



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

The Pluronic block copolymer surfactants used in this study were kindly supplied from BASF (Thailand) Ltd. The relevant properties of each are listed in Table 3.1. Silica (Tokusil 255) was donated by Tokuyama Siam Silica Co., Ltd. (PPG-Siam Silica Co., Ltd.). The average particle size and BET surface area were 50  $\mu\text{m}$  and 167  $\text{m}^2\text{g}^{-1}$ , respectively. 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 obtained from Univar, and concentrated hydrochloric acid of 37% purity which obtained from Labscan Asia Co., Ltd (Thailand). All chemicals were used as received.

Table 3.1 Properties of Pluronics

HLB range	Pluronics	Structure	EO/PO ratio	MEO	MPO	MW	HLB
1--7	L 31	EO1-PO17-EO1	0.1176	100	850	1000	6.8
	17R2	PO15-EO10-PO15	0.2500	430	1720	2150	6
7--12	P123	EO19-PO69-EO19	0.4286	1725	4025	5750	8
	25R4	PO19-EO33-PO19	0.2500	620	2480	3600	8
12--18	L64	EO13-PO30-EO13	0.6629	1160	1750	2900	15
	10R5	PO8-EO23-PO8	0.9898	970	980	1950	15

### 3.2 Experimental Procedures

#### 3.2.1 CMC determination of surfactants

The surface tensions of various concentrations of copolymer surfactants were determined using a DU NOUY ring tensiometer (Kruss, model K 10 ST). The concentration at which there was no further decrease in surface tension was considered as the CMC of that surfactant.

### 3.2.2 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/supernatant 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 (Shimadzu, model UV 2550).

### 3.2.3 Adsorption of surfactants onto silica

An adsorption isotherm was constructed from batch adsorption data to determine the adsorption isotherms of the tested Pluronic surfactants onto silica. Fifteen mL aliquots of various known concentrations of the Pluronics were added to 1.5 grams of silica in 24-ml screw-cap glass vials. The solution was shaken in a water bath for 48 hours at 29°C. The supernatant was separated from the mixtures by centrifugation (Hermle, model Z383) at 12,000 rpm for 25 min and then mixed with the molybdophosphoric acid reagent. The turbidity was estimated by measuring the absorbance of UV light at 268 nm and compared in the calibration graph. A simple mass balance was used to determine the amount of Pluronics adsorbed onto the adsorbent. The adsorption isotherms of adsorbent were constructed by plotting the amount of Pluronics adsorbed on adsorbent (mmol/g) versus the equilibrium concentration of Pluronics in the solution (mM). The concentration where the slope began to remain unchanged was referred to as the maximum coverage concentration and was used for further experiment procedures.

### 3.2.4 Adsolubilization of organics

#### 3.2.4.1 *Preparation of organic solutions*

The required organic solute concentrations were achieved by preparing two stock solutions. The first contained only surfactant at the required

concentration in deionized water. The second was identical except that it had been saturated with our solute. The 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 40°C for 3 days to speed saturation of the solution. They were then allowed to cool to 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. A 20-ml crimp-top glass vials seal with Teflon-lined septa with a minimum headspace was used with 0.2 g of silica and 20 ml of various surfactant / solute solutions. The vials were shaken in a water bath for 48 hours at 29°C, which was found to be sufficient to achieve equilibrium. The adsolubilization of organic solute was directly measured using Gas Chromatography equipment (Hewlett Packard, model 5890 series 2) with HP-5 column.

### 3.2.5 Determination of surface characteristics by using AFM

#### 3.2.5.1 *Sample preparations*

Samples of silica with adsorbed surfactant alone and with adsorbed surfactant and adsolubilized solute were left to dry at the ambient temperature. The particles were gently put onto a circular metal plate on which a piece of two-sided tape had been attached.

#### 3.2.5.2 *Surface determination*

The surface characteristics were examined using atomic force microscopy (MMAFM-2; Veeco Nanoscope V (Digital Instruments, Santa Barbara, CA) operating in tapping mode under ambient conditions. This method allows imaging of surface topography and phase scans of the modified surfaces. Images were taken for a scan size of 100 – 300 nm, scan rate of 1 Hz, aspect ratio: 1, integral gain: 0.5, and porportional gain: 0.7.