CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Surfactants

Sodium dodecyl sulfate (NaDS) and n-octanoic acid sodium salt (NaC_8) both with 99+% purity obtained from Sigma Chemical Co. (St. Louis, USA) were used as anionic surfactant without further purification. Nonylphenoxy poly (ethyleneoxy) ethanol (EO group = 9-10), branched with 99+% purity obtained from Rhodia Inc. (NJ, USA) was used as nonionic surfactant.

3.1.2 Fatty acids

Dodecanoic acid with 99+% purity obtained from Sigma Chemical Co. (St. Louis, USA) was used to prepare calcium dodecanoate (CaC_{12}) precipitate without further purification.

3.1.3 Reagents

Calcium chloride dihydrate and sodium hydroxide both with AR grade were obtained from Ajax Chemical Co. (Auburn, Australia)

Sodium chloride and methanol both with AR grade were obtained from Lab-Scan Ltd. (Thailand).

3.1.4 Water

Doubly distilled and deionized water was used for preparation of solutions throughout these experiments.

3.2 Methodology

3.2.1 Preparation of Calcium Soap Precipitate

Calcium dodecanoate precipitate (CaC_{12}) was prepared by first dissolving dodecanoic acid in hot methanol before reacting with calcium chloride solution. This solution was enhanced to completely precipitate by cooling to 0°C in a refrigerator. 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 desiccator. The purity of the precipitate was checked by HPLC.

3.2.2 Solid Substrate Preparation

The solid substrate was prepared by using a hydraulic press (Bio-rad P/N 15011) with a highly polished stainless steel punch and die of 13 mm diameter. The fine powder of calcium dodecanoate precipitate, which was used as the solid substrate, was compressed with 8 tons force with 3 minutes dwelling time to obtain smooth and reflective surface pellets.

3.2.3 Saturated Solution of Calcium Dodecanoate Preparation

CaC_{12} precipitate was dissolved in doubly distilled and deionized water before shaking in water bath at 40°C for the first two days and 30°C for the next three days. After that, the solution was filtered in order to separate out the excess CaC_{12} precipitate from the saturated solution and kept in water bath at 30°C for use throughout the experiments.

3.2.4 Surfactant Mixture Preparation

The surfactant solution of 50 mM sodium dodecyl sulfate (NaDS) in saturated CaC_{12} solution was prepared as a stock solution. Saturated CaC_{12} solution was used as a diluent to obtain surfactant mixture solution with various NaDS concentrations. NaCl salt was added for preparing the mixture surfactant with different salt concentrations. The same processes but differ in initial subsaturated surfactant concentration were carried out for all of the surfactant mixture solutions between

subsaturated sodium octanoate (NaC_8) and nonylphenoxy ethoxylate (NPE) in saturated CaC_{12} solution.

3.2.5 Contact Angle and Surface Tension Measurement

The contact angle and surface tension were measured by using DSA drop shape analysis instrument (KRUSS Model DSA 10 Mk2, Germany). The sessile drop technique was used in contact angle measurement and the pendant drop technique was used for surface tension measurement. This apparatus consists of a computer, CCD camera and a closed chamber that was connected to the temperature controller as shown in Figure 3.1. The temperature was controlled at 30°C. For contact angle measurement, the solid precipitated surface was placed in the chamber and 10 μL of the surfactant solution droplet was introduced onto the surface using a micro syringe. The photographic pictures of the droplets on the surfaces were captured by the camera, then the value of their contact angles were calculated from the drop profiles by using computer software. In case of surface tension measurement, the liquid drop was produced from the tip of the needle. The camera was used to take the drop profile picture of the droplet while it was still attached to the syringe needle. The values of the surface tension were calculated from the drop profiles of the surfactant solution.

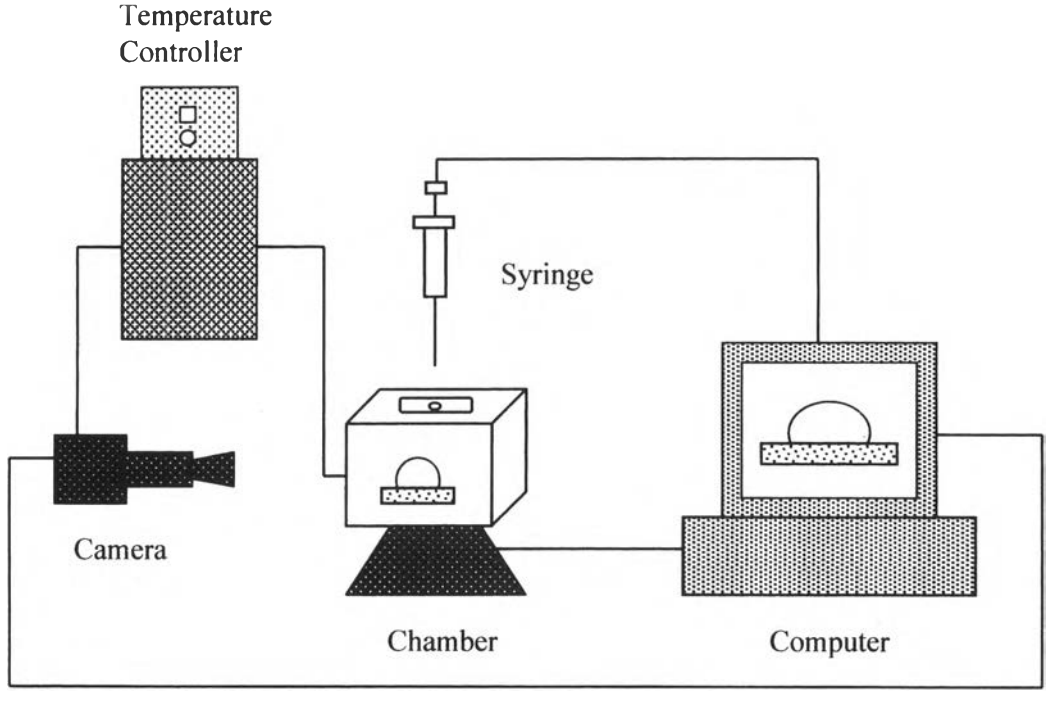

Figure 3.1 Schematic of the DSA instrument.

3.2.6 Adsorption Measurement

The surfactant solutions of 20 mL each were added into vials containing 0.5 g of solid CaC_{12} precipitate and allowed to equilibrate by shaking in a water bath at 30°C for 4 days. After that, the samples were centrifuged by a high-speed centrifuge (Sorval Super T21, Italy) at 3000 rpm for 10 minutes before filtered and then the supernatant solutions were analyzed for equilibrium surfactant concentrations by using HPLC and UV-visible spectroscopy. The amount of adsorption was determined from the difference between the initial and equilibrium concentrations of the surfactant.

3.2.7 Analysis

The concentration of NaDS was analyzed by HPLC (Hewlett Packard series 1050, USA) with a conductivity detector (Alltech Model 550) and C_{18} reverse phase silica column (Alltech Alltima 5 μm x 150 mm x 4.6 mm). The carrier solvent was composed of 60% methanol and 40% water at a flow rate of 0.5 mL/min. The concentration of NPE was analyzed by using UV-VIS spectrophotometer (Shimadzu 2550) at the wavelength 223 nm.

Table 3.1 Abbreviation of each surfactant used

Surfactant	Abbreviation
Sodium dodecylsulfate	NaDS
Sodium octanoate	NaC_8
Nonylphenoxy poly(ethyleneoxy) ethanol	NPE