

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

Chemical reagents were purchased from the companies as follows, and were used without further purification except 2-bromo-4-methyl phenol from Aldrich Inc. (USA.). Diethyl ether, methanol and methylene chloride were purchased from J.T. Baker Inc. (Phillipsburg, USA.); methylamine (40% in water), anhydrous sodium sulfate 2,4-dimethyl phenol from Fluka Chemicals (Buchs, Switzerland); *p*-cresol, paraformaldehyde from Sigma (USA.); 1,4-dioxane, sodium hydroxide, sodium chloride, magnesium chloride, potassium chloride and picric acid from Ajax chemicals (Australia); nickel(II) chloride and barium chloride from E. Merck (Germany); and lithium chloride were purchased from Riedel-de Haen (Germany).

3.2 Instruments and Equipments

3.2.1 Fourier Transform Infrared Spectrophotometer (FTIR)

FTIR spectra were obtained on a FT-45A Bio-Rad Spectrophotometer with 16 scans at a resolution of 8 cm⁻¹ in the frequency range of 4000-400 cm⁻¹. Both neat techniques on ZnSe plate and KBr pellet were used.

3.2.2 Nuclear Magnetic Resonance Spectrometer (^1H -NMR, ^{13}C -NMR)

^1H and ^{13}C -NMR spectra were obtained from DPX-300 Avance 300 MHz Digital NMR Spectrometer of Bruker, Switzerland, by courtesy of the National Metal and Material Technology Center (MTEC), Ministry of Science, Technology and Environment, Thailand.

3.2.3 Vortex Mixer

Vigorous shaking of the mixture of organic and aqueous solution was performed by Vortex mixer; GENIE-2 from Scientific Industries for 1 minute.

3.2.4 Ultraviolet-Visible Spectrophotometer

Picrate metal ion concentration in aqueous phase was determined by Ultraviolet-Visible Spectrophotometry, Perkin Elmer Lambda-16 UV-VIS spectrophotometer.

3.2.5 Density Determination Kit

The density measurement was done by Density Determination Kit, Sartorius YDK 01. The kit is composed of the 5 decimal balance equipped with beaker, sample holder, glass plummet and thermometer.

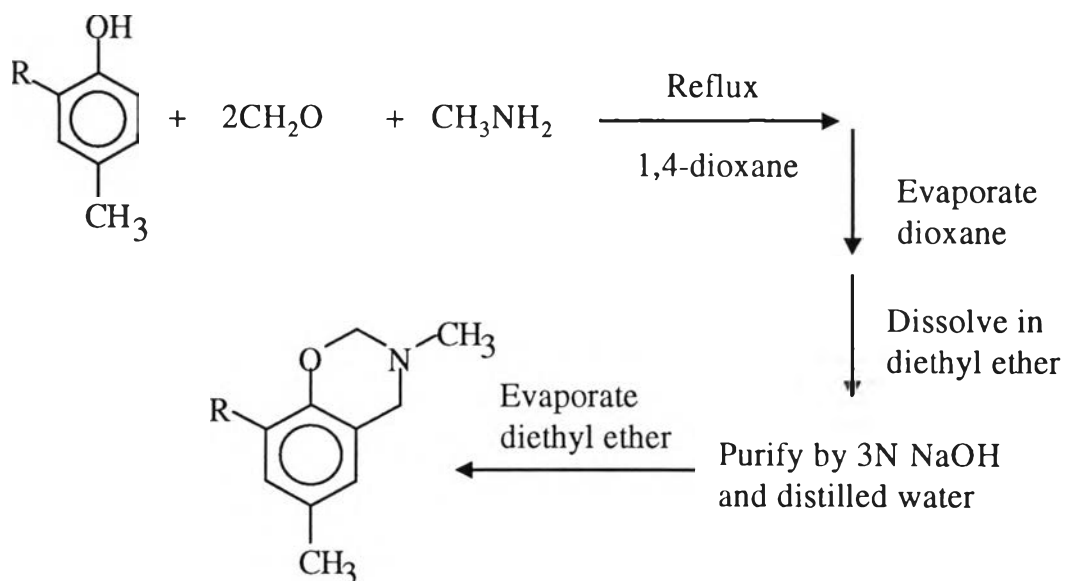
3.2.6 Atomic Absorption Spectrophotometer

Ion concentrations in aqueous phase were detected by a SpectrAA-300 from Varian, Australia. The hollow cathode lamp used depends on the type of ions. Ion solution standard was prepared according to the analytical method of Varian.

3.3 Methodology

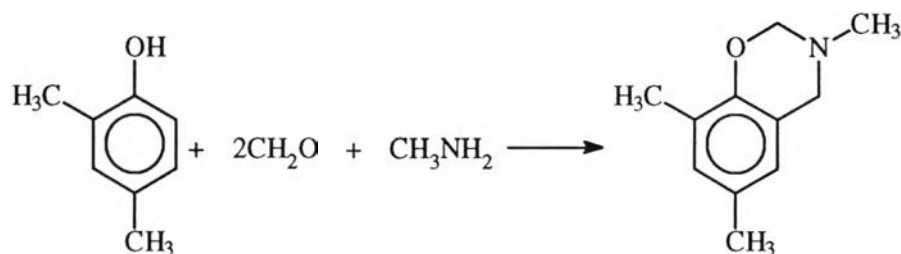
3.3.1 Preparation of Benzoxazine Monomer

The general method of synthesis of benzoxazine monomer is shown in scheme 1:



Scheme 3.1 Preparation of benzoxazine monomer.

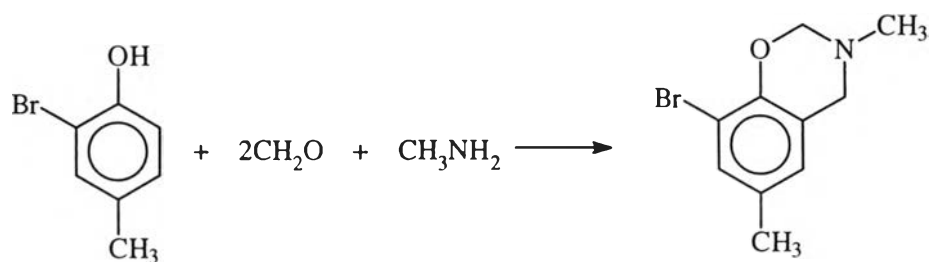
- (1) Preparation of 3-methyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine (Bm1)



Scheme 3.2 Synthesis of 3-methyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine (Bm1).

Methylamine solution (0.2 mole methylamine in 20 ml 1,4-dioxane) was added dropwise to a solution of 0.4 mole para-formaldehyde in 50 ml 1,4-dioxane while being stirred and chilled in ice bath for 20 minutes. The temperature was kept about 0-5°C. 0.2 Mole of 2,4-dimethyl phenol in 50 ml 1,4-dioxane was added with continuous stirring. The mixture was heated to 70-75°C and refluxed for 6 hours and the completion of the reaction was confirmed by thin layer chromatography. After cooling to room temperature, the solvent was removed. The resulting yellow oil was dissolved in 200 ml diethyl ether and washed with 3N aqueous sodium hydroxide solution to remove any unreacted -OH groups till the solution was clear. The solution was dried over anhydrous sodium sulfate for overnight. After that, the ether was removed and the benzoxazine monomer was a very pale yellow liquid. Further purification was done by vacuum distillation which produced a clear, colorless liquid at room temperature.

(2) Preparation of 3-methyl-3,4-dihydro-6-methyl-8-bromo-2H-1,3-benzoxazine (Bm2)

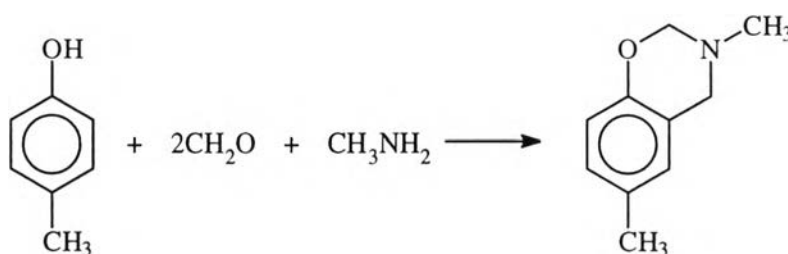


Scheme 3.3 Synthesis of 3-methyl-3,4-dihydro-6-methyl-8-bromo-2H-1,3-benzoxazine (Bm2).

A solution of 0.2 mole of *p*-formaldehyde in 80 ml 1,4-dioxane was stirred with 0.1 mole of methylamine solution in 20 ml 1,4-dioxane while

being chilled in an ice bath for 20 minutes. A solution of 0.1 mole (18.7 g) 2-bromo-4-methyl phenol in 100 ml 1,4-dioxane was added. The mixture was then heated to reflux (93-95°C) for more than 48 hours. After that, the solvent was removed under reduced pressure. The remaining material was dissolved in diethyl ether and washed by 3N aqueous sodium hydroxide solution and distilled water. The clear solution was added with sodium sulfate and kept for overnight. Then the ether was removed and the yellowish liquid was obtained which was further recrystallized in diethyl ether. The clear colorless cubic crystals were formed.

(3) Preparation of 3-methyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine (Bm3)



Scheme 3.4 Synthesis of 3-methyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine (Bm3).

p-Cresol (0.1 mole) in 25 ml 1,4-dioxane was added to a 0-5°C solution of *p*-formaldehyde (0.2 mole) and methylamine (0.1 mole) in 75 ml 1,4-dioxane. The solution was refluxed for 6 hours. The solvent was removed and the residue was dissolved in diethyl ether followed by washing with 3N aqueous sodium hydroxide solution and distilled water. After the clear solution was kept overnight in sodium sulfate and the ether was removed, the obtained monomer was white crystal and further purification was done by vacuum distillation.

3.3.2 Preparation of Ion Solution and Benzoxazine Solution

(1) Pedersen's Technique

Chloride salts of lithium, sodium, potassium, magnesium, calcium, and nickel ions were applied as an ion solution. 10^{-2} M of picric acid and 10^{-2} M of ion salt were dissolved in deionized water. The concentration of ion-picric acid stock solution prepared previously was adjusted to 0.0002 M to obtain the UV absorbance at 354 nm equals to 1. Benzoxazine solutions were prepared by dissolving monomer in methylene chloride to obtain 0.001, 0.01 and 0.1 M.

(2) Titration and AA techniques

Sodium hydroxide and picric acid were utilized for preparing ion solution in deionized water at 0.0002 M. Benzoxazine solution at a concentration of 0.1 M was prepared by dissolving monomer in methylene chloride.

3.4 Monomer Characterization

3.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

In the case of 3-methyl-3,4-dihydro-6,8-dimethyl-2H-1,3-benzoxazine, the obtained liquid sample was characterized by ZnSe cell. The solid samples of 3-methyl-3,4-dihydro-6-methyl-8-bromo-2H-1,3-benzoxazine and 3-methyl-3,4-dihydro-6-methyl-2H-1,3-benzoxazine were measured by KBr method. Solid samples were ground with dried KBr (spectroscopic grade) and subsequently pressed into pellets. A pure KBr pellet was used as background.

3.4.2 Density Measurement

The density of benzoxazine monomer was determined by the water displacement method and calculated as follows:

$$\text{For solid sample:} \quad \rho = \frac{W(a) \times \rho(\text{fl})}{W(a) - W(\text{fl})} \quad \text{Eq.(1)}$$

$$\text{For liquid sample:} \quad \rho(\text{fl}) = \frac{G}{V} \quad \text{Eq.(2)}$$

While

ρ = Density of solid sample (g/cm^3)

$\rho(\text{fl})$ = Density of liquid sample (g/cm^3)

$W(a)$ = Weight of solid in air (g)

$W(\text{fl})$ = Weight of solid in fluid (g)

G = Buoyancy of the glass plummet (g)

V = Volume of the glass plummet (cm^3)

The balance was tared in order to cut the weight of instrument in advance, the solid sample was then weighed on the upper pan of the sample holder for $W(a)$. The balance was tared again with the sample on the upper pan. Then the sample was removed from the upper pan and placed on the lower sieve of the sample holder which sank in the water. Only the number shown on the balance was recorded as $W(a)-W(\text{fl})$. The density of the solid sample was calculated.

The beaker and the glass plummet were set on the balance which was then tared. The liquid sample was added until the level of the liquid is higher than the glass plummet approximately 10 mm. Buoyancy of the glass plummet (G) was recorded due to only the number shown on the balance. The

volume of the glass plummet is 10 cm^3 . The density of the sample was calculated according to the equation(2).

3.5 Ion Extraction Observation

3.5.1 Pedersen's Technique

Pedersen's technique is applied to study the ion extraction property in liquid/liquid system. (Pedersen, 1968). Picric acid is utilized to form picrate salt with metal ions because of its very large acidity constant. Generally, the picrate salt will present in aqueous phase and give the yellow color to the phase while the organic phase is colorless. If the benzoxazine monomer provides a structure as a host molecule and acts as an ionophore, when benzoxazine monomer is added to the system, the picrate salt will be shifted to the organic phase as soon as the host-guest compound is formed. Thus, ion extraction can be investigated by determining the changing of picrate concentration in aqueous phase using UV-vis spectrophotometer at the absorption wavelength of the picrate.

In the present work, ion extraction property of benzoxazine was studied by Pedersen's technique. Picrate ion solution and benzoxazine solution were prepared as mentioned in 3.3.2 (1). Picrate ion solution and benzoxazine solution were taken of each for 5 ml and mixed vigorously for 1 minute. The mixture was left at room temperature till the aqueous phase and organic phase were separated completely. The aqueous phase was taken to determine the metal ion concentration by UV-vis spectrophotometer at 354 nm.

3.5.2 Titration Technique

Picric acid which has very high acidity constant can form salt complex with metal ion. Then picrate salt will form inclusion complex with

ionophore and shift to organic phase. Proton from picric acid will be left in aqueous phase and make pH decreasing. This concept was applied for titration technique. The solution was prepared according to 3.3.2 (2). 0.1 M benzoxazine monomer in methylene chloride was titrated into aqueous picrate ion solution and the pH was observed till the aqueous picrate is neutral.

3.5.3 Quantitative Analysis by Atomic Absorption Technique

The ion concentration was also detected by atomic absorption spectrophotometer. Standard ion solutions were prepared according to the analytical method in order to obtain calibration curve for determining unknown ion concentration. Sodium is partially ionized in the air-acetylene flame. To suppress ionization, potassium chloride solution was added to give final concentration of 2,000 ppm for potassium in all solutions including the blank. The solution was analyzed by using air-acetylene flame at 589.0 nm and flame stoichiometry was shown as oxidizing. Quantitative analysis was operated for the sample solution obtained from 3.3.2 (2).