CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Crude Oils

Crude oils were homogenized at 50 °C to remove of light hydrocarbon that effect crude oil stabilization. To separate sand particles, clay, water and other possible particles from crude oils, crude oil A was centrifuged at 3500 rpm for 10 hours using centrifuge Model Sorvall Legend X1R from Thermal Scientific (250 mL). Other crude oils were centrifuged at 14000 x gforce for 3 hours using 50 mL centrifuge tubes. The centrifuged crude oils were then stored in amber colored bottles with Polyseal^{TM} caps. The samples were purged inert nitrogen to prevent any oxidation during storage.

3.1.2 n-Heptane Precipitant

n-Heptane was used to precipitate asphaltenes from the crude oil. The properties of n-heptane is shown in Table 3.1.

Table 3.1 Physical properties at room temperature of n-heptane

Precipitant	n-Heptane
Density (g/ml)	0.6791
Viscosity(cP)	0.386
Solubility Parameter ($MPa^{1/2}$)	15.3
Purity	99.1 %
Source	Fisher

3.2 Equipments

3.2.1 Ultracentrifuge

An ultracentrifuge model Sorvall Legend X1R from Thermal Scientific was used to separate sand, clay, water and other possible particles from the crude oil.

3.2.2 Microcentrifuge

A Microcentrifuge Model 5418 from Eppendorf was used to separate asphaltenes precipitated from of the crude oil and n-heptane mixtures to measure amount of asphaltene precipitated as a function of time and precipitant concentration for centrifugation technique.

3.2.3 Ultrasonic Cleaner

An Ultrasonic Cleaner Model 1510 from Branson was used to break the asphaltene cake and remove the trapped oil.

3.2.4 Oven

An isotemp incubator from Fisher Scientific was used to evaporate n-heptane trapped in asphaltene cake.

3.2.5 Optical Microscope

An optical microscope (Model E600 from Nikon Eclipse) was used to detect the precipitation of asphaltenes from mixture of crude oil and precipitant. The microscope setup provided a 500x total magnification. It was connected to a monochrome Sony CCD video camera and linked to a Sony camera adaptor CMA-D2. WinTV 2000 software was used to view and capture the digital images (640 x 480 pixels).

3.2.6 Syringe Pump

Syringe pump model Harvard Apparatus 22 was used to control the heptane flowrate in the precipitant addition when preparing the solutions with crude oil for good degree of mixing.

3.2.7 Refractometer

A refractometer model DUR-HT from SCHMIDT+HAENSCH was used to measure refractive index of samples in order to estimate the solubility parameter (Eq 2.13).

3.2.8 Rheometer

A rheometer model AR 1000 from TA instrument was used to measure viscosity of each crude oil.

3.2.9 Small Angle X-ray Scattering (SAXS)

Small Angle X-ray scattering (SAXS) model APS and Bruker nanostar was used to estimate size of asphaltene nanoaggregates in toluene.

3.2.10 Inductively Coupled Plasma Mass Spectroscopy or ICP-MS

An ICP-MS was used to analyze metal contents (Ni, Fe, and V) in asphaltene samples.

3.2.11 Elemental Analyzer (EA)

An Elemental Analyzer was used to determine the amount of C, H, N, O, and S in asphaltenes.

3.2.12 Nuclear Magnetic Resonance (NMR)

A liquid stage NMR model Varian vnmrs 500 (Tellurium) was used to identify and characterize the chemical structure of asphaltenes.

3.3 Software

- Win TV 2000
- Rheology Advantage Instrument Control AR
- Small angle X-Ray Scattering System
- Vnmrj
- Mestrenova

3.4 Methodology

3.4.1 Determine Precipitation Onset Time

3.4.1.1 Sample Preparation

Samples of crude oil and heptane were prepared based on volume % of the precipitant concentration that was desired to study. The crude oils were prepared in 25 mL flasks. The crude oil was under agitation. The syringe pump was used to add heptane slowly at 1 mL/min for well mixing base on the final vol% of heptanes in mixture. To ensure the experimental accuracy, the mixture of crude oil and precipitant were measured base on mass basis using an analytical balance containing an error of ±0.0005 g and these values then converted to vol%. A small drop of sample was taken on 25x25 mm microscopy slide and cover by 22x22 mm microscopy slide at different time to observe asphaltene precipitation under optical microscope as shown in Figure 3.1.

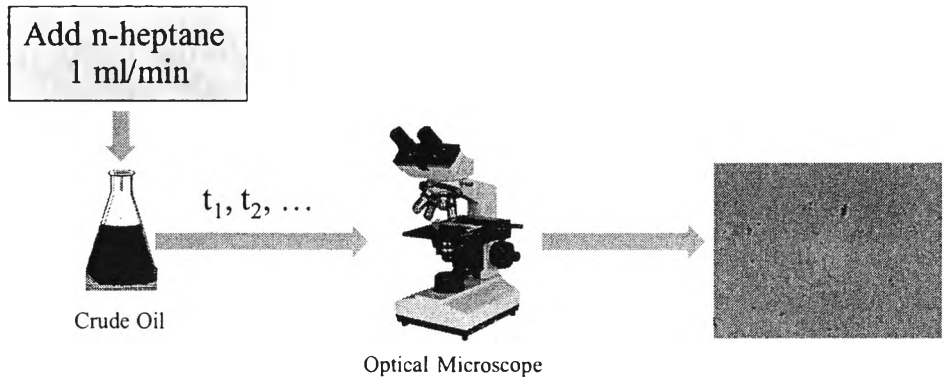

Figure 3.1 Schematic of onset precipitation time experiment.

3.4.1.2 Measuring Viscosity using Rotational Rheometer

The cone/plate geometry was used to measure viscosity of crude oils. The type of geometry used was the 40 mm stainless steel cone and 1.59°. The temperature was maintained at 20 °C by water thermostatic bath. Crude oil (5 mL) was dropped on sample platform. Therefore, cone was moved down and the viscosity measurement was operated at constant shear rate (1/s) from 0.05 to 100 s^{-1}. The steady state flow was used in this experiment using 5 % tolerance.

3.4.1.3 Measuring Refractive Index (RI)

Small drop of samples was taken to the bottom of prism. Then the top prism was closed. The light was shined to the prism and passed through sample. Temperature was controlled at 20 °C by connecting the refractometer to water bath. The refractive index was measured based on measuring the total internal reflaction angle (θ) from the interface between prism and fluid sample.

3.4.2 Centrifugation Experiments

Centrifugation experiments provided an estimate about the amount of asphaltenes precipitated as a function of time. A known amount of crude oil was mixed with heptane in 125 ml flasks to reach to desired concentration. Then, 1.5 ml of solution was withdrawn from flask at different times to be centrifuged at 14000 rpm (16000 x gforce) for 10 minutes. After centrifugation, supernatant was decanted

and cake was washed with heptane to remove trapped crude oil. The cake was then brought to oven to dry until the weight remained constant. The amount of asphaltene precipitated could be calculated as shown in Appendix A.2.

3.4.3 Fractionation Experiments

3.4.3.1 Collecting Total Asphaltenes from Crude Oil

Crude oil was mixed with heptane at 1:40 volume ratio (ASTM D2007-80 (1980)). The mixture was kept stirred for 24 hours. The precipitated asphaltenes were then centrifuged at 10000 rpm for 1 hour. The supernatant, which had no precipitated asphaltenes, was withdrawn from the centrifuged bottle. Heptane was then used to wash crude oil trapped in asphaltene cake. The washing process was repeated until supernatant was colorless. Finally the asphaltene cake was dried in oven and called total asphaltenes.

3.4.3.2 Collecting Asphaltenes Precipitated at Different Times and Concentration

Using centrifugation results as a guideline, fractionation experiments were conducted at 50 vol% of crude oil in heptane. Crude oil was mixed with heptane to reach to desired heptane concentration. After 1 hour the whole sample was centrifuged at 3500 rpm for 4 hours to separate all of the precipitated particles. The cake was then separated from supernatant to generate *cut 1* asphaltenes and supernatant is restored to a flask under agitation to let the remaining asphaltenes precipitate. Similar procedure was repeated after 72, 833 and 2253 hours to generate *cut 2*, *cut 3* and *cut 4*. After 50 vol% of heptane in crude oil solution reached equilibrium more heptane was added to reach to 75 vol% of heptane. The asphaltene cakes were separated after 1, and 1096 hours to generate *cuts 6* and *cut 7*. At each heptane concentration, after centrifuging last cut, the soluble asphaltenes were precipitated by adding more heptane in the ratio of 1:40 (crude oil : heptane).The soluble asphaltenes for 50 vol% and 75 vol% heptane in crude oil are called *cut 5* and *cut 8*, respectively. The schematic for this procedure is shown in Figure 3.2.

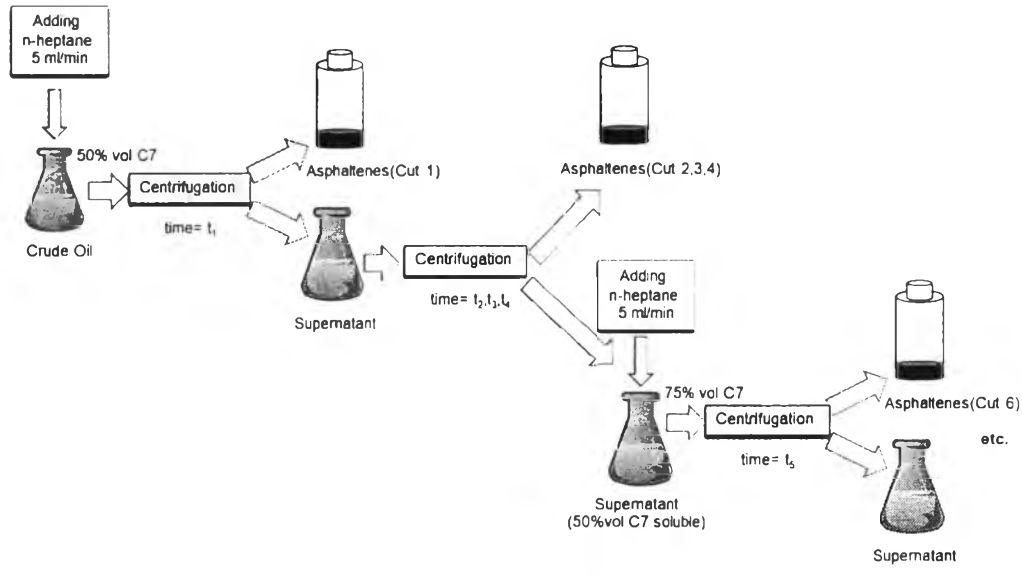

Figure 3.2 Schematic of collecting asphaltenes precipitated at different times and concentrations.

3.4.3.3 Washing the Asphaltene Cake

The Branson Ultrasonic Cleaners 2510 was filled with water at optimum level. After wiping remaining oil out from microcentrifuge tube, the tube was filled with heptane. It was then sonicated until the cake collapsed. n-Heptane washed out trapped crude oil in the cake. The sample was centrifuged at 14,000 rpm for 10 minutes. The supernatant was decanted and next washing step was repeated until the supernatant was colorless. The samples were then dried in the oven at 70 °C to evaporate the remaining heptane.

3.4.4 Characterization of Asphaltenes

3.4.4.1 Small Angle X-ray Scattering (SAXS)

SAXS was used to estimate size of asphaltenes nanoaggregates in toluene. Samples were prepared by dissolving 1%wt of asphaltenes in toluene, sonicated and left overnight. Two different SAXS facilities were used in this study. Part of the experiments were conducted at Argonne National laboratory, X-Ray generator for these experiments was operated at 12keV with a flow

cell technique for analysis. Rest of the experiments was conducted using Bruker nanostar in University of Michigan. The X-Ray generator was operated at 40 kV and 35 mA. Moreover, the conditions used were 0.5 second per frame and 900 second per sample.

3.4.4.2 Elemental Analyzer (EA)

Elemental composition of precipitated asphaltenes (C,H, N,O and S) was measured in Shell.

3.4.4.3 Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS)

Metal contents of precipitated asphaltenes (Ni and V) were analysed using inductively coupled plasma-mass spectroscopy in Shell.

3.4.4.4 Nuclear Magnetic Resonance (NMR)

^{13}C NMR experiments were carried out in Varian vnmrs 500 model spectrometer at resonance frequency 500 MHz. Asphaltenes were dissolved in deuterated methylene chloride at 1 wt% and 10 wt% for ^{1}H and ^{13}C NMR, respectively. The solution was added to 5 mm NMR tube. Base on most of literature reviews, the ^{13}C NMR spectrum were obtained by using an inverse-gated decoupling technique to suppress NOE effect with flip angle 75°, spectral width 220 ppm and 2000 scans. ^{1}H NMR experiments were operated with flip angle 45°, spectral width 14 ppm and 256 scans. Therefore, this study used the same condition as literature.