) were obtained from different oil field chemical companies.

3.2 Experimental Techniques

For the asphaltene precipitation modeling and validation studies, the experiment mainly consists of two parts. The first part is ambient titration using an Automated Flocculation Titrimeter (AFT) to determine the oil solubility parameter and the onset solubility parameter for the model. Another part is the high pressure system for titrating crude oil at high pressure and temperature and for performing pressure depletion of live oil.

For the asphaltene precipitation remediation and controlling studies, the experiment consists of three parts. The first part is ambient titration using the AFT to study the delay in the asphaltene precipitation onset when using asphaltene dispersants. The second part is using a turbidity measurement device to study the effectiveness of asphaltene dispersant on asphaltene settling. The last part is using a

particle size distribution measurement to study the effect of asphaltene dispersant on particle size.

3.2.1 Ambient Titration

The titration procedure was based on ASTM standard D6703-01 (ASTM, 2001). The asphaltene precipitation onset under ambient conditions was determined using an Automated Flocculation Titrimeter (AFT) by Western Research Institute with a LS-1 Tungsten Halogen light source, an USB2000 Miniature Fiber Optic Spectrometer by Ocean Optics, Inc. and a 0.2 mm path length quartz flow cell by Starna Cells, Inc. to measure light transmittance at 740 nm (effective particle detection is at 370 nm). The temperature was controlled with ± 0.01 °C precision by using a circulating water bath. A crude oil sample or a crude oil/toluene mixture of about 3 g was titrated with normal alkanes at a rate of 0.5 mL/min. The sample mixture was then circulated through the flow cell at 10 mL/min. The online data acquisition and system control were performed using a PC. The ambient titration system is illustrated in Figure 3.1 and the flow cell is illustrated in Figure 3.2.

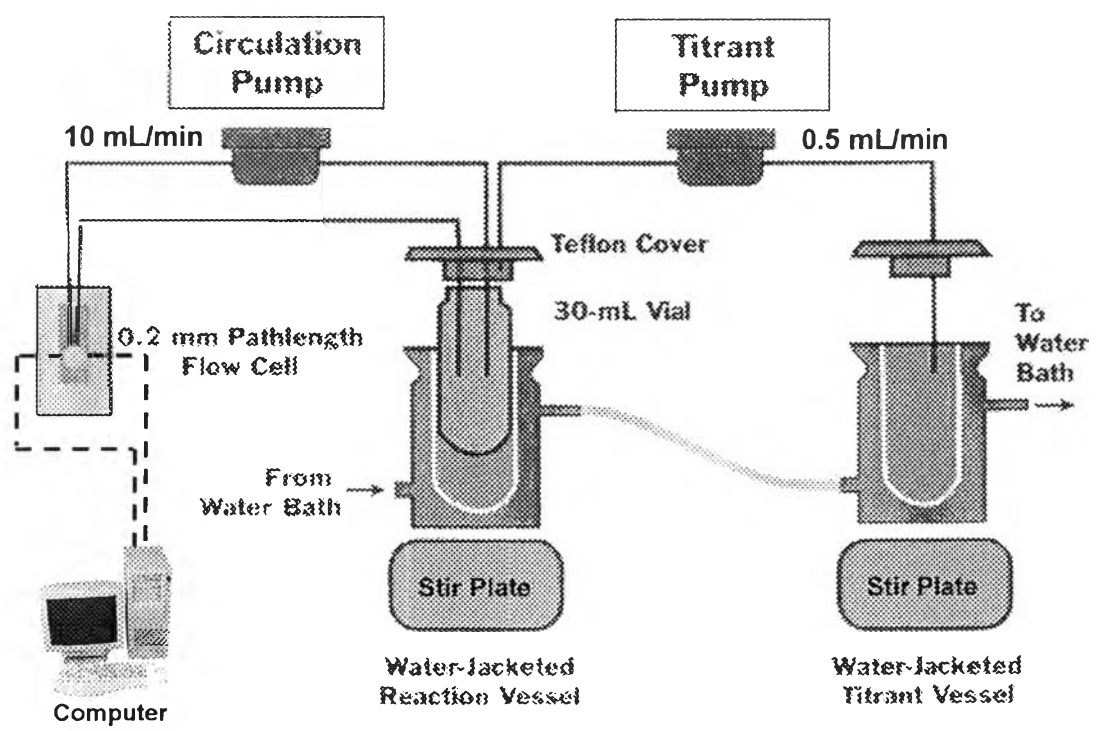


Figure 3.1 Schematic of ambient titration system

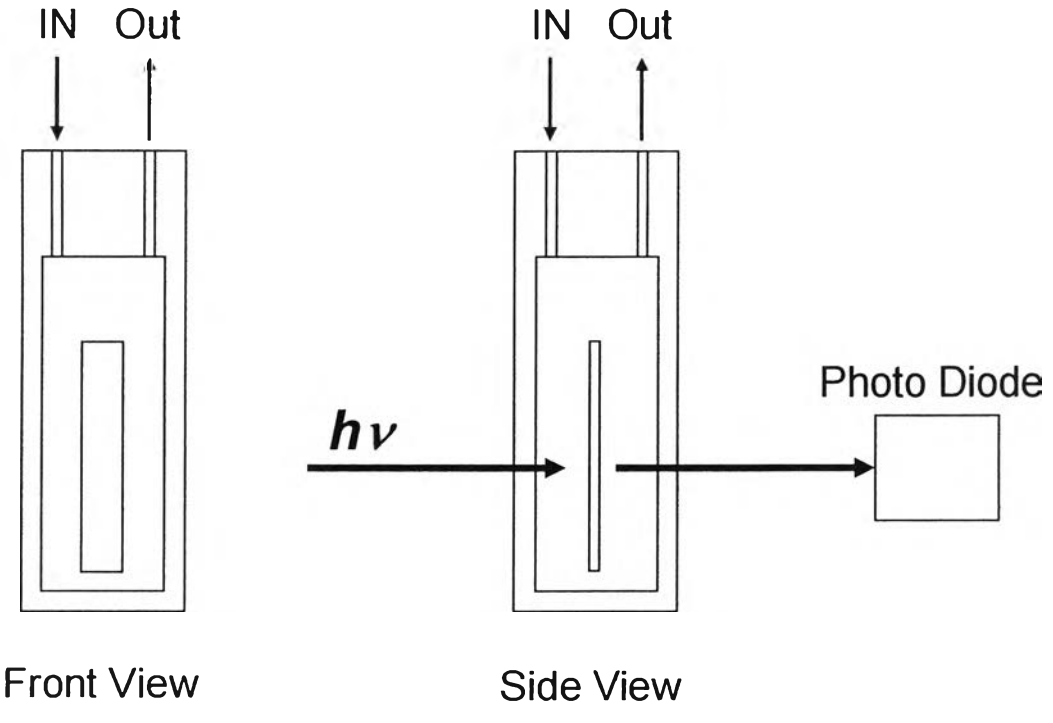


Figure 3.2 Flow cell

3.2.2 Density Measurement

The density of the crude oil at different temperatures was measured based on standard procedure ASTM D4052-96 (Reapproved 2002) using a DMA 5000 Densitometer by Anton PAAR. This densitometer has a measuring range of 0-3 g/mL, repeatability of 1×10^{-6} g/mL, a temperature accuracy of 0.001 °C, and a temperature range of 0-90 °C.

3.2.3 SARA Analysis

A SARA analysis of crude oil was performed by following the procedure described in section 2.1.

3.2.4 High Pressure System

The pressure vessel with a magnetic mixer was specially made for high pressure titration and pressure depletion test of asphaltenes. It was made from titanium by Phoenix Instruments to stand up to 15,000 psi and 200 °C. Window cells

were also incorporated for light transmission detection system. Three syringe pumps from ISCO were used to pressurize the system and charge crude oil sample or precipitant to the pressure vessel. Two ISCO pumps rated to 10,000 psi and 200 °C with the capacity of 103 mL and another pump rated to 2,000 psi and 200 °C with the capacity of 1,015 mL were used. The vacuum pump used was a Welch direct-drive high vacuum pump model 8905 acquired from Fisher Scientific. This pump had the free air displacement of 51 L/min and ultimate vacuum of 2 millitorr. All valves and in-line filters were purchased from High Pressure Equipment and all of them were rated at 15,000 psi. Asphaltene precipitation was detected using a laser near infrared (NIR) detector at 1550 nm and the signal was sent to a PC for analysis. NIR was selected because of larger path length (1/4 inch) and effective particle size detection is at 775 nm. Several photographs of high pressure system are shown in Figure 3.3 to Figure 3.7. The experimental diagram of a high pressure system is illustrated in Figure 3.8.

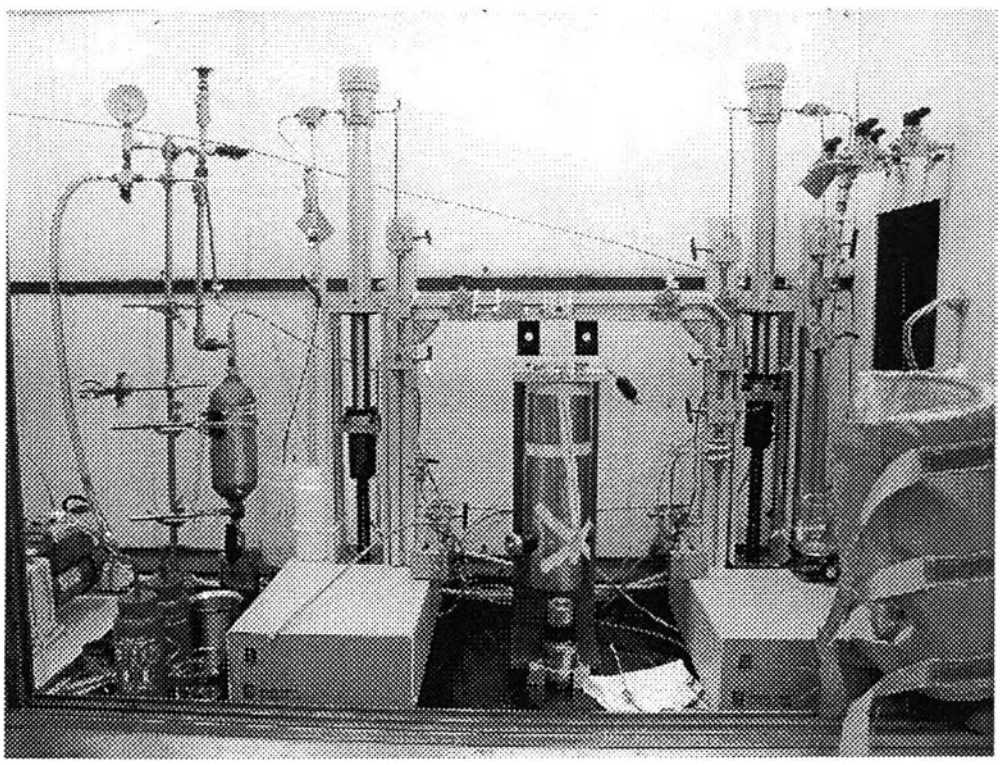


Figure 3.3 High pressure system

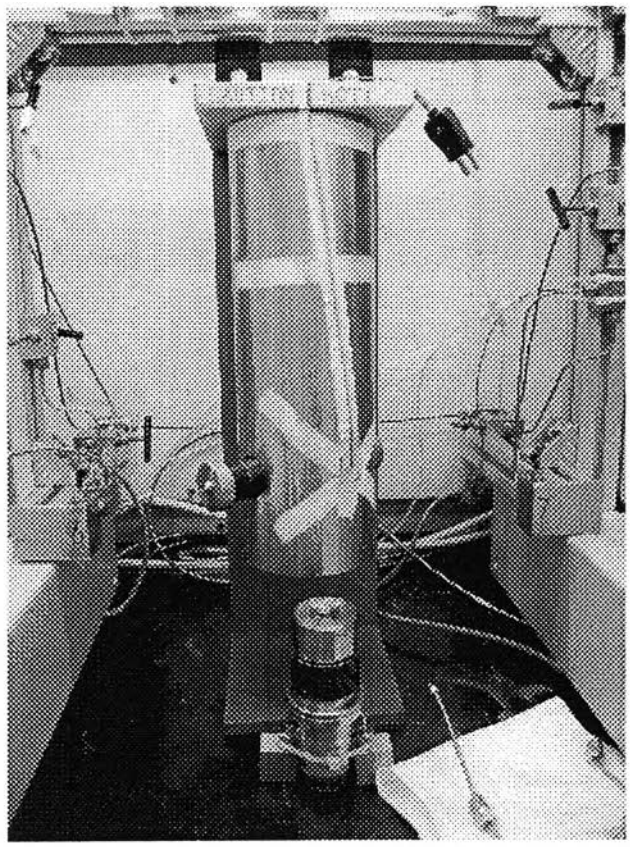


Figure 3.4 Titanium pressure cell

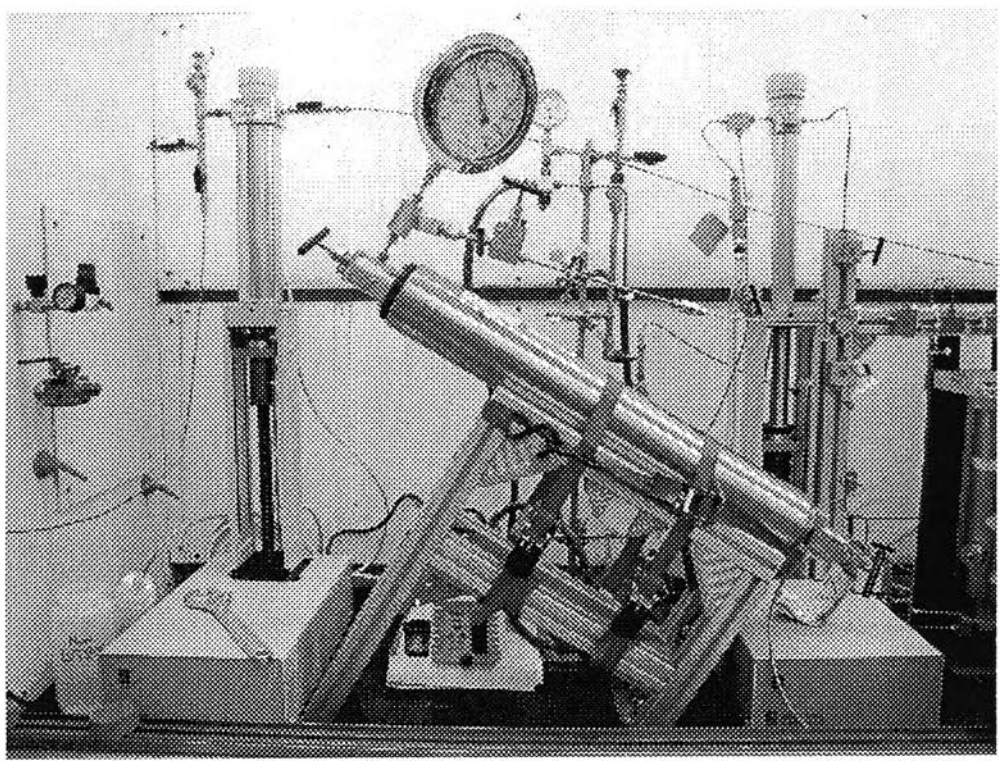


Figure 3.5 Pressure depletion setup

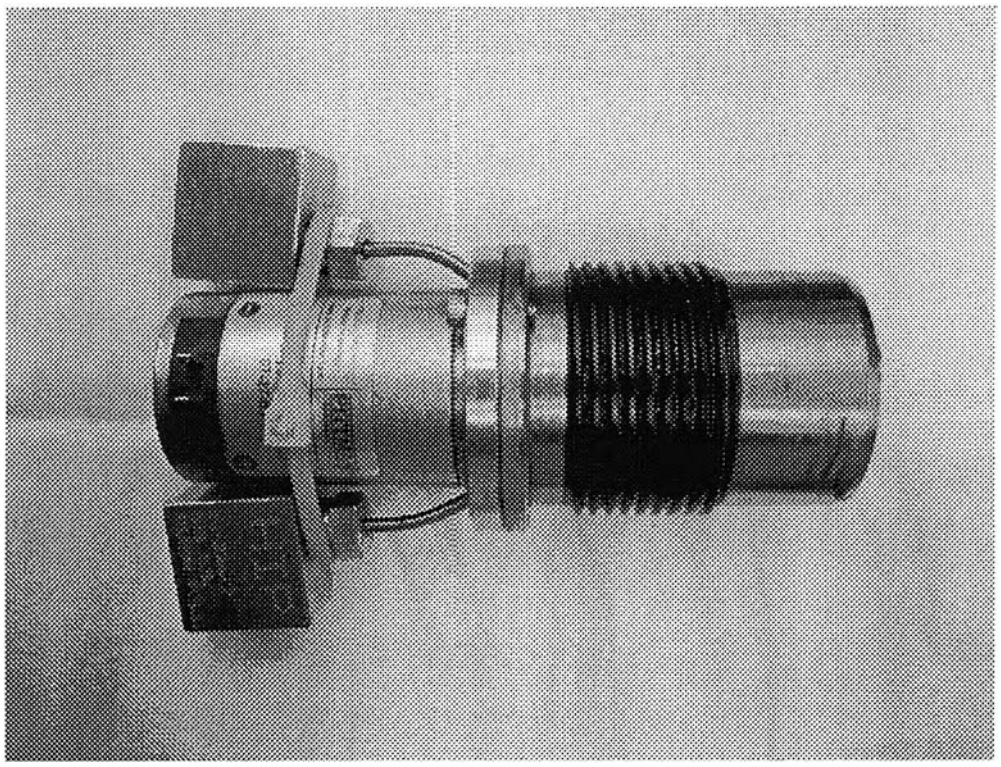


Figure 3.6 Magnetic mixer with motor

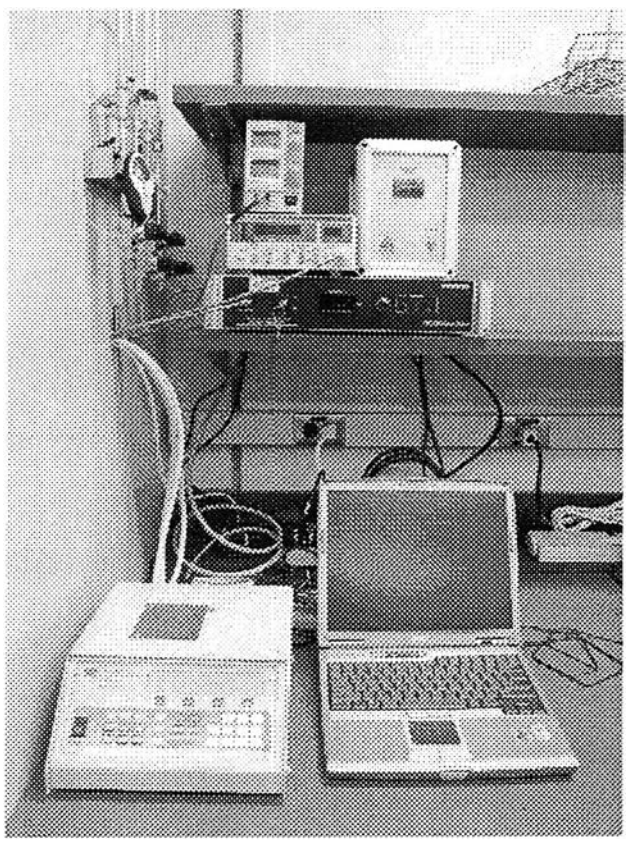
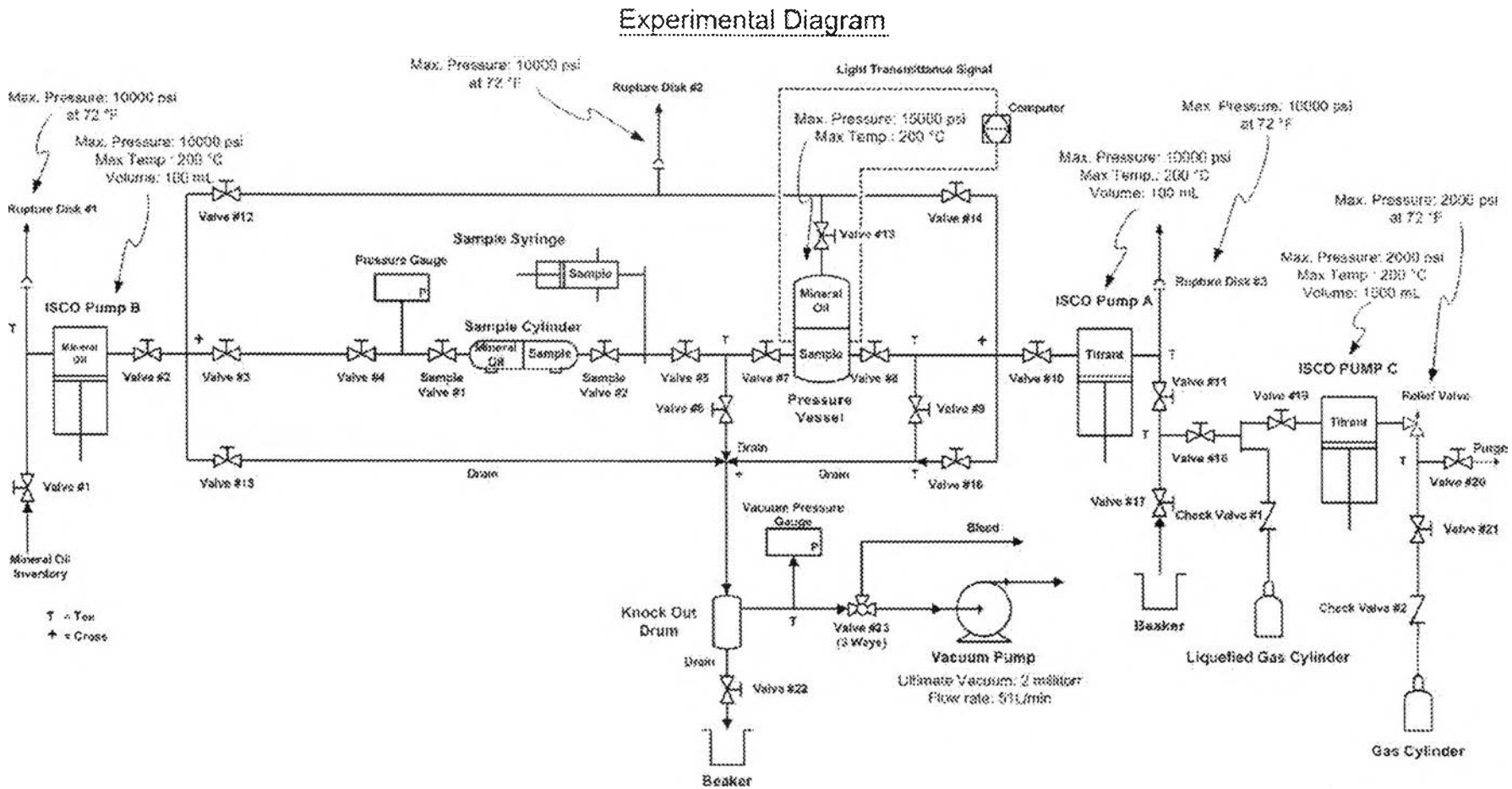


Figure 3.7 Controlling system



Note: All valves, tees, crosses and tubing are rated to 15000 psi

Figure 3.8 Experimental diagram of high pressure system

3.2.5 Turbidity Measurement

The turbidity measurements were obtained using a Turbiscan MA2000 from Formulaction that used a pulsed near infrared light source (850 nm) to measure the average transmittance. The asphaltenes were precipitated by adding 150 μL of crude oil sample to 7.5 mL of precipitant (e.g., *n*-pentane, *n*-heptane, and *n*-decane) in a test tube. The blend was agitated briefly and the transmittance of the blend was measured as a function of time at one minute intervals over a one-hour period. Initially, the entire tube was dark and transmittance approached zero. As asphaltenes settled, the upper portion of the solution became clearer and more light was transmitted as shown in Figure 3.9. For well-dispersed asphaltenes, the transmitted light was constant and the transmittance remained close to zero.

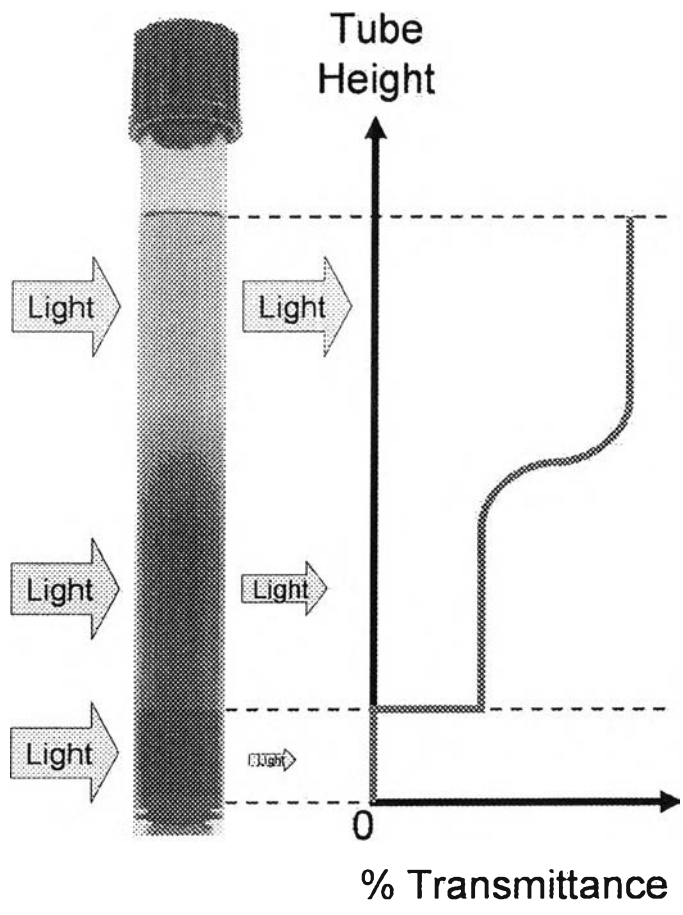


Figure 3.9 Dynamic turbidity measurement

3.2.6 Particle Size Distribution Measurement

A Mastersizer S by Malvern Instruments was used to measure the particle size distribution in the range of 0.05 μm to 900 μm. The asphaltene particles were precipitated out by adding 800 μL of crude oil sample to 400 mL of a precipitant, a crude oil to precipitant ratio of 1 to 500. The mixture was shaken very briefly to avoid shearing effects on the asphaltene particles. The same preparation method as the other measurements was applied to the crude oil/solvent (e.g., cyclohexane and toluene) system to determine the stable asphaltene size.

3.3 Experimental Methods and Calculations

3.3.1 Sample Preparation

3.3.1.1 Stock Tank Oil

The stock tank oils obtained from the field usually contain water, sand, clay, and/or foreign particles. These impurities were separated by centrifugation at 6000 rpm and 60 °C for 60 minutes. The top part above the emulsion pad was poured out and kept as centrifuged/ cleaned stock tank oil for further experimentation.

3.3.1.2 Stock Tank Oil with Asphaltene Dispersant

Solutions of stock tank oil containing 500 part-per-million (ppm) of asphaltene dispersant were prepared by adding 25 μL of asphaltene dispersant to 50 mL of stock tank oil. Solutions were placed in an oven at 55 °C for two hours and mixed for one hour. Lower concentration solutions were prepared by dilution of 500 ppm solution with neat stock tank oil.

3.3.2 Ambient Titration

Three grams of the crude oil/solvent mixture was put into a 30 mL vial. The selected precipitant (normal alkane) was then added automatically to the sample vial at a rate of 0.5 mL/min. The mixture of crude oil/solvent/precipitant was then flowed through the 0.2 mm path length quartz flow cell at a rate of 10 mL/min. The light transmittance was recorded and converted to absorbance via the PC. The typical titration data is shown in Figure 3.10.

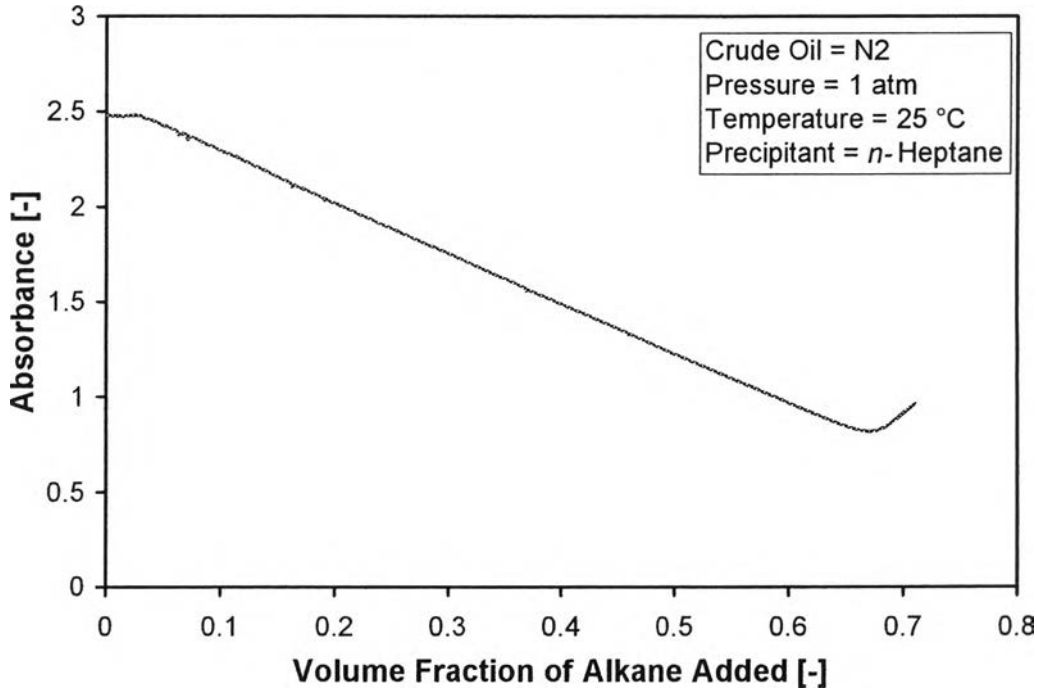


Figure 3.10 Typical titration data using the AFT system

Asphaltene precipitation onset point is usually defined as a point of maximum transmittance or a point of minimum absorbance; however, at this point, there are enough asphaltene particles that block the light and overcome the dilution effect. Therefore, the actual onset point precedes a minimum absorbance point. The actual onset point was determined mathematically as described in Kraiwattanawong's thesis (2005) by taking derivation of absorbance respected to volume fraction of normal alkane added, which was based on Beer's law and empirical fitting. The derivation of absorbance respected to volume fraction of normal alkane added is shown in Figure 3.11 and the mathematical fitting is shown in Figure 3.12.

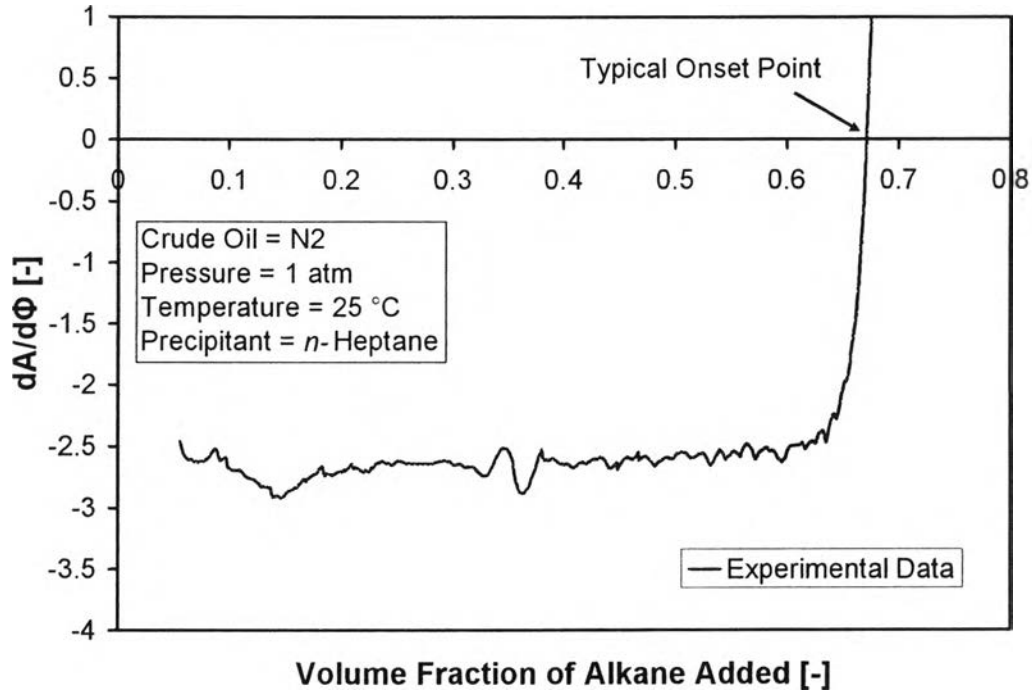


Figure 3.11 Derivation of absorbance respected to the volume fraction of alkane added

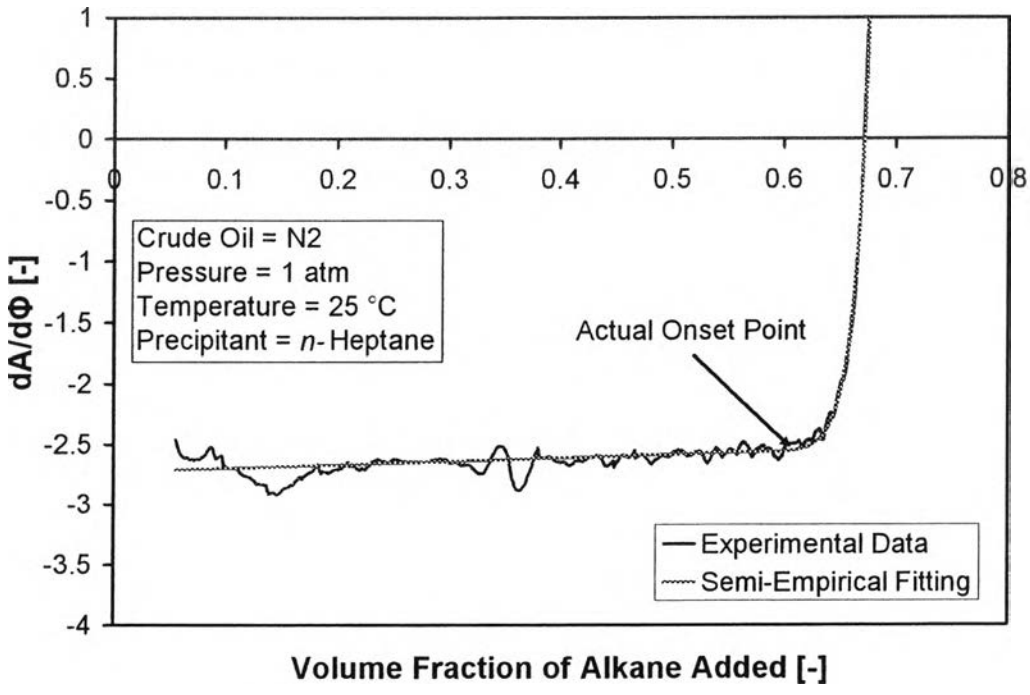


Figure 3.12 Semi-empirical fitting shows an actual onset point

A set of titrations with different ratios of solvent to crude oil were needed to calculate the oil solubility parameter and the onset solubility parameter. Typical titration results with different asphaltene precipitants are shown in Figure 3.13.

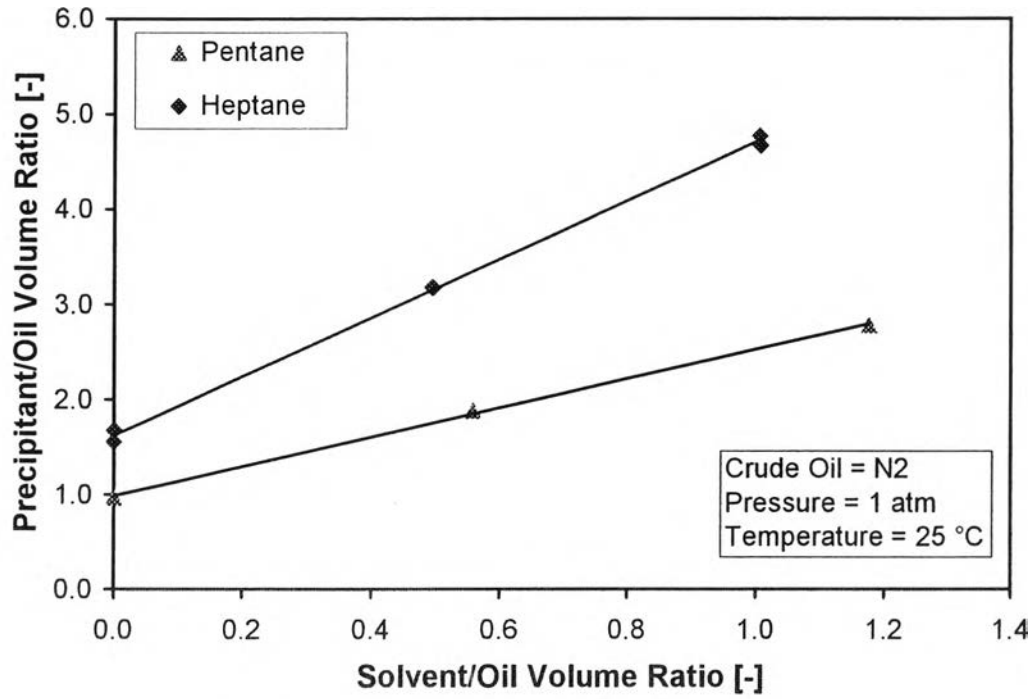


Figure 3.13 Typical titration results with different asphaltene precipitants

Using the simple mixing rule of solubility parameters and defining the solubility parameter of the mixture as the onset solubility parameter, it can be written as:

$$\delta_{onset} = \phi_o \delta_o + \phi_s \delta_s + \phi_p \delta_p \qquad (3.1)$$

Where δ_{onset} = onset solubility parameter ($MPa^{½}$)

ϕ_o = volume fractions of crude oil (-)

ϕ_s = volume fractions of solvent (-)

ϕ_p = volume fractions of precipitant (-)

δ_o = solubility parameters of crude oil ($MPa^{½}$)

δ_s = solubility parameters of solvent ($MPa^{½}$)

δ_p = solubility parameters of precipitant ($MPa^{1/2}$)

Equation (3.1) can be rewritten in terms of a volume ratio as:

$$\frac{V_p}{V_o} = \left(\frac{\delta_s - \delta_{onset}}{\delta_{onset} - \delta_p}\right)\frac{V_s}{V_o} + \left(\frac{\delta_o - \delta_{onset}}{\delta_{onset} - \delta_p}\right) \tag{3.2}$$

Where V_o = volume of crude oil (mL)

V_s = volume of solvent (mL)

V_p = volume of precipitant (mL)

Plotting V_p/V_o versus V_s/V_o, the oil solubility parameter (δ_o) and the onset solubility parameter (δ_{onset}) can be calculated from the slope and intercept of the line as follows:

$$Slope = \left(\frac{\delta_s - \delta_{onset}}{\delta_{onset} - \delta_p}\right) \quad or \quad \delta_{onset} = \left(\frac{\delta_s + Slope \cdot \delta_p}{1 + Slope}\right) \tag{3.3}$$

$$Intercept = \left(\frac{\delta_o - \delta_{onset}}{\delta_{onset} - \delta_p}\right) \quad or \quad \delta_o = Intercept \cdot \left(\delta_{onset} - \delta_p\right) + \delta_{onset} \tag{3.4}$$

The relationship between the oil solubility parameter (δ_o) and molar volume (v) (which also depends on temperature) was described by Hildebrand and Scott in 1964 which stated that $\ln\delta = \alpha \ln v$ where $\alpha \approx -1.25$ for normal liquids but α can range from 1.0-1.5, as shown in Figure 3.14. Therefore, the oil solubility parameter can be calculated base on the experimental data.

The onset solubility parameter (δ_{onset}) is a strong function of the precipitant type and temperature. The onset solubility parameter as proposed by Wang *et al.* (2004) can be plotted as a function of square root of molar volume of the precipitant. The onset solubility parameters are shown in Figure 3.15.

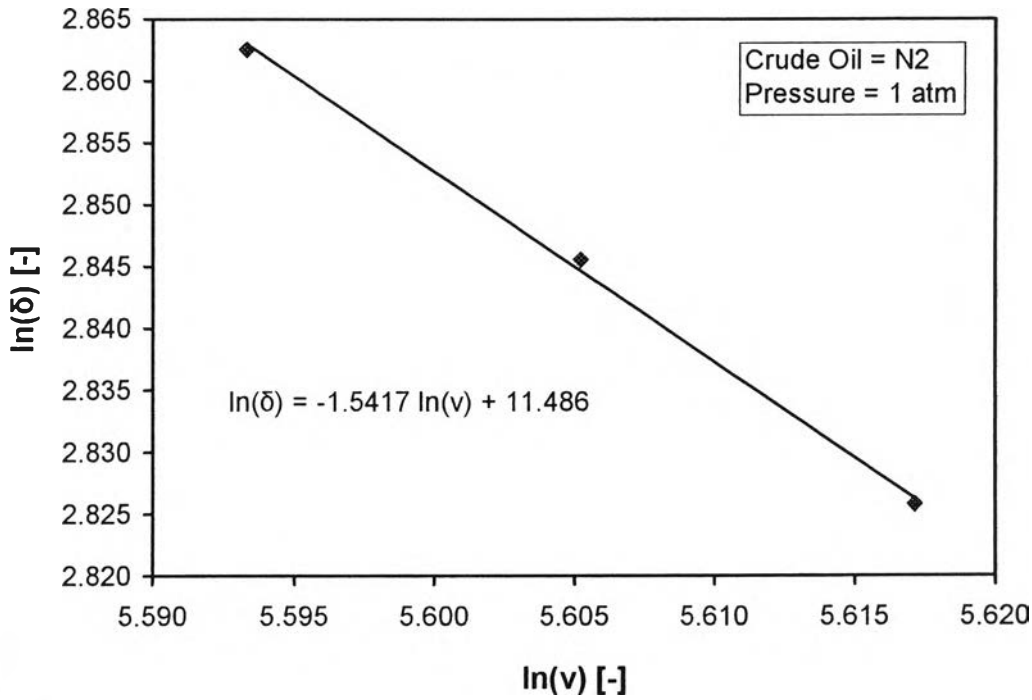


Figure 3.14 Oil solubility parameter as a function of the molar volume

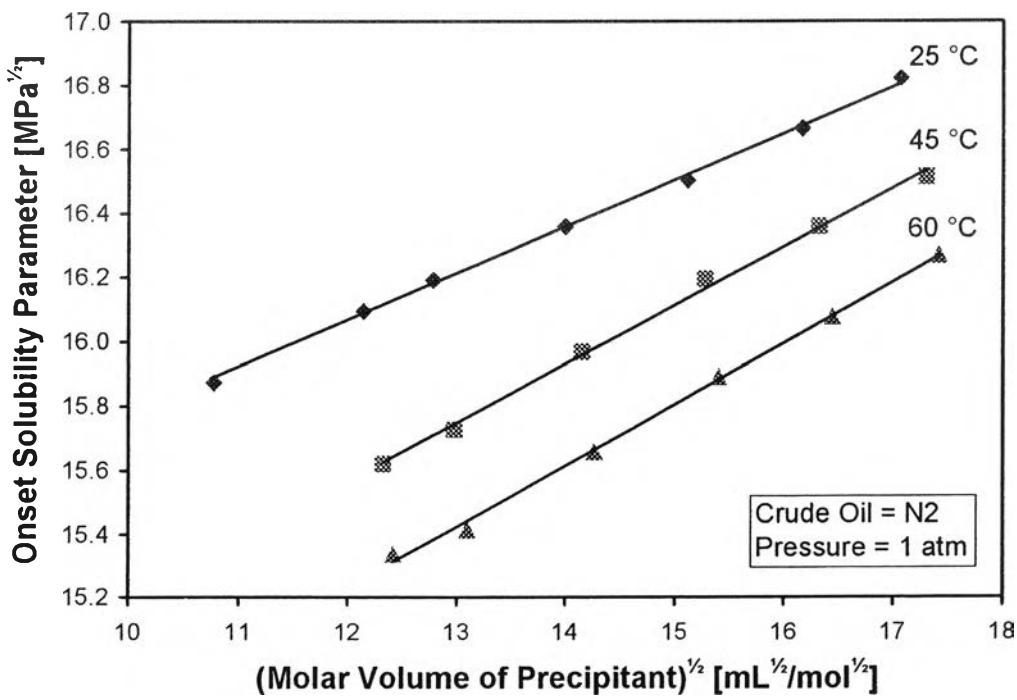


Figure 3.15 Onset solubility parameter as a function of temperature and the square root of the molar volume of the precipitant

3.3.3 High Pressure Titration with *n*-Pentane to *n*-Hexadecane

Under ambient conditions, the titration can be performed with liquid alkanes ranging from *n*-pentane to *n*-hexadecane. High pressure titrations have been performed to validate the model to predict the onset solubility parameter. For high pressure titration with liquid alkanes from *n*-pentane to *n*-hexadecane, the experimental setup follows the general experimental diagram as shown in Figure 3.8 and the standard operation procedure (SOP) is shown in Table 3.4.

3.3.4 High Pressure Titration with Ethane, Propane and *n*-Butane

For high pressure titration with alkane gases (ethane, propane and butane), propane and butane are in the liquid phase and can be introduced directly to ISCO pump B as liquid. However, ethane comes in the gas phase and needs a booster pump to pressurize ethane gas into liquid using ISCO pump C before transferring to ISCO Pump B for titration. The standard operating procedure for high pressure titration with propane and butane is shown in Table 3.5 and the standard operating procedure for high pressure titration with ethane is shown in Table 3.6.

3.3.5 Pressure Depletion

For pressure depletion, the live oil or the live oil/miscible injectant mixture is the only sample in the pressure vessel. Therefore, a titrant cylinder is not needed. The standard operating procedure for pressure depletion is shown in Table 3.7.

Table 3.4 Standard operating procedure for high pressure titration with *n*-pentane to *n*-hexadecane

Step-by-Step Procedure	Hazards or Consequences of Deviation	Control Measures
Step 1: Inventory Mineral oil. De-inventory Pump B. Close all valves. Open valves #2, 12, 13, 15 and 23. Start the vacuum pump and pull a full vacuum. (Note: Be sure to inventory a few ml of mineral oil into the dip tube for pump A to displace air in this line, valve #1) Close valves #2, 15 and 23 then turn off the vacuum pump. Open valve #1 and inventory Pump B to 100%. Close valve #1. Set the maximum pressure on Pump B to 50 psi. Open valve #2 and cycle Pump B to inventory and de-inventory pressure vessel. Close valve #2. Open valve #1 and cycle pump B until no bubbles are seen in the mineral oil bottle. Repeat until system is liquid full. Inventory pressure vessels 100% with mineral oil then de-inventory pump B through valve #1 to 30 ml. Close valve #1.	Open valves slowly. System is under vacuum and valves are being opened to ambient pressure.	Use nitrile gloves for splash protection.
Step 2: Inventory ISCO Pump A. Open valves #10, 11, 16 and 23. Pull system under vacuum. (Note: Be sure to inventory a few ml of titrant into the dip tube for pump A to displace air in this line, valve #17) Close valves #10, 16 and 23 and turn off the vacuum pump. Open valve #17. Cycle pump A 100%-0% until no bubbles are seen in the titrant beaker. Inventory pump A to 100%. Close valves #11 and 17.	Open valves slowly. System is under vacuum and valves are being opened to ambient pressure. Titrants are flammable and toxic.	Use nitrile gloves for splash protection.

Step 3: Inventory Pressure Vessel with Crude Oil. Open valves #6, 7, 8, 9, 16 and 23. Pull system under vacuum. Close these valves. Attach syringe with crude oil to valve #5. Open valve #5 to fill the line with crude oil. Close valve #5. Weigh syringe and record weight as tear weight. Connect again and open valves #5 and #7 and inventory pressure vessel with crude oil. Close valves #5 and 7. Remove syringe and weigh. Record added weight of crude oil. Turn heating mantle on.	Crude oil is toxic.	Use nitrile gloves for splash protection.
Step 4: Pressurize System. Set pump B to constant pressure mode and enter test pressure. Open valve #10 and set pressure of Pump A to test pressure. Set pump A to constant flow mode and enter titrant rate.	System under high pressure.	Close hood windows. Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.
Step 5: Start Experiment. Start mixer by setting power output to proper voltage. Start logging data, Open valve #8 and start pump B. Monitor system for flocculation.		Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.

Step 6: Stop Experiment. Close valves #8 and 10 and stop pump A. Stop logging data. Set pump A and B pressure to 50 psi. Turn heating mantle off.		Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.
Step 7: Cleaning. Place a beaker under the dip tube on valve 22. Open valves #6 and 7. Slowly open drain valve and let crude oil drain out of knock out vessel. Close valve 22. Open valve #23 and start vacuum pump and pull system under vacuum. Close valve #23 and stop vacuum pump. Open valve #22 and drain the knock out vessel. Close valve #22. Disconnect the fiber optic cable and unscrew the sapphire window on the pressure vessel. Open valve #23 and start the vacuum pump. Rinse the inside of the pressure vessel with toluene. Turn off vacuum pump and drain knock out vessel. Set pump B to refill 30 ml. Start pump B. Once pump B has refilled 30 ml (this pulls the piston in the pressure vessel up for cleaning) shut off pump B. Repeat the cleaning procedure for the pressure vessel until the solvent shows little sign of color from the crude oil. Reinstall the sapphire window and reconnect the fiber optic cable.	Toluene is used as a cleaning solvent.	During cleaning empty knockout vessel often to prevent liquid carryover into the vacuum pump line.

Table 3.5 Standard operating procedure for high pressure titration with propane and *n*-butane

Step-by-Step Procedure	Hazards or Consequences of Deviation	Control Measures
Step 1: Inventory Mineral oil. De-inventory Pump B. Close all valves. Open valves #2, 12, 13, 15 and 23. Start the vacuum pump and pull a full vacuum. (Note: Be sure to inventory a few ml of mineral oil into the dip tube for pump A to displace air in this line, valve #1) Close valves #2, 15 and 23 then turn off the vacuum pump. Open valve #1 and inventory Pump B to 100%. Close valve #1. Set the maximum pressure on Pump B to 50 psi. Open valve #2 and cycle Pump B to inventory and de-inventory pressure vessel. Close valve #2. Open valve #1 and cycle pump B until no bubbles are seen in the mineral oil bottle. Repeat until system is liquid full. Inventory pressure vessels 100% with mineral oil then de-inventory pump B through valve #1 to 30 ml. Close valve #1.	Open valves slowly. System is under vacuum and valves are being opened to ambient pressure.	Use nitrile gloves for splash protection
Step 2: Inventory ISCO Pump A. Open valves #10, 11, 16 18 and 23. Pull system under vacuum. Close valves #10, 16, 23 and turn off the vacuum pump. Open propane/butane cylinder valve. Set pump A to refill to 100%. Close butane cylinder valve and turn pump A off. Close valves #11 and 18.	Be sure to keep valve #17 closed for this titration. Open valves slowly. System is under vacuum and valves are being opened to ambient pressure.	Use nitrile gloves for splash protection

Step 3: Inventory Pressure Vessel with Crude Oil. Open valves #6, 7, 8, 9, 16 and 23. Pull system under vacuum. Close these valves. Attach syringe with crude oil to valve #5. Open valve #5 to fill the line with crude oil. Close valve #5. Weigh syringe and record weight as tear weight. Connect again and open valves #5 and 7 and inventory pressure vessel with crude oil. Close valves #5 and 7. Remove syringe and weigh. Record added weight of crude oil. Turn heating mantle on.	Crude oil is toxic.	Use nitrile gloves for splash protection.
Step 4: Pressurize System. Set pump B to constant pressure mode and enter test pressure. Open valve #10 and set pressure of Pump A to test pressure. Set pump A to constant flow mode and enter titrant rate.	System under high pressure.	Close hood windows. Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.
Step 5: Start Experiment. Start mixer by setting power output to proper voltage. Start logging data, Open valve #8 and start pump B. Monitor system for flocculation.		Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.

Step 6: Stop Experiment. Close valves #8 and 10 and stop pump A. Stop logging data. Set pump A and B pressure to 50 psi. Turn heating mantle off.		Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.
Step 7: Cleaning. Place a beaker under the dip tube on valve #22. Open valves #6 and 7. Slowly open valve #22 and let crude oil drain out of knock out vessel. Close valve #22. Open valve #23 and start vacuum pump and pull system under vacuum. Close valve #23 and stop vacuum pump. Open valve #22 and drain the knock out vessel. Close valve #22. Disconnect the fiber optic cable and unscrew the sapphire window on the pressure vessel. Open valve #23 and start the vacuum pump. Rinse the inside of the pressure vessel with toluene. Turn off vacuum pump and drain knock out vessel. Set pump B to refill 30 ml. Start pump B. Once pump B has refilled 30 ml (this pulls the piston in the pressure vessel up for cleaning) shut off pump B. Repeat the cleaning procedure for the pressure vessel until the solvent shows little sign of color from the crude oil. Reinstall the sapphire window and reconnect the fiber optic cable.	Toluene is used as a cleaning solvent.	During cleaning empty knockout vessel often to prevent liquid carryover into the vacuum pump line.

Table 3.6 Standard operating procedure for high pressure titration with ethane

Step-by-Step Procedure	Hazards or Consequences of Deviation	Control Measures
Step 1: Inventory Mineral oil. De-inventory Pump B. Close all valves. Open valves #2, 12, 13, 15 and 23. Start the vacuum pump and pull a full vacuum. (Note: Be sure to inventory a few ml of mineral oil into the dip tube for pump A to displace air in this line, valve #1) Close valves #2, 15 and 23 then turn off the vacuum pump. Open valve #1 and inventory Pump B to 100%. Close valve #1. Set a max pressure on Pump B to 50 psi. Open valve #2 and cycle Pump B to inventory and de-inventory pressure vessel. Close valve #2. Open valve #1 and cycle pump B until no bubbles are seen in the mineral oil bottle. Repeat until system is liquid full. Inventory pressure vessels 100% with mineral oil then de-inventory pump B through valve #1 to 30 ml. Close valve #1.	Open valves slowly. System is under vacuum and valves are being opened to ambient pressure.	Use Nitrile gloves for splash protection.
Step 2: Inventory ISCO Pump A. Open valves #10 11, 16, 18, 19, 21 and 23. Pull system under vacuum. Close valves #10, 11, 16, 18, 19, 23 and turn off the vacuum pump. Open ethane cylinder valve. Set pump C to refill to 100%. Close valve #21 and ethane cylinder valve. Pressurize pump C to 1000 psi. Open valves #11, 18, 19 and set pump A to refill to	Be sure to keep valve #17 closed for this titration. Open valves slowly. System is under vacuum and valves are being opened to ambient pressure.	Use Nitrile gloves for splash protection.

100%. Close valves #11, 18 and 19.		
Step 3: Inventory Pressure Vessel with Crude Oil. Open valves #6, 7, 8, 9, 16 and 23. Pull system under vacuum. Close these valves. Attach syringe with Crude oil to valve #5. Open valve #5 to fill the line with crude oil. Close valve #5. Weigh syringe and record weight as tear weight. Connect again and open valves #5 and 7 and inventory pressure vessel with crude oil. Close valves #5 and 7. Remove syringe and weigh. Record added weight of crude oil. Turn heating mantle on.	Crude oil is toxic.	Use Nitrile gloves for splash protection.
Step 4: Pressurize System. Set pump B to constant pressure mode and enter test pressure. Open valve #10 and set pressure of Pump A to test pressure. Set pump A to constant flow mode and enter titrant rate.	System under high pressure.	Close hood windows. Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.
Step 5: Start Experiment. Start mixer by setting power output to proper voltage. Start logging data, Open valve #8 and start pump B. Monitor system for flocculation.		Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.

Step 6: Stop Experiment. Close valves #8 and 10 and stop pump A. Stop logging data. Set pump A and B pressure to 50 psi. Turn heating mantle off.		Work behind hood doors when operating valves. Keep hood doors closed when system under pressure
Step 7: Cleaning. Place a beaker under the dip tube on valve #22. Open valves #6 and 7. Slowly open valve #22 and let crude oil drain out of knock out vessel. Close valve #22. Open valve #23 and start vacuum pump and pull system under vacuum. Close valve #23 and stop vacuum pump. Open valve #22 and drain the knock out vessel. Close valve #22. Disconnect the fiber optic cable and unscrew the sapphire window on the pressure vessel. Open valve #23 and start the vacuum pump. Rinse the inside of the pressure vessel with toluene. Turn off vacuum pump and drain knock out vessel. Set pump B to refill 30 ml. Start pump B. Once pump B has refilled 30 ml (this pulls the piston in the pressure vessel up for cleaning) shut off pump B. Repeat the cleaning procedure for the pressure vessel until the solvent shows little sign of color from the crude oil. Reinstall the sapphire window and reconnect the fiber optic cable.	Toluene is used as a cleaning solvent.	During cleaning empty knockout vessel often to prevent liquid carryover into the vacuum pump line.

Table 3.7 Standard operating procedure for pressure depletion

Step-by-Step Procedure	Hazards or Consequences of Deviation	Control Measures
Step 1: Inventory Mineral oil. De-inventory Pump B. Close all valves. Open valves #2, 3, 4, 12, 13, 15 and 23. Start the vacuum pump and pull a full vacuum. (Note: Be sure to inventory a few ml of mineral oil into the dip tube for pump A to displace air in this line, valve #1) Close valves #2, 15 and 23 then turn off the vacuum pump. Open valve #1 and inventory Pump B to 100%. Close valve #1. Set a max pressure on Pump B to 50 psi. Open valve #2 and cycle Pump B to inventory and de-inventory pressure vessel. Close valve #2. Open valve #1 and cycle pump B until no bubbles are seen in the mineral oil bottle. Repeat until system is liquid full. Inventory pressure vessels 100% with mineral oil then de-inventory pump B through valve #1 to 30 ml. Close valve #1.	Open valves slowly. System is under vacuum and valves are being opened to ambient pressure.	Use nitrile gloves for splash protection.
Step 2: Inventory Pressure Vessel with Live Oil. Open valves #5, 6, 7, 8, 9, 16 and 23. Pull the system under vacuum. Close these valves. Close valve #13. Set pump B to 2000 psi above live oil pressure. Open valves #2, 3, 4, and sample valve #1. Open sample valve #2 then valves #5 and 7 to fill the pressure vessel with live oil. Close valves #3, 4, 5, 7 and sample valve #1 and 2. Turn heating mantle on.	Live oil is toxic. Live oil is under high pressure.	Use nitrile gloves for splash protection.

Step 3: Pressurize System. Set pump B to pressure gradient mode and enter starting test pressure, ending test pressure and duration. Open valve #13.	System under high pressure.	Close hood windows. Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.
Step 4: Start Experiment. Start mixer by setting power output to proper voltage. Start logging data and start pump B. Monitor system for flocculation.		Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.
Step 5: Stop Experiment. Stop pump B. Stop logging data. Set pump B pressure to 50 psi. Turn heating mantle off.		Work behind hood doors when operating valves. Keep hood doors closed when system under pressure.

Step 6: Cleaning. Place a beaker under the dip tube on valve #22. Open valves #6 and 7. Slowly open valve #22 and let crude oil drain out of knock out vessel. Close valve #22. Open valve #23 and start vacuum pump and pull system under vacuum. Close valve #23 and stop vacuum pump. Open valve #22 and drain the knock out vessel. Close valve #22. Disconnect the fiber optic cable and unscrew the sapphire window on the pressure vessel. Open valve #23 and start the vacuum pump. Rinse the inside of the pressure vessel with toluene. Turn off vacuum pump and drain knock out vessel. Set pump B to refill 30 ml. Start pump B. Once pump B has refilled 30 ml (this pulls the piston in the pressure vessel up for cleaning) shut off pump B. Repeat the cleaning procedure for the pressure vessel until the solvent shows little sign of color from the crude oil. Reinstall the sapphire window and reconnect the fiber optic cable.	Toluene is used as a cleaning solvent.	During cleaning empty knockout vessel often to prevent liquid carryover into the vacuum pump line.