

## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Supramolecular Chemistry

Supramolecules originally can be claimed as a natural system when a specific molecule or a group of molecules forms a molecular asset to interact with another species of molecule or a group of molecules or ion species (Fritz, 1993). The ideal structure of supramolecules can be referred to the nucleic acid base on pairing system, the double helix of DNA. RNA system, and the oligopeptide molecules. Conceptually, supramolecules are formed by using interaction among two types of molecules under the secondary forces, such as hydrogen bonding, van der Waals, dipole-dipole interaction, polar or nonpolar attractive force, and  $\pi$ - $\pi$  stacking (Rebek, Jr. 1996).

Up to now, supramolecules have been known under the name of host-guest or inclusion compounds. The basic structure of inclusion or host-guest compound is defined as a molecular assembly of host concave and guest convex stabilized under those secondary forces (Fisher, 1894).

Artificial inclusion compounds have been received much attention in order to create a molecule or a group of molecules that can provide a specific interaction to accept another molecule or ion species as guests.

#### 2.2 History of Host-Guest Compound

Host-guest phenomena were first reported by Schlenk (1951) who proposed the honeycomb structure of urea and thiourea. In 1956, Clasen *et al.*

proved the concept of inclusion polymerization by urea and thiourea as a host molecule for butadiene monomer. Pedersen (1960) reported that crown ether interacted with alkali and alkaline earth metal ions as proven by analytical technique. Farina *et al.* (1964), verified that hydrotriphenylene was also a host compound for diene polymerization.

### **2.3 Expectation on Applications**

The host-guest compounds are the assets or assembly of molecules forming with the unique structure recognized each other at the molecular level (Atwood, 1991). In natural system the molecular recognition provides the unique properties that each of individual molecule can not perform, such as ion transport in biosystem, transfer RNA, messenger RNA, DNA, and so on (Lehn, 1995). In artificial system, host-guest compounds are expected for advanced application owing to the specific properties induced from the molecular recognition. The molecular recognition can be when the host interacts with either neutral molecule guest (Sone, 1989), or monomer species (Brochsztain, 1999) or ionic species (Cram, 1985). Thus, the applications of artificial host-guest can be raised as; ultra-high purification (Weber, 1984), dissolution improvement in organic synthesis (Sone, 1989) and polymer prodrug (Brochsztain, 1999) when the guest molecule is neutral species, or waste water treatment (Weber, 1984), ion catalyst (Kitagawa, 1998), when the guest molecule is ionic species, and stereoregular polymer synthesis (Chkvetadzewhen, 1996) when guest molecule is monomer species.

### **2.4 Types of Host Compounds**

The types of host compounds in either artificial or natural system can be categorized into two main types, i.e., macrocyclic and noncyclic type

(Atwood, 1991). Macrocyclic host molecules are defined as a group of molecules bonded covalently to form a cyclic ring with a space to entrap guest molecules. Noncyclic host molecules are a group of molecules aligned in a specific manner to form an assembly giving a channel or layer for guest. The unique feature of macrocyclic is the fixed cyclic structure with hydrophilic or hydrophobic or ionic ring, while that of the noncyclic one is a flexible structure based on hydrogen bonding and van der Waals forces.

The known structures of artificial host compounds for macrocyclic types can be raised as nonactin, enniatin, valinomycin and enterobactin, while for noncyclic types can be raised as DNA, RNA helices (Cram *et al.*, 1974). Macrocyclic artificial host-guest compounds are referred to crown ether, cyclodextrin, and calixarenes, as the first, second, and third host generation, respectively. For noncyclic types, the well-known hosts are cholic acid and its derivatives, and acetylenic alcohol derivatives.

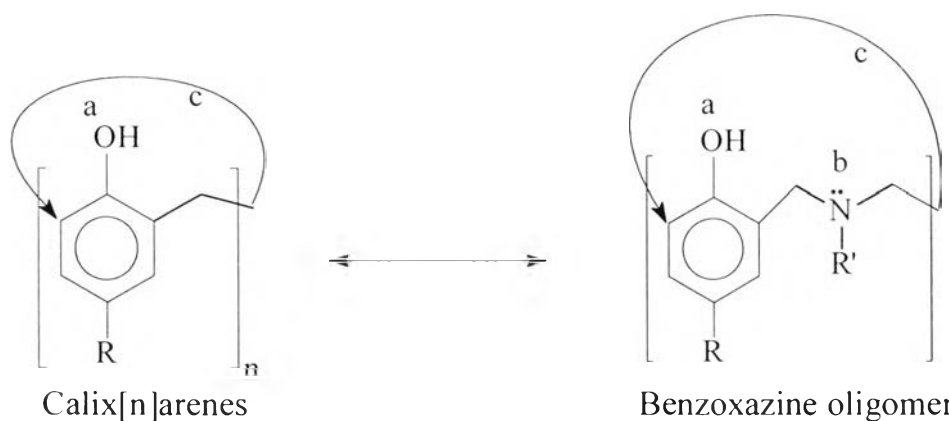
## 2.5 Types of Guest Compounds

In general, types of guests can be neutral species, reactive neutral species or monomer, and ion species. Crown ether is known for the ion dipole interaction to form inclusion complex with metals depending on the polyether ring, e.g., 14-crown-4, 15-crown-5 and 18-crown-6 with cavity diameter for guest in the range of 1.2~ 1.5, 1.7~ 2.2 and 2.6~ 3.2 angstrom, respectively (Pedersen, 1967). Up to now, many reports have clarified that crown ether can form complex with alkali, alkaline-earth metals, heavy metals and so on. Cyclodextrin is reported for the inclusion phenomena relating to the size of the cyclic structure (Breslow, 1993), i.e.,  $\alpha$ -cyclodextrin for benzene and phenol,  $\beta$ -cyclodextrin for naphthalene, 1-anilino-8-naphthalene-sulphonate and  $\gamma$ -cyclodextrin for anthracene, 1-anilino-8-naphthalene-sulphonate (Duchene and Wouessidjewe, 1992). Calixarenes are known to interact with either ion

species or neutral molecules. Calix-4, 5, and 6-arenes and their major derivatives are known to form complex with metal ions, such as lithium, sodium, potassium and so on. Sone *et al.* (1989), reported that calixarenes interacted with benzene, acetone, dioxane, dichloromethane and 1,2-dichloroethane in the ratio of 1:1, 1:1, 2:1, 2:1, 2:1, respectively. Miyata *et al.* (1990), reported that cholic acid and its derivatives entrapped alcohol derivatives, phenol derivatives and vinyl monomers mostly in a ratio of 1:1, 1:2, or 2:1, respectively.

## 2.6 Benzoxazine: A Novel Host Compound

The expectation for benzoxazine as a host compound is reasonable as compared to that of calixarenes, which is well known host-guest compound forming the complex with metal ions or organic molecules (Figure 2.1).



**Figure 2.1** Resemble structures of calix[n]arenes and the open ring benzoxazine oligomer.

The repeating unit of benzoxazine consists of the hydrophilic hydroxyl group at one side while the hydrophobic benzene ring at the other. There are lone pair electrons at oxygen in the hydroxyl group and nitrogen in the tertiary amine linkage at each monomer unit, as shown in Figure 2.1 (Dunkers, 1995), which is partially similar to the calixarenes. By varying the functional groups, R and R, can control the hydrophobicity of benzoxazines.

Siripattanasarakit *et al.* (1997), reported that Bisphenol-A based benzoxazine monomer and its oligomer acted as ionophore and showed that these benzoxazine compounds can interact with ion metals, alkali and alkaline earth metal ions. When solubility of the organic phase is close to 0.34 ion extraction abilities are shown significantly while ionophore concentration controlled the ion extraction ability. Phongtamrug *et al.* (1998), reported that benzoxazine monomer formed assembly to entrap alkali and alkaline earth metal ions via its inclusion phenomena. Ion extraction ability performed differently depending on the functional group of benzoxazine monomer. Techakamoluk *et al.* (1999), demonstrated that benzoxazine dimer was a host compound to interact with alkali and alkaline earth metal ions. The ion extraction ability of this dimer was significant when intramolecular hydrogen bonding of dimer was decreased while the lone pair electrons was increased.

## **2.7 Benzoxazine and the Approach for Ion Extraction Resin**

It is an interesting theme to apply ion extraction property for ion extraction resin. The material can be achieved by either curing benzoxazine monomer directly or coupling with a stable material, such as silica. Yoswathananont *et al.* (1999), reported that benzoxazine monomer can act as ion extraction resin via coupling benzoxazine on silica surface by using silane coupling agent in the monomer preparation step. This silica resin showed high ion extraction ability for alkali and alkaline earth metal ions with a good stability as used many times for extraction process.

### 2.7.1 The Chemistry of Silane Coupling Agent

Normally, silane coupling agents are monomeric species,  $R-Si(OR')_3$ , which R is a reactive group for polymer matrix. The reinforce bonding between silica and matrix resin can be performed by silane coupling

agent. The chemistry of silane coupling agent was shown by Ishida (1996), including the application as composite material. Ernst *et al.* (1985), reported that 3-chloropropyltriethoxysilane and 3-aminopropyltriethoxysilane can be an anchor on silica gel surface particle in three different types as clarified by  $^{29}\text{Si}$ -NMR.

### 2.7.2 Aminoalkoxysilane as an Amine in Benzoxazine Preparation

Aminoalkoxysilane-coupling agent was used as an amine in the method of benzoxazine synthesis (Lee *et al.*, 1998) and used as glass fiber reinforced polybenzoxazine composites. It was shown that the reaction was completed in nonpolar solvent to prevent alkoxy silane from hydrolysis due to water molecule formed as by-product in the process. Yoswathananont (1999), demonstrated the benzoxazine coupling onto the surface of silica by using aminopropyltriethoxy-silane. It is interesting to tailor the benzoxazine dimer coupling onto silica resin instead of monomer since it will use the molecular assembly in the step of entrapping with metal ions.

Recently, Laobuthee *et al.*, showed the successful preparation of benzoxazine monooxazine dimer which can be applied to this work. Thus, the present work makes use of monooxazine dimer concept but applies aminopropyltriethoxy-silane as a coupling agent for silica.

## **2.8 The Scope of the Present Work**

The present work is extended to study on the benzoxazine-silica resin by coupling the dimer derivatives on silica surface. The aim of the work is also to clarify the ion interaction ability in order to establish a new type of ion extraction resin.