

## CHAPTER III

### EXPERIMENTAL SECTION

#### 3.1 Kinetic Study of Asphaltene Dissolution by Amphiphile/Alkane Solutions.

##### 3.1.1 Materials

###### 3.1.1.1 *Asphaltenes*

The Mobil crude oil used in this study was provided by Mobil Research and Development. The asphaltenes were obtained from the precipitation of n-pentane insoluble fraction of Mobil crude oil followed a modified version of ASTM2007D. 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. Afterward, asphaltenes precipitants were collected from solution by passing the solution media through a fritted glass filter with Whatman 1 filter papers. The precipitants then were dried and asphaltenes were obtained which appeared as fine powders with a dark brown to black color.

### 3.1.1.2 *Amphiphiles*

Dodecylbenzene sulfonic acid (DBSA) and nonyl phenol (NP) were two oil-soluble amphiphiles selected for this study. These two alkylbenzene derived chemicals have been found to stabilize asphaltenes in alkane media effectively. The chemical structure, abbreviation, source, and purity of these amphiphiles were listed in Table 3.1

### 3.1.1.3 *Alkanes*

To study the effect of solvent types in the micellar fluid on the rate of dissolution, five alkanes were used as dispersing media in this experiment. Table 3.2 listed their general chemical structures and properties.

All chemicals used in this study are commercially available and no further purification is performed before their usage.

## 3.1.2 Experimental method

In order to carry out this study, an experimental apparatus was established as illustrated in Figure 3.1. This apparatus included a differential reactor to accommodate asphaltene deposits and a syringe pump to constantly inject the fluid in the syringe through the differential reactor to dissolve asphaltene deposits. In the dissolution experiments conducted at controlled temperatures, a water bath was used to accommodate the differential reactor. As shown in Figure 3.2, the differential reactor was

modified from a filter holder with a diameter of 25 mm. This differential reactor appeared as a circular disk with 22 mm in 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 were inert to any of the component in the micellar fluid, especially, dodecylbenzene sulfonic acid amphiphile. For each experiment, 0.025 gram of asphaltene powders was first placed in the reactor as the model deposit of asphaltenes. Asphaltene powders were loosely and uniformly placed in the reactor space such that they could easily contact the micellar fluid. The micellar fluid was injected upwardly into the reactor at a constant flow rate. This upward flow ensured that air remained in the reactor could be completely displaced out of reactor by the micellar fluid at the initial stage of the experiment. Because the filter membranes at both ends of the reactor were permeable to the micellar fluid and the dissolved asphaltenes, but impermeable to the un-dissolved asphaltene powder. Therefore, only the dissolved asphaltenes were flown with the micellar fluid out of the reactor and collected in glass vials. 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. In this study, asphaltene concentration in the solution was quantified from the absorbance of light at a wavelength of 400 nm using a Varian DMS200 UV/vis spectrophotometer. This UV/visible spectroscopy technique has been successfully used for this purpose because asphaltenes can absorb strongly over the entire range of visible light while the other, such as amphiphiles and solvents, cannot. Therefore once the linear

calibration curve of absorbance versus known concentration of asphaltenes sample using toluene as solvent is constructed, the concentration of asphaltenes can be measured using Beer's light absorbance law.

### **3.2 Study of Stability of Different Asphaltene Fractions in Selected Amphiphile/Alkane Solutions.**

#### **3.2.1 Materials.**

##### *3.2.1.1 Asphaltenes.*

In this study Mobil asphaltenes were further fractionated into four fractions using a binary pentane-methylene dichloride ( $\text{CH}_2\text{Cl}_2$ ) solution. The volume percentage of  $\text{CH}_2\text{Cl}_2$  in the solution was varied from 25 to 18 and to 10. The precipitated asphaltene fractions were referred to as fraction 1, fraction 2, and fraction 3 respectively. The residual asphaltenes were referred to as fraction 4. Fraction 1 appeared as black solid whereas fraction 4 was brown fine powder.

##### *3.2.1.2 Amphiphiles.*

Dodecylbenzene sulfonic acid (DBSA) and nonyl phenol (NP) are two oil-soluble amphiphiles used in this study. The concentration of these two amphiphiles were varied to find the minimum concentration required to completely stabilize asphaltenes.

### 3.2.1.3 *Alkane.*

Heptane was used as the dispersing media in this part of the study due to its suitable viscosity, boiling point, and cost.

### 3.2.2 Experimental Method

A systematic investigation of the stability of different asphaltene fractions was carried out using heptane-based solution containing different concentration amphiphiles .

The experiment was carried out by the following procedure. First, the minimum concentration of each amphiphile needed for complete asphaltene solubilization in alkane solvents was estimated from a preliminary study, and an amphiphile stock solution which contained a sufficient amount of amphiphiles to totally solubilize asphaltenes was prepared. The asphaltene stock solution was prepared by dissolving 1 wt% asphaltene powders in each amphiphile stock solution. Samples were prepared by mixing the amphiphile stock solution, the asphaltene stock solution and pure alkane by different proportions. Afterwards, samples were gently shaken at room temperature for 6-12 hours and then centrifuged at 3000 rpm for 30 minutes. The concentration of asphaltenes in the filtrate was measured by the absorbance of light at the wavelength of 400 nm.

Table 3.1 List of alkylbenzene-derived amphiphiles used in this study

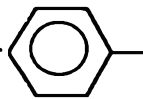
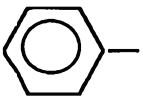
Alkylbenzene-Derived Amphiphiles			
Name	Abbrev	Chemical structure	MW
n-Nonyl phenol	NP	$n\text{-C}_9\text{H}_{19}$ — 	220.36
n-Dodecyl benzenesulfonic acid	DBSA	$n\text{-C}_{12}\text{H}_{25}$ — 	326.00

Table 3.2 List of alkane solvents used in this study

Aliphatic Solvents				
Name	Chemical structure	Abbrev.	Viscosity (cp@25oC)	MW
Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	C6	0.296	86.18
Heptane	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	C7	0.390	100.21
Decane	$\text{CH}_3(\text{CH}_2)_9\text{CH}_3$	C10	0.863	142.29
Dodecane	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	C12	1.390	170.34
Hexadecane	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$	C16	3.064	226.45

Table 3.3 List of the experimental conditions conducted in this study

Variables	Amphiphiles	Solvents	Amphiphile Concentration (%wt)	Temperature (oC)	Flwrate (ml/min)
Concentration	NP	C7,C12	2,4,7,10,20,30,	22	1
	DBSA	C7	1,1.5,2,3,5,10,20	22	1
	DBSA	C12	1,3,5,10,20	22	1
Flowrate	NP	C7	20	22	0.1,1
Solvent	NP	C6,C7,C10,C12,C16	20	22	1
	DBSA	C6,C7,C10,C12,C16	5	22	1
Temperature	NP	C7,C12	20	6,22,58	1
	DBSA	C7	5	22,58	1
	DBSA	C12	5	6,22,58	1

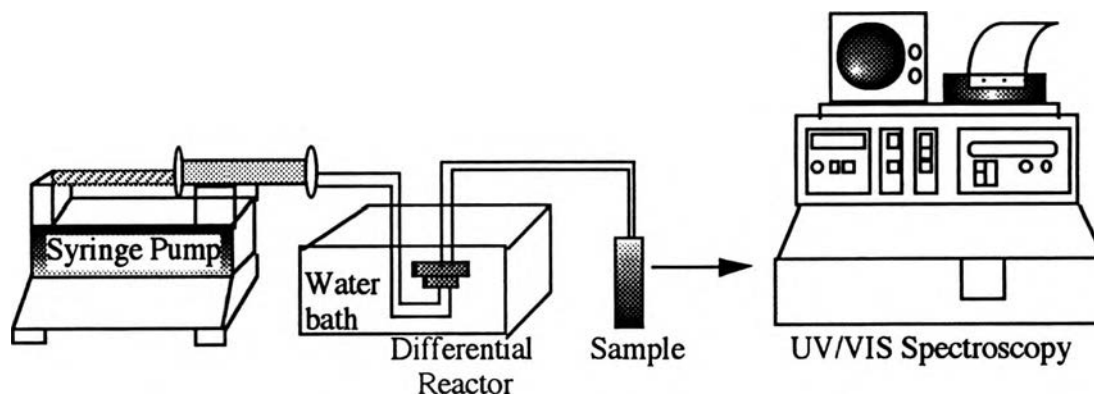


Figure 3.1 A schematic illustration of the experimental setup for the kinetic study of asphaltene dissolution.

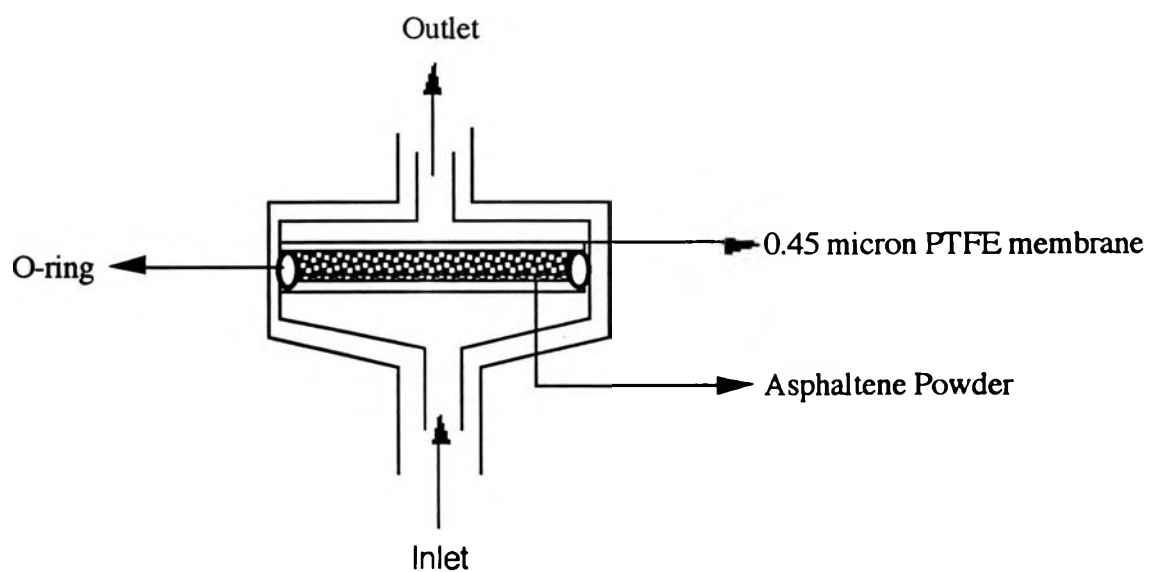


Figure 3.2 A detailed schematic drawing the differential reactor used in this study.