

## CHAPTER III

### EXPERIMENTAL

#### 3.1. Materials

##### 3.1.1 Surfactants

Sodium dodecyl sulfate (SDS) with 95.5% purity was obtained from Henkel Company. It was purified to be greater than 99% purity by crystallization in aqueous solution and recrystallization in methanol.

##### 3.1.2 Fatty Acids

Sodium salt of octanoic acid (99% purity), sodium salt of dodecanoic acid (99+% purity), decanoic acid (99+% purity), dodecanoic acid (99+% purity), tetradecanoic acid (99-100% purity), hexadecanoic acid (95% purity), octadecanoic acid (90+% purity) were obtained from Sigma Chemical Co.

##### 3.1.3 Reagents

Calcium chloride dihydrate (AR grade) obtained from J. T. Baker Chemicals and calcium hydroxide (AR grade) received from Fluka used as multivalent counterion. Sodium hydroxide which was used as monovalent counterion was Baker analyzed grade, manufactured by J. T. Baker. Methanol was HPLC grade, manufactured by J. T. Baker. The deionized and distilled water was used throughout this study. It had a conductivity of 2  $\mu\text{mho/cm}$ .

## 3.2 Equipment

### 3.2.1 High Performance Liquid Chromatograph (HPLC)

HPLC was used to determine the concentration of anionic surfactants, and fatty acids. Measurements were done with HPLC (Hewlett Packard series 1050) by injecting 300  $\mu$ l of ionic surfactant solution into a column Supelcosil LC-18, dimension 15 cm. x 4.6 mm. x 5  $\mu$ m. and detected the ions by conductivity detector (Alltech 350).

A fatty acid solution was separated by Hewlett Packard Spherisorb ODS2 column, dimension 12.5 cm. x 4 mm. x 5  $\mu$ m. and detected by UV detector (Hewlett Packard series 1050).

The mobile phase for analyzing anionic surfactants was composed of 85% methanol and 15% distilled water. The flow rate was 1 ml/min. The condition for analyzing dodecanoate concentration was MeOH : H<sub>2</sub>O equal to 80: 20 with flow rate of 0.7 ml/min. or MeOH : H<sub>2</sub>O equal to 85: 15 with the flow rate of 1 ml/min.

### 3.2.2 Atomic Absorption Spectrophotometer

Varian Specter AA300 was used to analyze the concentration of calcium and sodium. Absorption measurement of calcium was done in nitrous oxide-acetylene flame at 422.7 nm. wavelength, and sodium was done in air-acetylene flame at 589 nm. wavelength.

### 3.2.3 Hydraulic Press

The hydraulic press (BIO-RAD, P/N 15011) was used to make the pellets that were used as the solid substrate for dropping the saturated solution on. The preparation was done by applying loading 10 tons to press solid powder in 13 mm. diameter die to obtain a pellet.

### 3.3 Methodology

#### 3.3.1 Sample Preparation

3.3.1.1 *Sodium Salt of Fatty Acids* Sodium salt of fatty acids ( $C_{10}$ ,  $C_{14}$ ,  $C_{16}$ ,  $C_{18}$ ) were prepared from the free fatty acids. Each kind of free fatty acid was dissolved in hot methanol and reacted with sodium hydroxide solution, while the solution was placed on the hot plate and stirred until the solution was homogenous. The solution was left in a refrigerator at  $0^{\circ}\text{C}$  to complete precipitation. The precipitate was filtered and rinsed with excess distilled water to remove remaining sodium hydroxide and subsequently dried in an oven at  $70^{\circ}\text{C}$  for 1 day and stored in a desiccator. All of the precipitates were analyzed for the purity by HPLC.

3.3.1.2 *Calcium Salt of Fatty Acids* Calcium salt of surfactants was prepared by 2 methods. First method was used to prepare the calcium dodecyl sulfate ( $\text{Ca}(\text{DS})_2$ ), calcium octanoate and calcium dodecanoate from sodium salt of surfactants. Calcium chloride solution was added into the aqueous solutions of sodium salt of surfactants to obtain the precipitate of calcium salt of fatty acid. Next, the solution was left in a refrigerator over night to complete precipitation. The precipitate was filtrated and rinsed by distilled water. Finally, the filtrated particle was dried in an oven and stored in a desiccator to avoid moisture.

The second method was used to prepare the calcium salt of fatty acids ( $C_{10}$ ,  $C_{14}$ ,  $C_{16}$ ,  $C_{18}$ ) from free fatty acids. The fatty acid was initially dissolved in hot methanol and reacted with clear calcium hydroxide solution. The sequence of obtaining the precipitate was similar to that mentioned in the first method.

3.3.1.3 *Varying Composition between Surfactant and Counterion* In this study calcium salts of SDS, octanoic acid and dodecanoic acid were investigated in case of vary fraction. Solubility product constant

( $K_{sp}$ ) of each calcium salt of fatty acid was initially determined. Each solid of calcium salt of surfactants was dissolved in distilled water until the solution was saturated and kept in equilibrium at 30 °C in a water bath. The equilibrium concentrations of surfactant and calcium ions were analyzed by using HPLC and AAS. Finally,  $K_{sp}$  was calculated. Compositions of surfactant and counterion were varied in such a way that the product of the concentrations is equal to its  $K_{sp}$  value.

3.3.1.4 *Surface Preparation of Solid Sample* A pellet was made in the same manner as KBr pellet for IR sample preparation. First, the surfactants are ground by mortar until become fine powder. Then, one-gram of fine powder is transferred into stainless steel punch and die (13 mm diameter) and pressed at 10,000 kg force using a hydraulic press with a 3 min dwell time. The pellet obtained is moved from the die. The appearance of the surfaces was smooth and reflective. Those samples that exhibited non-uniform surfaces or sticking or picking occurred were rejected. The pellet disks were stored in a 30% relative humidity chamber at ambient temperature prior to use.

### 3.3.2 Contact Angle Measurement

3.3.2.1 *Contact Angle Measurement as a Function of Time* A pellet was placed inside a plexy glass chamber which temperature inside was controlled by thermostat at 30 °C. A dimension of the chamber was 21 cm. x 27 cm. x 15 cm. There was a rectangular gate (10 cm. x 15 cm.) at the front panel for insertion of sample. The topside of this chamber had a small hole for syringe insertion for dropping a solution onto the pellet as shown in Figure 3.1.

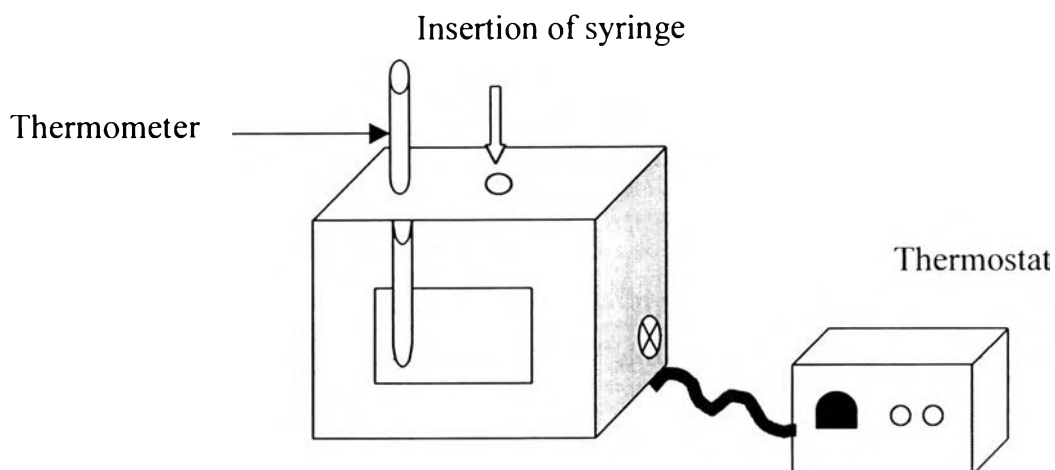


Figure 3.1 The chamber for contact angle measurement.

The chamber atmosphere was equilibrated with the liquid solution to prevent evaporation of drop and maintain at 30 °C. A drop of 20  $\mu\text{l}$  solution was placed on the solid surface using digital micro pipette. The picture of contact angle was captured by video recorder every 5 minutes.

*3.3.2.2 Advancing Contact Angle Measurement* The pellet, which used as a substrate was equilibrated by the liquid solution. A drop of 10  $\mu\text{l}$  solution was placed on the pellet by using a syringe. After that each 10  $\mu\text{l}$  of the solution was slowly applied by the syringe mounted above the drop until drop size became largest. The advancing contact angle was measured immediately (within 10 sec) by photographing after each addition of the solution. The contact angles of sessile drop on the solid precipitates are determined directly by drawing the tangent lines at the interface. The angle made between the solid-liquid tangent and the liquid-gas tangent is the contact angle.

*3.3.2.3 Receding Contact Angle Measurement* The pellet was equilibrated with the liquid solution. A drop of 90  $\mu\text{l}$  solution was placed on the pellet by using a syringe. The step of work was reversely done for advancing angle measurement by withdrawing 10  $\mu\text{l}$  of the solution into the

syringe until the size of the drop become too small but not smaller than 10  $\mu\text{l}$ . The receding contact angle was recorded by photographing every times when the liquid was pulled back.

Table 1 Abbreviations for each surfactant used.

Surfactant	Counterion	Abbreviation
Octanoic acid	H	HC <sub>8</sub>
	Na	NaC <sub>8</sub>
	Ca	CaC <sub>8</sub>
Decanoic acid	H	HC <sub>10</sub>
	Na	NaC <sub>10</sub>
	Ca	CaC <sub>10</sub>
Dodecanoic acid	H	HC <sub>12</sub>
	Na	NaC <sub>12</sub>
	Ca	CaC <sub>12</sub>
Tetradecanoic acid	H	HC <sub>14</sub>
	Na	NaC <sub>14</sub>
	Ca	CaC <sub>14</sub>
Hexadecanoic acid	H	HC <sub>16</sub>
	Na	NaC <sub>16</sub>
	Ca	CaC <sub>16</sub>
Octadecanoic acid	H	HC <sub>18</sub>
	Na	NaC <sub>18</sub>
	Ca	CaC <sub>18</sub>
Decyl sulfate	H	-
	Na	SDS
	Ca	Ca(DS) <sub>2</sub>