

CHAPTER III

EXPERIMENTAL SECTION

3.1 Sample Preparation

3.1.1 Asphaltene Preparation

The original asphaltene used in this study was isolated from Venezuela crude oil supplied by INTEVEP. The asphaltene sample was a heptane-insoluble fraction prepared from crude oil according to ASTM 2007D (1983). From Figure 3.1, 50 ml of crude oil was first mixed with 2 litres of warm heptane solvent for approximately one hour to precipitate asphaltene out of solution. Afterwards, the asphaltene precipitates was collected from the solution by passing the solution through the fritted glass filter with teflon filter membrane having 0.22 micron in a pore diameter and was then dried at 60 °C. This precipitated asphaltene sample appeared as fine powder with a dark brown to black color.

3.1.2 Asphaltene Fractionation

The original asphaltene obtained as described earlier was further fractionated into components of different polarities using binary mixture of a polar and nonpolar solvent as the precipitating medium. Methylenechloride (CH₂Cl₂) solution containing completely dissolved asphaltenes were successively diluted with adding n-pentane. According to this procedure, the partial precipitation of asphaltenes was obtained as a result of a gradual decrease in the asphaltene solubility.

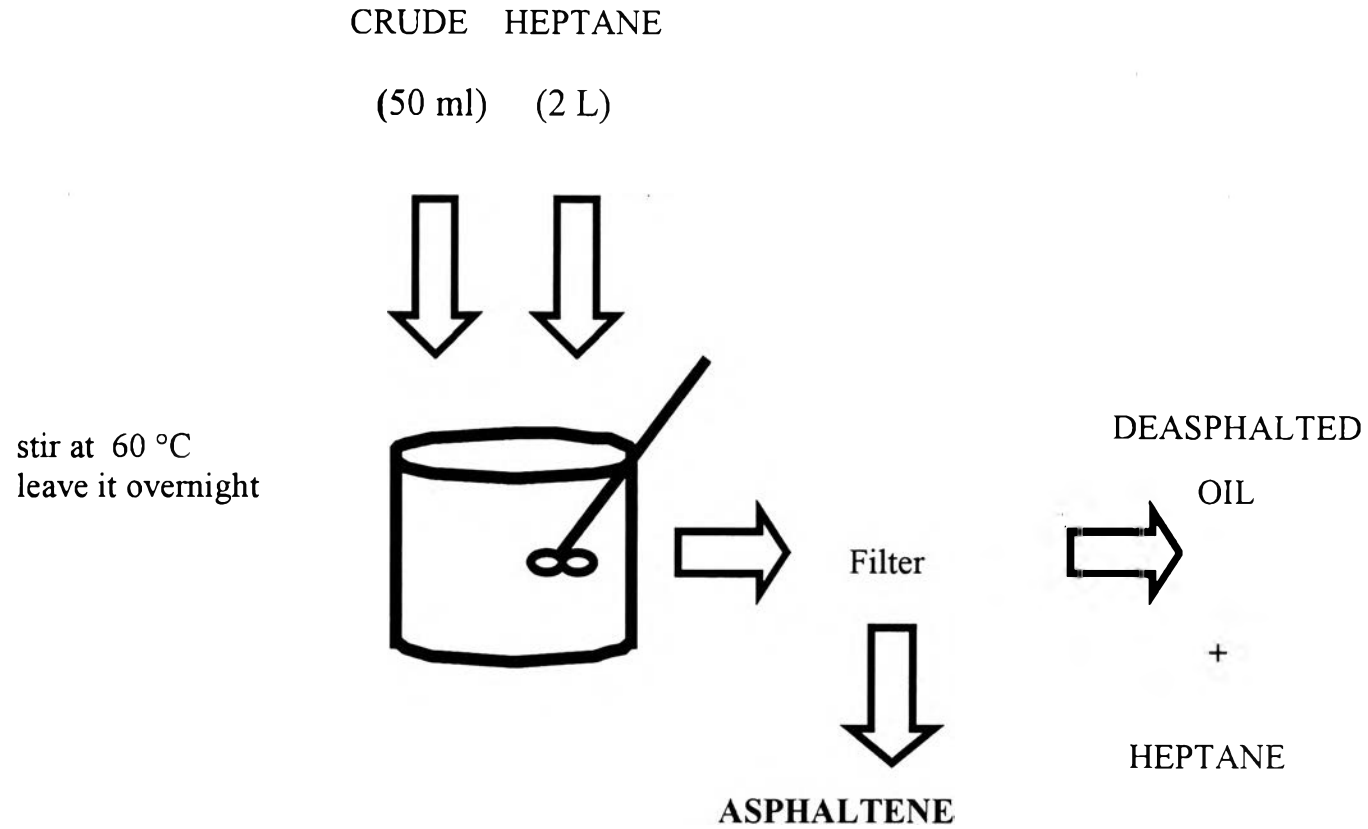


Figure 3.1 Schematic illustration of original asphaltene preparation.

Figure 3.2 shows the procedure of asphaltene fractionation. The original asphaltene powder was first dissolved completely by adding ten times by weight of CH_2Cl_2 by putting in a sonicator. Pentane was now gradually added up to 60% by vol. of CH_2Cl_2 . No asphaltene was precipitated up to this composition. More pentane was further added to make the composition 70:30 of the ratio of pentane and CH_2Cl_2 . The solution was then violently shaken and left at room temperature for at least 4 hours. Afterwards, the mixture was centrifuged at 3000 rpm for 30 minutes and subsequently, the precipitate was collected and called the first fraction (fraction 1). More pentane was added to the supernatant to make the composition of 80:20 of pentane: CH_2Cl_2 . After that, the similar procedure was carried out to obtain the precipitate called the second fraction (fraction 2). Likewise, taking the supernatant in each case, fraction 3 and fraction 4 were obtained at the compositions of 90:10 and 95:5 of pentane: CH_2Cl_2 , respectively.

3.2 Characterization of Asphaltenes

The characterization was carried out for fraction 1 (the most polar fraction), fraction 3, and fraction 4 (the least polar one). In order to differentiate between the most polar and the least polar asphaltenes, the two asphaltene fractions (fraction 1 and fraction 4) should have been taken for characterization. Due to the small amount fraction 4 in Venezuela crude oil, characterization with fraction 4 could not be performed. Hence, the asphaltene samples of fraction 1 and fraction 3 were characterized.

The Morphology of the asphaltene fractions was examined by Hitachi S-800 Scanning Electron Microscope (SEM).

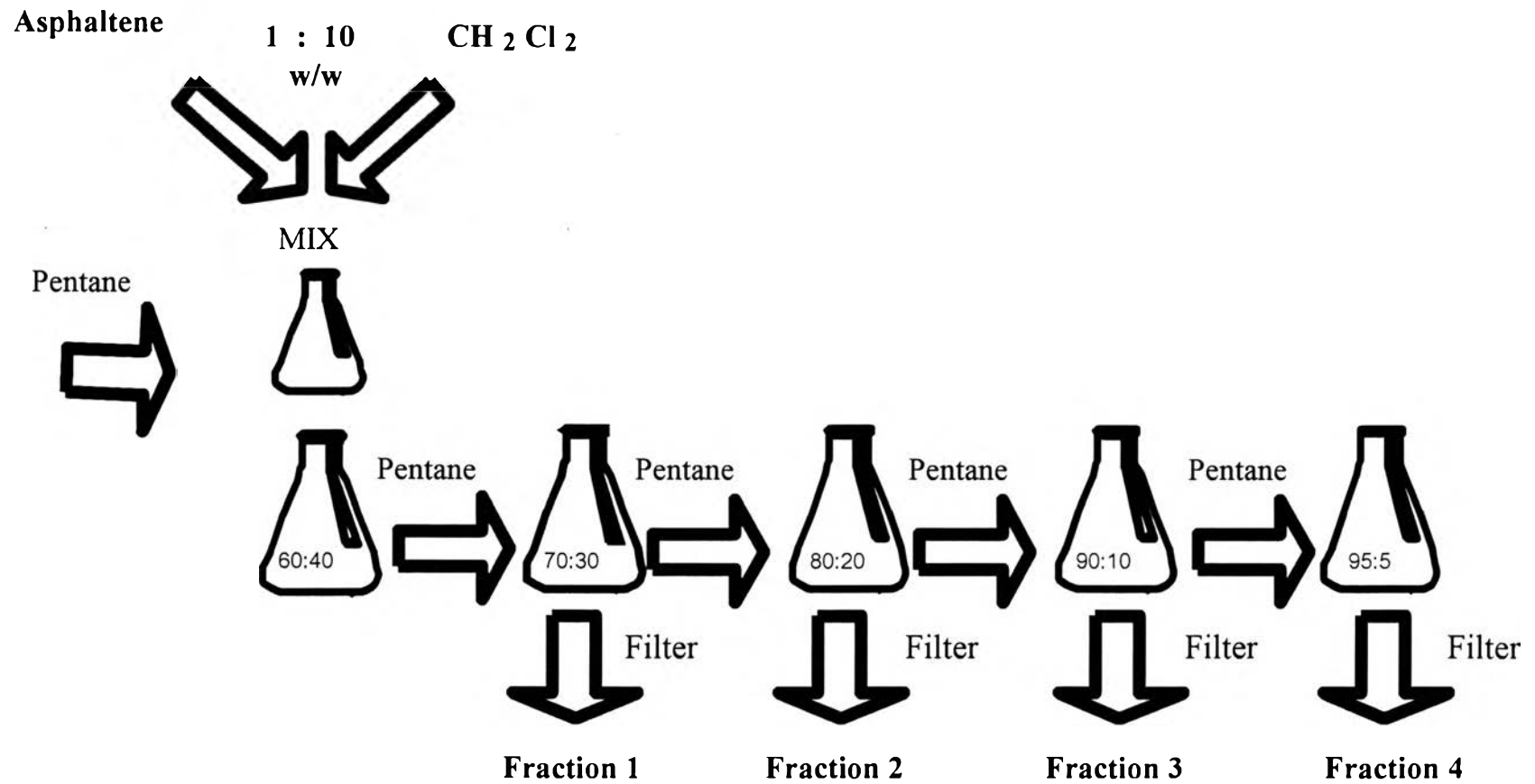


Figure 3.2 Schematic of asphaltene fractionation.

The specific surface area was measured by Micromeritics ASAP 2010 Brunauer-Emmett-Teller method (BET). This technique was done by measuring the absorption of N₂ gas at 77 K to determine the surface area of asphaltene fractions.

Elemental composition of the asphaltene samples was determined by using Elemental analyzer (Perkin Elmer 2400). This analytical technique gave the wt% of carbon, hydrogen, nitrogen, and sulfur. Oxygen content was calculated by subtracting the sum of those four values from one hundred. The amounts of other components were negligible because of their insignificant amounts.

Metal ion contents were analyzed by Inductive Coupled Plasma (ICP) emission spectrophotometer (XRAL activation services). All asphaltene fractions were analyzed for metal ions of iron (Fe), Vanadium (V), Nickel (Ni), and Zinc (Zn)

Functional groups of the asphaltene sample were investigated by a single-beam Matterson CYGNUS 100 FTIR Spectrophotometer. It was equipped with a wide-band mercury-cadmium-telluride (MCT) detector. Carbon tetrachloride (CCl₄) was used to dissolve the asphaltene sample because CCl₄ shows the low IR absorption background above 800 cm⁻¹. The CCl₄ solution of asphaltenes was put in a sonicator to ensure total dissolution of asphaltene before injecting the solution in the NaCl liquid sample cell with 0.3 mm in path length.

The structures of the asphaltene samples were investigated by the Jeol JNM-A 500 FT NMR Alpha FT NMR spectrometer (Jeol, Japan). Proton magnetic resonance (p.m.r.) spectroscopy was employed to investigate the structure of the asphaltic components of the asphaltene samples. This technique was to estimate aromatic structure within the asphaltene fractions. Chloroform was used as a internal standard.

3.3 Dissolution Study

An experiment was carried out by employing the apparatus illustrated in Figure 3.3. This apparatus consists of a differential reactor to accommodate asphaltene deposit and a syringe pump to constantly inject the fluid through the differential reactor to dissolve the asphaltene deposit. The dissolution experiment was conducted under the constant temperature at 17°C. As shown in Figure 3.3, the differential reactor was modified from a filter holder having 25 mm in a diameter. This differential reactor had a circular disk with 22 mm in a diameter and 3 mm in thickness. The edge of the reactor was made of an O-ring while both of the front and rear faces of the reactor were made of a pair of 0.45 micron Teflon filter membranes. These Teflon membranes were selected for this study because they are inert to any of the component in the micellar fluid, especially, dodecylbenzene sulfonic acid amphiphile. For each experiment, 0.01 gram of asphaltene powder (crushed before starting the dissolution experiment in order to get rid of mass transfer effects) was first placed in the reactor as the model deposit of asphaltenes. The asphaltene powder was loosely and uniformly placed in the reactor space so it could easily contact the micellar fluid. The micellar fluid is injected vertically upwards into the reactor at a constant flow rate. This upward flow was applied to ensure that any air remaining in the reactor could be completely displaced out of the reactor by the micellar fluid at the initial stage of the experiment. The filter membranes at both ends of the reactor are permeable to the micellar fluid and dissolved asphaltenes but impermeable to the undissolved asphaltene powder. Therefore, only dissolved asphaltene flew out of the reactor with the micellar fluid and was collected in glass vials. Afterwards, the concentration of dissolved asphaltene in the effluents collected at different elution times were measured by UV/VIS spectrophotometer.

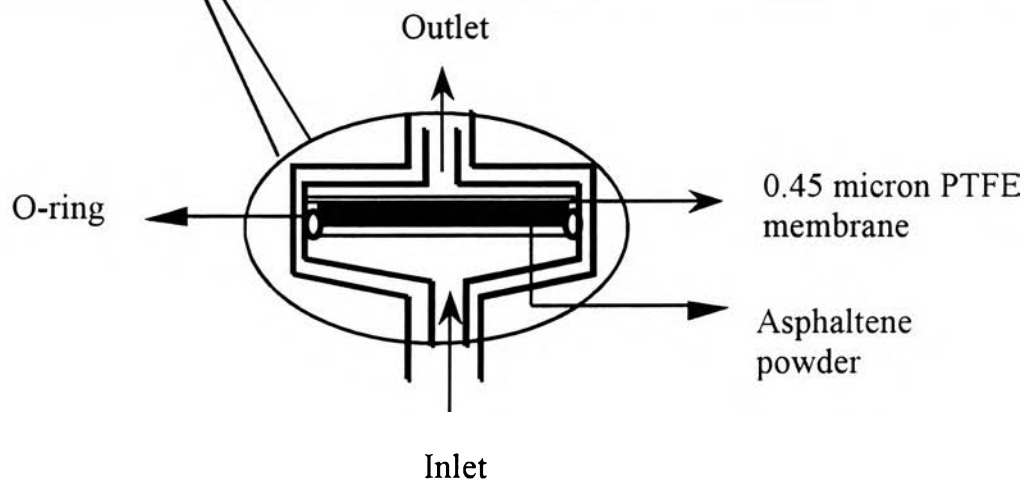
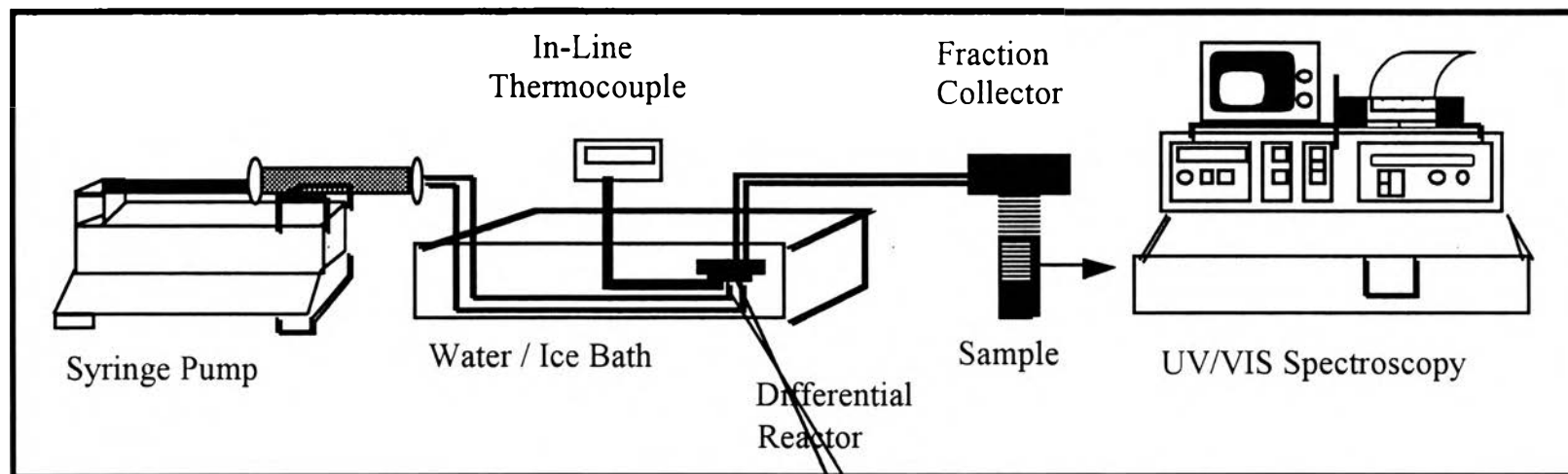


Figure 3.3 Schematic illustration of experimental setup of dissolution study.

Each experiment was carried out at 17°C and 1 ml/min in flow rate of the amphiphile solution. List of the experimental conditions conducted in the dissolution study was shown in Table 3.1

Table 3.1 Experimental conditions conducted in this study

Variable evaluated	Asphaltenes	Amphiphile concentration (wt%)*
asphaltene fraction	F1, F2, F3, F4	5
concentration	F1, F3	1, 3, 5, 7, 10

* wt% : weight percent of DBSA in heptane

3.4 Kinetics Analysis

In order to further analyze the kinetics and mechanism of asphaltene dissolution, the rate of dissolution of asphaltene precipitate, r_D , was assumed to be first order with respect to the undissolved asphaltene mass, i.e.,

$$-r_D = \frac{dM}{dt} = -k_s M \quad (3.1)$$

Integrating equation (1) gives

$$\ln \frac{M}{M_0} = -k_s t \quad (3.2)$$

where k_s is the apparent specific rate constant (min^{-1}) for asphaltene dissolution. M_0 and M are the mass of asphaltene precipitates initially placed and that remaining undissolved at time t , respectively.

3.5 Acid-Base Interaction Study

FTIR was used to quantify the acid-base interaction between asphaltene fractions and amphiphile to further unveil the mechanism of stabilizing of asphaltenes by amphiphile in alkane solutions. Dodecylbenzene sulfonic acid (DBSA) was used in this study. The IR absorption band responsible for the acid-base interaction between asphaltene and DBSA, namely, SO-H stretching bands, was determined. This broad bands range from 2000 to 3000 cm^{-1} for DBSA amphiphile. This experiment was studied the asphaltene-DBSA interaction. The CCl_4 solvent contained a sufficient concentration of 2.5 wt% DBSA amphiphile was used to dissolve asphaltene. Teflon tubes (Nalco Co.) were used to accommodate the solution in order to prevent the adsorption of asphaltenes and amphiphiles to the sample vial. After the asphaltene was completely dissolved in solution using the sonicator for 1 hour, the sample was agitated for at least 6 hours. Afterwards, the sample was measured by using the FTIR spectrophotometer. The procedure used to run the FTIR spectrophotometer was the same as previously described.