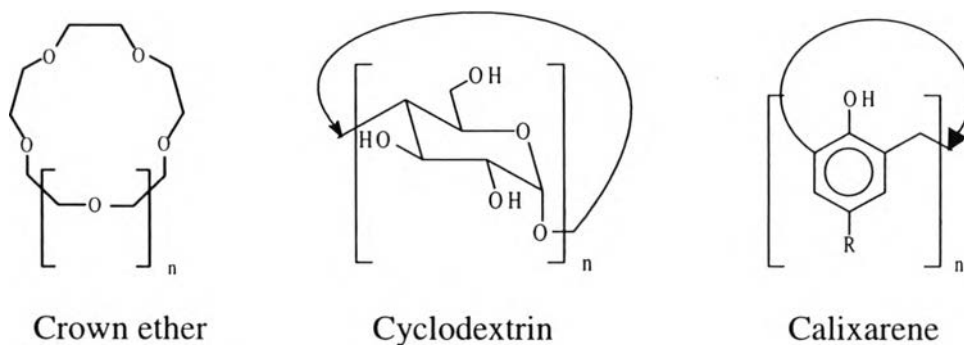


## CHAPTER II

### LITERATURE SURVEY

#### 2.1 Inclusion Compound or Host Guest Compound

The discovery of inclusion compounds can be referred to the report of Michael Faraday on the preparation of the clathrate hydrate of chlorine in 1823 ( J. E. D. Davies, 1983). Inclusion chemistry was established when C. J. Pedersen clarified the crown ether compounds as a host compound binding with metal ions such as potassium, sodium and some organic compounds in the mid 60s. Up to now, many types of host compound were found such as crown ether, cyclodextrin, calixarenes, (Figure 2.1) including some steroid compounds. Cyclodextrin is a cyclic polysaccharide obtained from starch by enzymatic degradation, which is soluble in water, and forms inclusion compounds with a wide variety of guest species in solution and solid state, including bioactive amino acid guests. Calixarenes, which are a particular class of phenolic compound produced by condensation of *p*-substituted phenols with formaldehyde, are reported as a series of derivatives and received much attention for a variety of molecular design. The complexes of calixarenes with metal ions or organic molecules lead to the expectation of separation system in the molecular level. Inclusion compound becomes extended area of polymer chemistry when C.J. Pedersen, D.J. Cram, and J-M Lehn were awarded Nobel Prize for the research works in 1987.



**Figure 2.1** Structures of crown ether, cyclodextrin, and calixarene.

## 2.2 Applications of Inclusion Compound

Inclusion compound opens up a wide area of applications owing to its specific microenvironment created by the host. The enclosure of the guest exerts an influence on the physical, spectroscopic, and chemical properties of the guest molecule themselves.

Inclusion compounds can be used as a sensor such as ion selective electrodes, industrial wastewater treatment resins, and the blood monitoring in clinical area (E. Weber, 1984). Cyclodextrin and the related hosts are reported for the potential use as a sensitive coatings media on chemical sensor devices (T.E. Edmonds, 1988).

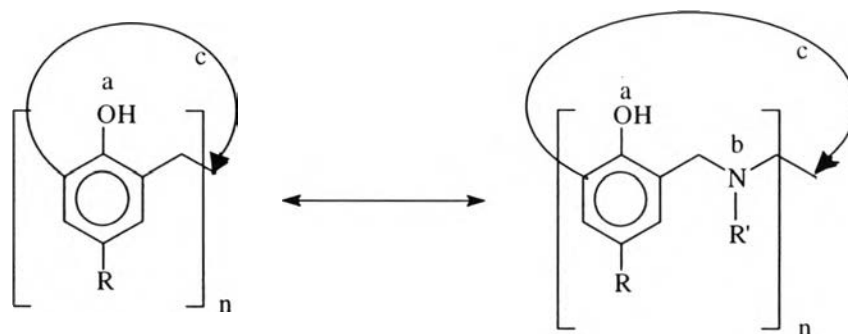
Applications of inclusion compounds are also included the retardation and the control activity of guest species, as seen in the commercial products of cosmetic, food, laundering, pharmacy, and agriculture.

### 2.3 Benzoxazine as an Azacalixarene

The chemistry of benzoxazine is received the attention from the early 1940's. Holly and Cope (1944) proposed the 3,4-dihydro-2H-1,3-benzoxazine structure by the condensation of formaldehyde with  $\sigma$ -hydroxybenzylamine. In 1949, Burke synthesized 3,4-dihydro-2H-1,3-benzoxazine by using p-substituted phenols, formaldehyde and a primary amine in a molar ratio of 1:2:1, respectively. The reaction is well known as a Mannich type of condensation. Ishida *et al.* reported the polymerization of benzoxazine monomer by thermal reaction with or without initiator and concluded that the ring opening polymerization occurs in the range between 160<sup>0</sup>C and 220<sup>0</sup>C (1994). In the presence of phenol, which can act as an initiator, the polymerization temperature of benzoxazine can be reduced to approximately 30<sup>0</sup>C – 50<sup>0</sup>C.

The chemistry of polybenzoxazine synthesis offers a wide range of molecular design by using derivatives of phenol, primary amine and aldehyde. Recently, Ishida and Chirachanchai focused on benzoxazine repeating unit to propose it as a host compound of azacalixarenes. The studies establish a basic understanding of benzoxazine host compound as a molecular assembly system.

As shown in Figure 2.2, it should be noted that the molecular structure of polybenzoxazine is somewhat similar to that of calixarene, i.e., phenol ring unit with methylene linkage, moreover, each unit of benzoxazine has the Mannich base linkage at which the lone pair electrons be provided to the system. Thus, it is expected that benzoxazine shows the inclusion property as seen in the case of calixarene.



Cyclic Calixarene

Polybenzoxazine

a : Hydroxy group.....Lone pair electrons and hydrophilicity

b : Nitrogen.....Lone pair electrons

c : Oligomer ring.....Stereospecific cavity

R, R' : Functional group.....Controllable hydrophobicity

**Figure 2.2** Cyclic calixarene and polybenzoxazine.

Preliminary study of Siripattanasarakit *et al.* on the oligobenzoxazine of bisphenol-A supported that benzoxazine performs as a host compound. Phongtamrug *et al.* demonstrated that the host property of benzoxazine can be derived even in the monomer level while the ion interaction ability depends on the structure of benzoxazine itself.

## 2.4 The Molecular Design of the Benzoxazine to Ion Extraction Resin

Based on the ion interaction ability of benzoxazine, it is an interesting theme to apply benzoxazine as an ion extraction material. In this case, the

material can be achieved by either curing benzoxazine monomer directly or coupling with a stable material, such as silica.

The present work, thus, focuses on the application of benzoxazine monomer for ion extraction resin by considering the possibility of coupling benzoxazine onto silica via silane coupling agent. The benzoxazine monomer coupled silica can be achieved by the molecular design to apply aminoalkoxysilane as an amine in the benzoxazine preparation and as a coupling group onto silica.

#### **2.4.1 The Chemistry of Silane Coupling Agent**

It is well known that a silane coupling agent is an important binder used to reinforce the bonding between silica and matrix resin. Silane coupling agents are monomeric species,  $R-Si(OR')_3$ , where R is a reactive group with a polymer matrix and (OR') is a hydrolyzable ester group. Ishida reported the chemistry of silane coupling agent including the application of various silanes for composite materials.

Ernst *et al.* (1985) used  $^{29}Si$ -NMR spectroscopy to quantify the anchoring of 3-chloropropyltrimethoxysilane and 3-aminopropyltriethoxysilane to the surface of silica gel particle and reported three different types of surface bonds, i.e., covalent linkages between the organosilane moiety by one, two, or three silanol groups.

#### **2.4.2 Aminoalkoxysilane as an Amine in Benzoxazine Preparation**

Ishida *et al.* (1998) proposed glass fiber reinforced polybenzoxazine composite by using aminoalkoxysilane coupling agent as an amine in the method

of benzoxazine synthesis. It is reported that the silane is successfully coupled onto benzoxazine resin and promoting the adhesion between glass fiber and polymer resin to obtain the composite. However, the reaction of silane with benzoxazine produces the water molecule by-product which hydrolyzes the alkoxy silane. If the alkoxy silane is hydrolyzed, the silane oligomer will be formed and the gelation may occur. In order to avoid these problems, the water molecule is separated from the product by using the nonpolar solvent.

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

The present work is originally to propose silica compound on benzoxazine oligomer chain linked on the surface by silane coupling agent as a novel type of ion extraction resin. Here, silylbenzoxazines are synthesized employing the method of benzoxazine synthesis and using an aminosilane as the primary amine. The success of the silica-benzoxazine preparation is also based on the solvent effect and the purification. The resins are applied as a stationary phase in the chromatographic separation to determine the ability of alkali and alkaline earth cation extraction.