CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

Hexadecyl trimethyl ammonium bromide (CTAB, 98% purity), tetradecyl trimethyl ammonium bromide (TTAB, 98% purity), and dodecyl trimethyl ammonium bromide (DTAB, 98% purity), cationic surfactants, were supplied by Fluka Co., Ltd. (Switzerland).

For anionic surfactants, sodium dodecyl sulfate (SDS, ≥99% purity) was purchased from Carlo Erba Co., Ltd. (BKK, Thailand), 4-octyl benzene sulfonate sodium salt (SOBS, 97% purity) and sodium octanoate (C8, >99% purity) were purchased from were purchased from Sigma Chemical Company (St. Louis, MO).

AR grade hydrobromic acid (HBr, 48% purity), purchased from Farmitalia Carlo Erba (Thailand Br) Co., Ltd. (BKK, Thailand) and sodium hydroxide (NaOH, 99% purity), purchased from RCI Labscan Co., Ltd. (BKK, Thailand) were used to adjust pH. Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) obtained from Fluka Co., Ltd. (Switzerland) was reagent grade and dried at 90°C for 12 h prior to use due to its hygroscopic nature. All chemicals were used without further purification.

3.1.2 Plastics

Polytetrafluoroetylene (PTFE) was purchased from Chemical Innovation Co., Ltd. High density polyethylene (HDPE) was obtained from Thai Polyethylene Co., Ltd. Polycarbonate (PC), grade Makrolon®PC, was obtained from Bayer Thai Co., Ltd. Polyvinylchloride (PVC), grade SG580, was obtained from Thai Plastic and Chemicals Public Co., Ltd. Acrylonitrile butadiene styrene (ABS) was obtained from IRPC Public Co., Ltd. Polymethyl methacrylate (PMMA) was obtained from Diapolyacrylate Co., Ltd. Polyhexamethylene adipamide (PA66), grade A31, was obtained from SY Smile Co., Ltd.. Polycaprolactone (PCL) was

purchased from Sigma-Aldrich Co., Ltd. All polymer pellets were ground into a powder by a hammer mill. The powder samples were then sieved to obtain particles sizes in the range of 45-125 μm. Finally, powders were rinsed with distilled water for 3-4 times and dried at room temperature before using them.

3.1.3 Carbon Black

Carbon black (type 400R) used in this study was manufactured by Cabot Corporation. The carbon black was thoroughly washed with distilled water several times in order to remove all ionic salts that may affect the adsorption isotherm results. After that, the washed carbon black was dried at 50°C in stagnant air for 5 d.

3.1.4 Paper Fiber

Paper fiber was prepared by pulping common office papers (Xerox, A4 80 GSM) at 5% consistency for 20000 beats at 3000 rpm in a disintegration machine (pulper) to obtain pulp slurry. The pulp slurry was then filtered and washed with distilled water several times over a number zero filter funnel (nominal maximum pore size of 160–250 μm) to remove all fillers and extraneous ions. The washing step was repeated until the concentration of calcium in the filtrate was less than 0.1 ppm as determined by an atomic absorption spectrophotometer (Varian, 300). The pulp fiber was then pressed to remove excess water and dried at 50°C for 2 d.

3.2 Methodology

3.2.1 Surfactant Tension Measurement

The surface tensions of surfactant solutions with various concentrations and pHs by adding an NaOH or HBr solution were measured by the pendant drop technique using a drop shape analysis instrument (Krüss, DSA10) at room temperature (30°C). The critical micelle concentration (CMC) of studied

surfactants was obtained from the break point of the semi-logarithmic plot of the surface tension (γ_{LV}) vs. initial surfactant concentration.

3.2.2 Contact Angle Measurement

The contact angles (θ) of all studied surfactant solutions and water on different plastic surfaces were measured using the sessile drop method by the drop shape analysis instrument (Krüss, DSA10). A volume of 45 μL drop of different surfactant solutions or distilled water was placed onto a studied plastic smooth sheet (size 3 cm. x 3 cm.), which was prepared by compressing the fresh plastic pellets into a smooth sheet beyond the melting point of each plastic, at 10 MPa for 5 min and cooling down at room temperature for 10 min, and the contact angle was measured after 1 min to allow equilibrium to reach. During the measurement, the chamber temperature was kept at 30°C and saturated with water vapor to prevent the evaporation effect.

3.2.3 Surface Area Measurement

The surface areas of plastic powder, carbon black and paper fiber were measured by a surface area analyzer (Quantachrome, Autosorb-1). The surface areas were calculated by measuring the amount of nitrogen gas adsorbed onto the solid surface at liquid nitrogen temperature (-196°C). The samples were out-gassed overnight before the nitrogen adsorption step.

3.2.4 PZC Measurement

Zeta potentials of both paper fiber and carbon black were determined by using a zeta meter (Zeta-meter, 3.0+). A quantity of 0.1 g of studied powdered plastic, 1.5 mg of carbon black or 0.1 g of the paper fiber was added to 40 mL of distilled water. The pH was adjusted by addition of a concentrated NaOH or HBr solution. The samples were then placed in an electrophoresis cell maintained at 30°C. The two electrodes placed at the ends of the cell were connected to a power supply, which created an electric field, causing the charged colloids to move. Velocities of individual particles were tracked via a grid in the eyepiece of the microscope. The

pH was adjusted so that the particles showed no net movement which then indicated the point of zero charge (PZC).

3.2.5 Adsorption Experiments

Adsorption experiments were conducted at 30°C using the solution depletion method in a series of vials with screw caps. For the study of adsorption on hydrophobic surfaces (polymers), 0.25 g of powdered plastic was added into 20 mL of a surfactant solution with different studied cationic or anionic surfactant concentrations. HBr or NaOH were added to adjust the solution pH at 3 or 9, respectively. Solutions were allowed to equilibrate in an incubator at 30°C and shaken by hand twice a day for 5 d. Supernatants were filtered using a Nylon syringe filter with 0.45 μm pore size and were analyzed for the amount of surfactant in the bulk phase by using a total organic carbon analyzer (Shimadzu, TOC-V CSH).

While the study of adsorption mechanism of carbon black and paper fiber, a quantity of 2.5 g of carbon black was added into 20 mL of a surfactant solution and 1.0 g of the prepared paper fiber was mixed with 25 mL of a surfactant solution with different concentrations of C8 or SDS with various calcium ion concentrations. The solution pH was adjusted at 7 or 9 by addition of NaOH. After mixing vigorously by hand, the vials were then allowed to equilibrate in a water bath shaker at 30°C for 4 d. The obtained supernatants from all vials were further filtered by using 0.22 μm cellulose acetate filter membranes and determined surfactant concentration by a TOC analyzer (Shimadzu, 5000A) for C8 and a high performance liquid chromatograph (HPLC) (Hewlett Packard, 1050) with an electrical conductivity detector (Altech, 550) for SDS. The calcium concentration was analyzed by an atomic absorption spectrophotometer (AAS) (Varian, 300).

The surfactant and calcium ion adsorptions were calculated by the concentration difference method. From the adsorption isotherm, the maximum adsorption on various plastics was then determined.