Chapter III

Experimental

3.1 Materials:

3.1.1 Crude oils

- supplied by oil companies

Table 3.1.1 Basic properties of crude oil used

Crude oil	A1
Density (g/mL)	0.8696
Asphaltene content (%g asphaltenes/g crude oil)	3.2532
Refractive index (n)	1.4964
Solubility parameter (δ, MPa$^{1/2}$)	18.15
Viscosity (μ, mPa s)	27.52

3.1.2 Solvents

- n-heptane 99.1 % purity

Table 3.1.2. Physical properties of n-Heptane precipitant at room temperature

Precipitant	n-Heptane
Density (g/ml)	0.679
Viscosity (cP)	0.386
Solubility parameter (MPa1/2)	15.3
Purity	99.1%
Source	Fisher Scientific

- Toluene 99% purity
- Deuterated methylene chloride

3.2 Equipment

3.2.1 Ultracentrifuge

A Sorvall Legend X11R Centrifuge from Thermal Scientific was used to pretreat Oil A1 by separating solid particles and water from Oil A1.

3.2.2 Microcentrifuge

Eppendorf Micro centrifuge Model 5418 was used to separate asphaltenes from the solution as a function of time for centrifugation experiment.

3.2.3 Ultrasonic Cleaner

Branson Model 1510 Sonicatior was used in the washing step in order to break asphaltenecake and disperse the trapped Oil A1 in the asphaltenes.

3.2.4 Iso-temp incubator

Fisher Scientific Isotemp Incubator was used to evaporate precipitants trapped in the asphaltenes.

3.2.5 Optical microscope

A Nikon Eclipse Model E600 optical microscope was used to detect asphaltene particle in the solution. It was connected to a monochrome Sony CCS video camera which was linked to a Sony camera adaptor CMA-D2. It was then connected to a computer which has a WinTV USB NTSC Model 40201 program to capture images.

3.2.6 Syringe pump

A precipitant was added into Oil A1 at a constant flow rate using Heardvard apparatus 22 Syringe pump in order to prepare the solutions.

3.2.7 Scale

In order to prepare the solutions to reach the desired precipitant concentration, the mass of solution was weighed using Scale from Fisher Scientific and the desired concentration can be calculated.

3.2.8 Small Angle X-ray scattering (SAXS)

Small Angle X-ray scattering (SAXS) model Brukernanostar was used to estimate size of asphaltenenanoaggregates in toluene and other solvents.

3.2.9 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

To analyze metal contents (Ni and V) in asphaltene samples, an ICP-MS was used.

3.2.10 Elemental Analyzer (EA)

To determine the amount of C, H, N, O, and S in asphaltene fractions, an Elemental Analyzer was used.

3.2.11 Nuclear Magnetic Resonance (NMR)

The chemical structure of asphaltene fractionswere identified and characterized bya liquid stage NMR model Varian vnmrs 500 (Tellurium).

3.2.12 Microcentrifuge tubes

1.5 mL Microcentrifuge tubes from Fisher Scientific were used to collect dry asphaltenes from centrifugation experiments.

3.2.13 22x22mm Microscope slides

22x22mm microscope slides from Fisher Scientific were used as cover slides when asphaltene samples were placed on the microscope peltier plate for onset experiments.

3.2.14 25x25mm microscope slides

Asphaltene samples were placed on 25x25mm microscope slides from Fisher Scientific and transferred to the microscope to detect the precipitation detection time of asphaltenes.

3.3 Software

3.3.1   Win TV 2000

3.3.2   Small angle X-Ray Scattering System

3.3.3   Vnmrj

3.3.4   Mestrenova

3.4 Methodology

3.4.1 Pretreatment of crude oil

The crude oil was pretreated to remove any sand particles or impurities by centrifuging at 10,000 rpm for 3 hours and stored in amber bottles to prevent light oxidation. The head space was purged with nitrogen to minimize oxidation and changes in crude oil properties.

3.4.2 Centrifugation experiment

Centrifugation experiments provide an estimate about the amount of asphaltenes precipitated as a function of time. A known amount of crude oil was homogeneously mixed with heptane in a 125 mL flask to reach a desired concentration. 1.5 mL of solution is withdrawn from the flask at different times and centrifuged at 14,000 rpm for 10 minutes. After centrifugation, the supernatant is decanted, and the asphaltene cake is washed with heptane several times to remove any trapped crude oil. The cake is then dried in an oven and the weight is measured until it remained constant.

3.4.3   Fractionation experiment

Using centrifugation results as a guideline, fractionation experiments were conducted at 50 vol% and 75 vol% of heptane mixed with crude oil. To remove remaining wax from crude oil, prior to any fractionation, 40 vol% of

heptane was added to crude oil and the solution was centrifuged at 10,000 rpm for 1 hour. The precipitated asphaltenes at initial times after 40 vol% heptane additionwere too small to be separated by centrifugation, hence only large particles of wax were separated.

After separating wax, more heptane was added to the supernatant using the syringe pump at 5mL/min to reach to 50 vol% heptane in crude oil. The solution was then left on a magnetic stirrer to ensure well mixing for 72 hours before centrifuging for 4 hours to obtain the first fraction of asphaltene (Cut 1). The supernatant is then transferred to another flask under agitation to let the remaining asphaltenes precipitate. A similar procedure is repeated after 833 hours to generate Cut 2. After 2253 hours, the precipitation of the asphaltenes reaches equilibrium for 50 vol% heptane and all precipitated asphaltenes are centrifuged to generate Cut 3. More heptane is then added to the supernatant to increase the heptane concentration to 75 vol% in crude oil. The precipitated asphaltenes at 75 vol% are fractionated after 1 and 1092 hours to generate Cut 4 and Cut 5, respectively. For each heptane concentration, after the last cut is centrifuged (thermodynamic equilibrium), 100 ml of supernatant is withdrawn to precipitate the soluble asphaltenes by adding heptane in the ratio of 40:1 (heptane : crude oil). The soluble asphaltenes for 50 vol% and 75 vol% are called Cut 6 and Cut 7, respectively. Figure 3.4.3.1 shows a schematic diagram of asphaltene fractionation procedure.
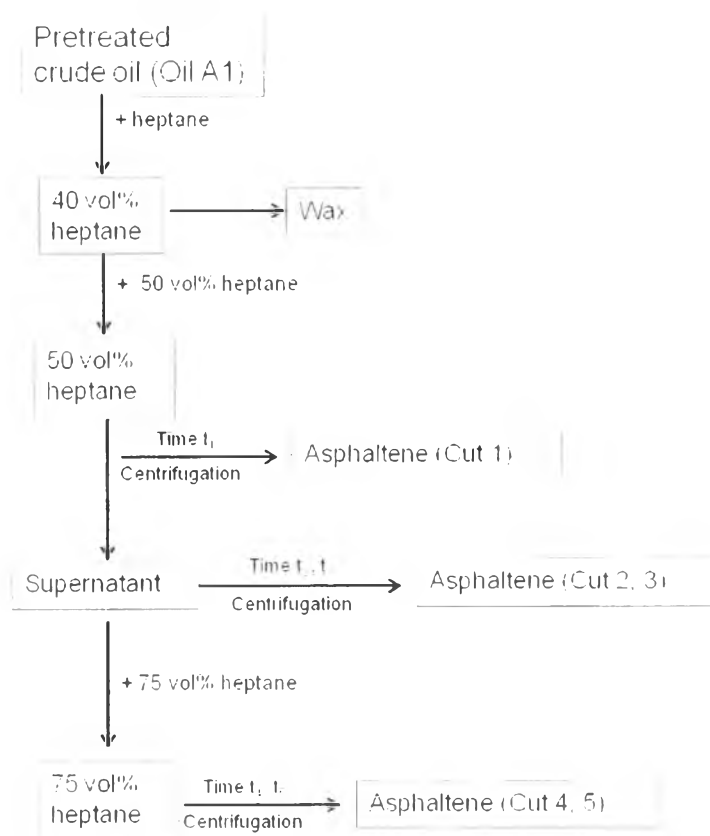
Pretreated
crude oil (Oil A1)

| + heptane

40 vol% ────────→ Wax
heptane

+ 50 vol% heptane

50 vol%
heptane

    Time t_1
    ───────────→ Asphaltene (Cut 1)
    Centrifugation

Supernatant   Time t, t
    ───────────→ Asphaltene (Cut 2, 3)
    Centrifugation

+ 75 vol% heptane

75 vol%   Time t, t
heptane ───────────→ Asphaltene (Cut 4, 5)
  Centrifugation

Figure 3.4.3.1 Schematic diagram of asphaltene fractionation procedure.

3.4.4 Asphaltene characterization

3.4.4.1 Heteroatom content: Elemental Analysis (EA)

An Elemental Analyzer will be used to determine the amount of C, H, N, O, and S in asphaltenes. Elemental composition of precipitated asphaltenes is measured in Shell Oil Company.

3.4.4.2 Metal content: Inductively Coupled Plasma MassSpectrometry (ICP-MS)

An ICP-MS is used to analyze metal contents (Ni, Fe, and V) in asphaltene samples. Metal contents of precipitated asphaltenes (Ni and V) are analyzed using inductively coupled plasma-mass spectrometry in Shell Oil Company.

3.4.4.3 Size of nanoaggregate: Small-Angle X-ray Scattering (SAXS)

SAXS is extensively used for the structural characterization of the dispersed particles in solution. Asphaltene molecules can scatter because of their high electron density. Their higher electron density is due to heteroatoms such as oxygen and nitrogen and metal compounds such as Ni and V. SAXS can be used in the range of nanoscale to measure the particle size, shape and polydispersity.

The scattering intensity is recorded as a function of the scattering vector as shown by Equation 1:

$$q = 4\pi \sin(\theta)/\lambda \tag{1}$$

Where q is scattering vector function, 2θ is the total scattering angle and λ is the X-ray wavelength.

For monodisperse particles, the intensity can be simplified to Equation 2:

$$I(q) = S(q) F(q) \tag{2}$$

Where $S(q)$ is structure factor and $F(q)$ is form factor.

In dilute solution, structure factor is equal to one and the size of asphaltene aggregates can be estimated by Guinier Approximation:

$$I(q) = I_0 \exp\left(-\frac{q^2 R_g^2}{3}\right) \qquad (3)$$

Where I_0 is the scattering intensity extrapolated to $q = 0$, R_g is the radius of gyration, and q is the scattering vector.

In this work, SAXS was used to estimate the 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 is operated at 12keV with a flow cell technique for analysis. The rest of the experiments were conducted using Bruker Nanostar at the University of Michigan. The X-Ray generator was set to operate at 40 kV and 35 mA. Moreover, the conditions used were 0.5 second per frame and 900 second per sample.

3.4.4.4 Aromaticity and Average alkyl chain lengths: Proton and Carbon Nuclear Magnetic Resonance (^{1}H and ^{13}C NMR)

Nuclear Magnetic Resonance (NMR) is a technique that measures the absorption of electromagnetic radiation during transition between spin states of atoms and molecules in presence of magnetic field. Sample is placed in a magnetic field, and then all nuclei in sample are charged at a characteristic frequency in the radio frequency range of the electromagnetic spectrum. The resonance frequency, energy of the absorption and the intensity of the signal are proportional to the strength of the magnetic field.

The resonance frequency can be used for defining the position of atom within a molecule and characterize the type of nucleus. Therefore, the bonding electrons create their own small magnetic field which modified the external magnetic field in nucleus. This variation is defined as chemical shift in parts per million.

Typically, ^1H NMR and ^{13}C NMR are used for characterization of asphaltenes. Asphaltenes are dissolved in deuterated toluene (C_8D_8), deuterated chloroform ($CDCl_3$), or deuterated methylene chloride, etc. The chemical shifts of solvent are shown in Table 3.4.4.4.1.

Table 3.4.4.4.1 Chemical shifts of solvents

Solvent	Chemical shift	
	^1H NMR	^{13}C NMR
Deuterated toluene	2.09, 6.98, 7.00, 7.09	20.4, 125.49, 128.33, 129.24, 137.24
Deuterated chloroform	7.24	77.23
Deuterated methylene chloride	5.32	54.08

^{13}C and ^1H NMR can provide information about asphaltene structure such as their aromaticity or average alkyl side chain lengths.

The ^{13}C NMR spectra can be divided into two different integration domains to determine the fraction of aliphatic and aromatic carbons in the structure of asphaltenes. The region of chemical shift in NMR spectra is shown in Table 3.4.4.4.2.

Table 3.4.4.4.2 Assignments of chemical shifts in ^{13}C NMR.

Chemical Shift Range (ppm)	Assignment
10-60	C_{al}: Aliphatic carbon
110-160	C_{ar}: Aromatic carbon

The average aromaticity of asphaltenes obtained from ^{13}C NMR experiments can be calculated by using Equation 4:

$$Aromaticity(f_a) = \frac{C_{ar}}{C_{ar}+C_{al}} \tag{4}$$

Where C_{ar} is the number of aromatic carbons and C_{al} is the number of aliphatic carbons in the molecule.

Proton nuclear magnetic resonance (^{1}H NMR) can be used to estimate the average alkyl side chain length that is connected to the aromatic core of asphaltenes.
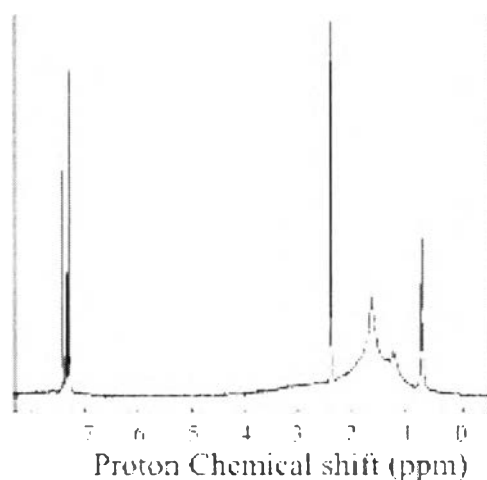

Proton Chemical shift (ppm)

Figure 3.4.4.4.1 ^{1}H chemical shift spectrum of an asphaltene solution in deuterated toluene solvent.

Figure 3.4.4.4.1 illustrates the proton NMR chemical shift spectrum and the average alkyl side chain length can be calculated using Equation 5:

$$\text{Average alkyl side chain length } (n) = \frac{H_\alpha + H_\beta + H_\gamma}{H_\alpha} \tag{5}$$

Where H_α, H_β and H_γ are the positions of hydrogen atoms on the alkyl chains attached to the aromatic cores. These values are obtained as the area under the ^1H NMR spectra at chemical shifts shown in Table 3.4.4.4.3.

Table 1.4.4.4.3 Assignments of chemical shifts in ^1H NMR.

Chemical Shift Range (ppm)	Assignment
0.5-1.0	H_γ : Hydrogen atoms of methyl groups of saturated compounds.
1.0-2.0	H_β : Hydrogen atoms of methylene groups of saturated compounds.
2.0-4.0	H_α : Hydrogen atoms of the groups bonded next to aromatic rings, heteroatoms or carbonyl carbon atoms.
6.0-9.0	H_{ar} : Aromatic hydrogen.

In this work, a liquid state NMR model Varian vnmrs 500 (Tellurium) at the Chemistry Department, University of Michigan was used to identify and characterize the chemical structure of asphaltenes. Asphaltene cuts were dissolved in deuterated methylene chloride at 1 wt% and 10 wt% for ^1H and ^{13}C NMR, respectively. The solution was transferred to a 5 mm NMR tube to fit the NMR equipment. The ^{13}C NMR spectra were obtained by using an inverse-gated decoupling technique to suppress NOE effect with flip angle of 75°, spectral width of 220 ppm and 2000 scans. ^1H NMR experiments were operated with flip angle of 45°, spectral width of 14 ppm and 256 scans.

3.4.5 Microscopy experiment

Microscopy experiments provide information about the aggregation rate of asphaltenes by detecting the onset of precipitation under the microscope. Samples were prepared by dissolving asphaltene fractions that precipitate at different times in toluene to create model oil. 2 wt% of asphaltenes were used for each samples. Heptane was added to the solution at a desired concentration and the samples were monitored at regular interval under the microscope to detect the precipitation onset time or detection time. Figure 3.4.5.1 shows the schematic diagram of an onset experimental procedure.
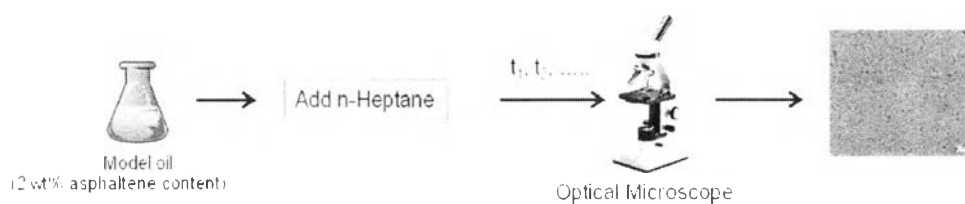

Model oil
(2 wt% asphaltene content)   Add n-Heptane $t_1, t_2, \ldots$ Optical Microscope

Figure 3.4.5.1 Schematic diagram showing onset experiment procedure.