

CHAPTER III

EXPERIMENTAL SECTION

3.1 Sample Preparation



3.1.1 Asphaltenes (original)

The asphaltene original sample used in this study was a pentane-insoluble fraction of crude oil provided by Mobil Research and Development. This asphaltene sample was prepared from crude oil according to a modified procedure described in ASTM 2007D (1983). In brief, one volume of crude oil was first mixed with ten volumes of warm pentane solvent for approximately one hour to precipitate asphaltenes out of solution. Afterwards, asphaltene precipitates were collected from solution by passing the solution media through a fritted glass filter with Whatman No. 1 filter papers and were dried at 60 °C. This precipitated Mobil asphaltene sample appeared as fine powders with a dark brown or black color. The solubility of this asphaltene sample was found to be 8.4 (cal/cm³)^{0.5} in the scale of Hildebrand solubility parameter. The elemental composition and chemical characterization of this asphaltene sample were also reported previously (Chang and Fogler, 1993 &1994).

3.1.2 Fractionated Asphaltenes

The asphaltene (original) was dissolved in 20 times of 50 % v/v of dichloromethane (CH₂Cl₂) - heptane by weight. For example, 20 g of asphaltene (original) would be dissolved with 400 g of 50 % v/v CH₂Cl₂ - heptane. Afterwards, 100 ml of the stock solution of asphaltene (original) and

50 % v/v CH_2Cl_2 - heptane were mixed with 100 ml of n- heptane for approximately one hour. The asphaltene precipitates, named as “asphaltene fraction 1”, were collected from the filtration set in the preparation of asphaltene (original). To obtain “asphaltene fraction 2, the preparation was conducted as well as the preparation for asphaltene fraction 1, but mixing 100 ml of the stock solution with a liter of n - heptane instead 100 ml of n - heptane.

Two alkylbenzene - derived amphiphiles, dodecylbenzene sulfonic acid (DBSA, $n\text{-C}_{12}\text{H}_{25}$ -- SO_3H) and nonylphenol (NP, $n\text{-C}_9\text{H}_{19}$ -- OH), and n - heptane as solvent, were used in this study. These two oil - soluble amphiphiles have been proved to be effective in the stabilization of asphaltenes in alkane media (Chang and Fogler, 1993 & 1994). All chemicals are commercially available and used directly for the study without further purification.

3.2 Experimental Procedure

To assess the rate of asphaltene dissolution, a differential reactor, shown in Figure 3.1-2, was used to carry out the experiments that were listed in Table 3.1. A syringe pump was used to inject the amphiphile/alkane micellar solutions (usually at 1 ml/minute) through the differential reactor to dissolve asphaltene deposits. A water bath was used to maintain a controlled temperature, ranging from 10 , 22, and 58 °C, for the flow system. In each experiment, 0.025 grams of asphaltene powders was first loosely and uniformly placed in the reactor. The differential reactor was modified from a filter holder with a diameter of 25 mm. The edges of the reactor were made of an O-ring while both of the front and rear faces were made of a pair of 0.45 micron Teflon filter membranes. These inert filter membranes were permeable to the amphiphile/alkane fluid and the dissolved asphaltences, but impermeable to the

un-dissolved asphaltene powder, Consequently, when the amphiphile/alkane fluid was injected upwards, only the dissolved asphaltenes were carried with the fluid out of the reactor and collected by glass vials. This upward flow ensured that air trapped in the reactor could be completely displaced from the reactor by the fluid at the initial stage of the experiment. Afterwards, the concentration of asphaltenes in the effluent collected at different elution times was measured by the absorbance of effluents at wavelength 400 nm using a UV/vis spectrophotometer.

3.3 Kinetics Analysis

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

$$-r_D = \frac{dM}{dt} = -kM \quad \dots\dots\dots(1)$$

Intergrating equation (1) gives

$$\ln \frac{M}{M_0} = -kt \quad \dots\dots\dots(2)$$

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

Table 3.1 List of the experimental conditions conducted in this study

Variable	Amphiphile Concentration (wt%)		Temperature (deg C)	Flow Rate (ml/min)	Solvent
Amphiphile Concentration	DBSA	2.5, 5.0, 7.5, 10.0	22	1.0	n-Heptane
	NP	5.0, 10.0, 15.0, 20.0	22	1.0	n-Heptane
Flow Rate	DBSA	10.0	22	0.2, 1.0, 5.0	n-Heptane
	NP	20.0	22	0.2, 1.0, 5.0	n-Heptane
Temperature	DBSA	10.0	10, 22, 58	1.0	n-Heptane
	NP	20.0	10, 22, 58	1.0	n-Heptane

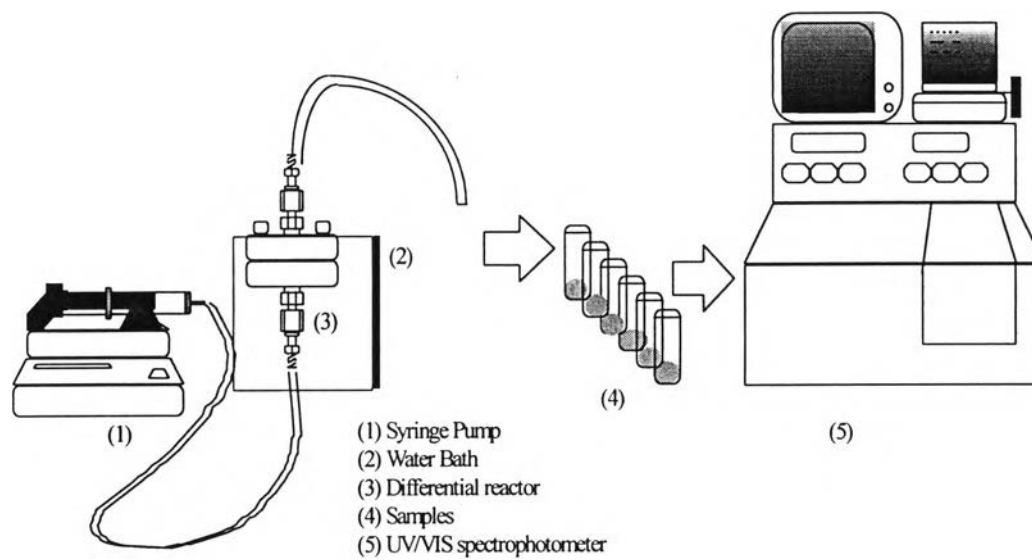


Figure 3.1 A schematic illustration of the experiment setup.

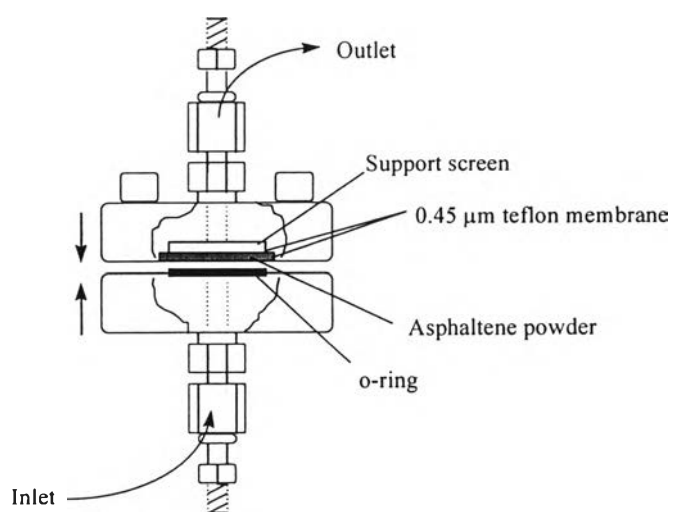


Figure 3.2 The enlarged view of the differential reactor.