CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Crude Oil

Asphaltene from crude oil GOM was used in the all experiments and the compositions are shown in Table 3.1.

Table 3.1 Composition of asphaltene from oil GOM

Composition	Asphaltene from oil GOM (%wt)
Carbon	84.14
Hydrogen	6.18
Nitrogen	0.81
Oxygen	4.67
Sulfur	4.72
Iron	87 ppm
Nickel	187 ppm
Vanadium	591 ppm

3.1.2 Solvent

- Tetrahydrofuran 99.9 % purity

Table 3.2 Physical properties of tetrahydrofuran at room temperature

Properties	Oil A
Solvent	tetrahydrofuran
Density (g/ml)	0.8892
Viscosity (cP)	0.456
Solubility parameter ($MPa^{1/2}$)	9.1
Purity	99.9 %
Source	Fisher Scientific

3.1.3 Precipitant

- n-hexane 95 % purity

Table 3.3 Physical properties of n-hexane precipitant at room temperature

Properties	Oil A
Precipitant	n-hexane
Density (g/ml)	0.6548
Viscosity (cP)	0.456
Solubility parameter ($MPa^{1/2}$)	9.1
Purity	99.9 %
Source	Fisher Scientific

3.1.4 Alkylbenzenes

- 4-n-nonylacetophenone 97% purity

Table 3.4 Physical properties of 4-n-nonylacetophenone at room temperature

Properties	4-n-nonylacetophenone
Molecular weight	246.39
Purity	97 %
Head Group	$-COCH_3$
Structure	$COCH_3$—⌬—C_9H_{19}
Source	Fisher Scientific

- 4-n-nonylaniline 98% purity

Table 3.5 Physical properties of 4-n-nonylaniline at room temperature

Properties	4-n-nonylaniline
Molecular weight	219.37
Purity	97 %
Head Group	$-NH_2$
Structure	NH_2—⌬—C_9H_{19}
Source	Fisher Scientific

- 4-n-octyloxybenzonitrile 98% purity

Table 3.6 Physical properties of 4-n-octyloxybenzonitrile at room temperature

Properties	4-n-octyloxybenzonitrile
Molecular weight	231.34
Purity	97 %
Head Group	-CN
Structure	CN—⌬—$O-C_8H_{17}$

- 4-n-nonylphenol 98% purity

Table 3.7 Physical properties of 4-n-nonylphenol at room temperature

Properties	4-n-nonylphenol
Molecular weight	220.36
Purity	98 %
Head Group	-OH
Structure	OH—⌬—C_9H_{19}

- 4-n-dodecylbenzaldehyde 98% purity

Table 3.8 Physical properties of 4-n-dodecylbenzaldehyde at room temperature

Properties	4-n-dodecylbenzaldehyde
Molecular weight	290.45
Purity	98 %
Head Group	-COH
Structure	COH—⌬—O-$C_{12}H_{25}$

3.2 Equipment

3.2.1 <u>Nikon Eclipse E600 Optical Microscope</u>

A Nikon Eclipse E600 optical microscope with 40X zoom was used to detect asphaltene precipitation in tetrahydrofuran solution. It was connected to a Nikon digital sight DS-U3 server and Nikon DS-Fi2 camera. Images were took and kept from camera through computer.

3.2.2 <u>Sorvall Legend X1R Centrifuge</u>

A Sorvall Legend X1R was used to pretreat crude oil GOM and extract asphaltene from crude oil GOM.

3.2.3 Hardvard Apparatus 22 Syringe Pump

In microscopy experiments, titrant was added to samples by Hardvard apparatus 22 syringe pump at 0.33 mL/min.

3.2.4 Mettler Toledo XS204 Scale

All solutions in this work were prepared by weighing the mass of solutions to reach the desired concentration.

3.2.5 Cooler RTE-111 Neslab

Asphaltene cake was washed in soxhlet by heating and cooling heptane continuously to make it condensed and dropped into a thimble. Heptane was chilled and kept at 10°C by cooler RTE-111 Neslab.

3.2.6 5510 Branson Sonicator

5510 Branson sonicator was used to make asphaltene completely dissolved in solvent and asphaltene solution ready for performing microscopy experiments.

3.2.7 Seveneasy Mettler Toledo pH Meter

Potentiometric titrations were conducted measuring potential values by Seveneasy Mettler Toledo pH meter.

3.2.8 Inlab Mettler Toledo Electrode

An Inlab Mettler Toledo electrode was connected to Seveneasy Mettler Toledo pH meter.

3.2.9 Fisherbrand 20-200 μL Micropipette

In potentiometric titration, acidic titrant was added to alkylbenzene solution by fisherbrand 20-200 μL micropipette.

3.3 Software

3.3.1 NIS-Element D

NIS-Element D was used to save and adjust picture properties from the camera. The length scale is also available on this program.

3.4 Experimental Procedures

3.4.1 Crude Oil Pre-treatment

GOM crude oil was centrifuged at 10,000 rpm for 3 hours in order to remove sand and other impurities. The supernatant was separated and transferred to amber bottle to storage.

3.4.2 Asphaltene Extraction Experiment

A known amount of pretreated crude oil GOM was mixed with heptane in the ratio of 1:40, stirred for at least 24 hours, and centrifuged in 250 mL tube at 10,000 rpm for 1 hour. Asphaltene cake at bottom was collected and rinsed by heptane in soxhlet washed for 4 days to remove remaining resins and dirt. The cake was then dried under a fume hood for several days until it dry.

3.4.3 Potentiometric Titration Experiment

The mixture was made to be 0.2 mmol alkylbenzene/ mol tetrahydrofuran. Acidic titrant used in this work is 0.6 mmol trifluoromethanesulfonic acid. A pH meter and a combination electrode were first calibrated using buffer solutions of pH 4, 7, and 10. The mixture was kept stirred and the titrant was added by micropipette 50 mL each time. The potential values will change slightly while titrating acidic titrant. The titrant will be added until the potential values reach and pass the equivalence point which is the point that mV of the solution changes rapidly. The schematic diagram of potentiometric titration is shown in Figure 3.1.

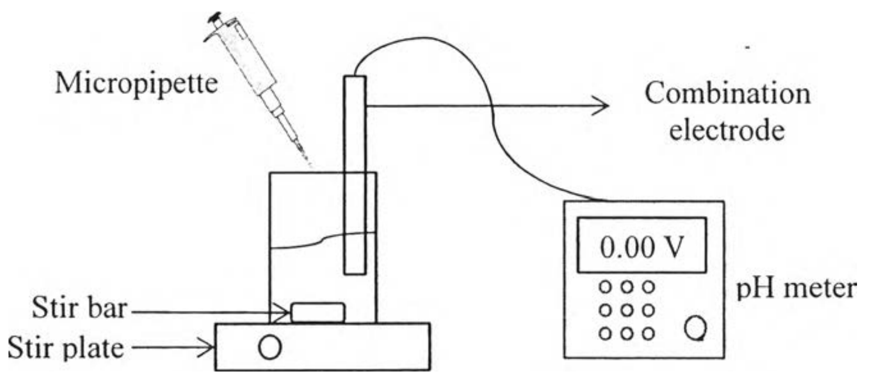

Figure 3.1 Schematic diagram of potentiometric titration.

The potential values from pH meter of dodecylbenzaldehyde were recorded and plotted as a function of titrant as shown in Figure 3.2a.

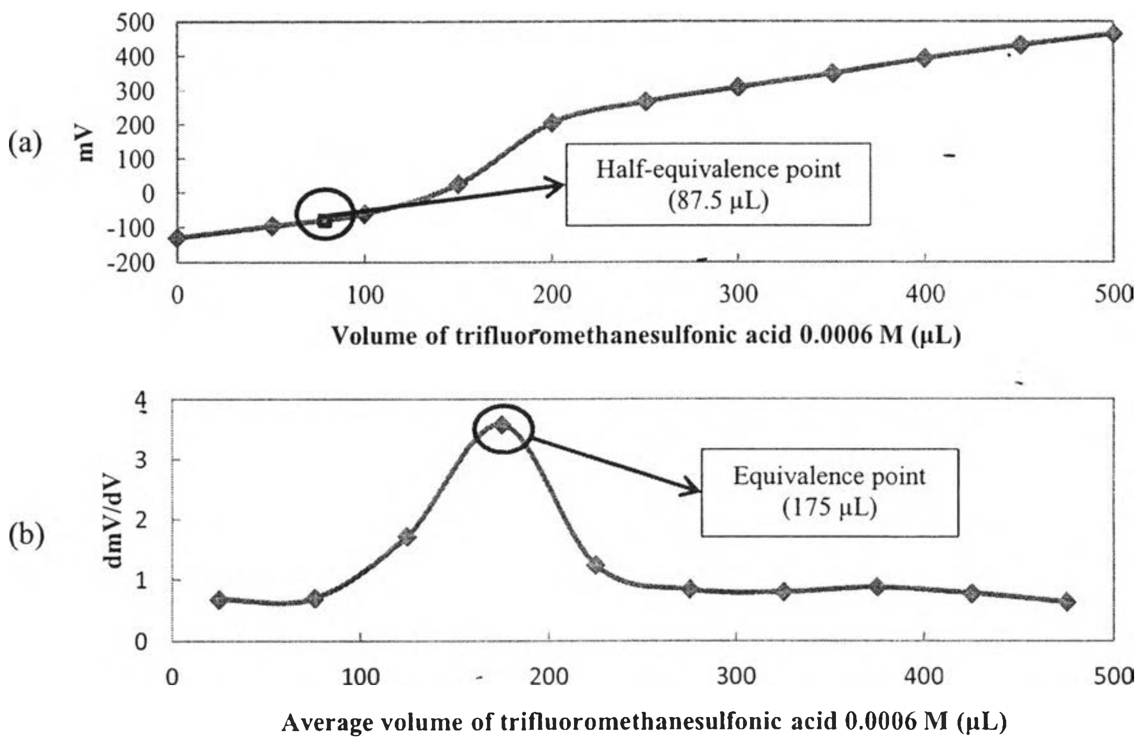

Figure 3.2 (a) Raw data between mV and volume of titrant collected from pH meter of dodecylbenzaldehyde. (b) First derivative plot of data from (a).

Figure 3.2a shows a plot of mV versus volume of titrant added for the titration collected from pH meter of dodecylbenzaldehyde titration. As can be seen from Figure 3.2a, the mV of solution slightly changes before 150 μL added titrant and significantly changes between 150-200 μL added titrant. The equivalence point is defined as the deepest change of potential values. The equivalence point is more accurately determined by converting data to derivative plot as shown in Figure 3.2b. The end point corresponds to the top of the peak that is apparent. In this case, 175 μL is the equivalence point, so the half-equivalence point will be at 87.5 μL. Then, the potential values at half-equivalence point can be converted to pKa by Nernst equation.

3.4.4 Microscopy Experiment

Stock solutions of alkylbenzene were first made at high concentrations. Then, those stock solutions of each alkylbenzene were diluted and added to asphaltene stock solutions. The desired concentration of asphaltene and alkylbenzene were made to be 0.01 wt % asphaltenes and 0.33 mmol alkylbenzene/ mol asphaltene, respectively. The samples were monitored using microscopy; the detection time was located when asphaltenes precipitate. A diagram of microscopy experiment is shown in Figure 3.3.

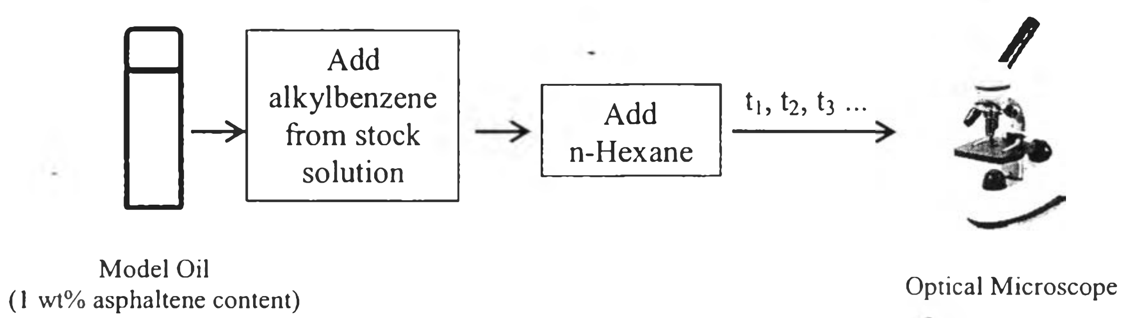

Figure 3.3 Schematic diagram of microscopy experiment procedure.