CHAPTER III
METHODOLOGY

3.1 Materials

3.1.1 Carbon Black

The carbon black (type 400 R) used in the study was manufactured by Carbot Corporation. Because calcium concentration was one of some parameters which was considered, and ionic salts including calcium are present highly in the carbon black, so it was necessary to remove these ionic salts by washing.

The carbon black was mixed with distilled and deionized water in the ratio of 1 to 4 and agitated thoroughly. After that the mixture was centrifuged at 2500 rpm for 15 minutes, and water was decanted off. This procedure was repeated 4 times which were sufficient to reduce the calcium concentration in the rinse water to less than 0.2 ppm. Finally the washed carbon was dried at 50 °C for 5 days. The surface area of washed carbon black determined by BET surface area was 96 m^2/g.

3.1.2 Surfactant

Sodium dodecyl sulfate (SDS, $C_{12}H_{25}SO_4Na$) with a purity of 99% was purchased from Sigma Chemical Company (St. Louis, MO) and used without further purification.

3.1.3 Calcium Chloride as Counterion

The reagent grade calcium chloride dihydrate ($CaCl_2.2H_2O$) obtained from Fluka Co., Ltd. (Switzerland) was used in the study. Due to the

chemical hygroscopic nature, it was necessary to dry at 90 °C for 12 hours just prior to manufacturing the stock solution.

3.1.4 pH Adjusting Solution

Sodium hydroxide (NaOH) manufactured by J.T. Baker Chemicals B.V. (Deventer, Holland) was used as received.

3.2 Experimental Procedure

3.2.1 Adsorption Isotherm Experiment

This experiment was carried out in order to find the amount of solution adsorbed on the solid surface as a function of solution concentration.

Twenty ml of solution was added to 2.5 g of washed carbon black in a screw cap vial. The filled vials were allowed to equilibrate at 30 °C for 4 days in a shaking bath. After this time, the equilibrated samples were centrifuged twice by a high speed refrigerated centrifuge (Sorval Super T21) at 30 °C, 16500 rpm for 20 minutes. The supernatant liquid was taken out by disposal pipette, and kept in screw cap vial for further analysis. The supernatant liquid was then analyzed for the residual concentrations of surfactant and calcium.

SDS concentrations were determined by High Performance Liquid Chromatography or HPLC (Hewlett Packard series 1050) with an electrical conductivity detector (model 550 Alltech Associates, Inc.). The conductivity detector was set up at condition of positive signal and temperature of detector was adjusted at 30 °C. The sensitivity of detector for high surfactant concentration and low surfactant concentration was manipulated to 500 μS and 100 μS respectively. Because chloride salt was used in the experiments, it was necessary to separate the surfactant response from chloride response on the HPLC (Bitting and Harwell, 1987).

The separation was accomplished using bicratic operation or gradient elution mode of two mobile phases through C_{18} reverse phase silica column. The primary mobile phase was 30 % by volume of mixture of methanol in water. At this point, surfactant adsorbed on the reverse phase silica and chloride salt eluted from the column. During HPLC operation, the composition of mobile phase was changed gradually from 0 to 2.5 minutes. After that the composition was maintained at 80 % by volume of methanol in water. Finally, the mobile phase was switched back to 30 % methanol to complete cycle. The SDS concentration was analyzed twice in order to obtain mean value of area under curve and the experimental error was less than 5%.

Calcium concentrations were analyzed by Atomic Absorption Spectrophotometer (AAS Varian 300). The accuracy from measurement was less than 3%.

3.2.2 Zeta Potential Determination

The zeta potential of carbon particles in aqueous solution was determined by Zeta Meter 3.0+.

The suspension placed in the electrophoresis cell was prepared by placing 1.5 mg of carbon black in 40 ml of solution. The suspension was required to equilibrate at 30 °C for 24 hours. The pH of equilibrated samples was measured. Before measurement, the electrophoresis cell was cleaned with distilled and deionized water and dried thoroughly. Approximately 5 ml of suspension was rinsed through the cell, and then remainder was loaded into the cell. Before tracking the particles, the appropriate tracking voltage for the colloidal system was selected. For the suspension, which had a high specific conductance, low voltage was required.

For each sample, the zeta potential was measured about 12 values, in order to take an average mean value of zeta potential with small standard deviation. Final surfactant concentrations were calculated by

assuming an adsorption of surfactant on the basis of the separately determined adsorption data.