CHAPTER III
EXPERIMENTAL

3.1 Materials

Two types of crude oils, named NM1 and NM5, were used to precipitate asphaltenes. These crude oils were provided from PDVSA - Intevep Company, Venezuela. HPLC grade n-heptane was selected as a solvent for precipitating asphaltenes from these two crude oils. Solvents used in the dissolution study composed of the mixture of aromatic/alkane solvent. HPLC grade toluene and heptane obtained from Fisher were used as aromatic and alkane solvents, respectively.

3.2 Asphaltene Precipitation

Asphaltenes were precipitated from PDVSA – Intevep crude oil By mixing one volume of crude oil with 40 volumes of heptane at 65 ^{o}C and stirred for 45 minutes as modified from ASTM 2007D. The mixture was allowed to settle at room temperature for 8 hours and was then filtered through a 0.45 μm membrane. The precipitated asphaltenes were washed on the filter with heptane until the filtrate was colorless. The filtrated asphaltenes were dried overnight in a vacuum desiccator at room temperature and the mass of asphaltene was determined when the sample had a constant weight.

3.3 Fractionation Procedure

The asphaltene sample was fractionated to different polarity fractions by using binary mixture of CH_2Cl_2 and n-heptane. The original asphaltene was completely dissolved with pure CH_2Cl_2, and then n-heptane was added to

was completely dissolved with pure CH_2Cl_2, and then n-heptane was added to this solution. As the amount of n-heptane (nonpolar solvent) is increased in the binary mixture, the polar effect of CH_2Cl_2 decreases. The asphaltene fraction precipitated out first is the most polar fraction, followed by precipitation of less polar fractions upon the addition of more n-heptane.

One weight of the original asphaltene was completely dissolved with 10 times by weight of CH_2Cl_2. Heptane was added in the discrete increments of 5 %vol until the first fraction (F70/30) was precipitated out at 30 % vol CH_2Cl_2 and 70 % vol heptane. The precipitate was separated by centrifugation at 3500 rpm for 30 minutes and more heptane was then added to supernatant to obtain the next fraction (F80/20), which precipitated out at 20 % vol CH_2Cl_2 and 80 %vol heptane. The third and the fourth fractions (F90/10 and F95/5) were obtained at 10 and 5 % vol CH_2Cl_2 in a similar manner. All asphaltene precipitates were dried in a vacuum desiccator overnight and the mass of each asphaltene precipitate was determined.

3.4 Asphaltene Dissolution Study

The experimental study of asphaltene dissolution was conducted by using apparatus illustrated in Figure 3.1 The rate of dissolution was obtained by using a differential reactor. A syringe pump was used to inject the toluene/heptane solution through the differential reactor upwardly to dissolve an asphaltene sample at a fixed flow rate. All experiments were done at room temperature (22 ^{o}C). In each experiment, 25 mg of asphaltene powder was first placed uniformly between two Millipore hydrophobic type HVHP membranes (pore size 0.45 micron, 25 mm diameter), which were sealed by a Teflon O-ring mounted inside the differential reactor as shown in Figure 3.2. The toluene/heptane solution dissolved asphaltene as it flowed through the reactor and a 1/6 " ID Teflon tube were collected at different times

in glass vials using a fraction collector (LKB 2211 SuperRac). The apparatus was arranged such that the solvent flows up and

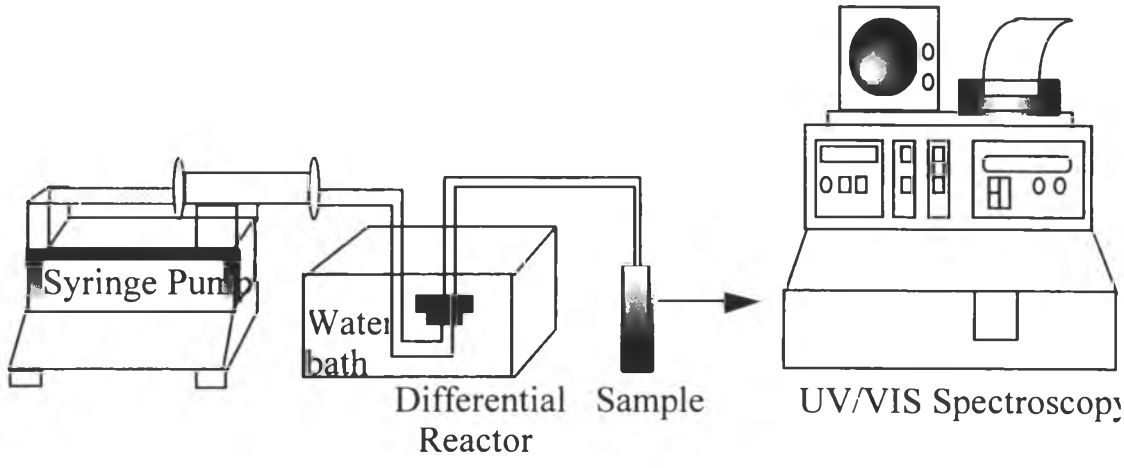

Figure 3.1 Schematic of the experimental setup for dissolution study.

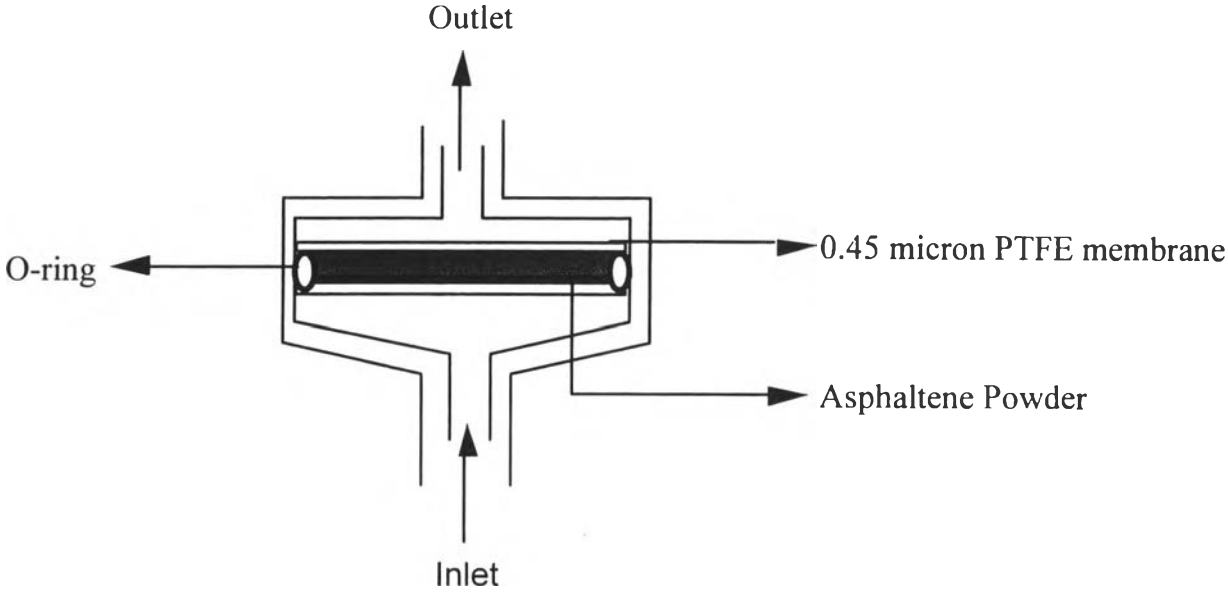

Figure 3.2 The configuration of a differential reactor.

entered the reactor from the bottom in order to ensure that any air trapped in the reactor was completely displaced from the reactor by the fluid at the initial stage of the experiment. The effluent samples were analyzed for asphaltene concentration using UV-Vis spectroscopy at a wavelength of 400 nm.

3.5 Measurement of Asphaltene Solubility

Solubility of asphaltene was determined by adding 0.5 g asphaltene powder with 3 ml of toluene. Afterwards, the sample mixture was put in soniccator bath to completely dissolve the asphaltene. If all the asphaltene powder dissolved, then the more was added until the solution reached the solubility limit of asphaltene in toluene. The sample was left to reach equilibrium for 10 h and then centrifuged at 3,500 rpm for 30 min. The supernatant was taken to analyze for asphaltene concentration using UV-Vis spectroscopy at a wavelength of 400 nm. To determine the solubility of asphaltene in toluene/heptane mixture, heptane was added into the solution. When heptane was added to the solution, asphaltene precipitated out of the solution due to the reduced asphaltene solubility in heptane. The solubility of asphaltene in toluene/heptane mixture was then determined in the same manner as in pure toluene.

3.6 Characterization Techniques of Asphaltenes

The chemical compositions of two types of crude oils were analyzed by SARA analysis (Saturate, Aromatic, Resin, and Asphaltenes). These data were provided from PDVSA-Intervep company, Venezuela. The morphology of asphaltene precipitates was analyzed using scanning electron microscope (SEM).