



CHAPTER III EXPERIMENTAL SECTION

3.1 Materials

Chemical reagents were purchased from the companies as follows, and were used without further purification. Paraformaldehyde, *p*-cresol and phenol were purchased from SIGMA (USA). 3-Aminopropyltriethoxysilane, sodium sulfate anhydrous, 2,4-dimethyl phenol, lithium chloride, and silica gel (particle size = 0.063-0.2000 mm) were the products of Fluka chemicals (Buchs, Switzerland). Chloroform and diethyl ether were purchased from J.T. Baker Inc. (Phillipsburg, USA). Picric acid, magnesium chloride, potassium chloride, sodium hydroxide and sodium chloride were obtained from Ajax chemicals (Australia). Barium chloride and calcium chloride were purchased from E. Merck (Germany). All solvents were used as received and stocked over 0.4 nm molecular sieve before use.

3.2 Instruments and Equipment

3.2.1 Fourier Transform Infrared Spectrophotometer (FTIR)

Fourier transform infrared (FTIR) spectra were taken from Bruker Equinox 55 spectrophotometer with 16 scans at a resolution of 4 cm⁻¹ in the frequency range of 4000-400 cm⁻¹. Both techniques on ZnSe plate and KBr pellet were used.

3.2.2 Proton Nuclear Magnetic Resonance Spectrometer ($^1\text{H-NMR}$)

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were obtained from Fourier Transform NMR spectrometer ACF 200 MHz of Bruker, Switzerland. Sample was dissolved in deuterated chloroform with tetramethylsilane as an internal standard.

3.2.3 Vortex Mixer

Vigorous shaking of the organic-aqueous mixture was performed by Vortex mixer (GENIE-2, Scientific Industries).

3.2.4 Ultraviolet-Visible Spectrophotometer

Percent extraction of picrate metal salt was determined by Ultraviolet-Visible Spectrophotometry, Perkin Elmer Lambda-16 UV-VIS spectrophotometer.

3.2.5 Atomic Absorption Spectrophotometer

Ion concentration in aqueous phase was determined by an atomic absorption spectrometer Varian SpectrAA-300. The hollow cathode lamps used were sodium cathode lamp for sodium, potassium cathode lamp for potassium, magnesium cathode lamp for magnesium, barium cathode lamp for barium, and calcium cathode lamp for calcium. Ion solution standard was prepared according to the analytical method of Varian.

3.2.6 Elemental Analysis

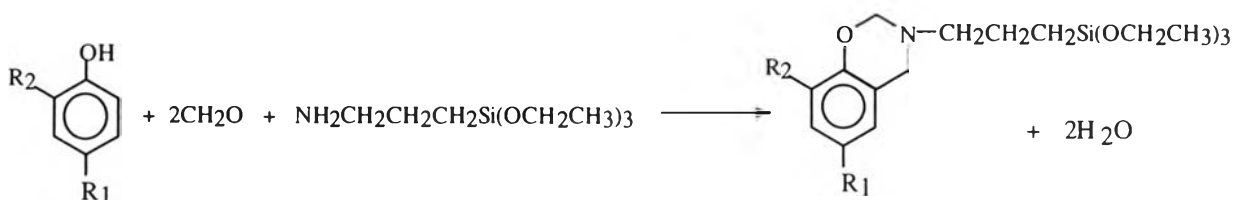
The percent elements were obtained from PE 2400 Series II CHNS/O Analyzer with combustion temperature at 975 °C, reduction temperature at 500 °C and vial receptacle for 1000 runs. The sample was put in tin foil and

weighed approximately for 1-2 mg and analyzed under air atmosphere with O₂ as a combustion gas and He gas as a carrier gas.

3.3 Methodology

3.3.1 Preparation of Silylbenzoxazine Derivatives

The general method of synthesis of silylbenzoxazine is shown in Scheme 3.1.



When R₁ : -H and R₂ : -H for **(1)**

R₁ : -CH₃ and R₂ : -H for **(2)**

R₁ : -CH₃ and R₂ : -CH₃ for **(3)**

Scheme 3.1 Preparation of silylbenzoxazine derivatives

(A) Synthesis of 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine**(1)**

A portion of paraformaldehyde (6.3063 g, 0.2 mole) in 25 mL of chloroform was measured into a 100 mL three neck flask, with continuous stirring. 3-aminopropyltriethoxysilane (22.137 g, 0.1 mole) in 10 mL of chloroform was then added to the paraformaldehyde solution, of which was heated to 85⁰C. The mixture was allowed reacting for 10 minutes. Phenol (9.411 g, 0.1 mole) in 25 mL of chloroform was further added into the reaction to proceed for 3 hrs. The obtained solution was evaporated to remove the solvent

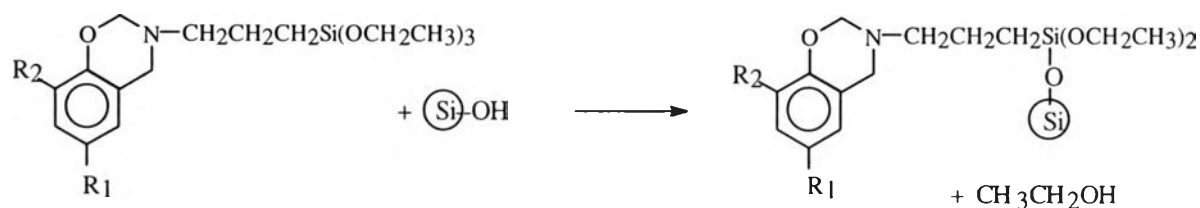
and then dried over sodium sulphate anhydrous. The crude product was then purified by vacuum distillation to remove unreacted starting materials to obtain a colorless liquid at room temperature.

(B) Synthesis of 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine(**2**) and 3-triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine(**3**)

Similarly, (**2**) and (**3**) were prepared as the procedure of (**1**) with *p*-cresol and 2,4-dimethyl phenol as a starting material, respectively.

3.3.2 Preparation of Benzoxazine Monomer Coupled with Silica

The general method of preparation of benzoxazine monomer coupling with silica is shown in Scheme 3.2.



When R_1 : -H and R_2 : -H for (**4**)

R_1 : -CH₃ and R_2 : -H for (**5**)

R_1 : -CH₃ and R_2 : -CH₃ for (**6**)

Scheme 3.2 Preparation of benzoxazine monomer coupled with silica

(A) Preparation of Silica Coupled with 3-triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine(**4**), 3-triethoxysilyl-n-propyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine(**5**) and 3-triethoxysilyl-n-propyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine(**6**)

3-Triethoxysilyl-n-propyl-3,4-dihydro-2H-1,3-benzoxazine (8 mmol, 3 g) was stirred with silica (1 g) and heated to 200°C without solvent for 3 hrs to obtain yellow silica particles. The product was washed thoroughly with chloroform to exclude the unreacted silylbenzoxazine and THF to eliminate the physisorbed silane on silica, followed by drying in vacuo at room temperature for 3 hrs to obtain a light yellow powder.

Similarly, (**5**) and (**6**) were prepared as the procedure of (**4**).

3.4 Ion Extraction Studies

Ion extraction property was studied using Pedersen's technique for both silylbenzoxazine, (**1**)-(b3), and silica surface modified with benzoxazine-functional silanes, (**4**)-(b6). Chloride salts of lithium, sodium, potassium, magnesium, calcium, and barium ions are used as metal ions. $7 \times 10^{-5} \text{M}$ of picric acid and 0.1M of ion salts were dissolved in deionized water so that the UV absorbance at 354 nm becomes one absorbance unit. Benzoxazine solution was prepared by dissolving each monomer, (**1**)-(b3), in chloroform to obtain concentrations of $7 \times 10^{-3} \text{M}$, $7 \times 10^{-2} \text{M}$, and $7 \times 10^{-1} \text{M}$.

Ion extraction was studied as follows; five mL of aqueous alkali or alkaline earth picrate salt solution and 5 mL of benzoxazine solution were mixed vigorously for 1 minute. The mixture was left at room temperature till the aqueous phase and organic phase were completely separated. The aqueous phase

was taken to determine the metal ion concentration by ultraviolet-visible spectrophotometer at 354 nm, i.e., the wavelength of maximum absorption of the picrate ion.

The ion extraction ability of benzoxazine monomers coupled with silica was determined as follows. Six mL of picrate ion solution was shaken with 5 g of each silane-treated silica, (4)-(6), for 3 minutes in a column at room temperature. The solution was drained and the procedure was repeated 10 times. Ion extraction was evaluated by the change picrate concentration in the aqueous phase and observed by ultraviolet-visible and atomic absorption spectrophotometry.