

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

##### 3.1.1 Surfactant

Sodium dodecyl sulfate (NaDS) with 99+% purity obtained from Sigma Chemical Co. (St. Louis, USA) was used as an anionic surfactant without further purification.

##### 3.1.2 Fatty Acid

Dodecanoic acid (C<sub>12</sub>) with 99+% purity obtained from Sigma Chemical Co. (St. Louis, USA) was used to prepare calcium salt of fatty acid without further purification.

##### 3.1.3 Reagents

Calcium chloride dihydrate with UNIVAR grade and methanol with HPLC grade were obtained from Ajax Chemical Co. (Auburn, Australia) and were used to prepare calcium salt of fatty acid without further purification.

##### 3.1.4 Water

Doubly distilled and deionized water with a conductivity of 2  $\mu$  mho/cm was used for preparation of solutions throughout these experiments.

## 3.2 Methodology

### 3.2.1 Preparation of Calcium Soap Precipitate

Dodecanoic acid was initially dissolved in hot methanol and then reacted with calcium chloride solution to obtain calcium soap precipitate. Next, the solution was cooled to 0°C in a refrigerator to complete precipitation. The precipitate was filtered and rinsed with excess water to remove the remaining methanol and calcium chloride before drying in an oven at 40°C for 24 hours and stored in a dessicator. The purity of the precipitate or calcium dodecanoate ( $\text{CaC}_{12}$ ) can be checked by HPLC. The surface area of  $\text{CaC}_{12}$  precipitate determined by BET (Quantachrome Surface Area Analyzer model Autosorp I, USA) was equal to 3.476 m<sup>2</sup>/g.

### 3.2.2 Saturated Solution Preparation

$\text{CaC}_{12}$  was dissolved in doubly distilled and deionized water until the solid no longer dissolved. Then, the solution was placed in a water bath at 30°C and shaken periodically to equilibrate for 4 days.

### 3.2.3 Surfactant Mixture Preparation

The surfactant solution of 100 mM of NaDS in saturated  $\text{CaC}_{12}$  solution was prepared as a stock solution. Then the solution was diluted with a saturated  $\text{CaC}_{12}$  solution to obtain surfactant mixtures with various NaDS concentrations.

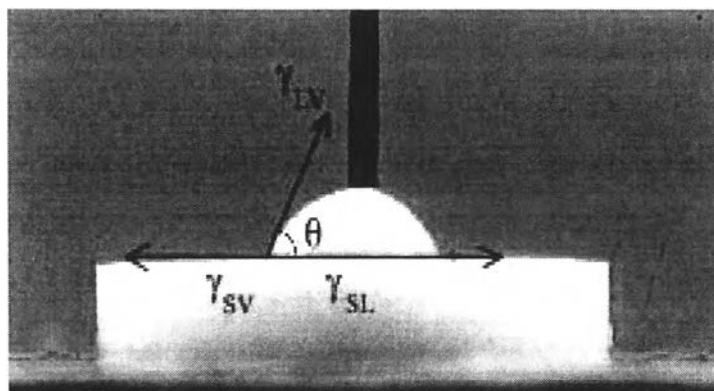
### 3.2.4 Solid Sample Preparation

The solid samples were made by using a hydraulic press (Bio-rad P/N 15011) with a highly polish stainless steel punch and die of 13 mm

diameter (Britain). The sample was compressed at 8 tons force with 3-minute dwelling time to obtain smooth and reflective surface. Samples with non-uniform surfaces were rejected. The pellets were stored in a controlled humidity desiccater at ambient temperature prior to use.

### 3.2.5 Contact Angle Measurement

The contact angles were measured by using the sessile-drop technique. The apparatus consisted of a camera with micro lens and a closed plexiglas chamber with the dimensions of 21 cm x 27 cm x 15 cm. There was a rectangular gate of 10 cm x 15 cm at the front panel for insertion of the sample and a hole of 0.5 cm at the top of the chamber for microsyringe injection for adding or withdrawing solution onto the droplet. The chamber was connected to the thermostat to control temperature. Before measurement, the chamber environment was preheated at  $30 \pm 1^\circ\text{C}$  by switching on the thermostat and saturated with water vapor to prevent drop evaporation effect. When the temperature reached  $30^\circ\text{C}$ , the precipitated surface was placed in a closed plexiglas chamber. The solution drop was introduced onto the surface through a microsyringe and made to advance or retreat by adding or withdrawing a small volume of solution (20-70  $\mu\text{L}$ ). The advancing or receding contact angles were measured by taking photographic pictures 15 second after adding or withdrawing the solution. The contact angles were determined directly from the photographs by drawing the tangent lines between liquid drop and the solid surface using computer with photoshop program as illustrated in Figure 3.1. The measurement was made on both sides of the drop and the average was taken. The contact angles were reproducible to within  $\pm 5^\circ$ .



**Figure 3.1** The sessile-drop contact angle method;  $\theta$  is contact angle,  $\gamma_{sv}$ ,  $\gamma_{sl}$ , and  $\gamma_{lv}$  are solid-vapor, solid-liquid, and liquid-vapor interfacial tensions, respectively.

### 3.3.6 Surface Tension Measurement (ASTM D 1331-89)

The surface tension of surfactant solution was determined by using a DuNuoy–ring technique (KRUSS digital tensiometer, Model K10ST, Germany) with a platinum–iridium ring which had wetting length 199.95 mm, ring-radius 9.6545 mm, and wire radius 0.185 mm. All surface tension measurements were controlled at  $30 \pm 0.5^\circ\text{C}$ . The ring was rinsed by water and heated in a gas flame of an alcohol burner to remove impurity before using. The precision of the surface tension of water was  $\pm 0.3\%$ . The vessel was rinsed with the solution sample before using. The solution was added into the vessel and then the ring was dipped into the solution. Then, the instrument was switched on and the surface tension measured when equilibrium was attained. Each surface tension was an average from at least ten readings. All the necessary precautions were taken to maximize accuracy (Lunkenheimer and Wantke, 1981). The critical micelle concentrations

(CMC) were determined from a break point in plots of surface tension as a function of bulk surfactant concentration.

### 3.2.7 Adsorption Measurement

The subsaturated NaDS adsorption onto surfactant precipitate was determined by measuring the concentration of NaDS before and after adsorption. The NaDS in saturated solutions of  $\text{CaC}_{12}$  of 20 mL was added into a vial containing 0.5 g of  $\text{CaC}_{12}$  precipitate and allowed to equilibrate at 30°C for 4 days in a water bath shaker. Then, the samples were centrifuged by a high-speed centrifuge (Sorval Super T21, Italy) at 3000 rpm for 10 minutes filtered, and the supernatant solutions analyzed for equilibrium NaDS concentration. The concentrations of NaDS adsorbed were determined by HPLC. The amount of NaDS adsorbed on  $\text{CaC}_{12}$  precipitate was plotted as a function of NaDS concentrations.

### 3.2.8 Analysis

The concentration of NaDS was analyzed by HPLC (Hewlett Packard series 1050, USA) with a conductivity detector (Alltech Model 550) and  $\text{C}_{18}$  reverse phase silica column (Altect Altima 5  $\mu\text{m}$  x 150 mm x 4.6 mm). The temperature of the detector was adjusted to 30°C. The carrier solvent was composed of 60% methanol and 40% water at a flow rate of 0.5 mL/min. Each analysis of the sample solution was repeated twice to obtain the reported average concentration.