CHAPTER I

INTRODUCTION

In recent years, fine separation is essential in technologies, such as separation of isotopes, separation of isomer, separation of ions and decontamination of waste-waters or other concentration processes. Although ion exchange membranes are primarily required to separate selectively cations from anions and vice versa, separating different ions with the same electrical sign and same charge has also been required. In industrial level, those techniques are also required for product synthesis, water treatment and water purification.

At present, there are some problems in separation of ions, such as Urenium ion from sea water or heavy metal from sea water. Ion exchange resin has been introduced to solve this problem. In order to achieve ion exchange property, Host-Guest or inclusion compound has been studied for years. Over the past decade, inclusion compound has received much attention and the understanding of the molecular recognition of the inclusion phenomena has grown rapidly. There are many aspects of the researches and concerning applications (Diemer, R.B., Jr. et al., 1991), such as drug delivery system for pharmaceutical, increasing compound solubility for food and cosmetic industrial (Iwamoto, T., et al., 1978), synthetic enzyme mimicry (Green, B.S., et al., 1982; Diederich, F., 1983; Stoddart, J.F., 1987), and separation of chemical species (Pedersen, C.J., 1967).

Benzoxazine is a novel type of phenolic material. Ishida, H. et al. (1994) proposed that benzoxazine has a great deal of flexibility in molecular design comparing to ordinary phenolics. Benzoxazine is synthesized by Mannich reaction from phenol and amine, and contains both hydroxyl and amine group in the unit. Polyfunctional benzoxazine is a thermosetting resin, which has been developed as a novel material for various applications. Polyfunctional benzoxazines show excellent mechanical properties and is expected for an improved composite material (Ishida, H., 1995). Kinetic studies of the curing system were performed using differential scanning calorimetry (Ishida, H. and Rodriguez, Y., 1995). H. Ishida and D.J. Allen (1996) investigated the mechanical, physical and rheologocal properties of polybenzoxazines and their copolymers with epoxy and revealed that these materials have high glass transition temperatures, high moduli, low water absorption and good dielectric properties.

However, it should be noticed that the benzoxazine may show the property of inclusion compound owing to the specific structure of monomer unit as found in the case of calixarene. In order to consider benzoxazine as a novel inclusion compound, it is important to overview the well-known inclusion compound. Traditional Host-Guest compounds can be summarized as follows.

Crown-ether is a cyclic oligoether, which shows the negatively polarized cavity. Through this property, crown-ether is capable of accommodating metal ions to form crown cation inclusion complexes (Coronates). In particular, alkali and alkaline earth metal ions are proven to be appropriate to the cavity with the increase of the dipole interaction with crown-ether to form a structural Host- Guest compound. Host crown-ether which

contains 5-10 oxygen atoms can form stable complexes with Li, Na, NH_4, K, Cs, etc. (Izatt, S.R. et al., 1985). 18 - crown - 6 has been shown to be a useful ion size selective masking reagent in the synergistic extraction of alkaline earths into cyclohexane (Yamakishi, T. et al., 1996).

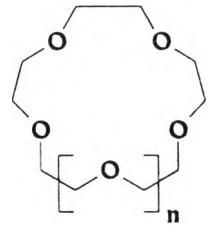
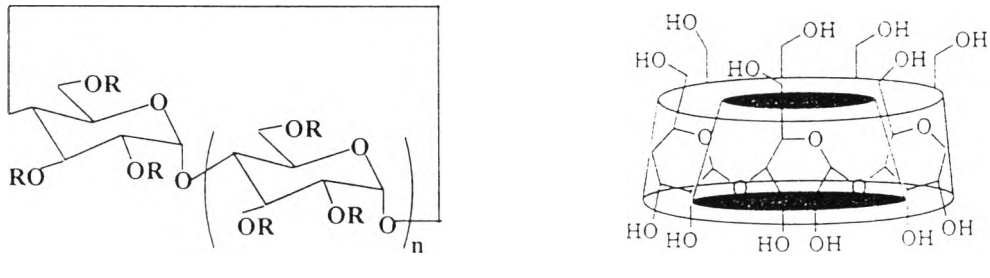


Fig. 1 Crown macroring inclusion compounds (Coronates).

Cyclodextrin is a cyclic oligosaccharide obtained from starch by enzymatic degradation. Cyclodextrin is composed of glucose unit and forms cone structure, as seen in the case of calixarene. Thus, cyclodextrin may be considered as natural analogy of the artificial calixarenes (Diemer, R.B., Jr., 1991). Several enzymes can be obtained by cyclodextrin as a host in synthesis process. (Moon, H.T. et al., 1993). Another useful application is enhancement of the efficiency of guest binding (Breslow, R., 1993).



A B

Fig. 2 A : Cyclodextrins

B : Three-dimensional cone-structure of β-cyclodextrin.

Calixarene is a particular class of metacyclophane host bearing protonizable hydroxyl groups. Calixarene can be characterized as a cone- or calix-like conformation compound (calix means beaker in Latin and Greek) (Ohseto, F. et al., 1995). Through its specific conformation, it is well known as a Host-Guest compound or inclusion compound, which can form the complex with metal ions or organic molecules. Calixarene is considered as a carrier-mediated of alkali-metal cation in H_2O - organic solvent and H_2O - liquid membrane.

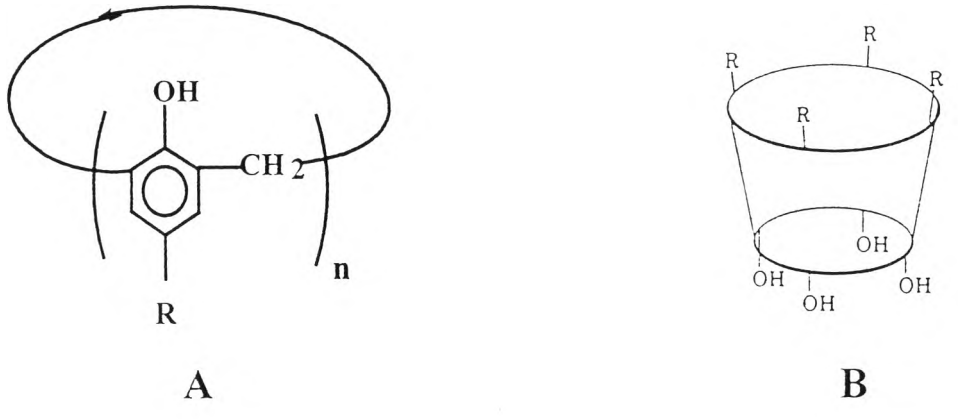
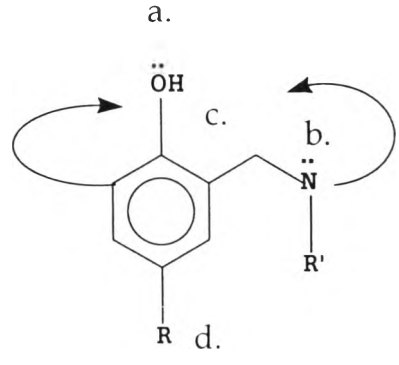


Fig. 3 A : Calixarenes

B : Cone- or calix-like conformation of calixarenes.

As shown in Fig. 4, benzoxazine monomer unit 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 on each monomer unit. By varying the functional group R and R', hydrophobicity of monomer unit can be controlled. Thus, it can be expected that when monomer unit of benzoxazine forms an oligomer, it will possibly show a specific conformation and act as host

molecule. The property of oligo or polybenzoxazine as a host molecule can be achieved by the molecular design of the monomer unit as known in the case of calixarenes.



a : Hydroxyl group.....Lone pair electron

.....Hydrophillicity

b : Nitrogen.....Lone pair electron

c : Oligomer ring.....Stereospecific cavity

d : Functional group.....Hydrophobicity (Controllable)

Fig. 4 Benzoxazine structure.

In order to confirm the possibility for a host molecule, it is very important to study benzoxazine material unit by unit as a dimer, trimer, tetramer and so on. However, since the present work is a very first step to explore benzoxazine oligomer as a host molecule, the scope of this work will deal mainly on the oligomers derived from the thermal curing of benzoxazine monomer rather than the stepwise synthesis of a controlled structure. The benzoxazine monomer which is studied in the project is bisphenol-A and methylamine-based benzoxazine as shown in Fig. 4. Alkali and alkaline earth

ions are used as guests and oligo-benzoxazine are studied as an ion extraction host molecule.

In this work, the inclusion phenomena induced by the molecular assembly of benzoxazine is studied by varying ion guests, size of oligomer and type of aqueous/organic phase concerned in the ion extraction system.