CHAPTER III
EXPERIMENTAL

3.1 Materials

Zuata crude oil used to precipitated asphaltenes was provided by Conoco oil company. n- Heptane, AR grade and HPLC grade obtained from aldrich were used to precipitate asphaltene and used as the solvent in the dissolution study, respectively. Dodecylbenzene sulfonic acid (DBSA), 95-98%, was obtained from Pfaltz & Bauer MSDS. Potassuim hydroxide (laboratory grade) and Hydrochloric acid were used as the titrants in potentiometric titration. Toluene (HPLC grade) Isopropanol (99.5 %) and CO_2 – free water were purchased from Aldrich for preparing the titration solvent. 9-Antracene carboylic acid obtained from Aldrich and Triethylamine from Fisher were used to sharpen the titration curve.

3.2 Methodology

3.2.1 Original Asphaltene Preparation

The original asphaltene used in this study was separated from Zuata crude oil supplied by Conoco Inc. This asphaltene sample was the heptane-insoluble fraction prepared by mixing heptane with crude oil at ratio 10:1 for 1 hour. This process was done at 60 °C. The mixture was left at room temperature for at least 12 hours before passing the solution through the fretted glass filter with teflon filter membrane having pore size of 0.45 micron and the precipitate was then dried at room temperature under nitrogen environment for 2-3 days.

3.2.2 Thermal Aging Procedure

The original asphaltene was kept in vacuum oven at 25 in Hg vacuum at different temperatures and different periods of time under nitrogen and air environment.

3.2.3 Acid/Base Titration

3.2.3.1 Reagent Preparation

0.03 N KOH standard alcoholic and 0.03 N HCl standard alcoholic solutions and titration solvent were prepared by the method described in Appendix A. These standard solutions were then standardized with potassium phathalic acid. The exact normalities of KOH and HCl standard alcoholic solutions were then calculated. Titration solvent having toluene: isopropanol: water ratio of 66: 33.5: 0.5 was also prepared in a large quantity.

3.2.3.2 Blank Titration (Base Titration)

For each set of samples, 0.0538 g of 9-antracene carboxylic acid was firstly weighed into 125 ml of titration solvent. A small amount of KOH standard alcoholic solution was then added into the system. The volume of the KOH solution and the correspondent mV were read until the titration was completed. The end point was taken at the sharpest inflection point of the titration curve.

3.2.3.3 Blank Titration (Acid Titration)

0.5 ml of triethylamine which was already diluted with titration solvent at a ratio of 1:19 (=0.18 mmol of triethylamine) was pipetted into 125 ml of titration solvent. A small amount of HCl standard alcoholic solution was then added into the system. The volume of the titrant (HCl) and the correspondent mV were progressively recorded until the titration was completed.

3.2.3.4 Acid/Base Titration

The acid/base numbers of asphaltene samples were determined by potentiometric titration modified from ASTM664D (1983). For base titration, briefly, approximately 0.5 g of sample was mixed with 0.0538 g of 9-antracene carboxylic acid and 125 ml of the titration solvent consisting of 66.5 % toluene, 33.5 % anhydrous isopropanol and 0.5 % water. 9-antracene carboxylic acid was used in order to sharpen the inflection point of titration curve. Afterwards, approximately 0.03 N KOH standard alcoholic solution was added in a small portion and waited until the potential equilibrium was reached. The volume of KOH standard alcoholic solution added and correspondent cell potential readings were recorded until the titration was completed. The same procedure was taken for acid titration but the sample was mixed with 0.18 mmol triethylamine and then titrated with 0.03 N HCl standard alcoholic solution instead. Base and acid numbers of all samples were then calculated as shown in Appendix A.

The potentiometric measurement was obtained by using a potentiometric titrimeter (Orion research microprocessor ionalyzer/ 901) connected with combination electrode (glass indicating electrode and calomel referent electrode).

3.3 Dissolution Study

An experimental study of asphaltene dissolution was conducted by using the apparatus illustrated in Figures 3.1 and 3.2. The apparatus consisted of a differential reactor, a syringe pump, a water bath and a sample collector. The asphaltene sample was firstly placed uniformly in the reactor between two HV 0.45-micron membranes. The dissolving solution containing 10 wt. % of DBSA in n-heptane was injected at a constant flow rate of 1 ml/min by a syringe pump. The system temperature was kept constant at 20 °C. A low

flow rate and a high concentration of DBSA were used in this study in order to prevent a stable steric layer causing asphaltenes to aggregate into large colloid due to the shortage of DBSA (Chang and Fogler, 1994a). The effluents were collected via the sample collector at different elution times. Afterwards, the concentrations of disssolved asphaltene were measured by a UV/Vis Spectrophotometer at a wavelength of 400 nm.

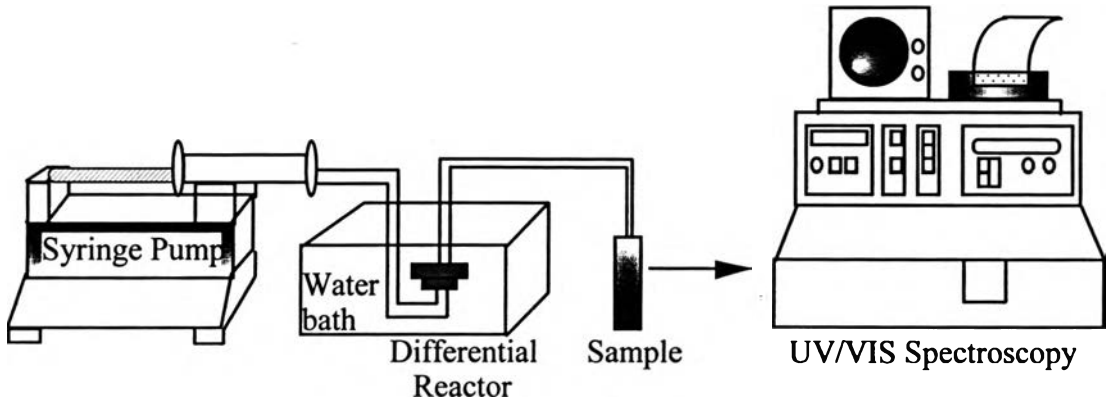

Figure 3.1 Schematic of the experimental setup for dissolution study

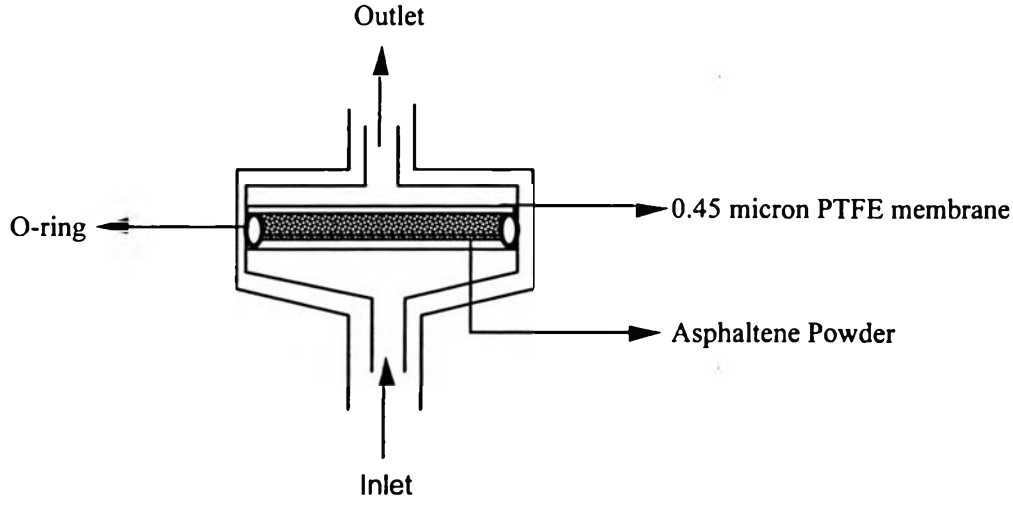

Figure 3.2 The configuration of a differential reactor

3.4 Asphaltene Characterization

Elemental compositions of asphaltene samples were determined by using an elemental analyzer. The technique could provide weight % of carbon, hydrogen and nitrogen. The oxygen content was roughly estimated by subtracting with weight % of these three fractions.

Functional group analysis of asphaltene samples was performed by using Mattson Galaxy series FTIR 3000. Asphaltene samples were firstly dissolved in toluene and put in a sonicator bath. However, the asphaltenes aged under air environment at 120 °C for 7 day, at 150 °C for 3 days and at 180 °C for 3 days couldn't be completely dissolved. These three samples were filtered with 0.45 μm filter members before injected into ZnCN cell. The concentration of all asphaltene solutions was 1 mg/ml.

Molecular weights of some asphaltene samples, which were aged in different conditions, were determined by a gel permeation chromatography using pyridine as a solvent at 80 °C.