

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

Dehydol LS5, LS7, LS8, and LS9 linear alcohol ethoxylates— $C_{12-14}EO_5$, $C_{12-14}EO_7$, $C_{12-14}EO_8$, and $C_{12-14}EO_9$, respectively—and methyl ester sulfonate (MES) with a purity of 99 % were used in this work. They were supplied by Cognis (Thailand) Co., Ltd. Nonylphenol ethoxylate 9 (NPE-9) was also used in this study, which were purchased from Dow Chemical Co., Ltd. with a purity of 99 %.

Glycerol ($HOCH_2CH_2CH_2OH$, 99 % purity) was supplied from Labscan. Nitrobenzene ($C_6H_5NO_2$, 99 % purity) was purchased from Carlo Erba. Ethanol (C_2H_5OH , AR grade) was purchased from Merck. Ethylene glycol ($HOCH_2CH_2OH$, AR grade) was purchased from LabScan.

All chemicals were used without further purification. All aqueous solutions of surfactants were prepared with DI water.

3.1.2 Plastics

Three types of plastics were used in this work; Poly(tetrafluoroethylene) (PTFE), Poly(vinyl Chloride) (PVC), and Poly(methyl methacrylate) (PMMA). PTFE (Zonyl[®] MP 1300 and Teflon[®] 807-N) was purchased from Dupont (Thailand) Co., Ltd.. PVC and PMMA were kindly provided by Thai Plastics and Chemicals Public Co., Ltd, and Diapolyacrylate Co., Ltd., respectively. PTFE and PVC were in the powder form and were used as received.

3.2 Equipment:

1. Tensiometer with Wilhemy Plate (Krüss, K10T)
2. Grinding machine (Mikro-Feinmühle-Culatti)
3. Sieve (diameter size of 74, 125, 300, and 425 μm)

4. Surface Area Analyzer (BET) (Quantachrome, Autosorb-1)
5. Temperature-controlled incubator (BINDER, KB400/E2)
6. Syringe filter (Verticlean™, nylon 0.45 μm)
7. Total Organic Carbon analyzer (Shimadzu, TOC-V_{CSH})
8. Compression Molding (Wabash, V50H-18-CX)
9. Contact Angle Tester (Krüss, DSA10)

3.3 Methodology

In this work, the experiments were divided into four main parts; surface tension measurement; Powder and Plate Preparation and Characterization; Adsorption Experiment; and Contact Angle Measurement.

3.3.1 Surface Tension Measurement

The surface tension of surfactant solution was determined by Wilhelmy plate technique using tensiometer (Krüss, K10T). All surface tension measurements were controlled at 30 °C. The solution was first half filled into a 20 ml vessel, then a platinum plate with the surface being tested. It was slowly immersed in the solution in order to register the height at which this occurred as the ‘zero depth of immersion’. The plate was then wetted to a set depth to ensure that there was indeed complete wetting of the plate (zero contact angle). When the plate was later returned to the zero depth of immersion, the force it registers could be used to calculate surface tension. The surface tension was measured after 30 min at least to allow equilibrium to occur.

The CMC of surfactants were calculated at the concentrations that the plots of the surface tension versus the surface concentration showed abrupt in the slope. Surface tensions at the CMC (γ_{CMC}), the effectiveness (π_{CMC}), and the minimum area per molecule at the interface (a^s), were also calculated from those plots.

Pure liquids (water, ethylene glycol, nitrobenzene, glycerol, and ethanol) were measured their surface tension. These results were used in Zisman plots.

3.3.2 Powder, and Plate Preparation and Characterization

Hydrophobic materials were used in 2 processes; powder preparation for adsorption experiment and smooth hard surface for contact angle measurement.

3.3.2.1 Powder Preparation and Characterization

PMMA was ground into small particles by using a grinding machine, and then sieving to get particles that were in the range of 74 μm to 125 μm in diameter. Specific surface areas (a_s) of the powders were determined by surface area analyzer (Autosorb-1). Characterized powders were further used in adsorption experiment.

3.3.2.2 Plate Preparation and Characterization

All polymers (PTFE, PVC, and PMMA) were compressed into smooth hard surfaces by using compression molding (Wabash) at appropriate conditions. Prepared plates were used in contact angle measurement.

3.3.3 Adsorption Experiment

0.25 g of hydrophobic powder was filled in surfactant solution with known various concentrations and volume into 20 ml screw cap vial. Vial were shaken and placed in temperature controller incubator and shaken gently 2 times per day for 5 days. Supernatant part of solutions were taken, filtered with 0.45 μm nylon syringe filter, and analyzed equilibrium surfactant concentration by using Total Organic Carbon analyzer (Shimadzu). Carbon concentrations were recorded and converted into surfactant concentrations. Surfactant adsorptions on plastic surfaces were calculated from the concentration difference method, and the adsorption isotherms were plotted.

3.3.4 Contact Angle Measurement

The contact angles of all studied solutions and pure liquids on the studied surfaces were measured with the sessile drop technique by the contact angle tester (Krüss, DSA10). A volume of 10 μl drop of surfactant solution was dropped on

prepared polymer surfaces by using a micro syringe. Each drop had been formed on the tip of syringe and were released from a small height (<1 cm) to minimize inertial effects. The contact angle was measured after 1 min to allow equilibrium to occur by using drop shape analysis software. The water contact angle was measured to ensure that the surface was not contaminated after the procedure.

All experiments were performed at controlled temperature, $30\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$, with relative humidity kept below 35 %. Experiments of each mixture were repeated more than five times on each substrate and the largest difference in the final contact angle observed never exceeded 3° .