CHAPTER III
EXPERIMENTAL

3.1 Materials

The triblock copolymer surfactants (Pluronics) which used in this study were kindly supplied from BASF (Thailand) Ltd. The properties of each are listed in Table 3.1. Hydrophobic silica (AEROSIL R974) was donated by Evonik Degussa (Thailand) Ltd. with a reported average particle size of 50 μm and BET surface area of 170 m^2g^{-1}. Phenol with a purity of 99% was purchased from Merck Ltd. (Thailand). 2-naphthol with a purity of 99% and naphthalene with a purity of 98% were provided from Aldrich Chemical Company (Steinhiem, Germany). 1-dodecanol, sodium dodecyl benzene sulfonate (SDBS), and 1-tetradecanol were provided from Aldrich Chemical Company (Thailand). Analytical grade of molybdophosphoric acid and barium chloride dihydrate with a purity of 99%, were obtianed from Univar, and concentrated hydrochloric acid with a purity of 37% which obtained from Labscan Asia Co., Ltd (Thailand).

Table 3.1 Properties of Pluronics

Pluronics	Structure	EO/PO ratio	MEO	MPO	MW	HLB
P123	EO19-PO69-EO19	0.4286	1725	4025	5750	8
25R4	PO19-EO33-PO19	0.2500	620	2480	3600	8
L64	EO13-PO30-EO13	0.6629	1160	1750	2900	15

3.2 Experimental Procedures

3.2.1 Adsorption Isotherms

Surfactant adsorption isotherms were constructed from batch adsorption data to determine the adsorption isotherms of the surfactants onto hydrophobic silica. The impact of linker molecules on surfactant adsorption were determined by preparing a concentrated solution containing both surfactant and linker molecules and then diluting it with distilled water to provide a series of solution with varying concentration but constant surfactant to linker mole ratio (3:1). 15 mL of various

known concentrations of surfactant/linker molecules was added to 0.15 grams of hydrophobic silica in 24-ml screw-cap glass vials. The vials were shaken in a water bath at 29 °C for 4 days. After 4 days, the solid was separated by filtration and the supernatant surfactants were mixed with the molybdophosphoric acid reagent.The mixtures from this step were separated by centrifugation (Hermle, model Z383) at 12,000 rpm for 25 min. The equilibrium surfactant concentrations were analyzed by measuring the absorbance of UV light at 268 nm. A simple mass balance was used to determine the amount of Pluronics adsorbed onto hydrophobic silica. The adsorption isotherms were constructed by plotting the amount of Pluronics that adsorbed onto hydrophobic silica (mmol/g) versus the equilibrium concentration of Pluronics in the solution (mM).

3.2.1.1 Determination of Surfactant Concentrations

The surfactant concentration was evaluated using a method developed by Nuysink and Koopal (1982). This method is based on a principle of turbidity caused by the complexation between molybdophosphoric acid and the PEO block of Pluronics, which is proportional to the Pluronics concentration. The molybdophosphoric acid reagent was prepared by dissolving 0.5 g of molybdophosphoric acid ($H_3MO_{10}PO_{32}.24H_2O$) with 0.5 g of barium chloride dihydrate ($BaCl_2.2H_2O$) in 1.5 ml of concentrated hydrochloric acid (HCl). The volume was then increased to 250 mL by the addition of distilled water. The initial and final surfactant concentrations were determined by mixing aliquots of surfactant solution (2 ml) with the molybdophosphoric acid reagent (30 ml) and then measuring turbidity using a UV-Visible spectrophotometer (Shimadsu, model UV 2550).

3.2.2 Adsolubilization Isotherms

3.2.2.1 Preparation of Organic Solutions

The required organic solute concentrations were achieved by preparing two stock solutions. The first was contained only surfactant/linker molecules at the required concentration in distilled water. The second was contained with surfactant/linker molecules and organic solutes. The various concentrations of organic solute were produced by mixing known amounts of the two solutions.

3.2.2.2 Adsolubilization Studies

Batch adsolubilization experiments were performed to determine the quantity of organic solutes that would preferentially partition into the adsorbed layer of surfactant on the hydrophobic silica. The experiments were carried out by placing 0.15 g of hydrophobic silica in 20-ml crimp-top glass vials with 15 ml of the solution having constant surfactant/linker concentration but varying quanties of organic solute. The vials were shaken in a water bath at 29 °C for 4 days, which was found to be sufficient to achieve equilibrium.

3.2.2.3 Determination of Organic Solute Concentrations

The adsolubilized amount of organic solute was directly measured by using a UV-Visible spectrophotometer (Shimadsu, model UV 2550). The equilibrium concentrations of phenol, 2-naphthol, and naphthalene were analyzed by measuring the absorbance of UV light at 270 nm, 328 nm, and 277 nm, respectively. After that, adsolubilization amount of organic solute of interest could be then determined, a simple mass balance was used to determine the amount of organic solute that adsolubilized into the adsorbed layer of surfactant on the hydrophobic silica. The adsolubilization isotherms were constructed by plotting the amount of organic solute that adsolubilized into adsorbed layer of surfactant (mmol/g) versus the equilibrium concentration of Pluronics in the solution (mM).