

CHAPTER III

RESULTS AND DISCUSSION

3.1 Characterization of Benzoxazine

Structural Characterization

The methylamine-based benzoxazine monomer was prepared according to Ning, X. et al., 1994 and the structure was characterized by FTIR.

IR (KBr, cm^{-1}) ; 3400-3200 (N-H)

1499 (tri-substituted benzene ring)

1240-1020 (C-N-C : antisymmetric),

830-740 (C-N-C : symmetric)

1240-1210 (C-O-C : antisymmetric),

1040-1020 (C-O-C : symmetric)

2810-2794 (N-CH₃)

Oligomer was obtained by thermal polymerization. In the present work, in order to establish the inclusion phenomena at this very first step, the applied monomer was prepared by curing at 100°C for 4 hours. When the curing proceeds, the sample will change from the white powder to the pale yellow rigid sheet. An attempt to qualitative the degree of polymerization was done by FTIR. It is expected that when the oligomer is formed, hydroxyl group will be increased and the methylene-amine-methylene bridge will occur, thus the IR peak at 3500-3300 and 1480 will appear significantly. Fig. 6 reveals that B-m monomer forms oligomer quantitatively.

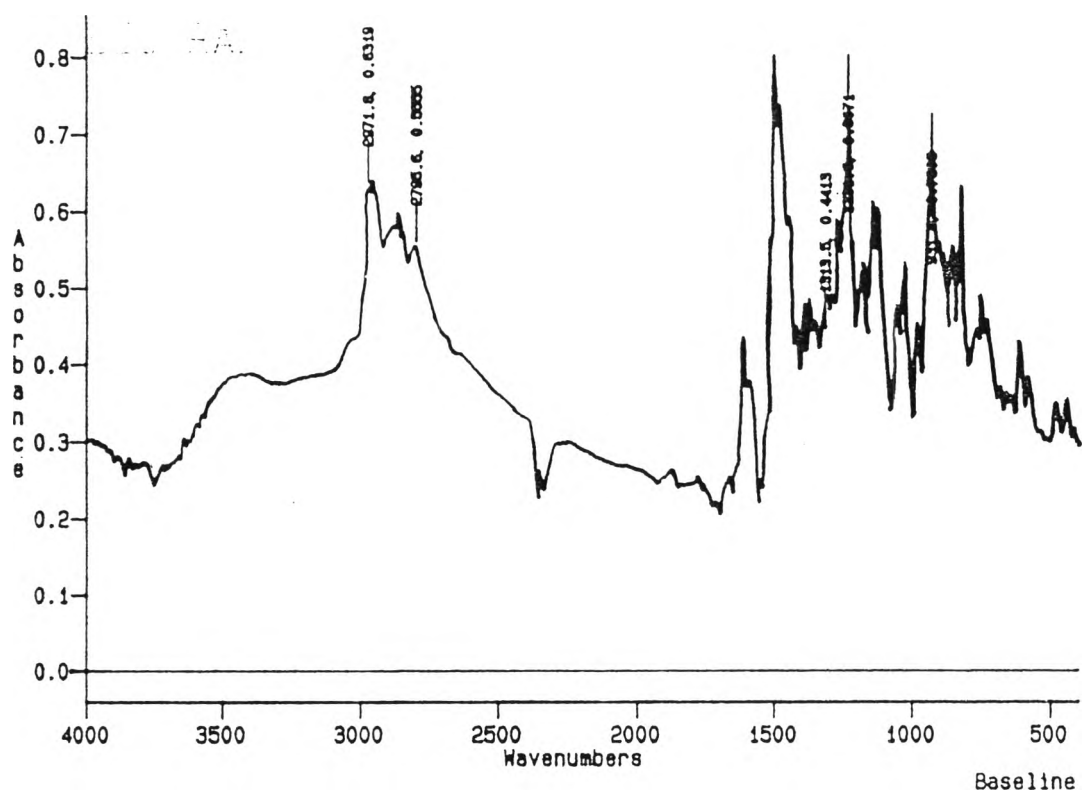


Fig. 6 FTIR spectra of B-m oligomer.

3.2 Molecular Weight Determination

In order to investigate oligobenzoxazine for a function of host compound, it is important to study the molecular weight. Since the oligobenzoxazine is difficult to dissolve in most organic solvents, the molecular weight can not be measured by the gel permeation chromatography technique.

It is found that oligomer can swell in the methylene chloride solvent, and the determination of the molecular weight can be possibly determined by the light scattering technique. However, there were some problems about the undissolved particles (even the filtration was operated) due to the oligomers which could not swell and act as an impurity in the system, which made the results unrepeatable. Hence, the molecular weight of oligomer can not be achieved by the ordinary techniques.

3.3 Ion Extraction Property

By considering benzoxazines structures, it can be expected that benzoxazines give a specific confirmation as a host compound to form complexes with some guest molecules. As known in all cases of Host-Guest compounds, when the guest molecules are trapped inside the host cavity, the inclusion phenomena can be confirmed by some analytical techniques, such as ultraviolet spectrophotometry, infrared spectroscopy, atomic absorption spectroscopy, nuclear magnetic resonance spectroscopy, mass spectroscopy, etc.

Since the structure of benzoxazine monomer unit is very similar to that of calixarene, it is very interesting to consider the inclusion phenomena of benzoxazines by referring to calixarenes.

Calixarenes can be formed as many types of host compounds, such as Calix[4]arenes, Calix[6]arenes, Calix[8]arenes, which show the well known inclusion phenomena by trapping various types of metal ions. It is reported that the specificity and selectivity of calixarenes are considered from the result of specific confirmation of the compound.

In the present work, in order to explore the inclusion phenomena of oligobenzoxazine, metal ions are focused as guests and the ion extraction property of oligobenzoxazine was studied.

Pedersen's technique is applied to study the ion extraction property in liquid/liquid system. (Pedersen, C.J., 1968). Normally, the picrate will present in aqueous phase and give the yellow color to the phase while the organic phase is colorless. If the oligobenzoxazine provides a structure as a host molecule and acts as an ionophore, when oligobenzoxazine is added to the system, the metal ion will be shifted to the organic phase as soon as the ion complex is formed. Thus, ion extraction can be investigated by determining the changing of picrate concentration in aqueous phase and quantitative can be achieved by ultraviolet spectrophotometer at the absorption wavelength of the picrate.

In order to identify oligobenzoxazine as an ionophore, and explore the inclusion phenomena, it is necessary to study some factors concerning directly the structure of host-guest compounds. In the present work, the following factors are investigated;

1. Factor of molecular assembly
2. Factor of organic phase in liquid-liquid system
3. Factor of metal ion species
4. Factor of B-m concentration

3.3.1 Factor of Molecular Assembly

Host-Guest compound can be formed from either the monomers gathering or the oligomer linking to each other, and as a result, forming a molecular assembly. Generally, when the molecular assembly is established, some significant properties will appear owing to the specific confirmation of the assembly system.

In this study, it is expected that the molecular assembly will lead to the ion complex formation and the percentage of ion extraction will be changed according to the inclusion phenomena.

As shown in Fig. 7, liquid/liquid system was operated by using aqueous/ CH_2Cl_2 . In the case of B-m monomer, when the monomer concentration is increased, the percentage of ion extraction is found to be increased for all types of metal ions. This suggested that B-m have the interaction with ion species and act as an ionophore. It also implies that the formation of ion complex with B-m monomer is established as a molecular assembly.

In the case of B-m oligomer, it is found that the percentage of ion extraction is as high as that of B-m monomer. Fig. 10 showed that B-m oligomer can trap Na ion almost 100 % while B-m monomer showed the lower (90 %) extraction affinity (Fig. 7), when the B-m concentration is 2g / 100 ml

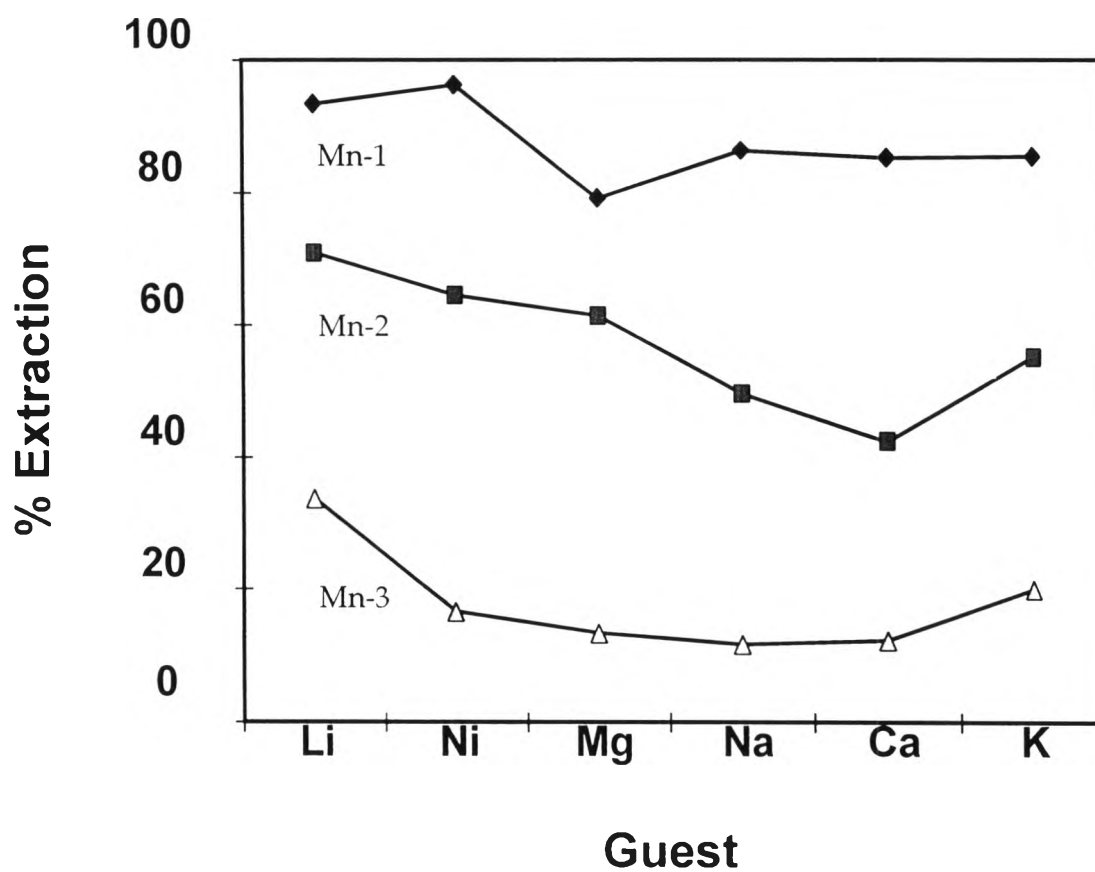


Fig. 7 Extraction percentage of metal picrate by B-m monomer.
Ionophore concentration : **Mn-1** = 2 g/100ml in CH_2Cl_2 ,
Mn-2 = 0.2 g/100ml in CH_2Cl_2 and **Mn-3** = 0.02 g/100ml in CH_2Cl_2 .

in CH_2Cl_2 . Fig. 8 - Fig. 12 show the ion extraction percentage of the same condition when the organic phases are CHCl_3 and toluene, indicating that all oligomers show the high ion extraction percentage as the monomer. However, there are some differences between the type of organic phases which will be discussed in the next section.

The results imply that ion extraction mechanism is accomplished by the molecular assembly formation in the ion extraction mechanism. Yamagishi T. et al. proposed that the ionic affinity of the cavity which presented in the molecular assembly is based on the pseudo-cyclic conformation (Yamakishi, T. et al., 1996). In this study, it can be concluded that the assemblies of benzoxazine monomer and oligomer maybe form a flexible structure, thus the ion extraction can be performed to various metal ion species and the selectivity is not very much significant between monomer and oligomer.

3.3.2 Factor of Organic Phase in Liquid/Liquid System

The organic phase in liquid/liquid system is one of the important role in the ion extraction step. Tsurubou, S. et al. (1995) reported that when the size of solvent is much smaller than the ion or ion complex, the disturbance of the solvent molecule will be less. Thus, the ion can be interacted easier to the ionophore, in other words, the ion extraction can be controlled by the size of the organic solvent in the liquid/liquid system.

The ion extraction selectivity can be established when the appropriate solvent is applied under a certain hydrodynamic continuum atmosphere (Wandlowski, T. et al. 1989). In the present work, methylene chloride, chloroform and toluene which are different in the solvent molecule size are used to study the factor of organic phase in the liquid/liquid system. If the

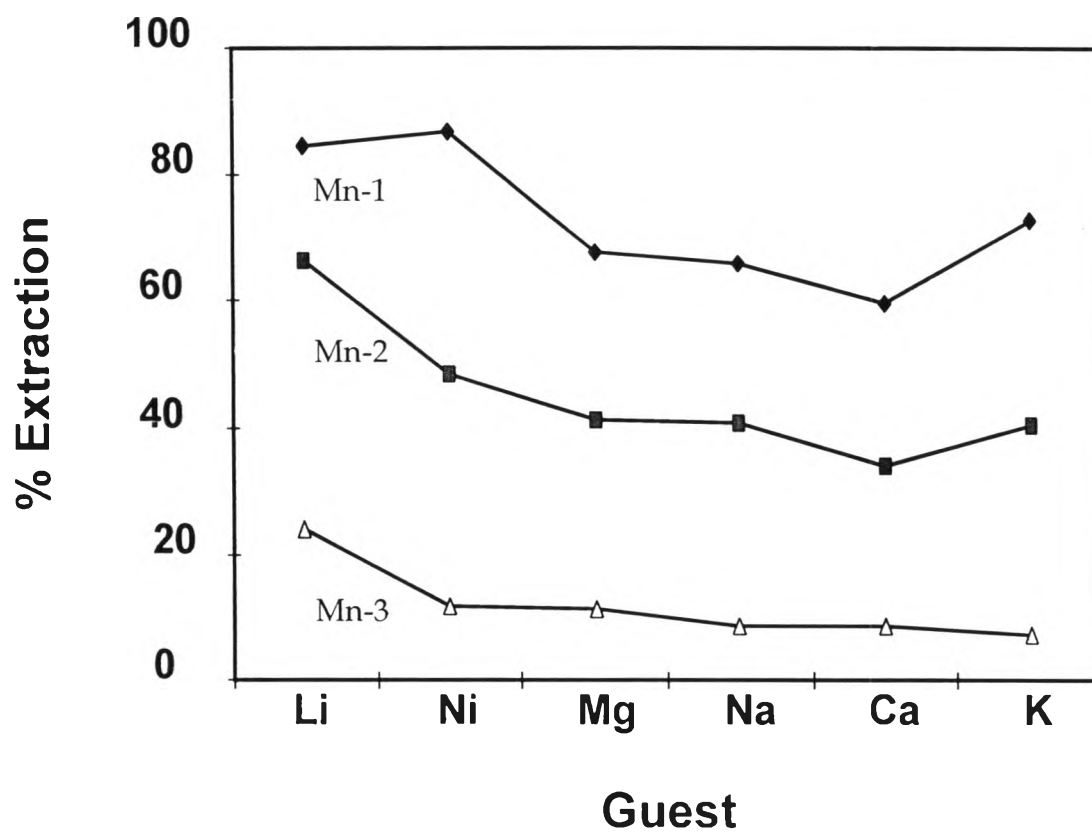


Fig. 8 Extraction percentage of metal picrate by B-m monomer.
Ionophore concentration : **Mn-1** = 2 g/100ml in CHCl_3 ,
Mn-2 = 0.2 g/100ml in CHCl_3 and **Mn-3** = 0.02 g/100ml in CHCl_3 .

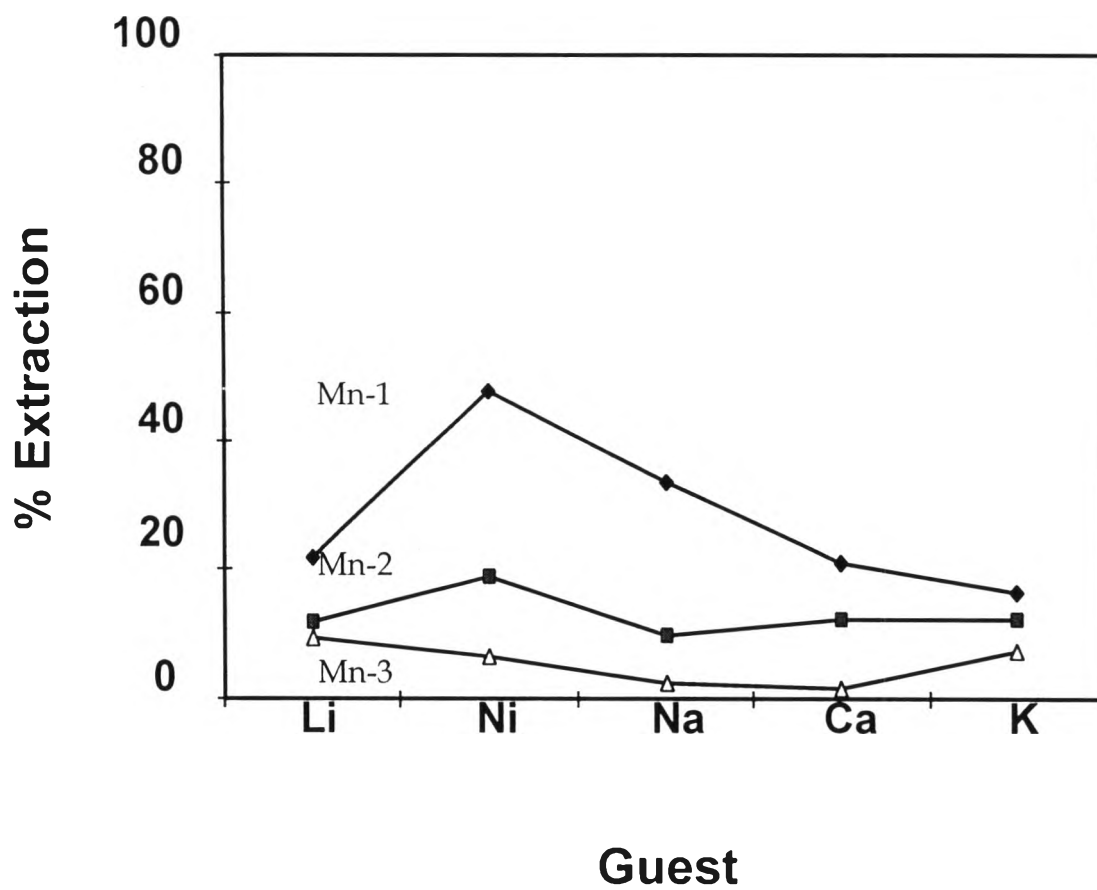


Fig. 9 Extraction percentage of metal picrate by B-m monomer. Ionophore concentration : **Mn-1** = 2 g/100ml in toluene, **Mn-2** = 0.2 g/100ml in toluene and **Mn-3** = 0.02 g/100ml in toluene.

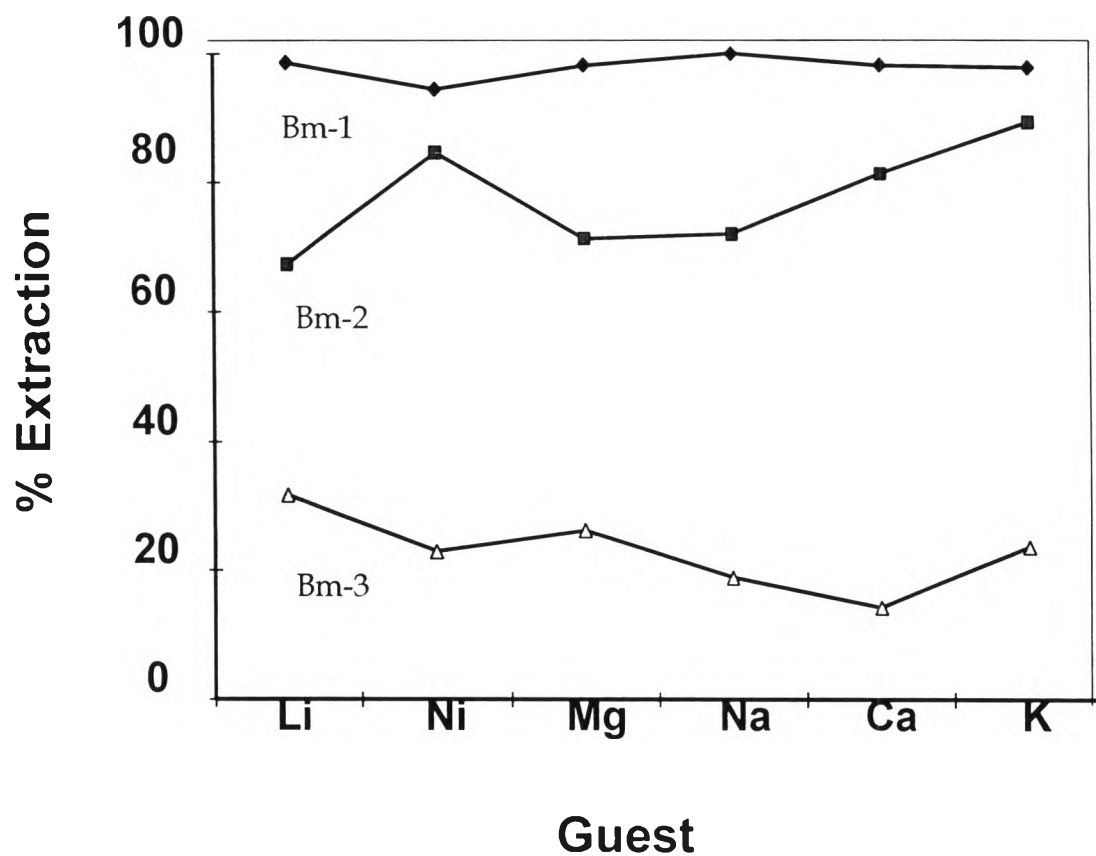


Fig. 10 Extraction percentage of metal picrate by B-m oligomer.
Ionophore concentration : **Bm-1** = 2 g/100ml in CH_2Cl_2 ,
Bm-2 = 0.2 g/100ml in CH_2Cl_2 and **Bm-3** = 0.02 g/100ml in CH_2Cl_2 .

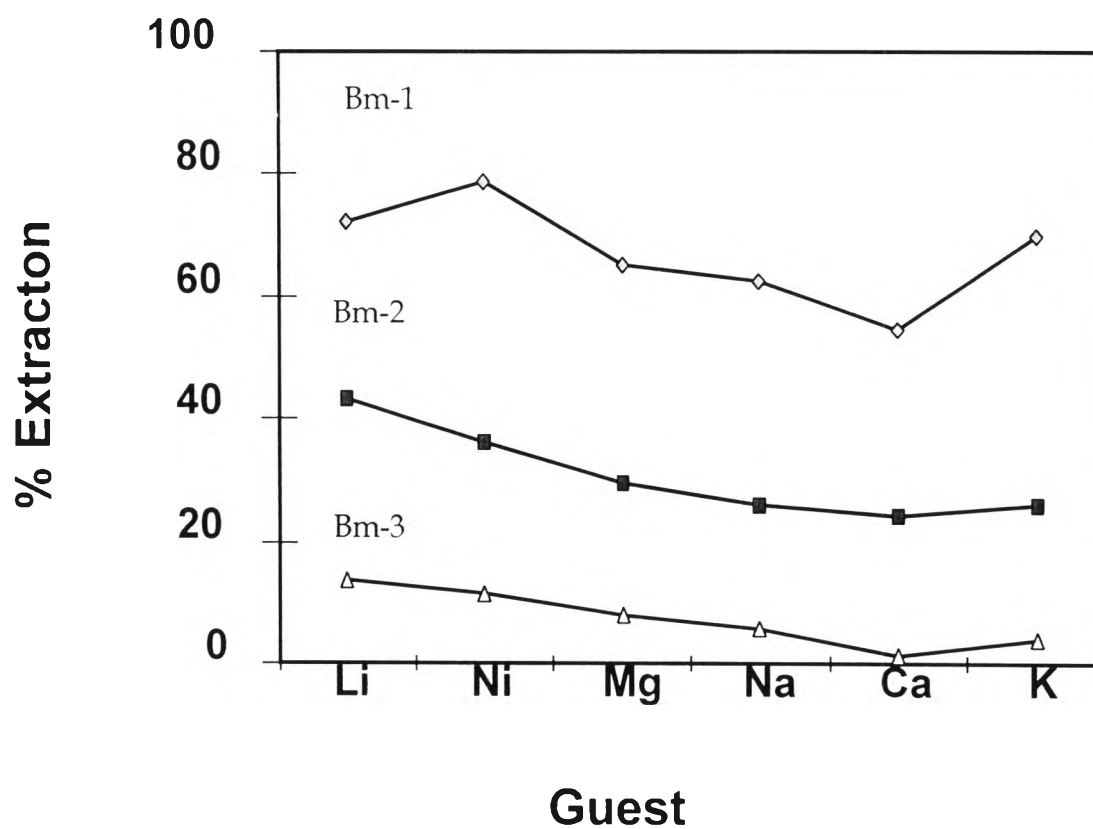


Fig. 11 Extraction percentage of metal picrate by B-m oligomer.
Ionophore concentration : **Bm-1** = 2 g/100ml in CHCl_3 ,
Bm-2 = 0.2 g/100ml in CHCl_3 and **Bm-3** = 0.02 g/100ml in CHCl_3 .

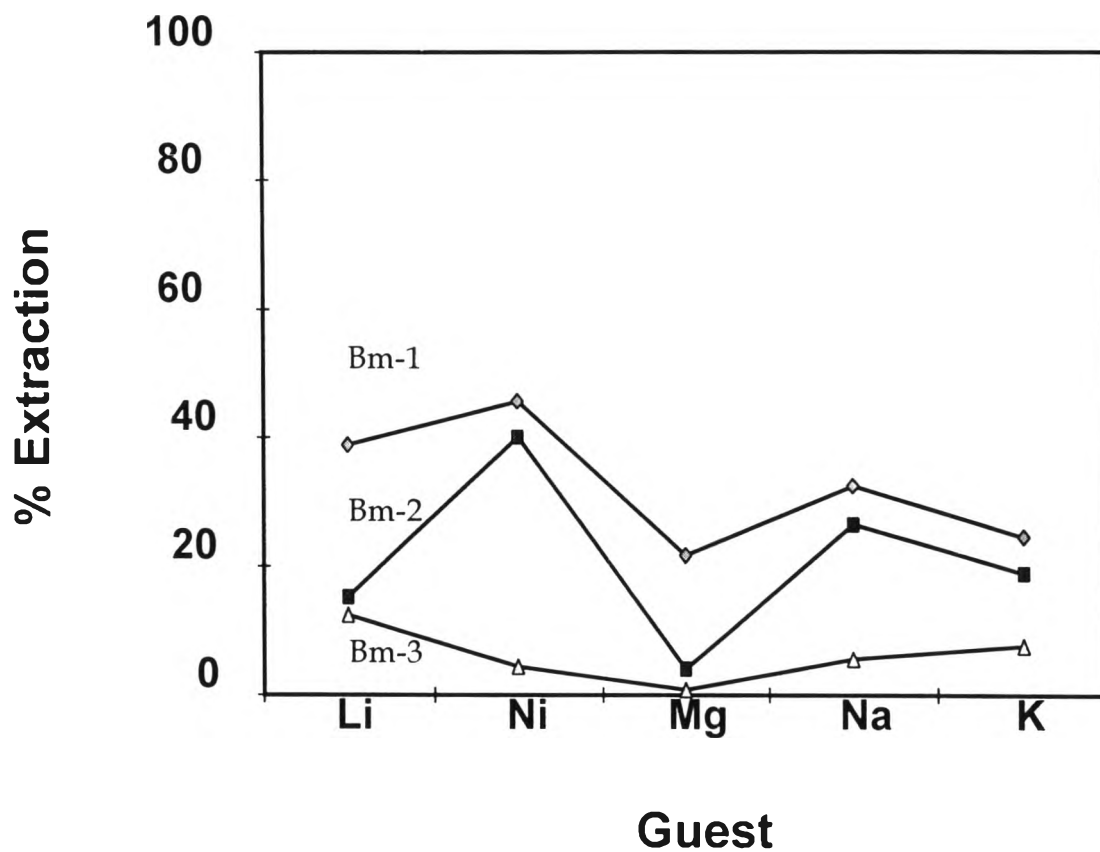


Fig. 12 Extraction percentage of metal picrate by B-m oligomer.
Ionophore concentration : **Bm-1** = 2 g/100ml in toluene,
Bm-2 = 0.2 g/100ml in toluene and **Bm-3** = 0.02 g/100ml in toluene.

hydrodynamic continuum is achieved in the system, it can be concluded that benzoxazines act as an ionophore to form the ion complexes.

As shown in Fig. 7 and Fig. 12, the ion extraction percentage is differed among the type of organic phase. It is found that under CH_2Cl_2 , the extraction percentage for all metal ions are confirmed to be higher than CHCl_3 and toluene for both cases of B-m monomer and oligomer. The lowest ion extraction percentage in toluene maybe refer to the hindrance effect of toluene molecule.

The hydrodynamic continuum effect implies that B-m forms inclusion cavity and allows the organic solvent to involve with the host-guest formation. Referring to calixarenes and crown-ether systems (Wandlowski, T. et al., 1989), it can be concluded that benzoxazines act as an ionophore in liquid/liquid system through the inclusion phenomena.

3.3.3 Factor of Metal Ion Species

Generally, host compound will provide the specific cavity for guest molecules owing to its molecular assembly structure. In this study, the ionophore was varied in order to investigate the guest responsive structure owing to the assembly formation of B-m monomer and oligomer. Alkali, alkaline earth and Ni (the transition metal) are used for the ion extraction observation.

As summarized in Table.1, six types of metal ion were applied in order to observe the ion extraction ability of B-m. It can be expected that there will be an appropriate ion size that fits the cavity of the ionophore. As shown in Fig. 7 to Fig. 12, Li and K tend to show higher ion extraction percentage. It

should be noted that the size of K is two folds larger than that of Li, while the ion extraction percentages are similar. This maybe explained that the cavity size of the ionophore is about the range of 0.6 Å. However, the results exhibit high percentage of ion extraction towards the metal ions and the selectivity owing to the size of ion species is not distinguished.

Table 1 Size of metal ion species

Ion Species	Size (Å)
Li	0.6
Ni	0.62
Mg	0.65
Na	0.95
Ca	0.99
K	1.33

Miyata, M. et al. (1990) reported that when the host molecule performs a flexible structure for the guest, various types of guest molecules will be allowed in the cavity, as seen in the case of Cholic acid. In this case, it can be concluded that B-m provides the guest responsive structure while inclusion phenomena is performed, with the low selectivity.

3.3.4 Factor of B-m Concentration

It is well known that inclusion phenomena is related to the interaction of the host and guest molecules. When the host concentration is higher in the

excess guests circumstances, it can be expected that the more amount of guests will be included in the host compound.

In this study, the B-m ionophores are varied from 0.02 to 2 g/100 ml. in CHCl_3 , CH_2Cl_2 and toluene organic phase. It is found that in the case of CHCl_3 , CH_2Cl_2 , when the ionophore (both B-m monomer, Fig. 7 and Fig. 8 and B-m oligomer, Fig. 10 and Fig. 11) concentrations are increased to 100 times (from 0.02g/100 ml to 2g/100 ml) the ion extraction percentage are increased at least for 60%. It should be noted that in the case of toluene organic phase which the ion extraction percentage are relatively low (as discussed in 3.3.3), the relationship of the ionophore concentration and ion extraction ability is not significant (approximately 10-30%).

Although ionophore concentration and ion extraction ability are related directly, as known in all cases of inclusion compound, it is very important to take it into the consideration that there are other effects that will overlap the ion extraction ability which makes the apparent value be differed from the expectation. In the case of toluene, it can be said that hydrodynamic continuum factor is mainly operated on the system and, thus, the ion extraction ability for all cases are not shown out through the factor of concentration.

3.4 The Comparison Between B-m and Other Ionophore

Calixarenes, crown-ether, and cyclodextrin; are well known for the inclusion compounds and some practical applications are established. According to the ionophore property, it is to the interest to review the ion extraction ability comparing to the benzoxazine system.

The ion extraction ability of the well known ionophores; which are calix[4]arene, calix[6]arene, calix[8]arene, and 18-crown-6; for the ion extraction in the cases of Ca, Li and Na ions are summarized, as shown in Fig. 13 - Fig. 15, respectively.

In order to compare the ion extraction ability to the mentioned ionophores, the similar experiments were operated. Benzoxazine monomers were used as the ionophore with the concentration of 2.7×10^{-3} M. The results were compared, as shown in Fig.13 - Fig. 15.

In the cases of Li and Ca ion, the ion extraction shows the performance in the range of 20-50% for the calixarenes and crown ether, while the extraction percentage of benzoxazine shows at nearly 80%. According to the high ion selectivity performance for calix[4]arenes on Na ion, it is also found that the ion extraction percentage is as high as that of benzoxazine (nearly 90% for both cases).

By considering the ion extraction ability of benzoxazines, it can be expected that the benzoxazine can be a novel type of ionophore, owing to the inclusion structure provided by the molecular assembly. It is also very interesting that benzoxazines show rather high ion extraction percentage comparing to other well known ionophores. However, the improvement of ion selectivity is required for the future work.

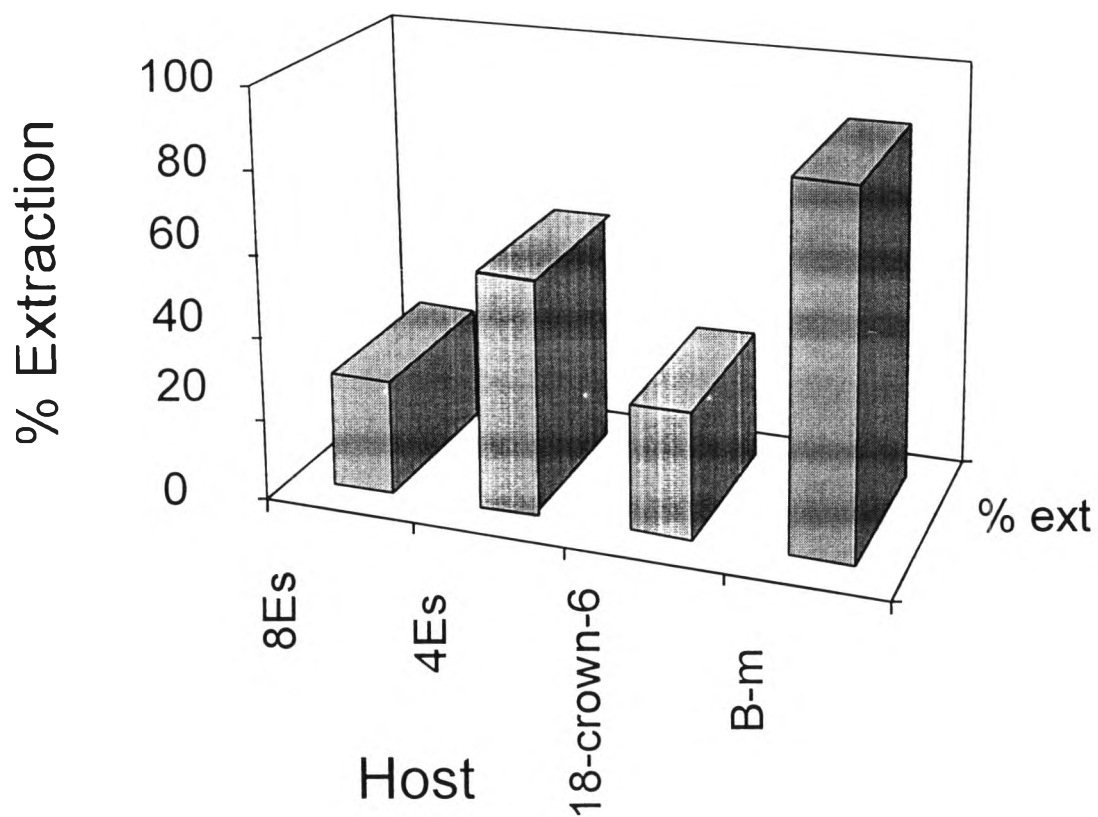


Fig. 13 Comparison of the extraction percentage of calcium picrate.
Ionophore concentration = 2.7×10^{-3} M in CH_2Cl_2 .
8Es : octamer of calixarene, 4Es : tetramer of calixarene, 18-crown-16 : crown-ether (From Yamagishi et al., *Polym. Bull.*, **33**, 281.) and B-m : B-m monomer.

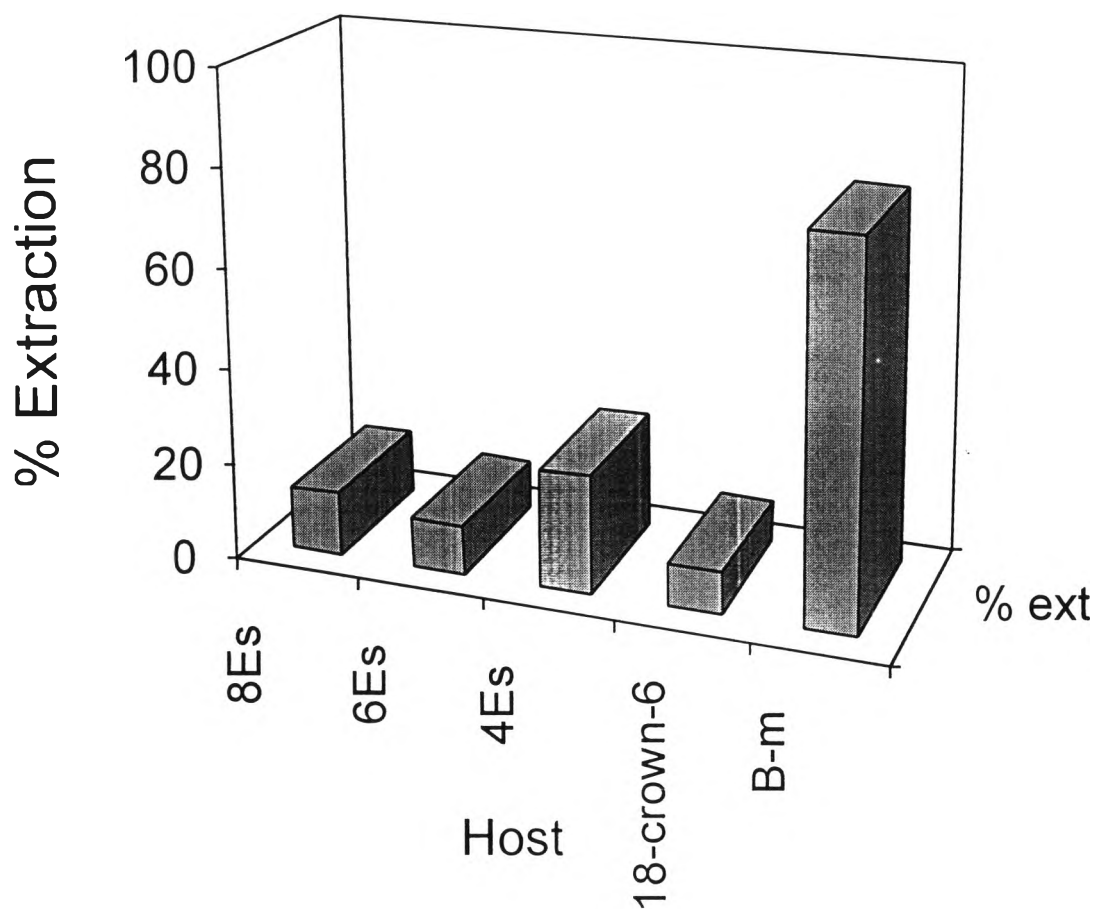


Fig. 14 Comparison of the extraction percentage of lithium picrate. Ionophore concentration = 2.7×10^{-3} M in CH_2Cl_2 . 8Es : octamer of calixarene, 6Es : hexamer of calixarene, 4Es : tetramer of calixarene, 18- crown-16 : crown-ether (From Yamagishi et al., *Polym. Bull.*, **33**, 281.) and B-m : B-m monomer.

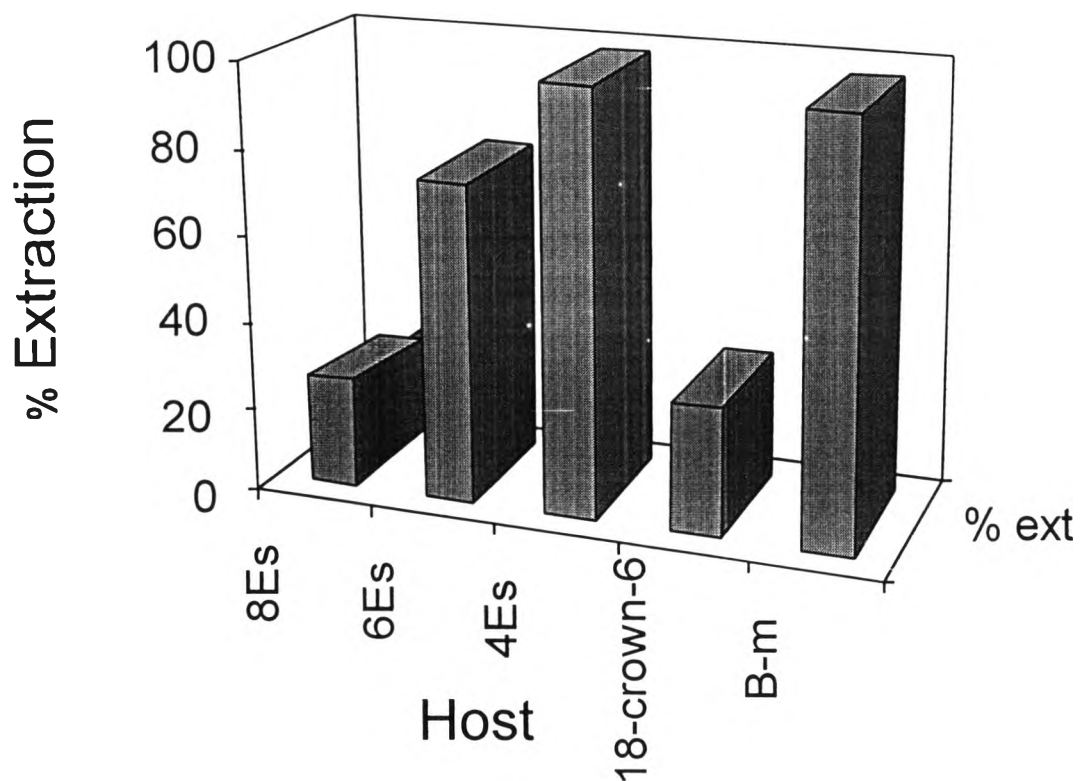


Fig. 15 Comparison of the extraction percentage of sodium picrate. Ionophore concentration = 2.7×10^{-3} M in CH_2Cl_2 .
8Es : octamer of calixarene, 6Es : hexamer of calixarene, 4Es : tetramer of calixarene, 18- crown-16 : crown-ether (From Yamagishi et al., *Polym. Bull.*, **33**, 281.) and B-m : B-m monomer.