# CHAPTER III
# EXPERIMENTAL

## 3.1 Materials.

### 3.1.1 Surfactants

Anionic surfactants, sodium dodecyl sulfate (SDS), sodium decyl sulfate (SDeS), and n-octanoic acid sodium salt ($NaC_8$), all with 99+% purity were supplied by Sigma Chemical Co. (St. Louis, USA) and nonionic surfactant such as nonylphenol ethoxylate (EO group = 9), branched with 99 % from Huntsman Chemical Co. (Melbourne, Australia) was used. Calcium dodecyl sulfate solid was obtained from the reaction of sodium dodecyl sulfate and calcium chloride as shown:

$$2\ C_{12}H_{25}O_4S\ Na + CaCl_2 \longrightarrow (C_{12}H_{25}O_4S)_2\ Ca + 2NaCl$$

The product was refrigerated at to force precipitation then was filtered using the suction pump and was washed with deionized water to remove remaining NaCl salt solution and dried in an oven for 24 hours at 40°C. Calcium chloride dehydrate with analytical grade 99 % was obtained from Ajax Chemical Co. (Auburn, Australia) and methanol with HPLC grade was obtained from Lab-Scan Ltd (Bangkok, Thailand). Doubly distilled and deionized water was used for preparation of all sample solutions.

## 3.2 Sample Preparation

### 3.2.1 Solid Substrate Preparation

Fine 100 mg of CDS powder was compressed to form one solid substrate, an application of 10 tons force with 4 minutes dwelling time for smooth and reflective surface of the pellets using hydraulic press (Bio-rad P/N 15011) with the highly polished stainless steel, 13 mm diameter.

### 3.2.2 CDS Saturated Solution Preparation

One gram of CDS powder was dissolved in doubly distilled and deionized 2 liters of water until saturated then filtered to separate the excess solid. The saturated solution was checked its purity by HPLC using mobile phase ratio of

80% methanol and 20% water then was kept in the water bath at 30°C for use throughout the entire experiments.

3.2.3 Surfactant Mixture Preparation

The saturated CDS solution was used to dilute various concentrations of each different surfactant mixtures. As stock solutions, 500mM of $NaC_8$, 1mM of NPE , and 120 mM of SDeS were prepared.

**3.3 Methods**

3.3.1 Surface Tension Measurement

Kruss K10T model was used which has automatic sensing of maximum force in ring method to prevent the lamella from breaking and allows to repeat measurements and liquid surface height is sensed automatically when using the plate method to provide accurate results, results are reproducible to +/- 0.1 mN/m, and digital platinum resistance thermometer allows sample temperature to be read quickly and precisely. The aqueous solution phase and mixture solution between saturated CDS and subsaturated surfactant solutions with varying concentration were measured by filling the sample vessel at least 20 mL with surfactant solution. Every measurement burning of platinum ring was done to free from contaminants, then digital display of the equipment will give the value of surface tension in mN/m.

3.3.2 Contact Angle Measurement

The sessile drop method is used to measure the contact angle. Measurement is carried out with the Kruss drop shape analysis system. For dynamic measurements, each image of sessile drops on substrate captured by a charge-coupled device was digitized to 744576 pixels per image with 256 different black/white contrasts per pixels and stored in a computer. The resolution of the images is 5.210-3 mm/pixel. For contact angle measurement, the solid precipitate surface was placed in the chamber and 10 μL of the surfactant solution droplet was dropped onto the surface using micro syringe. The photographic pictures of the droplets onto the surface were captured by camera at the controlled temperature of 30°C. The analysis of each stored image for contact angles dealt with the shape of

each sessile droplet as a spherical cap resting on a flat surface and the value of the contact angle was calculated from the drop profiles through software program.

3.3.3 Adsorption Measurement

The surfactant solutions of 20 mL each were added into vials containing 0.5 g of solid CDS precipitate and shaken in a water bath at 30 °C for 5 days then samples were put in a high-speed centrifuge Sorval Super T21, Italy) at 3,000 rpm for 10 minutes before filtering with a filter paper (pore size 0.2 μm) to obtain supernatant solutions which were analyzed for equilibrium surfactant concentrations by using HPLC and UV-VIS spectrophotometer for SDeS and NPE respectively. The amount of adsorption was determined from the difference between the initial and equilibrium concentrations of the surfactant (solution depletion method).

3.3.4 Analysis

The concentration of SDeS was analyzed by HPLC (Perkin Elmer Series 200 binary pump, Avondale, USA) with a conductivity detector (Alltech Model 550) and $C_{18}$ reversed-phase silica column (Alltech Altima, 5 micron, 150 x 4.6 mm). The temperature of the detector was adjusted to 30°C. The carrier solvent was composed of 80% methanol and 20% water at a flow rate of 0.5 mL/min. Each 100 μL sample solution was injected and ran for 15 minutes and result eventually displayed in terms of chromatogram showing separate peaks of different retention time which are were calculated automatically in μV-μS.. The concentration of NPE was analyzed by using a UV-VIS spectrophotometer (Shimadzu 2550, Japan) at a wavelength of 222 nm using the saturated CDS in reference cell. Each sample solution was analyzed in duplicate.