CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Crude Oil

Asphaltene extracted from crude oil A1 and K1 provide by oil companies were used in this work. Their elemental analysis data are provided in Table 3.1

Table 3.1 Elemental analysis of A1 and K1 asphaltenes

Asphaltenes	C (wt%)	H (wt%)	N (wt%)	O (wt%)	S (wt%)	H/C	Ni (ppm)	V (ppm)
K1	84.25	6.36	1.29	1.91	4.5	0.91	185	571
A1	81.5	7.79	1.05	2.21	7.2	1.15	152	479

3.1.2 Solvents

- Toluene 99.1 % purity from Fisher Scientific
- N-heptane 99.1 % purity

Table 3.2 Physical properties of n-Heptane precipitant at room temperature

Properties	Oil A
Solvent	n-heptane
Density (g/ml)	0.6790
Viscosity (cP)	0.386
Solubility parameter ($MPa^{1/2}$)	15.3
Purity	99.9 %
Source	Fisher Scientific

3.2 Equipment

3.2.1 Optical microscope

An optical microscope from Nikon (model: Eclipse E600) with 40× objective lens and 10× eyepiece was used to detect appearance of 0.5 micron-sized clusters of asphaltenes.

3.2.2 Camera

A Camera form Nikon DS-Fi2 was used for shooting images off from optical microscope.

3.2.3 Ultracentrifuge

The Sorvall Legend X1R centrifuge from Thermal Scientific was used to separate precipitated asphaltenes in fractionation experiment.

3.2.4 Microcentrifuge

An Eppendorf microcentrifuge Model 5418 was used to separate small quantity of asphaltenes precipitated from solution as a function of time.

3.2.5 Syringe pump

A precipitant, n-heptane, was added into model mixture at fixed flow rate using Hardvard apparatus 22 in order to obtain heptane-toluene solutions performed in microscopy experiment.

3.2.6 Scale

The Mettler Toledo XS204 scale was used to prepare model solutions.

3.2.7 Sonicator

The 5510 Branson sonicator was used in model mixture preparation in order to break asphaltene particles and provide complete dissolution in solvent.

3.3 Software

3.3.1 NIS-Element D (for microscopy experiment)

3.3.2 D8tools (for small angle X-ray scattering experiment)

3.3.3 Igor Pro 6.32A (for estimate size of asphaltene nanaoaggregates)

3.4 Experimental Procedures

3.4.1 Asphaltene extraction

A1 and K1 crude oils were separately centrifuged at 10,000 rpm for 3 hours to remove water, sand, and other solid particles. To extract the asphaltenes from crude oil, pretreated crude oil was mixed with heptane in 1:25 volume ratio and was stirred for 24 hours. Then, the mixture was centrifuged with Sorvall Legend X1R at 3,500 rpm for 1 hour to separate asphaltenes from solution. Precipitated asphaltenes were Soxhlet washed with heptane for 24 hours to eliminate the impurities trapped in the cake. The asphaltenes were dried in oven for A1 and vacuum oven for K1 at 75 °C for 24 hours to evaporate residual heptane.

3.4.2 Model mixture preparation

To prepare 3 wt% and 8 wt% asphaltene model mixtures for fractionation and centrifugation experiments, extracted asphaltenes were separately dissolved with toluene and were then sonicated to allow a complete dissolution.

3.4.3 Time and solubility based fractionation

For K1 asphaltenes, each model mixture (3 and 8 wt% asphaltene model mixture) was mixed with heptane using syringe pump at the flow rate of 5 mL/min to reach 48 vol% of heptane concentration. The solution was stirred for 24 hours to ensure well mixing and was then centrifuged for 2 hour at 5,000 rpm to generate the first fraction of precipitated asphaltenes denoted as cut 1. After centrifugation, the supernatant was transferred to another flask under agitation to allow the remaining asphaltenes to precipitate. After 25 days, this solution was centrifuged again in order to generate cut 2. More heptane was then added to the supernatant from cut 2 to reach 60 vol% heptane concentration. The similar procedure was repeated to generate Cut 3 and Cut 4 at 1 day and 25 days, respectively. Then, more heptane was added into solution to reach 70 vol% heptane solution. The solution was centrifuged again to obtain Cut 5 after stirring for 24 hours. In order to separate all soluble asphaltenes in the supernatant after generating Cut 5, additional heptane was to approach in 1:25 toluene:heptane volume ratio and was then centrifuged after 1 day to obtain Cut 6.

Fractionation procedure of A1 asphaltenes is similar to K1 asphaltenes. Each model mixture was mixed with heptane to reach 60 vol% heptane solution. The solution was centrifuged after being stirred for 1 day and 25 days to obtain Cut 1 and Cut 2, respectively. Then, more heptane was added to the solution to reach 70 vol% heptane concentration in order to generate Cut 3 and Cut 4 by centrifuging asphaltenes out of solution after 1 and 25 days. After that, additional heptane was added again to reach the final heptane concentration in 1:25 toluene:heptane volume ratio. This solution was centrifuged to generate Cut 5. An example schematic diagram of fractionation procedure of A1 and K1 asphaltenes were illustrated in Figure 3.1 and Figure 3.2, respectively.

3.4.4 Microscopy experiments

All asphaltene sub-fractions were separately dissolved with toluene and sonicated to generate 1 wt% model mixtures. A known volume of heptane was added into each model mixture using syringe pump at the flow rate of 0.33 mL/min to reach a desired heptane concentration at total volume of 3 mL.

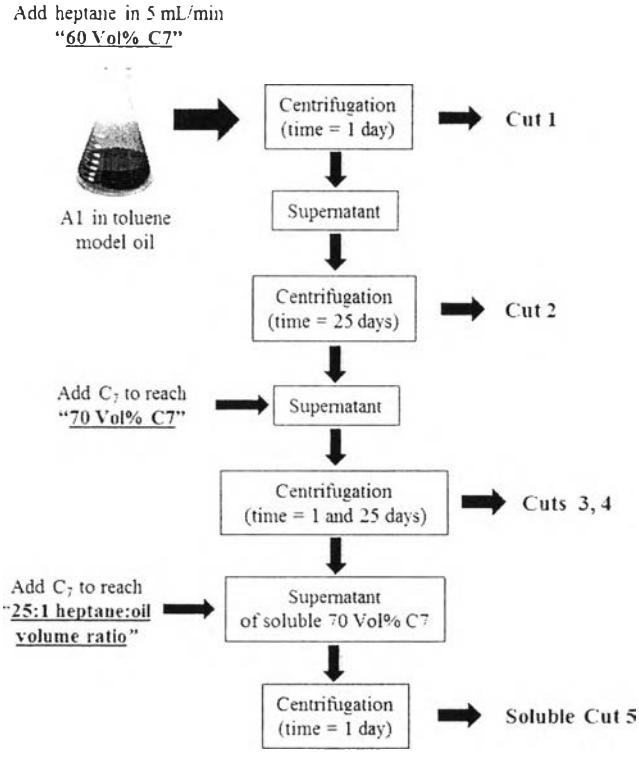

Figure 3.1 A schematic diagram of A1 fractionation procedure.

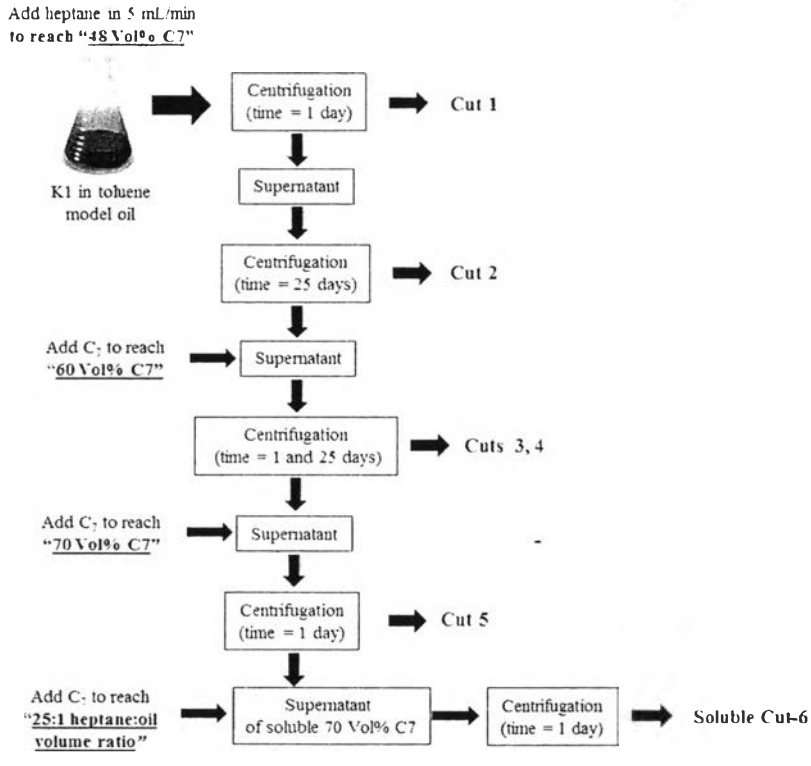

Figure 3.2 A schematic diagram of K1 fractionation procedure.

The sample was monitored as a function of time under an optical microscope from Nikon (model: Eclipse E600) along with Nikon camera (DS-Fi2) to determine the detection time of asphaltene precipitation which is the time that 0.5 μm destabilized asphaltenes are detectable in microscope.

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3.4.5 Small angle X-ray scattering experiments

Bruker Nanostar Equipment at University of Michigan was used to perform Small Angle X-ray scattering (SAXS) in order to determine the radius of gyration or the size of nanoaggregate of precipitated asphaltenes. Sample was

prepared by dissolving precipitated asphaltenes in toluene (1 wt%). The X-ray generator was operated at 40 kV and 35 mA with 0.5 second per frame and 900 second per sample

3.4.6 Centrifugation experiments

Unfractionated K1 asphaltenes were blended with toluene to prepare 3 wt% and 8 wt% asphaltene- content model mixtures. Similar to microscopy experiments, heptane was separately added to each model oil to reach desired precipitant concentrations at total volume of 20 mL. Four samples of 1.5 mL were withdrawn from each sample at different times and were then centrifuged by an Eppendorf 5418 centrifuge at 14000 rpm for 10 mins. The supernatant was decanted after centrifugation. The asphaltene cake was dried in an oven until the weight remained constant.