CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Crude Oils

Two crude oils from different locations were used in this study. These crude oils labeled as N2 oil and GM2 oil come from the North Slope, Alaska and the Gulf of Mexico, respectively. Both oils are classified as light oils because of relatively low viscosity and low asphaltene content. The SARA analysis and physical properties of the crude oils are shown in Tables 3.1 and 3.2. The molecular weight of GM2 oil is 246.86 g/mol as determined by Pencor Laboratories by freezing point depression. The SARA analysis of GM2 oil was determined by Baseline Resolution Weatherford Laboratories *(See Appendix E for SARA separation procedure)*.

Crude oils from field samples generally contain impurities like sand particles, clay and water. It is essential to remove these impurities in order to have a consistent, homogenous crude oil sample. The crude oils were centrifuged for 3 hours at 10,000 rpm using a Thermoscientific Sorvall Centrifuge. Afterwards, the centrifuged oils are stored in 60mL amber bottles which are purged with inert nitrogen. The bottles are capped with Polyseal™ caps and sealed with Teflon tape. This storage procedure is observed to preserve the integrity of the crude oil sample. All experiments are done at ambient conditions. (*See Appendix B – C for implications of improper storage conditions*).

Table 3.1 SARA fractionation analysis of N2 and GM2 crude oils

Solubility Class	**N2 Oil**	**GM2 Oil**
Saturates (wt %)	55.1 %	46.2 %
Aromatics (wt%)	23.6 %	41.7 %
Resin	17.3 %	8.4 %
Heptane–Asphaltenes	2.7 %	3.6 %
Unrecovered fraction	1.3 %	0.1 %

Table 3.2 Physical properties of N2 and GM2 crude oils

Property	**N2 Oil**	**GM2 Oil**
Density at 25C (g/mL)	0.8737	0.8688
Viscosity at 25C (cP)	13.87	15.69

3.1.2 n-Alkane Precipitants

N-alkanes were used as precipitants to induce precipitation of asphaltenes from crude oil. Table 3.3 shows the properties and source of the n-alkanes used in this study.

Table 3.3 Physical properties of n-alkane precipitants used at room temperature.

Precipitant	Density (g/mL)	Molar Volume[1] (mol/mL)	Solubility Parameter[1],δ ($MPa^{0.5}$)	Viscosity[2] (cP)	Purity	Source
n-hexane	0.659	131.6	14.8	0.307	99.5%	Fluka
n-heptane	0.680	147.5	15.2	0.417	99.1%	Fisher
n-octane	0.703	163.5	15.5	0.546	99.0%	Aldrich
n-nonane	0.718	179.7	15.6	0.714	99.0%	Acros Organics
n-decane	0.730	195.9	15.8	0.907	99.0%	Fisher
n-pentadecane	0.773	276.4	16.25	2.841	99.0%	Acros Organics

(1) Barton, 1991. (2) http://www.engsolcom.com

3.2 Equipment

3.2.1 Optical microscope setup

An optical microscope (Nikon Eclipse E600) is used to observe the precipitation of asphaltenes from crude oil–precipitant mixtures. The microscope has

a 10x objective magnification and uses a Nikon LU Plan ELWD 50x lens which provides a 500x total magnification. It is connected to a monochrome Sony CCD video camera and linked to a Sony Camera Adaptor CMA-D2. The analog signal from the camera is digitally converted by an analog-digital converter using WinTV USB NTSC Model 40201. WinTV software is used to view and capture the digital images at 640 x 480 pixels.

3.2.2 Microcentrifuge

An Eppendorf Micro Centrifuge 5415C is used to separate the precipitated asphaltenes from the crude oil–precipitant mixtures.

3.3 Methodology

3.3.1 Sample Preparation

The precipitant–crude oil mixture sample is prepared based on the desired volume % of the precipitant to be studied. Determining the onset of precipitation, centrifuged crude oil is put in a 25mL flask with a magnetic stirrer. In order to accurately prepare the desired amount of crude oil, measurements were done gravimetrically on an analytical balance with precision of up to ±0.0005g. As a base case, a small drop of neat crude oil is analyzed under a microscope to detect whether impurities are present in the oil. If there are impurities present, the crude oil undergoes further centrifugation. The flask is then covered with an aluminum foil to minimize any evaporation losses when adding precipitant. The desired amount of precipitant is added gradually into the well-stirred crude oil using a syringe pump. Samples are capped with a stopcock lined with Dow Corning high vacuum grease and are continuously stirred for the entire duration of the experiment. All experiments are conducted at room temperature.

For the experiments used to determine the amount of precipitated asphaltenes, 132mL of crude oil–precipitant mixture is prepared using the same procedure described above.

3.3.2 Detection of the Onset of Asphaltene Precipitation

The onset of asphaltene precipitation is observed from the evolution and growth of asphaltene precipitates to the detectable size that is seen under the microscope. After the final addition of the precipitant on the crude oil sample (time t=0), a sample drop is analyzed under the microscope. Using the Nikon Eclipse E600 optical microscope with a 50x lens, the edge of the sample is first located and the focus knob is adjusted to attain a sharp edge. Transparent particles such as water or air bubbles may be present in the sample but they can be easily distinguished by tuning the focus knob of the microscope counterclockwise and these particles change hue intensity from clear to black and appear circular in shape. Meanwhile, opaque particles like asphaltenes change hue intensity from black to clear and appear as loose fractals. On the other hand, waxes do not appear under monochromatic light and will not be captured in the image. The crude oils were checked for any presence of waxes by using a cross–polarizing lens and waxes were not detected. Afterwards, eight pictures were taken from different locations within the sample drop for each time. The precipitation of asphaltenes from crude oil–precipitant mixtures can be very slow depending on the concentration of precipitant in the mixture. Thus, the evolution and growth of asphaltene precipitates were carefully monitored by frequently taking pictures over time.

The micrographs were compared to standard polystyrene particles dispersed in water with diameters of 0.2 μm, 0.5 μm, 0.75 μm, 1 μm, 5 μm, and 10 μm. The maximum resolution of the optical microscope used is at 0.2 μm using a mid-spectrum wavelength of 550nm. However, 0.2-0.3 μm particles appear hazy due to poor resolution for particles of this size.

3.3.3 Determination of the amount of precipitated asphaltenes as a function of time

The amount of asphaltenes that precipitate as a function of time was determined using a centrifugation–based separation technique. An Eppendorf Micro Centrifuge 5415C is used to separate asphaltene precipitates from the crude oil–precipitant mixture. Two 1.5 mL samples were withdrawn from the crude oil–precipitant mixture and placed in pre-weighed microcentrifuge tubes. The samples

were weighed and are then centrifuged at 14,000 rpm for 10 minutes, which corresponds to a relative centrifugal force of 16,000 G. Precipitated asphaltenes settle at the bottom of the tube as a tight cake. The supernatant was then carefully decanted while avoiding any loss of asphaltene cake. Excess oil mixture from the inside walls of the tubes was carefully wiped out with a tissue without touching the centrifuged cake. Sampling was done at different times to determine the amount of precipitated asphaltenes as a function of time.

A small amount of excess crude oil–precipitant mixture is trapped within the asphaltene cake. This excess amount is removed by washing the asphaltene cake with the same precipitant that was used in the preparation of the sample. If n-heptane is used to precipitate asphaltenes from the crude oil, then n-heptane would be used to wash the cake. About 1.5mL of the appropriate precipitant is added to the asphaltene cake in the tube. An ultrasonic water bath (Branson Ultrasonic Cleaners 2510) is used to break up the cake and facilitate efficient washing. Sonication is done for 1-2 minutes or until the cake is broken apart by the alternating low and high pressures created by the ultrasonic sound. The sample is then shaken in the Fisher Scientific Vortex Mixer for 1 minute. It is centrifuged at 14,000 rpm for 10 minutes. The supernatant is then decanted and collected in vials. The washing procedure is done three times after which the supernatant becomes very faint in color, indicating that there is only a negligible amount of oil left in the asphaltene cake.