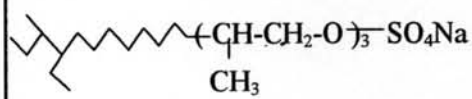
CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Surfactants

There were two types of surfactants used in this research work which are branch alcohol propoxylate sulfate sodium salt, Alfotera 145-3PO, and secondary alcohol ethoxylate, Tergitol 15-S-5. Branch alcohol propoxylate sulfate sodium salt, Alfotera 145-3PO in 28.7% solution used in this research was a commercial grade anionic surfactant supplied by Dow Chemical Co. Secondary alcohol ethoxylate, Tergital 15-S-5 in 100% solution used in this research was a commercial grade nonionic surfactant supplied by Dow Chemical Co. Table 3.1 shows general properties of the two studied surfactants used in this study.

Table 3.1 Properties of surfactants used in this study

Chemical name	Chemical structure	Mol. wt.	HLB
Alfoterra 145-3PO		595	-
Tergitol 15-S-5	$CH_3(CH2)_{15}$-$O(CH_2CHO)_5H$	415	10.6

3.1.2 Studied Oil

Motor oil used in the study is commercially available for use in gasoline engines, type SAE 10W-30 (Castrol GTX). As the motor oil used in this research is a commercial product and can vary in composition, the same batch of oil was used throughout this research.

3.1.3 Distilled Water

Distilled water was used throughout this research for preparing aqueous surfactant solutions and hard water for washing step and rinse step.

3.1.4 Electrolyte

Sodium chloride (NaCl), analytical purity grade, was used as an electrolyte and purchased from LabScan Asia CO, Ltd.

3.1.5 Dyed Oil

Oil red O (Solvent Red 27, CI. NO. 26125) was purchased from Aldrich Chemical Company, Inc. It was used for preparing dyed oil solution before being applied on the fabric.

3.1.6 Fabrics

Fabrics for detergency tests, the standard unsoiled cotton, polyester and polyester/cotton blend (65/35), were purchased from Test Fabrics Co. (Middlesex, NJ, USA). The specific surface areas of the three testing fabrics are shown in Table 3.2.

Table 3.2 The surface area of the standard fabrics.

Fabrics	**Specific surface area (m^2/g)**
Cotton fabric	4.326
Polyester/Cotton blend (65/35)	3.215
Polyester fabric	2.500

3.1.7 Commercial Detergent

A commercial liquid detergent available in Thai market was also used in order to compare the detergency performance with the selected formulation. The composition of the commercial detergent contained of 4% sodium linear alkybenzene sulphonate; 2% ethoxylate alcohol; and, 8.5% sodium lauryl ether sulphate.

3.1.8 Other Chemicals

Dichloromethane, analytical reagent grade, was used for diluting dyed oil before applied on fabrics. It was purchased from LabScan Asia CO, Ltd.

Iso-propanol, analytical reagent grade, was used to extract the oil from fabric in detergency tests for determining the oil removal from fabrics after washing. It was purchased from LabScan Asia CO, Ltd.

3.2 Methodology

3.2.1 Phase Study

Phase studies were performed by adding an aqueous surfactant solution in flat-bottomed screw-capped tubes. Then the oil was added at a water-to-oil volumetric ratio of unity (1:1). The aqueous surfactant solutions added were prepared with different hardness concentrations. The surfactant and NaCl are based on the aqueous phase with different hardness concentrations (water + surfactants + electrolyte (NaCl) +hardness). When surfactant concentrations are reported, these are based on the total mass. The mixture in each vial was shaken well for 3 min in a water bath for attainment of equilibrium at 30°C which could be reached within a few days to a month, depending on the combination of the system. After equilibration, the height of each liquid phase was measured using a cathetometer (Model TC-II from Titan Tool Supply) having a high precision of $\pm$0.01 mm. The solubilization parameter (SP) as mL of either oil or water dissolved per g of total surfactants. The solubilization parameters of oil (SPo) and water (SPw) are designed as:

$$SPo = \frac{Vo}{Ms} \quad \text{and} \quad SPw = \frac{Vw}{Ms} \qquad \text{..... (Eq.3.1, 3.2)}$$

Where Vo is Volume of oil solubilized, Ms is weight of surfactant, Vw is volume of water solubilized. The IFT values between two equilibrated phases were measured by a spinning drop tension meter (model 500; University of Texas, Austin, TX).

3.2.2 Conductivity Measurement

In microemulsion studies, the measurement of electrolytic conductivity is an approach used to determine microemulsion type (Salager *et al.*, 1983 and 2000; Minana-Perez *et al.*, 1986). This method can be used effectively to determine the type of microemulsion at a low surfactant concentration which is not possible to be observed by human observation. In this study, an oil-to-water ratio of 1:1 was used to form different types of microemulsions by varying NaCl and hardness concentrations. For each condition, the electrolytic conductivity was measured, under gentle stirring with a magnetic stirrer, by using a conductivity meter (Cybersan, con110). Since, the aqueous phase contains a certain concentration of NaCl, the inversion from a water-in-oil microemulsion to an oil-in-water microemulsion is easily monitored by a change of two or more orders of magnitude in conductivity (ms/cm or μs/cm) (Salager *et al.*, 2000). The conductivity results were used to plot the fish diagrams to show the boundaries of microemulsion types.

3.2.3 Fabric Preparation and Soiling Procedure

The fabric was pre-washed to eliminate residues of mill finishing agents that might influence oil removal results. The pre-washing method followed ASTM standard guide D4265-98 (Annual Book of ASTM Standards, 2000). The oil was dyed by the oil-soluble Oil-Red-O dye using the standard method (Goel, 1998), before being applied on the fabrics. Approximately 0.1 g of the oil-soluble dye having λ_{max} around 520 nm in 100 mL of the oil was prepared for use as colored soil for detergency experiments. The colored oil was filtered until clear. The soiling procedure was done by diluting 10 mL of the clear dyed oil with dichloromethane (or dimethyl chloride) to 100 mL. The fabric was folded and put in a glass container into which the dyed oil solution was poured until the fabric was completely submerged. It was allowed to stand for 1 min. The soiled fabric was then unfolded and laid on a flat plate in a ventilated hood at room temperature overnight in order to dry the soiled fabric. After drying, the soiled fabric was cut into 3x4 inch swatches in the warp and weft directions. It has to be marked to assure that all specimens in the same test series are strained and graded with the same fabric orientation. All soiled swatches

were kept in a sealed glass container before use. By using this soiling method, the average weight ratio of oil to fabric was approximately 0.15. All soiled swatches were freshly prepared for each set of laundry experiments since a different aging of the soil on textile has an effect on detergency results.

3.2.4 Laundry Procedure

Detergency experiments were carried out by using a terg-o-tometer (Copley, Model DIS 8000). The terg-o-tometer simulates home washing-machine action in a bench scale unit. The washing experiments were performed in 1000 mL washing solution with 20 min washing time with an agitation speed of 110 rpm. A 3-min first rinse and 2-min second rinse were performed with deionized water (DI water or distilled water) under the presence and absence of hardness. Temperatures of both washing solution and rinse water were maintained at 30°C. Three swatches were washed in each bucket for one cycle as replicates.

3.2.5 Detergency Measurement

Detergency performance is quantified by 2 methods as reflectance measurement and oil removal measurement. For Reflectance measurement, detergency performance was determined by reflectance measurement of pre-wash and post-wash swatches and calculated in terms of the percentage of detergency (%D). Reflectance measurements of the unsoiled swatches, the pre-wash soiled swatches and post-wash soiled swatches were conducted by a colorimeter (Hunter Lab, Color Flex). The percentage of detergency is calculated by the following equation (Annual Book of ASTM Standards, 2000).

$$\%Detergency = [(A - B)/(C_0 - B)] \times 100 \quad \text{..... (Eq.3.3)}$$

Where A is the average reflectance of the soiled swatches after washing, B is the average reflectance of the soiled swatches before washing and C_0 is the average reflectance of the unsoiled swatches before washing.

For oil removal measurement, detergency performance was quantified by percentage of oil removal. Oil removal is a portion of residual oil on the swatches to be washed out during the detergency process. The residual oil was extracted by submerging a swatch in isopropanol overnight at room temperature, and then the absorbance of the extracted solution was measured at 520 nm wavelength by an ultraviolet/visible spectrophotometer (Hewlett-Packard, 8452A). The residual concentration of oil is calculated from the calibration curve of control oil solution, which plots between colored oil concentration and absorbance. The oil removal (%) was obtained from the values of oil levels on the swatch before and after wash. For comparisons, a commercial liquid detergent product (CP) was also used for the detergency experiments under the same laundering conditions.

3.2.6 Dynamic Interfacial Tension Measurement

Dynamic IFT was measured by a spinning drop tension meter (University of Texas, 500). The heavy phase (or dense phase) was the aqueous washing solution and the light phase was the dyed oil. A volumetric ratio of the aqueous solution to the oil of (100:1) was used to measure IFT values. The diameters of the oil drop were measured as a function of time. The interfacial tension is calculated from the following equation:

$$IFT = e(Vd)^3 n^2 \Delta\rho \qquad \text{..... (Eq.3.4)}$$

Where IFT is interfacial tension (mN/m), e is 3.427×10^{-4} (mN cm^3 min^2/m g mm^3), V is 0.31 (mm/sdv), d is diameter of the measured droplet (sdv), n is number of revolution or speed (rpm) and $\Delta\rho$ is the density difference between the heavy phase and the light phase (g/cm^3).

3.2.7 Contact Angle Measurement

Contact angles of the oil drops containing different surfactant concentrations at the fabric/water interface were determined by using plates which were made by fusing the testing fabric used in the washing experiments onto clean

glass slides. The fused fabric surface became smoother than that of standard Mylar plate, giving more reproducible contact angles.

3.2.8 Work of Adhesion and Work of Cohesion Measurement

The oil removal can be explained by the work of adhesion and the work of cohesion. The measurements combine with the interfacial tension data and the contact angle data. The work of adhesion (W_a or $W_{O/B}$) and the work of cohesion (W_c) are calculated from the following equation 3.5 and 3.6, respectively.

$$W_{O/S(B)} = \gamma_{SB} + \gamma_{OB} - \gamma_{SO} = \gamma_{OB}(\cos\theta + 1) \quad \text{..... (Eq.3.5)}$$

$$W_C = 2\gamma_{o/w} \quad \text{..... (Eq.3.6)}$$

Where, γ_{OB} or $\gamma_{o/w}$ represents the interfacial tension between oil and washing solution and θ represents the contact angle. W_a represents the affinity of the oil for the substrate and may be taken as an indicator of the efficiency of the "roll up" process (defined as complete drop removal). W_c is indicative of the tendency of the oil drop to fragment and may be taken to reflect the emulsification mechanism (defined as partial drop removal).

3.2.9 Adsorption Isotherm Experiment

This experiment was carried out in order to find the amount of surfactant adsorbed on the fabric as a function of surfactant concentration. Adsorption isotherm experiments were carried out using different concentrations of a mixed surfactants system of 0.1wt.% Alfotera 145-3PO and 5wt.% Tergitol 15S5 at 5 wt.% NaCl. Surfactant stock solutions were diluted with deionized water and added to screw cap vials containing 1 g of fabric. The filled vials were allowed to equilibrate at 30°C in a shaker bath for 2 days. After equilibrium, the filtered samples were analyzed for TOC by using a total organic carbon analyzer (TOC) (Shimadzu, TOC 5000).

3.2.10 Determination of Surface Area of Fabric

Pure cotton, pure polyester and polyester/cotton blend fabrics weighing 1 g were cut into very small pieces and degassed at 100 °C overnight. Then, surface area was determined by nitrogen adsorption BET measurement on a surface area analyzer (Quanta Chrome, Autosorb-1).