

CHAPTER III

METHODOLOGY



3.1 Materials

3.1.1 Surfactants

There were two types of surfactants used in this research: Alfoterra 145-4PO, which is an extended surfactant with its structure of C14-C15 branched alcohol propoxylate sulfate (4 propoxy groups); and another anionic surfactant, sodium dioctyl sulfosuccinate (Aerosol-OT or AOT).

Alfoterra 145-4PO with 30.8% purity, an experimental (not yet commercially available) surfactant specially synthesized by the Sasol Company (formerly Condea Vista Company) of Rosebank, South Africa, was used in this study. Alfoterra 145-4PO is a hydrophilic anionic surfactant. Sodium dioctyl sulfosuccinate (Aerosol-OT or AOT) with 100% purity was purchased from the Fluka Company. AOT is a hydrophobic anionic surfactant with a negative charged sulfosuccinate head group and an alkyl chain length of twenty carbon units. The properties and selected characterizations of these surfactants are shown in Table 3.1.

3.1.2 Oils

The NAPLs used in this study are diesel and motor oil as LNAPLs in the column study. Diesel was selected as a model oil contaminant in this research work. It was purchased from PTT Public Co., Ltd. With regard for the motor oil, which is commercially available for use in diesel engines, type SAE 15W-40 (dynamic plus) was used to make the model oily soil. It was purchased from PTT public Co., Ltd. The physical and chemical properties of these studied oils are shown in Table 3.2.

The two oils used in this study were unused oils in order to avoid a parameter (wear metals) or particulate and other chemical that usually found in used oil and may affect on experimental results.

Since the diesel and motor oil used in this research were commercial products that could vary in composition, a single batch of oils were used throughout this research. The oils were kept in a refrigerator at 4 °C until they were used.

3.1.3 Electrolyte

The electrolyte used in this research was sodium chloride (NaCl), analytical purity grade with 99% purity, purchased from Carlo ERBA Reagent Co., Ltd.

Table 3.1 Properties and selected characterizations of surfactants.

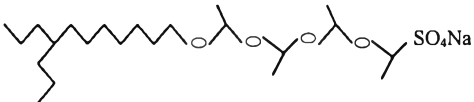
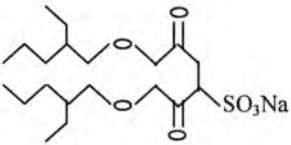
Chemical name	Chemical structure	Type	MW	HLB
C14-C15 branched alcohol propoxylate sulfate (4 propoxy groups) (Alfoterra 145-4PO)		Anionic	536	-
Sodium dioctyl sulfosuccinate (Aerosol-OT or AOT)		Anionic	444	10.2

Table 3.2 Physical and chemical properties of diesel and motor oil. (MSDS, 2005)

Properties	Diesel	Motor oil
Physical state	Liquid	Liquid
Carbon number	C ₉ -C ₂₀	C ₁₆ -C ₂₀
Appearance	Colorless to straw	Bright light brown liquid
Odor	Kerosene-like odor	Petroleum odor
Solubility	Insoluble in water	Insoluble in water
Specific gravity (H ₂ O = 1)	0.816	0.880
Boiling point	150-300 °C	> 300 °C
Flash point	187 °C	210 °C
Vapor pressure (mmHg)	0.5 (at 20 °C)	< 1 (at 20 °C)
Viscosity (cSt)	1.7-3.4 (at 40 °C)	100-126 (at 40 °C)

3.1.4 Substrate

The substrate for the experiment in the column study was 20-30 mesh Ottawa sand. 20-30 mesh Ottawa sand, nonporous silica sand, was purchased from Fisher Scientific. Pennell (1993) reported that the specific surface area of this sand was 0.1 m²/g.

3.1.5 Water

Ultra pure water was used throughout this research for preparing the aqueous surfactant solution and other chemical solutions. It was also used as the rinsing water and for cleaning the glassware.

All chemicals were used as received without further purification.

3.2 Methodology

This study was divided into two parts: the phase behavior study, and the column study. Figure 3.1 shows the experimental procedure diagram. The details of the experiment procedure and measurements are explained in more detail below.

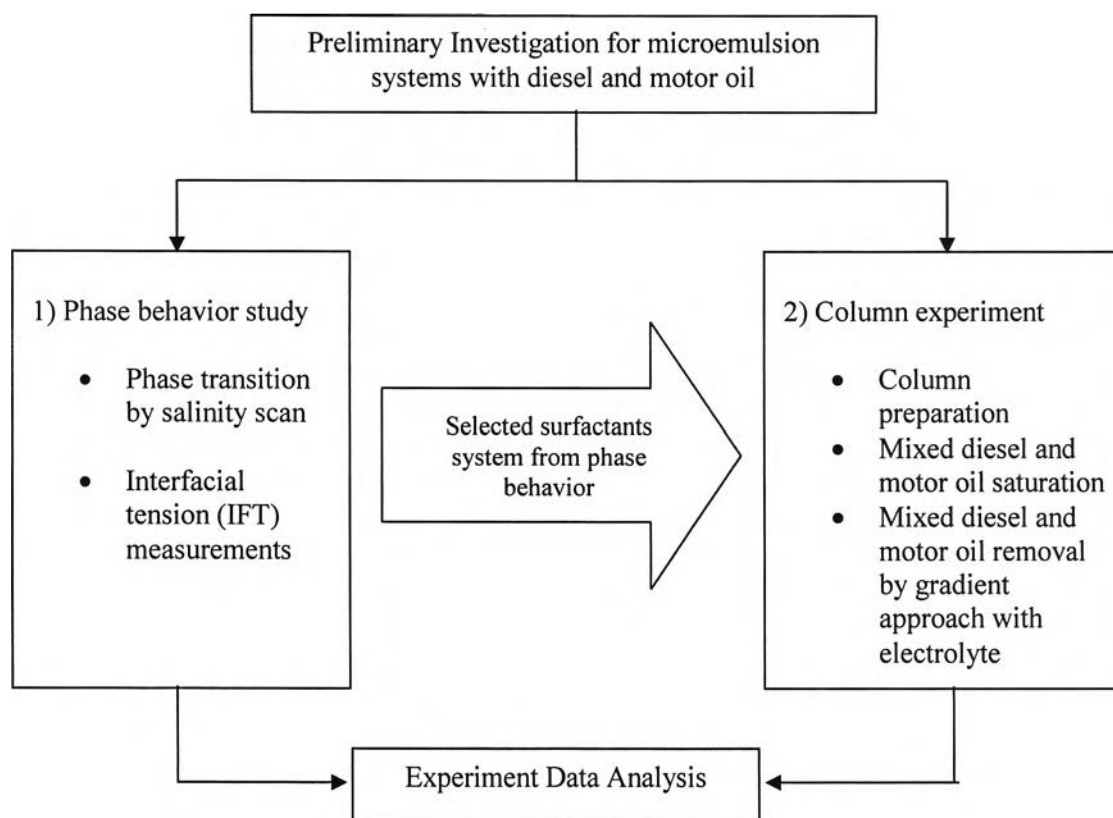


Figure 3.1 Experimental procedure diagram.

3.2.1 Phase behavior study

The preliminary study for the investigation of surfactant systems was conducted with diesel and motor oil in several surfactant systems. Then the phase behavior of the selected system that was able to form microemulsion was examined. From the preliminary results, the system of mixed anionic surfactants, C14 and C15 branched alcohol propoxylate sulfate (4 propoxy groups) (Alfoterra 145-4PO), and sodium dioctyl sulfosuccinate (AOT), were found to be able to form microemulsion with the two oils, diesel and motor oil. The phase behavior for this system was carried out by varying the salinity concentration.

In the microemulsion formation study, the experiment was prepared in 15 ml flat-bottom-screw-cap tubes. Firstly, the well-mixed aqueous solutions comprised of surfactant, water, and salinity at different concentrations was added in the tubes. Then the

oil was added as an aqueous solution to the oil volumetric ratio of unity. After that, each tube was gently shaken by hand for 1 min and left until it reached equilibrium in an incubator at 30 °C as illustrated in Figure 3.2.

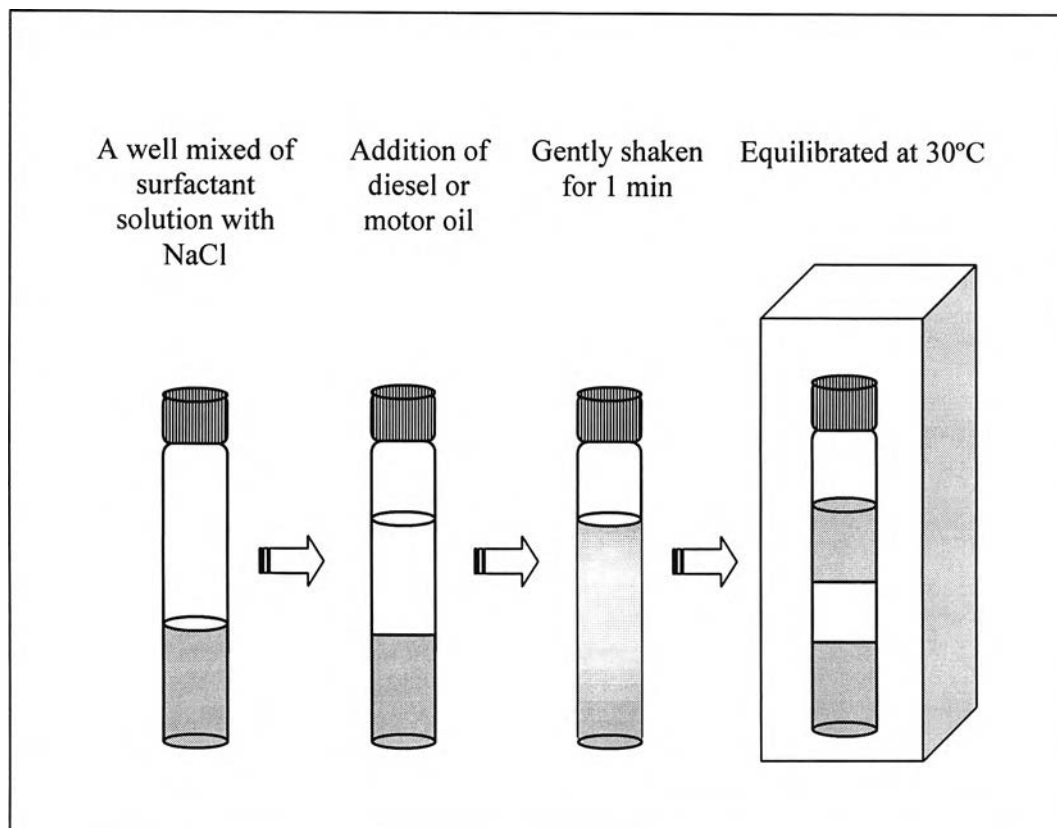


Figure 3.2 Schematic experiment of the phase study.

The equilibrium of the system was observed when the volume of each phase did not change. The phase transitions from Winsor Type I to Type III to Type II microemulsion were visually observed. Interfacial tension (IFT) was measured to characterize the microemulsion formation. The IFT between the equilibrated phases (excess oil and water phases) of each system was measured by a spinning drop tensiometer (Data physics, Model SVT20) to select the best microemulsion system that shows the minimum IFT. From this stage of the experiment, the two optimum salinities that gave minimum IFT for diesel and motor oil was obtained for further use in the column study.

3.2.2 Column study

Column studies were used for determining the performance of the surfactant gradient approach using a salinity scan for mixed diesel and motor oil removal from Ottawa sand. Figure 3.3 shows the experiment of column study.

3.2.2.1 Soil column preparation

The preparation procedure for the soil column was adapted from Pennell (1994) and Childs et al. (2004). The column used in this study consisted of a chromatography column with 2.5 cm ID KONTES equipped with an adjustable flow adapter. Ottawa sand with 20-30 mesh was packed in the column under vibration. The pore volume of the column was determined by measuring the volume replaced in the pores of the packed column. The water was prepared in a separate container and the initial volume of the water was measured. A small amount of water was poured into the column followed by a certain amount of sand until the sand level was a little lower than that of the water. Then the water and sand were gradually added into the column by this manner until the desired level of sand was reached. The volume of water in the container was measured over again after packing the column. The difference of volume before and after packing indicated the pore volume of the column since the water replaced the space of air originally present in the column. Approximately 40 pore volumes of de-aired water was pump upward into the column using a peristaltic pump (Watson-Marlow, Model 323S/D) at a flow rate of 0.60 ml/min. After that, 0.01 M $\text{Ca}(\text{NO}_3)_2$ was put into de-aired water in order to synthesize groundwater and 20 pore volumes of synthesized ground water were introduced at a flow rate of 0.60 ml/min through the column in an upward direction to saturate the column.

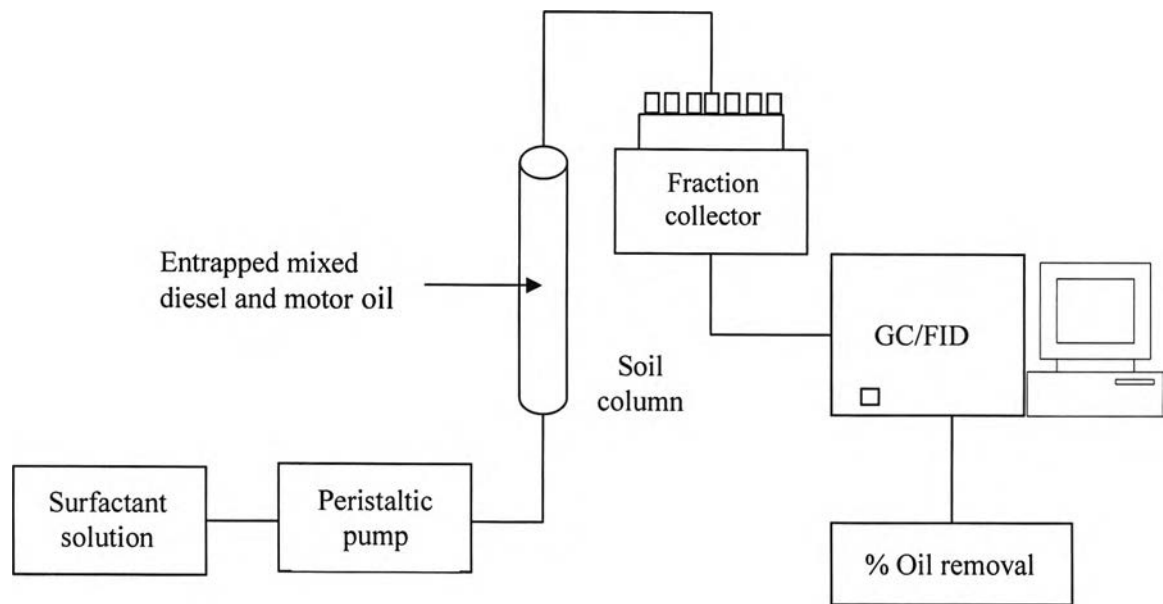


Figure 3.3 Schematic diagram of soil column experiment.

3.2.2.2 Mixed diesel and motor oil saturation

Residual mixed diesel and motor oil saturations were established into the column by a peristaltic pump. To saturate residual oils, 1.5 pore volumes of mixed diesel and motor oil were pumped into the packed column in a downward direction and then the free phase mixed diesel and motor oil was displaced with water in a downward direction at a flow rate of 0.60 ml/min. 10 pore volumes of de-aired water was pumped upward into the contaminated column at a flow rate of 0.60 ml/min and the volume of the displaced free phase mixed diesel and motor oil was measured. The volume of the entrapped mixed diesel and motor oil was calculated from a mass balance as in equation (1) (Pabute, 2005).

$$A = x - (y + z) \quad (1)$$

Where

A = Volume of residual mixed diesel and motor oil in the column (ml)

x = Volume of mixed diesel and motor oil before the contamination procedure (total mixed diesel and motor oil introduced to the column) (ml)

y = Volume of mixed diesel and motor oil after the contamination procedure (exiting column during mixed diesel and motor oil flushing) (ml)

z = Volume of the free phase of mixed diesel and motor oil leaving the column during water flushing (ml)

3.2.2.3 Mixed diesel and motor oil removal from the soil column

The study for the oil removal was conducted with 3 experimental columns using surfactant solutions with the following conditions: (1) a surfactant solution at optimum salinity for diesel, (2) a surfactant solution at optimum salinity for motor oil, and (3) a surfactant gradient approach. In the first two columns, the surfactant solutions at optimum salinity of diesel (0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT, and 1 wt% NaCl) and motor oil (0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT, and 5 wt% NaCl) were pumped continuously through the column in an upward mode at a flow rate of 0.60 ml/min. for 20 pore volumes.

For the third column, the four different solutions were flushed continuously into the column with surfactant gradient system as following details. The first solution included 2 pore volumes of 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT, and 0 wt% NaCl, the second solution included 8 pore volumes of 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT, and 1 wt% NaCl, the third solution included 2 pore volumes of 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT, and 3 wt% NaCl, and the last solution included 8 pore volumes of 0.2 wt% Alfoterra 145-4PO, 0.5 wt% AOT, and 5 wt% NaCl. The column effluents were then continuously collected in 0.20 pore volume increments of 8 ml using a fraction collector (Amersham Bioscience, Model Frac 100). The characteristics of the effluents were observed to determine the mixed oils solubilization and the mixed oils free phase as mixed oils mobilization. The effluent of the mixed diesel and motor oil removal from each column was extracted by hexane. Then the hexane solution was analyzed for diesel and motor oil concentrations by gas chromatography.

3.2.2.4 Analysis of diesel and motor oil

To control experimental analysis for obtaining reliable and accuracy of the results, duplicate analysis was conducted by GC/FID for all of column effluent samples. The average concentrations of individual oils, diesel and motor oil, were used to analyze the oil removal from Ottawa sand.

The saturated mixed diesel and motor oil was removed from the column during surfactant solutions flushing was determined in forms of solubilization and mobilization. The mobilization is free oil separated from aqueous phase while solubilization is the mixed oil solubilized in micelle in aqueous surfactant solution phase. The free mixed oil was determined by volume measurement of the free oil phase while the total mixed oil as well as total individual concentrations of diesel and motor oil removal was analyzed by a gas chromatography. Consequently, it can be categorized into three ways as following details: (a) total diesel, (b) total motor oil, and (c) total mixed diesel and motor oil. The details for analysis and calculation are as follows.

$$T_{\text{mix}} = T_{\text{mix}} (\text{mobilize}) + T_{\text{mix}} (\text{solubilized}) \quad (2)$$

$$T_{\text{mix}} = T_{\text{diesel}} + T_{\text{motor oil}} \quad (3)$$

Where

T_{mix} = Total of mixed oil removal (mg)

$T_{\text{mix}} (\text{mobilize})$ = Total of mixed oil removal in mobilization form (mg)

$T_{\text{mix}} (\text{solubilized})$ = Total of mixed oil removal in solubilization form (mg)

T_{diesel} = Total of diesel removal (mg)

$T_{\text{motor oil}}$ = Total of motor oil removal (mg)

Due to these two oils are miscible, $T_{\text{mix}} (\text{mobilize})$ were determined by volume measurement of free phase of mixed oils as mentioned earlier and calculated in form of weight (mg). The total of mixed diesel and motor oil removal (T_{mix}) as a summation of T_{diesel} and $T_{\text{motor oil}}$ which were determined by GC/FID. Next, solubilization was calculated as the different between the total of mixed diesel and motor oil removal and mobilization.

For determination of Tdiesel and Tmotor oil, total effluent containing solubilization and mobilization phases were extracted by hexane and analyzed for the concentrations by gas chromatography (Hewlett-packard, Model 6890) with an Flame Ionization Detector (FID); column DB-5 with 30 m x 0.53 mm ID, 1.5 μ m film thickness; carrier gas: helium at 48.5 cm/sec; oven temperature: 300 °C for 10 min; injector temperature: 280 °C; detector temperature: 300 °C.