

## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 Materials

Venezuela Crude Oil, used in this study, was provided by INTEVEP.

Ferric chloride ( $\text{FeCl}_3$ ), dodecylbenzene sulfonic acid (DBSA), hydrochloric acid (HCl), Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), n-heptane ( $\text{C}_7\text{H}_{16}$ ), and pentane ( $\text{C}_5\text{H}_{12}$ ).

#### 3.2 Asphaltene Preparation from Asphaltic Sludge

Asphaltic sludge was prepared by mixing  $\text{FeCl}_3$  in HCl with crude oil at  $80^\circ\text{C}$  and stirred for 30 minutes. The mixture was allowed to settle for at least 1 hour. Then asphaltene was separated from asphaltic sludge by adding 100 volumes of warm heptane to one volume of asphaltic sludge. Asphaltene precipitates was then vacuum filtered through a  $0.22\ \mu\text{m}$  membrane. The filtrate was dried in an oven at  $60^\circ\text{C}$  and the mass of asphaltene was determined. Two  $\text{FeCl}_3$  concentrations used were 3000 and 9000 ppm. Two HCl concentrations used were 2.2 and 4.4 M. For aging asphaltic sludge, the settling time was varied at 0.4, 10, and 15 days. The matrix of experiments 3.2 is presented in Table 3.1.

Table 3.1 The matrix of experiment 3.3

FeCl <sub>3</sub> (ppm)	HCl (M)	Asphaltic Sludge's Settling time (days)
nil.	2.2	0.4
nil.	4.4	0.4
nil.	4.4	10
nil.	4.4	15
3000	nil.	0.4
3000	4.4	10
9000	nil.	0.4
9000	2.2	10
9000	4.4	0.4
9000	4.4	10
9000	4.4	15

### 3.3 Asphaltene Preparation from Crude Oil

Asphaltene was precipitated from Venezuela crude oil by mixing one volume of crude with 40 volumes of heptane at 60°C and stirred for 30 minutes. The mixture was allowed to settle overnight. Asphaltene precipitates were then vacuum filtered through a 0.22 μm membrane. The filtrate was dried in an oven at 60°C and the mass of asphaltene was determined.

### 3.4 Asphaltene Re-precipitation

Asphaltene obtained directly from crude oil was re-dissolved with pure toluene and then re-precipitated it with acidic solution in the presence and/or absence of ferric ion. The re-precipitated asphaltenes was washed using warm heptane and then vacuum filtered through a 0.22  $\mu\text{m}$  membrane. The filtrate was dried in an oven at 60°C and the mass of asphaltene was determined.

### 3.5 Asphaltene Dissolution

To assess the rate of asphaltene dissolution, present the experiment set up in Figure 3.1. The 5% by volume DBSA/heptane solution was pumped into the reactor using a syringe pump at a rate of 5 ml/minute. A ice/water bath was used to maintain the temperature precisely. In each experiment, 0.010 grams of the asphaltene fraction was first loosely and uniformly placed between two Teflon membranes (pore size 0.22  $\mu\text{m}$ , 25 mm dia). The membranes were held apart inside the reactor (modified Millipore filter holder) by an O-ring. The DBSA/heptane solution dissolved the asphaltene fraction as it flowed through the reactor and samples were collected at different times in glass vials using fraction collector (LKB 2211 SuperRac). The apparatus was arranged such that the solvent flowed upwards and entered the reactor from the bottom, which ensured that any air trapped in the reactor was completely displaced from the reactor by the fluid at the initial stage of the experiment. The samples were analyzed using UV/vis spectrometry.

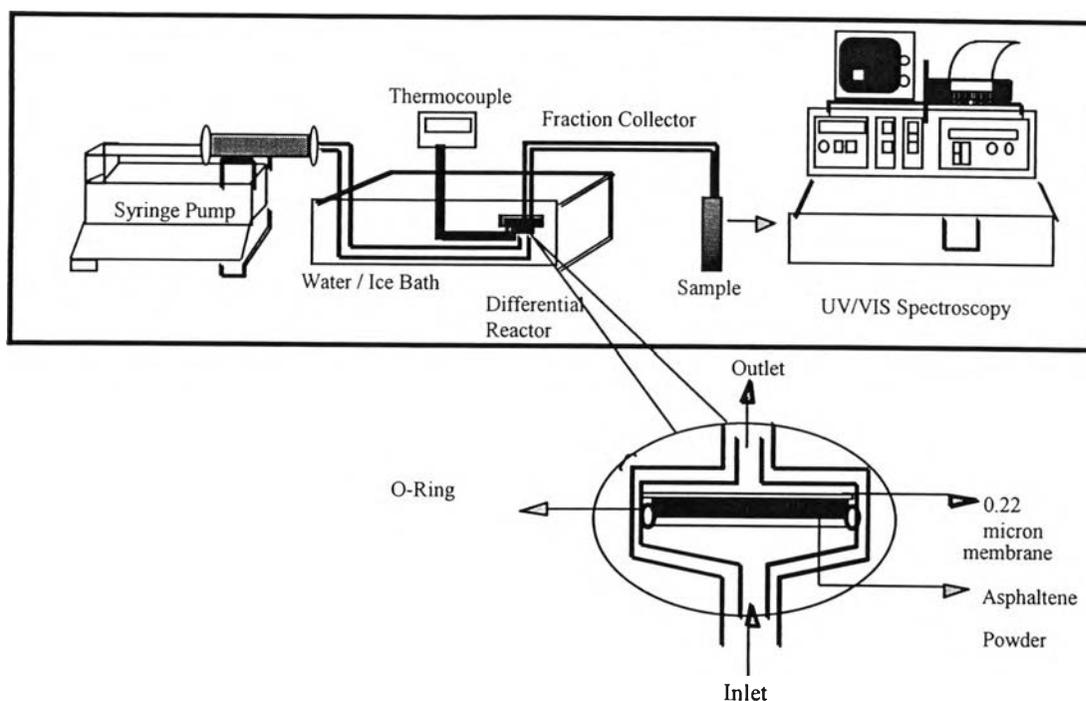


Figure 3.1 Asphaltene dissolution experimental apparatus.

### 3.6 Asphaltene Fractionation

Asphaltene was fractionated to different polarity fractions by using binary mixture of  $\text{CH}_2\text{Cl}_2$  and n-pentane. The original asphaltene was completely dissolved with 10 times by weight of pure  $\text{CH}_2\text{Cl}_2$ . Then this solution was added with n-pentane to obtain the composition of  $\text{CH}_2\text{Cl}_2$ /pentane at 60/40. The solution was allowed to settle for at least 5 hours and was then centrifuged. The asphaltene precipitated was in the fraction of F60/40. The supernatant was removed from the container. The precipitate was dried in an oven at  $60^\circ\text{C}$  and the mass of asphaltene precipitate was determined. The supernatant was added with more n-pentane to obtain the composition of  $\text{CH}_2\text{Cl}_2$ /pentane at 50/50 and was follow repeated by the previous fractionation

technique. Similarly, taking the precipitate in each case, fraction of 40/60, fraction of 30/70, fraction of 20/80 and fraction of 10/90 were obtained.

### **3.7 Asphaltene Characterization**

Venezuela asphaltenes from different precipitating conditions were characterized. Asphaltene characterization includes functional groups, morphology, metal ion analysis and  $^1\text{H-NMR}$ .

**Functional Groups:** The functional groups of asphaltene samples were investigated by FTIR spectroscopy using carbon tetrachloride as solvent.

**Morphology:** The morphology of asphaltene precipitates was analyzed using Scanning Electron Microscope (SEM).

**Metal Analysis:** The metal ion contents were analyzed using ICP by XRAL Activation Services, Ann Arbor, Michigan

**Asphaltene Structure:** Proton NMR was used to analyze asphaltene samples.