

CHAPTER II

LITERATURE SURVEY

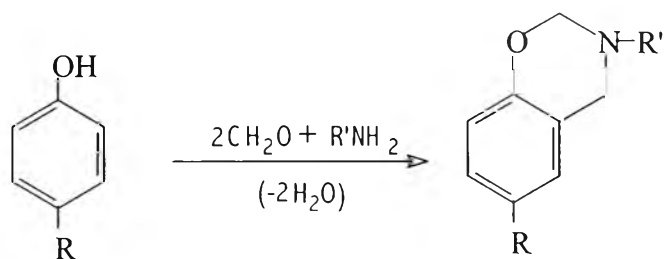


2.1 Inclusion Compound or Host-Guest Compound

The term host-guest is defined by D.J. Cram as follows. The complex composes of two or more molecules or ions holding together in an unique structural relationship by either of the following force, i.e., electrostatic force, hydrogen bonding, ion pairing, π -acid to π -base interaction, metal-to ligand binding, Van der Waals attractive forces, solvent reorganizing, and partial covalent bond such as intramolecular transition state. Host-Guest or inclusion compound has received much attention in the field of separation especially the selective binding with a variety of metal ions. The traditional host-guest compounds can be raised as crown-ether (C.J. Pedersen, 1967), cryptands (J.M. Lehn, 1969), cyclodextrin (R. Breslow, 1993) and calixarene (C.D. Gutsche, 1989).

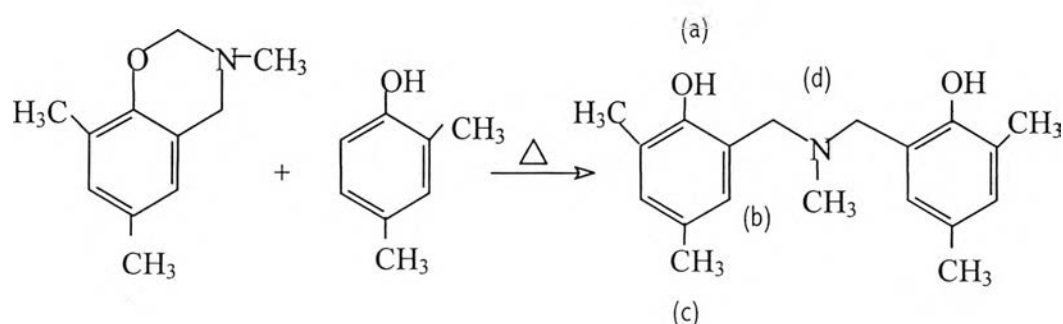
2.2 Benzoxazine : Structure and Conformation

Generally, benzoxazine was originally reported by Holly and Cope in 1944, prepared by Mannich reaction from phenol, formaldehyde and amine. Subsequently, Burke and co-workers (1949) reported that benzoxazine reacts specifically with the ortho position of phenolic compound to form a dimer with methylene-amine-methylene bridge structure. The formation of benzoxazine proceeds according to Scheme 2.1.



Scheme 2.1 Synthesis of benzoxazine monomer.

Dunkers and Ishida synthesized the model dimer of polybenzoxazine based on 2,4 dimethylphenol and methylamine. The formation of dimer benzoxazine proceeds according to Scheme 2.2. Oligomer of phenol-formaldehyde demonstrates conformation with both intramolecular hydrogen bonding between the hydroxyl groups and the nitrogen of the mannich bridge, and intermolecular hydrogen bonding among the hydroxyl groups. Intramolecular H-bonding was reported for the conformation of a pseudo cyclic shape.



Scheme 2.2 Synthesis of benzoxazine dimer.

2.3 Applications of Inclusion Compounds for Metal Ion Entrapment

Inclusion compounds show a potential of versatile applications, such as in 1967, Pedersen exhibited cyclic polyethers complex forming with metal ion in the two phase extraction. The salt-polyether complexes formed by ion-

dipole interaction between the cation (alkaline and alkaline earth metal ions) and the negatively charged oxygen atoms of the polyether ring.

In 1986, Arduni exhibited that the ether ester ligand derived from *p*-*t*-butylcalix(4)arene shows host-guest property. The study on x-ray crystallography and ^1H with ^{13}C -NMR clarified the encapsulation of sodium cation with a 1:1 stoichiometry.

2.4 Inclusion Compound from Calixarene to Benzoxazine

The expectation for benzoxazine as a host compound is reasonable when relates the structure to be calixarene which is well known host-guest compound forming the complex with metal ions or organic molecules (Figure 2.1). The repeating unit of benzoxazine has the hydrophilic hydroxyl group at one side while the hydrophobic benzene ring at the other. Moreover, there are lone pair electrons at oxygen in the hydroxyl group and nitrogen in the tertiary amine linkage an each monomer unit (Scheme 2.2) which are partially similar to the calixarenes.

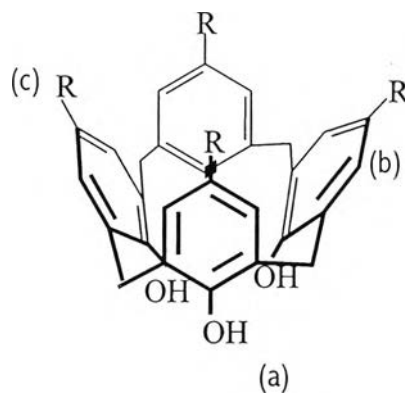


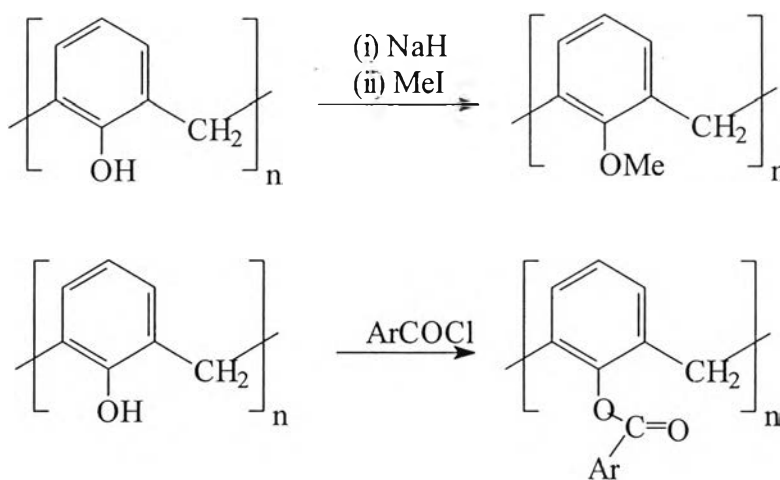
Figure 2.1 Structure of calix[4]arene.

- (a) : Hydroxyl groupHydrophilicity
- (b) : Benzene RingHydrophobicity
- (c) : Functional groupHydrophilicity
- (d) : NitrogenLone pair electron

Chirachanchai *et al.* (1997) demonstrated bisphenol-A benzoxazine oligomer derivative for the ion phenomena. The studies concluded that the ion entrapment efficiency of benzoxazine is related to the Flory-Huggins parameter between the organic solvent and benzoxazine structure.

Phongtamrug reported that benzoxazine monomer also exhibited the ion extraction property with various types of ions. The ion extraction ability of the oligomer and monomer do not show the selectivity either ion sizes or ion charges, leading to the conclusion in molecular assembly formation of benzoxazines.

Roundhill D. M. reported the modified structure of calixarene on the lower rim at phenolic oxygen atoms as shown in Scheme 2.3. Hence, it is our interest to systematic study on benzoxazine opening structure and clarify the molecular assembly for metal ion entrapment of a series of modified benzoxazines.



Scheme 2.3 Esterification at hydroxyl group of calixarenes.

2.5 Scope of the Present Work

In order to clarify the structure of benzoxazine related to the host property, a series of benzoxazine structure has to be studied. The present work focuses on the benzoxazine dimer with a variation of phenol derivatives.

The benzoxazine dimers are also modified by acid chloride at hydroxyl group of phenol ring to clarify the effect of electron rich system to the molecular assembly of benzoxazine. The completion of the work leads to the understanding of the relation between host structure and efficiency in complex formation with alkaline and alkaline earth metal ions.