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. Hydrophobic silica (AEROSIL R974) was donated by Evonik Degussa (Thailand) Ltd. The average particle size and BET surface area were 50 µm and 170 m^2g^{-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 obtianed 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	L31	EO1-PO17-EO1	0.1000	100	1000	1100	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	0.7143	1500	2100	3600	8
12--18	L64	EO13-PO30-EO13	0.6571	1150	1750	2900	15
	10R5	PO8-EO23-PO8	0.9898	970	980	1950	15

3.2 Experimental Procedures

3.2.1 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 copolymers, which is proportional to the copolymers 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 1800).

3.2.2 Adsorption of Surfactants onto Hydrophobic Silica

An adsorption isotherm was constructed from batch adsorption data to determine the adsorption isotherms of the tested copolymer surfactants onto hydrophobic silica. Fifteen mL aliquots of various known concentrations of the copolymers were added to 0.15 grams of hydrophobic silica in 24-ml screw-cap glass vials. The solution was shaken in a water bath for 4 days at 29°C. The supernatant was separated from the mixtures by filtration 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 copolymers adsorbed onto the hydrophobic silica. The triplicate experiments were carried out for all experiments and the mean values were used to plot the isotherms. The adsorption isotherms of adsorbent were constructed by plotting the amount of copolymers adsorbed onto hydrophobic silica (mmol/g) versus the equilibrium concentration of copolymers 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.

3.2.3 Adsolubilization of Organic Compounds

3.2.3.1 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.

3.2.3.2 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 0.15 g of silica and 15 ml of various surfactant/solute solutions. The vials were shaken in a water bath for 4 days at 29°C, which was found to be sufficient to achieve equilibrium. The adsolubilization of organic solute was directly measured using a UV-Visible spectrophotometer (Shimadzu, model UV 1800). The triplicate experiments were carried out for all experiments and the mean values were used to plot the isotherms.