

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

Surfactant

Sodium dodecyl sulfate (SDS) was obtained from Henkel Company and its purity was greater than 96.5 wt%. It was recrystallized in order to increase its purity. The recrystallization process (Perrin, 1988) was done by dissolving SDS into distilled water, and precipitating SDS at low temperature by leaving the filtrate overnight in a refrigerator. In the second step, the SDS precipitate was redissolved in absolute methanol (HPLC grade) and allowed to recrystallize in the refrigerator for overnight. The SDS crystals were filtered and dried. The recrystallized SDS was analyzed for purity by using high performance liquid chromatography (HPLC). It was found to be about 98.9 wt% purity.

Soap

Sodium salt of caprylic acid (n-octanoic acid) with 99+% (capillary GC) purity was manufactured by Sigma Chemical Co. It was used without further purification .

Calcium chloride dihydrate

The calcium chloride dihydrate was analytical reagent grade, manufactured by J.T. Baker Chemical B.V.- Deventer – Holland. It was also used without purification .

Water

Distilled and deionized water was used throughout this study. Its conductivity was 2 $\mu\text{mho/cm}$.

3.2 Analysis Methods

The concentrations of both anionic surfactant and soap were determined by a high performance liquid chromatography. Measurements were done with :

Hewlett Packard series 1050

On-line Vacuum Degasser G1303A

Alltech 350 Conductivity detector

C₁₈ Reverse phase, Supelco, pack column

The mobile phase composition was 85 % methanol (HPLC grade) and 15 % water in 1.0 M sodium perchlorate (NaClO_4) solution. The flow rate was 1.0 ml/min.

An atomic absorption spectrophotometer (AAS Varian 300) was used to analyze the calcium concentration . Conditions were done with :

Ca-lamp

Air-Acetylene frame

3.3 Experimental Methods

3.3.1 Precipitation Phase Boundaries

All experiments in this study were performed at a constant temperature of 30°C by placing all samples in a temperature controller. To

determine the precipitation phase boundaries (hardness tolerance), a series of solutions, with varying concentrations of SDS and soap (when present) and with varying calcium chloride dihydrate concentrations were prepared. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to adjust pH of the prepared solutions. A pH meter (Orion, Model 420 A) was used for pH measurement. Titration of each series of solution, SDS and SO with varying calcium chloride concentrations were made. Surfactant solutions can remain supersaturated for long periods of time before precipitation occurs (Peacock and Matijevic, 1980). Therefore, all solutions were cooled down to 5°C for 24 hours in order to force precipitation. The solutions were then placed in the 30°C water bath, shaken periodically, and allowed to equilibrate for at least 4 days before analytical determinations were made. If a solution was outside of the precipitation region, crystals would redissolve so that the solution became clear. If crystals remained in the solution after equilibration, the initial solution composition was considered to be inside the precipitation region. Using this procedure, the boundary of the precipitation region could be determined. Using simple visual detection with a flashlight and dark background, the concentration of Ca^{2+} that determined a point on the precipitation phase boundary could be defined. Other workers (Matherson et al., 1985) used laser scattering to obtain more accurate phase boundaries in similar systems. It was found that the laser technique could give improved detection which resulted in precipitating anionic / cationic surfactant systems (Stellner et al., 1988). However, the observed precipitation phase boundaries were not significantly different from those obtained using laser techniques. Therefore, visual detection employed in determination of the crystal formation in this experimental study was acceptable.

The composition of both SDS and soap was determined by HPLC. The difference between the initial concentration and the supernatant solution was equal to the concentration of the precipitate formed. The amount of Ca^{2+} remaining in the supernatant solution was analyzed by using an atomic absorption spectrophotometer.

3.3.2 CMC Determination

Surface tension measurements were used to determine the critical micelle concentrations (CMC) of aqueous solutions. The CMC was found by a break in the surface tension versus logarithm of surfactant concentration curve. A DuNuoy – ring tensiometer (Kruss Digital Tensiometer, Model K10ST) with a platinum – iridium ring was used and all the necessary precautions were taken to maximize accuracy (Lunkenheimer and Wantke, 1981). Solution temperatures were held constant at 30°C for each measurement.

3.3.3 Contact Angle Measurement

Contact angles were measured directly by photographing the liquid droplets on the compressed precipitate solid. Solid $\text{Ca}-(\text{DS})_2$ and $\text{Ca}-(\text{O})_2$ were prepared by adding CaCl_2 into the SDS and SO solutions and collected the precipitates. Pellets of SDS, SO, $\text{Ca}(\text{DS})_2$ and $\text{Ca}-(\text{O})_2$ were prepared by the hydraulic press. The saturated solutions of SDS and SO were 0.8 M and 1 M, respectively. For $\text{Ca}-(\text{DS})_2$ and $\text{Ca}-(\text{O})_2$, the saturated solutions used to form a drop on the pellet were made from the solution after its precipitation and filtering. To determine the contact angle, a droplet of each solution placed on the surface of pellet was photographed and measured directly. Temperature was held constant at 30°C for all experiments.