CHAPTER III
EXPERIMENTAL

3.1 Materials

Crude oil that used to precipitate asphaltenes was provided from PDVSA-Intevep Company, Venezuela. n-Heptane, HPLC grade, was selected as a solvent for precipitating asphaltenes from crude oil. In fractionation study, pentane, HPLC grade, and methylenechloride, certified ACS grade, were used. Solvents used for dissolution study were divided into two types. The first one was amphiphile/alkane solution, which consists of dodecylbenzenesulfonic acid (DBSA), 95-98 % produced by Pfaltz & Bauer MSDS, and heptane, HPLC grade. The other one was aromatic solvent, toluene with certified ACS grade.

3.2 Preparation of Asphaltene Precipitates

Asphaltene samples were obtained from COL-2 crude oil by solvent extraction. The crude oil was first mixed with warm heptane (85 ^{o}C) in a ratio of 1 to 10 by volume for approximately 45 minute to precipitate asphaltenes out of solution as modified from ASTM 2007D. The mixture was then allowed to stand for 12 hours and it was subsequently passed through a fritted glass filter with a Whatman No.4 filter paper. The asphaltene samples collected on the filter paper were dried at room temperature.

3.3 Fractionation Procedure

A binary mixture of methylenechloride (CH_2Cl_2) and pentane was utilized as a solvent for fractionation. As the amount of pentane (nonpolar) is increased in the binary mixture, the polar effect of CH_2Cl_2 decreases. The

asphaltene fractions, which precipitate out first, are the most polar fraction, followed by precipitation of less polar fractions upon addition of more pentane (Nalwaya *et al.*, 1999).

One weight of the unfractionated asphaltene was dissolved in 10 weights of CH_2Cl_2. Pentane was added in discrete increments of 5 vol.% until the first fraction (F60/40) precipitated out at 40 vol.% CH_2Cl_2 and 60 vol.% pentane. The precipitate was separated by centrifugation at 3000 rpm for 20 minutes and more pentane was then added to supernatant to obtain the second fraction (F70/30) precipitated out at 30 vol.% CH_2Cl_2 and 70 vol.% pentane. The third and fourth fractions (F80/20 and F90/10) were obtained at 20 and 10 vol.% CH_2Cl_2 in a similar manner.

3.4 Thermal Aging Study

The asphaltene samples obtained from Col-2 crude oil were kept in a vacuum oven at various temperatures (22, 80, 120, and 150 ^{o}C) under vacuum pressure 15 in Hg. The samples were taken out after certain time of aging and stored in sealed bottles to prevent exposure of asphaltenes.

3.5 Dissolution Procedure

The rate of dissolution was obtained by using a differential reactor as shown in Figure 3.1. A syringe pump was used to inject the amphiphile/alkane micellar solution through the differential reactor upwardly to dissolve asphaltene deposits at a fixed flow rate. The solution flew through a 1/16" ID stainless steel coil before entering the differential reactor. The temperature was controlled by immersing the coil in the Polystat programmable water bath. In each experiment, 0.01 grams of the asphaltene powder was first placed uniformly between two Millipore hydrophobic type HVHP membranes (pore size 0.45 micron, 25 mm dia.) which were then sealed by a Teflon O-ring mounted inside the differential reactor as shown in Figure 3.2.

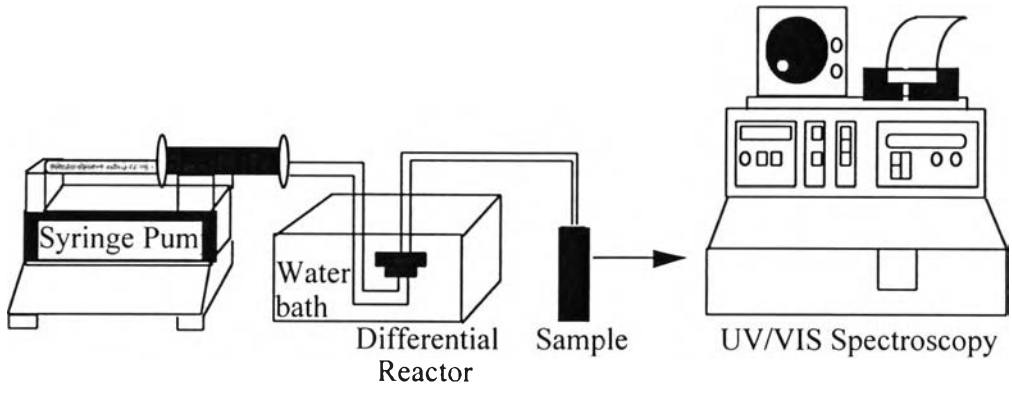

Figure 3.1 A schematic illustration of the experimental setup for the dissolution study

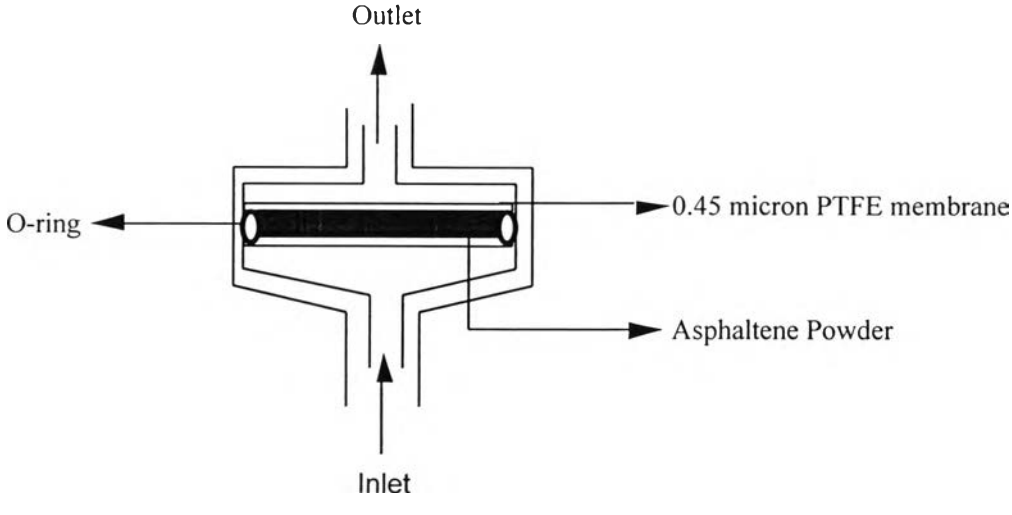

Figure 3.2 The enlarged view of the differential reactor

The dissolved asphaltene in amphiphile/alkane solution was then passed through a 1/16" ID Teflon tube through an LKB 2211 SuperRac fraction collector. Samples were then collected at different times in glass vials. The samples were analyzed for asphaltene concentration using UV/vis spectrophotometer at a wavelength of 400 nm.

3.6 Kinetic Analysis

Rate of dissolution of asphaltene, r_D, is assumed to be first order with respect to the undissolved asphaltene mass:

$$-r_D = \frac{dM}{dt} = -kM \tag{3.1}$$

Integrating equation (3.1), it gives

$$\ln\frac{M}{M_0} = -kt \tag{3.2}$$

Where k is the apparent specific rate constant for asphaltene dissolution (min^{-1}). M_o and M are the mass of asphaltene precipitates initially placed and that remaining undissolved at time t, respectively. k can be obtained from the slope of the plot of t versus $ln(M/M_0)$.

3.7 Asphaltene Characterization

Asphaltenes from different aging conditions were characterized to determine functional groups and molecular weight. The techniques used to characterize these physical structures are described below :

Functional group: Fourier Transform Infrared Spectroscopy (FT-IR).

Molecular weight: Gel Permeation Chromatography (GPC).

Morphology: Scanning Electron Microscope (SEM).