CHAPTER III
EXPERIMENTAL

3.1 Materials

A commercially available silica powder (Tokusil 255) was donated by Tokuyama Siam Silica Co., Ltd. and used as the solid substrate in all adsorption experiments. The average particle size and BET surface area were 50 μm and 167 m^2g^{-1} as reported by the manufacturer company. The triblock copolymers, Pluronic L64, $PEO_{13}PPO_{30}PEO_{13}$ (MW=2,900, HLB 15), was kindly obtained as a gift from BASF (Thailand) Co., Ltd. The cationic surfactant, cetyltrimethyl ammonium bromide (CTAB); (>96% purity, MW=364.448) was obtained from Fluka Co., Ltd. (Buchs, Switzerland). The anionic surfactant, sodium dodecyl sulfate (SDS); (>95% purity based on total alkyl sulfate, MW=288.38) was obtained from Sigma-Aldrich Co., Ltd. (Steinheim, Germany). The nonionic surfactant, polyoxyethylene octyl phenol ether ($OPEO_{10}$ or Triton X-100, MW=625) was obtained from Fluka Co., Ltd. (Steinheim, Switzerland). Phenol of 99% purity was purchased from Merck Ltd. (Thailand). 2-naphthol of 99% purity and naphthalene of 98% purity were provided from Aldrich Chemical Company (Steinhiem, Germany). Analytical grade of molybdophosphoric acid and barium chloride dihydrate of 99% purity, were purchaesed from Univar Co., Ltd (Thailand), and concentrated hydrochloric acid of 37% purity which supplied from Labscan Asia Co., Ltd (Thailand). All chemicals were used as received from commercial sources and used without further purification. Deionized water was used throughout the experiments.

3.2 Experimental

3.2.1 Critical Micelle Concentration (CMC)

The aqueous surfactant solutions were diluted by distilled water at different concentrations. Surface tension versus concentration was measured by using the drop shape analysis instrument (Krüss, DSA10). During the measurement,

the chamber was kept at 30°C. The surface tension as a function of the log of surfactant concentration was constructed for each aqueous surfactant solution. The best linear fit to the descending and horizontal lines of the plot was obtained, and their intersection is used to calculate the critical micelle concentration (CMC).

3.2.2 Preparation of Surfactant Concentration and the molybdophosphoric acid reagent

Various surfactant concentrations were prepared by diluting the surfactant stock solution with deionized water in the 100 ml volumetric flask. The molybdophosphoric acid reagent was prepared for the determination of Pluronic concentration by precipitation and complexation method (Nuysink and Koopal, 1981). 2.0 g of molybdophosphoric acid ($H_3Mo_{10}PO_{32}.24H_2O$) and 2.0 g of barium chloride dehydrate were dissolved in 6.0 ml of concentrated hydrochloric acid and made up to 1000 ml by deionized water. This reagent was used for complexation with Pluronic L64 supernatant before characterization.

3.2.3 Adsorption of surfactants onto silica

Both single surfactant and mixed ، conventional surfactant with EO/PO-based block copolymer were used to modify the silica surface. Single surfactant systems were prepared by using different type of surfactant such as cetyltrimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), polyoxyethylene octyl phenol ether ($OPEO_{10}$ or Triton X-100), and Pluronic L64 block copolymer surfactant. Silica powder was dehydrated in an oven at 80°C for four hours before used.

3.2.3.1 Preparation of surfactant-modified silica

The silica powder and differential surfactant concentrations were contained in the 24-mL vials. Those vials were placed into the mechanical shaker bath at 150 rpm and kept at constant temperature of 30°C for 48 hours until the solution achieved equilibrium except in the case of Pluronic surfactant. Those latter vials were kept for 4 days. After equilibration, the silica was separated from the solution by filtering with circle filter paper Whatman no.42. After that the supernatant solutions were sampling to characterize further experiment procedures.

The mixed surfactant systems were also studied by preparing various mixtures of conventional surfactants and block copolymer surfactant:

(i) cationic surfactant, cetyltrimethyl ammonium bromide (CTAB) with block copolymer surfactant, Pluronic L64 (ii) anionic surfactant, sodium dodecyl sulfate (SDS) with block copolymer surfactant, Pluronic L64 (iii) polyoxyethylene octyl phenol ether ($OPEO_{10}$ or Triton X-100) with block copolymer surfactant, Pluronic L64. 15 mL aliquots of surfactant mixture were mixed well with 0.15g silica in 24-mL screw-cap glass vials. Similar adsorption experiments were carried out for the mixed surfactant system.

3.2.3.2 Characterization procedure

The surfactant concentrations were analyzed either by UV-visible spectroscopy (Shimadzu, model UV 2550) and total organic carbon analyzer; TOC (Shimadzsu, TOC 5000). For CTAB and SDS, supernatant concentrations were measured by using total organic carbon analyzer; TOC. For Triton X-100 and Pluronic L64, the supernatant concentrations were measured by using UV-visible spectroscopy at wavelength 285 nm and 216 nm, respectively (Arunwuttipong, 2006; Nuysink and Koopal, 1981). The adsorption of surfactant on the silica was determined by comparing the sample data against known calibration curve.

In the case of Pluronic L64, the method used is an indirect method by measuring the molybdophosphoric acid reagent concentration before and after reacted with PEO group in the Pluronic L64 structure (Nuysink and Koopal, 1981). Pluronic L64 concentrations in supernatant were determined by reacting with molybdophosphoric acid reagent to form precipitates with large anions in the presence of cation as Ba^{2+}. 2 ml of Pluronic L64 supernatant was pipetted into a dry centrifuge tubes. Then, 30 ml of molybdophosphoric acid reagent was added in order to form complexation with Pluronic L64 solution. These centrifuge tubes were placed on the mechanical shaker bath. They were shaken gently, at constant temperature of 20°C for 20 minutes until no more precipitate was observed. After that, the samples were seperated by centrifugation to separate the precipitated complex from the solution (Hermle, model Z383) at 10000 rpm for 20 minutes. Next, 0.75 ml of supernatant was gently transferred into a 50-ml standard flask and made up to volume with deionized water and was centrifuged again at 5000 rpm for 5

minutes. The absorbance of supernatant was measured by UV-visible spectrometer at 216 nm in a 1-cm quartz cuvette against water.

3.2.4 Adsolubilization of organics

3.2.4.1 Preparation of organic solutions

The desired organic solute concentrations were achieved by preparing two stock solutions. The first contained only surfactant at the desired concentration in deionized water. The second was identical to the first one except that it had been saturated with the solute. Various concentrations were then achieved by mixing known amounts of the two solutions. This procedure worked well for phenol. Nevertheless, for 2-naphthol and naphthalene the surfactant/solute solutions were heated to 30°C for 3 days to speed saturation of the solution. They were then allowed to be cooled at room temperature before use.

3.2.4.2 Adsolubilization

Batch adsolubilization experiments were performed to determine the quantity of organic solutes that would preferentially partition into the adsorbed layer of surfactant on the silica. Mixtures of conventional surfactant and block copolymer which used as nonionic surfactant were used to treat the silica surface in order to solubilize the desired organic solutes: phenol, 2-naphthol, naphthalene into admicelle. A 20-ml aliquot of each surfactant solution was pipetted into 20-mL crimp-top glass vials, followed by addition of an excess organic solute, and then the vials were subsequently sealed with Teflon caps. The solutions were shaken in the laboratory shaker bath at 150 rpm for 2 days at 30°C to let the organic solubilize in the aqueous solutions. The remaining organic solute in the solution was measured using UV-visible spectroscopy (Shimadzu, model UV 2550). Phenol, 2-naphthol, naphthalene concentrations were measured at wavelength 270 nm, 274 nm and 275 nm, respectively (Silverstein, 2005).

3.2.5 Data Analysis of Adsorption and Adsolubilization Isotherms

The amount of adsorbed surfactant onto the silica surface was calculated using mass balance principle i.e. the difference between initial and final amount of surfactant in solution before and after shaking would be the amount of mass transferred on to the surface of silica (Asok and Anjali, 2005).The adsorption isotherm was plotted between the amounts of adsorbed surfactant (mmol/g of silica)

versus equilibrium surfactant concentration (mM) whereas the adsolubilization was plotted between the amounts of adsolubilized organic (mmol/g of silica) versus the equilibrium surfactant concentration of organic/maximum of solubility.