CHAPTER III

METHODOLOGY

3.1 Materials
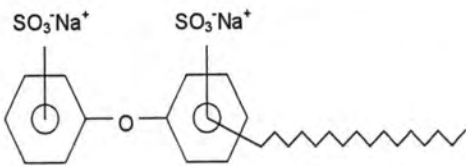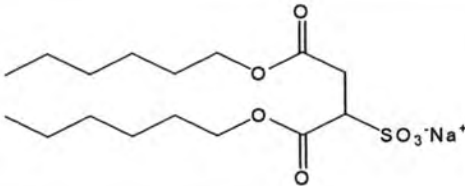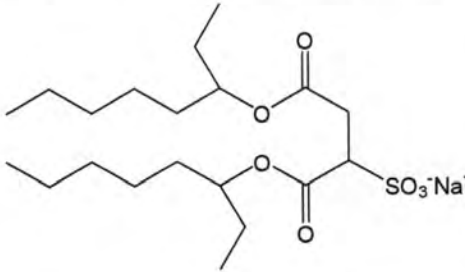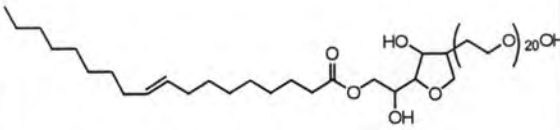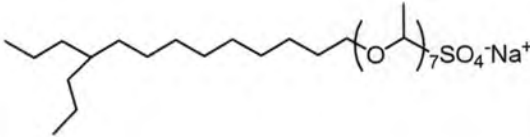
3.1.1 Organometallic contaminants and organic oils

Analytical grade TEL and DBTDC purchased from Sigma-Aldrich Co. were used as contaminants. The *n*-alkane series including pentane (C-5, Fluka), hexane (C-6, Lab-Scan), octane (C-8, Carlo Erba), and decane (C-10, Fluka) were used to establish the empirical relationship between S* and ACN of oil.

3.1.2 Surfactants

There are three major kinds of surfactant used in this research, which are anionic, nonionic and extended anionic surfactants. The anionic surfactants consisted of monoalkyl, diphenyloxide disulfonates (DPDS or trade name of Dowfax 8390 with 36% active) supplied by Dow Chemical Co., Ltd. (West Virginia, USA), sodium dihexyl sulfosuccinate (trade name of Aerosal MA or in short AMA with 80% active); and sodium dioctyl sulfosuccinate (trade name of Aerosal OT or in short AOT with 100% active) were purchased from Fluka Company (USA). The nonionic surfactant, sorbitan monooleate or trade name of Tween80 (20 ethoxy groups with 100% active) was purchased from BDH company (UK). The C16 and C17 branched alcohol propoxylate sulfate with 7 propoxy groups (trade name of Alfoterra 167-7PO with 30.9% active) was used as an extended anionic surfactant donated by Sasol North America Inc. (LA, USA). Some selective properties of these surfactants are shown in Table 3.1. All chemicals in this research were used as received without any further purification.

Table 3.1 Surfactants properties used in this study

Surfactants	Type	Structure	MW (g/mol)	HLB
Monoalkyl, diphenyloxide disulfonates (Dowfax 8390)	anionic		642	71.5*
Sodium dihexyl sulfosuccinate (AMA)	anionic		388.45	16.6*
Sodium dioctyl sulfosuccinate (AOT)	anionic		444.57	10.2*
Sorbitan monooleate (20 ethoxy groups) (Tween80)	nonionic		1308	15.0**
C16 and C17 branched alcohol propoxylate sulfate (Alfoterra 167-7PO)	extended anionic		757	37.1*

Note: * HLB value for anionic surfactants were calculated based on Davies method.

** HLB value for nonionic was developed by Griffin (Tadros, 2005).

3.1.3 Electrolyte

The electrolyte for salinity scan used in this research was an analytical grade sodium chloride (NaCl) with 99% purity purchased from Lab-Scan Ltd. (Ireland).

3.1.4 Synthetic soil

Ottawa sand or silica sand (20-30 mesh) with low iron was used as synthetic soil in this study purchased from Fisher Scientific Co., Ltd. (UK).

3.2 Experimental Procedures

3.2.1 EACN determination of TEL

Equal volume of oil and aqueous surfactant was added in 1 mL tube (0.5 mL each) with stopper. Firstly, aqueous surfactant phase contains mixture of AOT 2 wt% (45 mM), Tween80 2 wt% (15.3 mM) and sodium chloride at various concentration were added into these tubes, then equal volume of n-alkane was added into the tubes. The tubes were immediately sealed, gently shook for 1 min, and equilibrated for 1 day. Solubilization parameter (SP) was quantified by measuring the change of the volume of oil phase and aqueous phase as indicated by a changing of solution height using the digimatic height gages (Model series 192, Mitutoyo). The graphs between SP obtained from oil and aqueous surfactant phases and wt% NaCl were plotted and the S^* was then determined by an intercept of these two graphs. The same procedures were done with other n-alkanes in the series. The empirical relationship between S^* and alkane oils' ACN was established. The mixture of TEL and hexane in a mole fraction ratio of 0.2:0.8 was prepared and used for investigating the EACN of TEL. The experiments needed to be set up in a hood under a nitrogen atmosphere glove bag purchased from Sigma-Aldrich (Germany) in order to prevent TEL degradation and a direct contact to air. The same procedure was applied to other surfactant systems: AOT 2 wt% and AMA 2 wt% (51.5 mM).

3.2.2 DBTDC preparation as TEL surrogate

A number of solutions containing organotin (DBTDC) mixed with solvent(s) at various mole fraction ratios of DBTDC in solvent(s) (such as hexane) were prepared. These mixed oils were tested if they can form microemulsion by the above mentioned procedure with surfactant systems. The mixed oils that yield the same S^* as TEL, was used as the TEL surrogate for further study.

3.2.3 Phase behavior study

The surfactant solutions such as Dowfax8390, AMA, AOT, Tween80, and Alfoterra 167-7PO were prepared at 4 wt% total concentration with varied salt concentration. The microemulsion formation systems were conducted in 1 mL tubes with equal volume of surfactant aqueous solution and oil surrogate. These tubes were then immediately sealed with stopper and gently shook for 1 minute. The samples were stood for 3 days in ambient temperature to ensure that the solutions reached the equilibrium. The supersolubilization region was verified only by visualization as obtained from the point where located in Winsor type I region and gave the transition phase between Winsor type I and III microemulsion.

3.2.4 Solubilization study

The solubilization ability of oil surrogate was investigated using 4 wt% total surfactant concentration (at supersolubilization condition) of three promising surfactant systems screened from previous part. The 10 mL amber tubes with screw cap tubes were used in this experiment. An excess amount of oil surrogate was added into the tube followed by an addition of 5 mL of surfactant solution. The test tubes were subsequently sealed and gently shaken. The aqueous surfactant solutions were carefully collected at 24 hours to ensure that the solubilization of oil surrogate in surfactant micelles reaches an equilibrium condition. The concentration of TEL surrogate (organometallic compound mixed with alkane) was determined by gas chromatography with frame ionization detector (GC-FID) for alkane and inductively

coupled plasma atomic emission spectrometry (ICP-AES) for organometallic compound. The same manner was applied with other surfactant solutions at their supersolubilization condition. The oil solubilization among three promising surfactant systems was compared.

3.2.5 Column study

Column study was established for determining the solubilization potential of the screened surfactant for oil surrogate removal from Ottawa sand.

3.2.5.1 Soil column preparation

The column experiment was conducted in a wet packed silica sand in glass column (2.5 cm inner diameter and 30 cm length) equipped with an adjustable flow adapter purchased from KONTES (Chromatography columns, KONTES CHROMAFLEX^{TM}) to a height of ~15 cm from the bottom end plate. The pore volume was evaluated by determining the volume of water replaced in the sand pore packed in a column. The initial volume of water held in a separate container was measured first. Then, a small amount of water and sand were gradually added into the column until the desired level of wet sand was reached. After packing the column, the volume of remained water in the container was measured over again in order to quantify the certain volume used which represents the pore volume of the column. Approximately 40 pore volumes of degassed water was pump upward into the column using a piston pump (Model QG6, Fluid Metering Inc.) at flow rate of 0.40 mL/min (4.77 cm/hr). The column was then flushed with 20 pore volumes of degassed water containing 0.01 M Ca(NO$_3$)$_2$ at a flow rate of 0.40 mL/min in an upward direction to imitate the groundwater condition prior to contaminate the soil column with TEL surrogate (adapted from Child et al., 2004).

3.2.5.2 Surrogate oil saturation

Residual oil surrogate saturation was conducted by injecting surrogate oil in a downward direction and then flushing with 10 pore volumes of degassed water in an upward direction at a flow rate of 4 mL/min (10 times the flow rate of surfactant solution) to remove the untrapped oil (Acosta et al., 2003a). Residual saturation was calculated based on the difference of initial and final volume oil injecting into the column (see Appendix D).

3.2.5.3 Surrogate oil removal from soil column

Three surfactant systems selected from phase behavior study (section 3.2.3) were flushed into the column individually in downward mode at a flow rate of 0.4 mL/min. The fraction collector (Model Frac 920, Amersham Bioscience) was used to collect the elution from column every 0.25 pore volume as equivalent to 7.6 mL. Then, the removed oil surrogate (organometallic compound mixed with alkane) was determined solely on the total tin (Sn) concentration analyzed by ICP-AES. The characteristics of effluents were observed to determine the surrogate oil solubilization and the free phase oil as oil mobilization. Consequently, the efficiency of oil surrogate removal from soil was calculated based on the amount of tin solubilized and mobilized in the flushing solution.

3.3 Analysis for oil surrogate concentration

3.3.1 Determination of total tin concentration

The oil surrogate (organotin mixed with alkane) concentration was measured based on the total concentration of tin that can solubilized into the surfactant micelles, whereby organotin derivertives were not considered. Consequently, the sample preparation to convert organotin (DBTDC) to tin ions was done as follows.

First step, the samples were digested in an Ethos Plus microwave system with hi-pressure Teflon vessels. Approximately 0.3 mL of samples was pipetted directly into the teflon vessel, then 3 mL nitric acid and 9 mL hydrochloric acid were added and homogenously mixed. A three-step program was set with power of 1,000 Watts: 12.5 minutes to 175°C; 9.5 minutes at 175°C; and vent for 30 minutes. The volume of the final solution was made up to 25 mL with miliQ water (18.2 MΩ). It should be noted that the microwave program was a modified version of EPA method 3051 for oil/sediments/sludges and soils (adapted from Hargreaves et al., 2004). Modifications included the use of aqua regia ($HCl:HNO_3$ of 3:1 by volume) at the first step and heating at 175°C for 9.5 minutes instead of 5.5 and 4.5 minutes, respectively.

Second step, the digested samples were measured for total tin concentration by ICP-AES (Model Vista-MPX, Varian) at emission line at 189.927 nm.

3.3.2 Determination of decane concentration

For quantifying decane dissolved in surfactant solutions, the decane standard with similar metrics as the samples from section 3.2.4 was prepared to construct the calibration curve. For the AMA/Dowfax8390 and AMA surfactant systems, hexane was utilized as the extractant, while dichloromethane was used as the extractant for AMA/Tween80 surfactant system. The extraction step was done by adding 1.5 mL of extractant and NaCl of approximately 1 g into 8 mL vial that contained 3.5 mL of standard at known concentration. The vial was sealed, gently shaken for 1 minute and equilibrated for 20 minutes. Then, the sample in solvent phase was collected in GC vial and further injected to GC-FID (Model 6890N, Agilent Technologies) using DB-1 (100% Di-methyl polysiloxane) as an analytical column. The injector and detector temperatures were 250°C and 280°C, respectively. The column temperature was held at 120°C at 4 minutes, then it was ramped at the rate of 10°C/min from 120°C to 150°C and held for 2 minutes. The retention time of decane at this operating condition is 4.9 min. The same manner was done for determining decane solubilized in surfactant solutions (samples).