CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Surfactants

Cationic surfactants, tetradecyl trimethylammonium bromide, hexadecyl trimethylammonium bromide, and octadecyl trimethylammonium bromide obtained from Fluka were purum grade and used without further purification. Sodium dodecyl sulfate (>99% purity) from Sigma Chemical Co.; sodium tetradecyl sulfate (95% purity), and sodium octadecyl sulfate (93% purity), both from Aldrich Chemical Co., were all used without further purification.

3.1.2 Fatty Acids

Doubly distilled and deionized water was used to prepare solutions throughout the experiments. Fatty acids used in this study were dodecanoic acid (>99%, Sigma) and hexadecanoic acid (95% purity, Sigma). Calcium salts of fatty acids were prepared by adding excess amount of calcium chloride into surfactant solutions. The precipitate obtained from reaction was filtered and rinsed with distilled water and dried in an oven at 70° C for 24 hours.

3.1.3 Reagents

Sodium chloride (UNIVAR grade) and sodium bromide (UNILAB grade) were from Ajax Chemical Co. Calcium chloride dihydrate (AR grade) was manufactured by J. T. Baker. Doubly distilled and deionized water was used to prepare solutions throughout the experiments.

3.2 Methodology

3.2.1 Preparation of Saturated Solution

All surfactant solutions were prepared at saturated condition for contact angle measurement. The saturated solutions of cationic surfactants were prepared by dissolving the surfactant in doubly distilled and deionized water until no more dissolution occurs. In the case of tetradecyl and hexadecyl trimethylammonium bromide, the solutions were saturated by adding sodium bromide in different quantities to satisfy the solubility product. In the case of sodium dodecyl sulfate, sodium chloride was used instead of sodium bromide. Since the solutions can remain supersaturation for a long time, all the solutions were cooled to 0°C to force precipitation and were placed in a water controlled bath at 30°C, shaken periodically, and allowed to equilibrate for at least 4 days.

3.2.2 pH Adjustment

The effect of pH on contact angle of two saturated solutions of dodecanoic and hexadecanoic acids was studied by adjusting the pH with hydrochloric acid and sodium hydroxide and measuring the pH with a pH meter (Benchtop pH/ISE Meter, Model 420A with triode pH electrode Model 91-578N).

3.2.3 Solubility Product

The saturated solution of surfactant ions in equilibrium with its precipitates was filtered using a 0.22 μm cellulose acetate membrane and the filtrate solution was analyzed for the equilibrium concentration of surfactant.

The concentrations of surfactant solutions were measured using a total organic carbon analyzer (TOC-5000A, Shimadzu). The bromide concentrations were measured by ion chromatograph (Hewlett Packard Series

1050) with Alltech Anion/R column (10 µm, 150 mm x 4.6 mm) and conductivity detector (Alltech 350). The sample solution was loaded into a 100 µL sample loop and injected into the column using pure methanol as a mobile phase at the flow rate of 1 mL/min. The sodium and calcium concentrations were measured by using atomic absorption spectrophotometer (Varian Spectra AA300). 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.

3.2.4 Solid Sample Preparation

The samples were compressed using a highly polished stainless steel punch and die (13 mm diameter) at 10 tons force using a hydraulic press (Bio-rad, P/N 15011) with 3 min dwelling time and subsequently careful moval from the die. The surface was smooth and reflective. If any sample pellets exhibited non-uniform surfaces, or where sticking or picking occured, they would be rejected. The pellets were stored in a desicator at ambient temperature before use.

3.2.5 Contact Angle Measurement

The sessile drop method was used for measurement of the contact angles. The measurement was done in a closed plexiglass chamber with dimensions of 21 cm x 27 cm x 15 cm. The chamber atmosphere was saturated with water to prevent drop evaporation and was maintained at 30+1 °C by a thermostat. The pellet was placed inside the chamber and a drop of a saturated solution (20 µL - 80 µL) of its own precipitate was placed on the surface using a 100 µL syringe inserted from the top of the chamber. The three-phase contact line of the liquid drop was made to advance or retreat by adding or withdrawing each 10 µL of solution. The photographic pictures of advancing and receding contact angles were taken after adding or withdrawing the solution and waiting for 15 seconds. The contact angles were measured directly from the photographs by drawing tangent lines between the drop and the surface using a computer program as illustrated in Figure 3.1. The reported value of the contact angle was the average of those from the left and right sides of the drop.

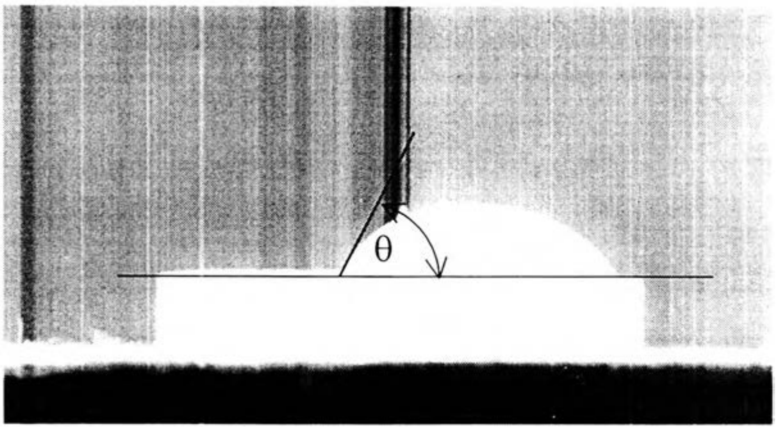

Figure 3.1 Photograph of surfactant solution placed on its precipitate

3.2.6 Cyclic Experiment

Following the aforementioned experiments to measure θ_A and θ_R, at the same place on the solid (syringe is not moved), the advancing, then receding contact angles are measured as was done previously on the virgin surface. This is the 2nd cycle. This procedure was repeated again for the 3rd and subsequent cycles.

The contact angle dependence on time for the cyclic experiment was studied by placing a drop of solution (50 μL) onto the surface and a photograph was taken from t=0 s to t= 20 min in order to measure advancing contact angle. After that, the solution was made to advance until the drop volume was 80 μL and then retreated (70 μL - 40 μL) to measure receding contact angle dependence on time for different drop volumes. The procedure was repeated for subsequent cycles.

3.2.7 Surface Tension Measurement

The surface tension of the solution was measured at 30±0.5 °C using a DuNuoy-ring technique (Kruss digital tensiometer. Model K10ST) with a platinum-iridium ring. The values represent the equilibrium surface tensions which were independent of time and were reported as the average of at least three determinations.