

A Novel Ion Extraction Material Using Host-Guest Properties of Oligobenzoxazine Local Structure and Benzoxazine Monomer Molecular Assembly

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ABSTRACT: Bisphenol-A based benzoxazine monomer (BA-m) and its oligomer are applied as an ionophore to study by Pedersen's technique, the ion interaction with alkali and alkaline earth ions. Ion extraction efficiencies are significant when the solubility parameter of the organic phase is close to that of BA-m or the χ -parameter is 0.34. Ionophore concentration controls the amount of metal ion extraction. Both BA-m and its oligomer show high entrapment efficiency over 70% extraction, for all types of ions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2561–2568, 2000

Key words: benzoxazine; oligobenzoxazine; ionophore; host-guest compound; molecular assembly; solubility parameter; χ -parameter

INTRODUCTION

Fine separation is essential in technologies such as separation of isotopes, isomers, and ions, decontamination of waste water, and 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 is also important. At present, there are some difficulties in excluding various ions from the system to obtain ultra high purity substances. To achieve high efficiency of an ion exclusion system, an ion exchange resin has been widely used.

Host-guest or inclusion compound is a novel approach to control the ion extraction process on the molecular level via the interaction between host and guest compound. Over the past decade, inclusion compounds have received much attention because the understanding on the molecular recognition of the inclusion phenomenon has grown rapidly. Thus, the inclusion phenomenon is widely studied in many applications, such as in the drug delivery system for the pharmaceutical industry,¹ increasing compound solubility for the food and cosmetic industries,² and in synthetic enzyme mimicry,^{3–5} including the separation of chemical and ion species.⁶

Polybenzoxazine is a class of phenolic material that undergoes ring-opening polymerization. Ning and Ishida⁷ reported that benzoxazine resin has a great deal of molecular design flexibility compared with ordinary phenolics. Benzoxazine is synthesized by the Mannich reaction from phenol, formaldehyde, and amine. Polyfunctional

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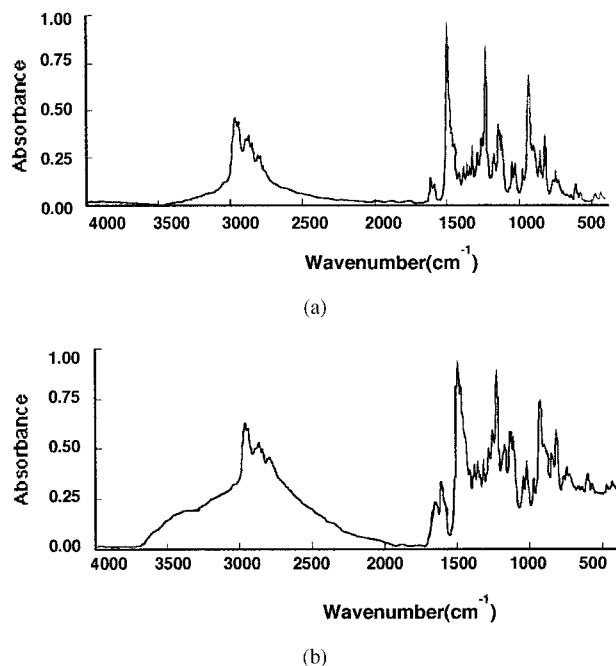


Figure 1 FTIR of (a) BA-m monomer and (b) BA-m monomer after heat under vacuum at 100°C for 4 h.

benzoxazines show an excellent balance of mechanical and physical properties,^{8,9} including high glass transition temperatures, high moduli, low water absorption, and good dielectric properties.^{10,11}

However, the structure of the polybenzoxazine repeat unit is similar to that of calixarenes which are well known host compounds. The benzoxazine local structure (Scheme 1) has a hydrophilic hydroxyl group and a tertiary nitrogen on one side with a hydrophobic benzene ring on the other. Moreover, there are lone pair electrons at the oxygen in the hydroxyl group and the nitrogen in the tertiary amine linkage of the Mannich base in each repeat unit. By varying the functional groups, the hydrophobicity of the monomer unit can be controlled. Thus, the benzoxazine chains will possibly act as a host compound because of the specific structure combined with the possible conformation of a cyclic phenolic, as seen in the case of calixarenes,¹² or pseudo-cyclic phenolic as seen in the case of all linear ortho-phenolic resins.¹³

Hence, it is our interest to originally propose the inclusion property of a benzoxazine compound derived from the unique structure of a benzoxazine monomer and its oligomer. The present work concentrates on the ion interaction ability, especially with alkali and alkaline earth metal

ions, to clarify the host-guest phenomenon of the benzoxazine owing to its specific local structure.

EXPERIMENTAL

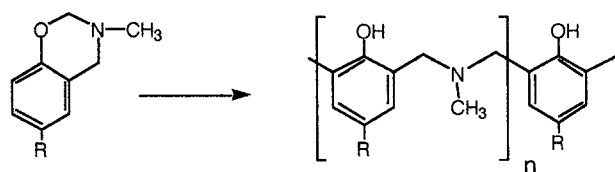
Polycarbonate-grade bisphenol-A was supplied by Siam Chemical Industry, Co., Ltd. (Thailand). Analytical grade 1,4-dioxane, sodium hydroxide, potassium nitrate, chloroform, and picric acid (Ajax Chemicals, Australia), formaldehyde and anhydrous diethyl ether (J. T. Baker, Inc., Phillipsburg, NJ), methylamine (40% in water) and anisole (Fluka Chemicals, Buchs, Switzerland), toluene (99.5%), trichloroethylene, 1,2-dichloropropane, and methylene chloride (Farmitalia Carlo Erba, Spain) were used without purification. Anhydrous sodium sulfate, nickel (II) nitrate, magnesium sulfate, sodium chloride (Farmitalia Carlo Erba, Spain), lithium chloride (Riedel-de Haen, Germany), and calcium chloride (E. Merck, Darmstadt, Germany) were applied as metal salts. All solvents were stocked with a 4-Å molecular sieve to eliminate the majority of water impurity before use.

The benzoxazine monomer and oligomer structures were studied by Fourier transform infrared spectroscopy (FTIR) (FT-45A, BioRad) at a resolution of 8 cm⁻¹. The concentration of picrate metal ions in the aqueous phase was measured by ultraviolet-visible spectroscopy (UV-Vis, Lambda-16, Perkin-Elmer) with a scan speed of 240 mm/min at room temperature. A Vortex mixer (Genie-2, Scientific Industries) was used to vigorously shake the mixture of organic and aqueous solution for 1 min. A centrifuge (Z 230 A, Hermle) was used for clear separation of a mixture to organic and aqueous phases at 3000 rpm for 3 min.

Purified bis(3,4-dihydro-2H-3-methyl-1,3-benzoxazinyl) isopropane (hereafter abbreviated as BA-m) was prepared from bisphenol-A, formaldehyde, and methylamine according to the method reported by Ning and Ishida⁷ as shown in Scheme 2.

Benzoxazine oligomers were obtained by heating the monomer powder under vacuum at 100°C for 4 h to obtain a pale yellow rigid sheet. The polymerization was confirmed by FTIR. The sheet was then ground to a powder and stored at low temperature until use. The local structure of the oligomer is shown in Scheme 1.

Alkali, alkaline earth, and other metal ion solutions were prepared by dissolving the corre-



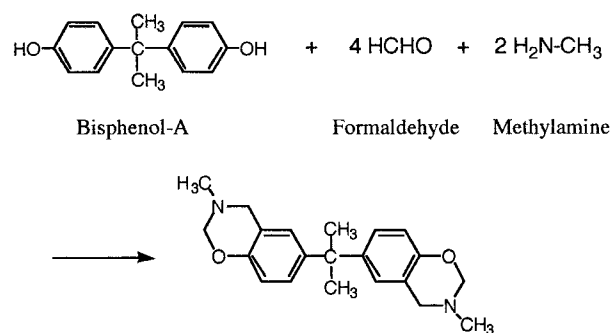
Scheme 1 Benzoxazine local structure.

sponding salts in water. Picric acid at a concentration of $10^{-2}M$ and an additional $2 \times 10^{-2}M$ of an ion salt were dissolved in deionized water. The concentration of each ion stock solution was diluted to obtain 1 absorbance unit at the wavelength of 354 nm as observed by UV spectroscopy, which is equal to 6.89×10^{-5} mol/L. The monomer and oligomers were dissolved in methylene chloride, chloroform, and toluene at the concentration of 0.200, 2.00, and 20.0 g/L, respectively. To study the effect of the organic phase on the ion extraction property of the BA-m monomer, in the liquid-liquid separation system, other solvents, i.e., anisole, trichloroethylene, and 1,2-dichloropropene, were also used.

The ion extraction phenomenon was observed using the Pedersen's technique in liquid-liquid systems.¹⁴ Five milliliters of ionophore in organic solution and 5 mL of ion solution were mixed vigorously for 3 min, followed by centrifuge for 1 min. The ion concentration of the aqueous phase was determined by a UV-Vis spectrophotometer at 354 nm. Ion extraction was accomplished at room temperature by varying the organic phase.

RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of BA-m before and after polymerization. The hydrogen bonded



Bis(3,4-dihydro-2H-3-methyl-1,3-benzoxazinyl) isopropane (BA-m)

Scheme 2 Preparation of BA-m.

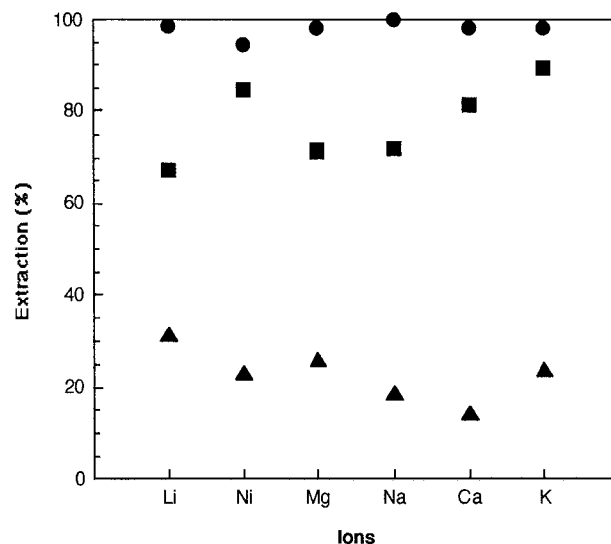


Figure 2 Extraction efficiency of various metal picrates by the BA-m oligomers. Ionophore concentration in CH_2Cl_2 as the organic solvent: ●, 20 g/L; ■, 2 g/L; and ▲, 0.2 g/L.

hydroxyl peaks are observed while the characteristic oxazine ring band is changed (1499 cm^{-1}) as reported elsewhere.⁷

To identify oligobenzoxazine as an ionophore and explore the inclusion phenomenon, it is necessary to study some structural factors of host-guest compounds. In the present work, the following factors are investigated: type of organic phase in liquid-liquid systems, variation of metal ions, and the concentration of both BA-m monomer and ion.

According to Pedersen's¹⁴ technique, the picrate ion will be shifted from the aqueous phase to the organic phase where the ionophore is present and act as an ionophore to entrap the metal ion. Here, when the oligobenzoxazine provides a structure as a host molecule and acts as an ionophore, the metal ion will transfer to the organic phase as soon as the oligobenzoxazine is added to the system and an ion complex is formed. Thus, ion extraction can be investigated by determining the change of picrate concentration in the aqueous phase and its concentration can be quantitatively determined by UV spectroscopy at the absorption wavelength of the picrate. Ion extraction was studied by varying the organic phase in the liquid-liquid system to observe the ion interaction with BA-m.

Figure 2 indicates that when the concentration of BA-m oligomers is higher, the ion extraction is more significant. When the oligomer concentra-

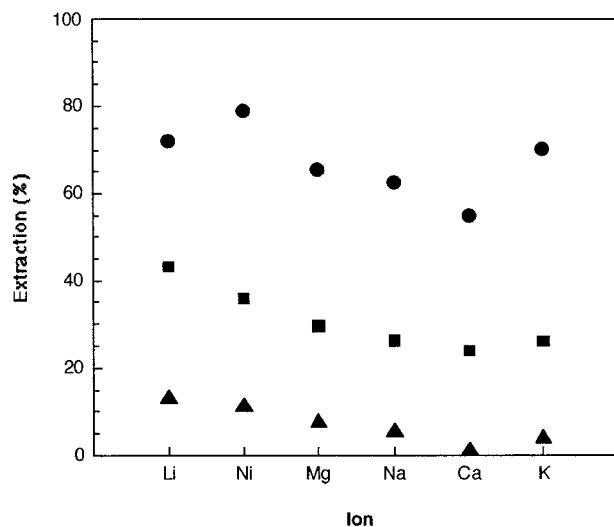


Figure 3 Extraction efficiency of various metal picrates by the BA-m oligomers. Ionophore concentration in CHCl_3 as the organic solvent: ●, 20 g/L; ■, 2 g/L; and ▲, 0.2 g/L.

tion is 20 g/L in CH_2Cl_2 , the ion extraction is nearly 100% of which the ion concentration is 6.89×10^{-5} mol/L. The BA-m oligomers show ion sensitivity to all types of metal ions. Figures 2–4 show the ion entrapment efficiency of the BA-m oligomers when the organic phase is varied from CH_2Cl_2 , CHCl_3 , and toluene. At the same oligomer concentration, the efficiency of ion extraction is highest in CH_2Cl_2 , followed by CHCl_3 , and

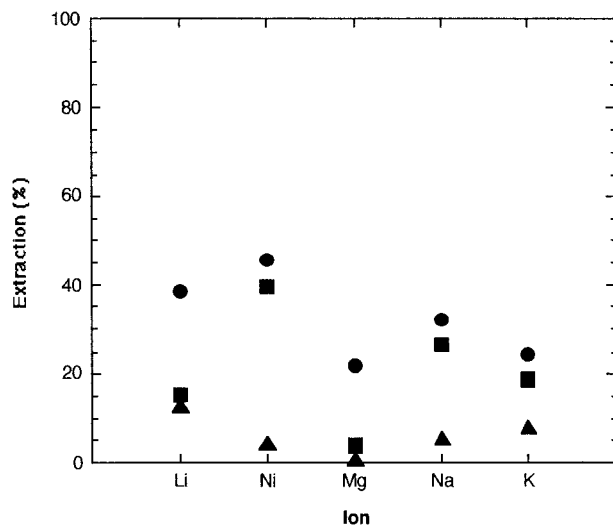


Figure 4 Extraction efficiency of various metal picrates by the BA-m oligomers. Ionophore concentration in toluene as the organic solvent: ●, 20 g/L; ■, 2 g/L; and ▲, 0.2 g/L.

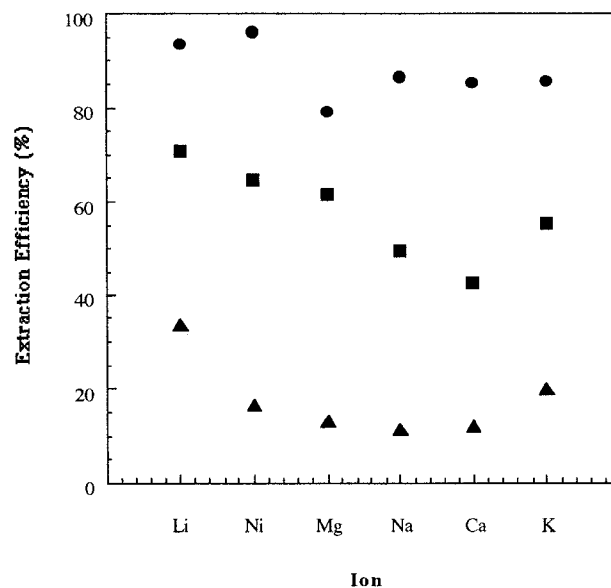


Figure 5 Extraction efficiency of various metal picrates by the BA-m monomer. Ionophore concentration in CH_2Cl_2 as the organic solvent: ●, 20 g/L; ■, 2 g/L; and ▲, 0.2 g/L.

finally toluene. When the oligomer concentration is increased, the percentage of ion extraction increases for all types of metallic ions. This suggests that the BA-m oligomers interact with ion species and act as ionophores. Similar to Figure 2, both Figures 3 and 4 show little selectivity toward any specific ions but high ion sensitivity to all types of metal ions.

To clarify the ion interaction mechanism, the BA-m monomer was studied as an ionophore because of its well defined structural unit. The results from the $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2$ system are shown in Figure 5. Here, it is clear that the monomer also performs as an ionophore. Ion extraction in a liquid-liquid phase system is significant in CH_2Cl_2 but is low for a toluene organic phase (Figures 5–7). In the case of the BA-m monomer, it is found that the percentage of ion extraction is nearly as high as that of the BA-m oligomers. Figure 5 shows that the BA-m oligomers can trap almost 100% of the sodium ion whereas the BA-m monomer shows a slightly lower (90%) extraction affinity when the BA-m concentration is 2.00 g/L in CH_2Cl_2 . It suggests that the lone pair electrons of the oxygen and/or nitrogen might be involved because there are no hydroxyl groups in the BA-m monomer.

The amount of ion entrapped increases nonlinearly as a function of the monomer concentration

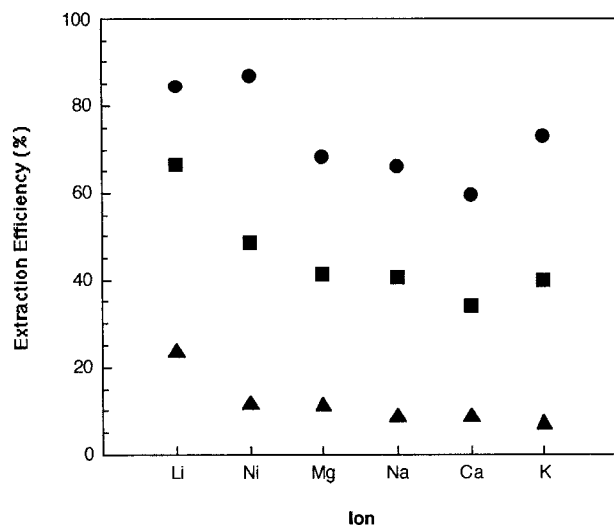


Figure 6 Extraction efficiency of various metal picrates by the BA-m monomer. Ionophore concentration in CHCl_3 as the organic solvent: ●, 20 g/L; ■, 2 g/L; and ▲, 0.2 g/L.

as shown in Figure 8 where the percent entrapment of the calcium ion is plotted as a function of the BA-m monomer concentration in CH_2Cl_2 . As the ion entrapment efficiency increases, the efficiency approaches an asymptotic value. It should be noted that the ion extraction property of benzoxazine is accomplished through various sizes of benzoxazines, oligomers, and even the monomer whereas the ion extraction percentage of metal

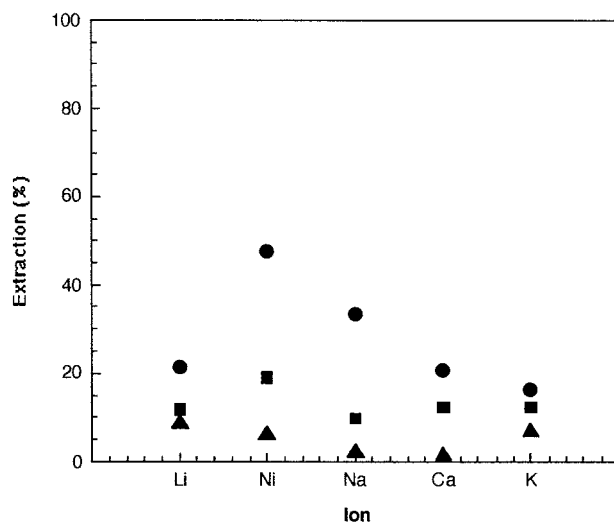


Figure 7 Extraction efficiency of various metal picrates by the BA-m monomer. Ionophore concentration in toluene as the organic solvent: ●, 20 g/L; ■, 2 g/L; and ▲, 0.2 g/L.

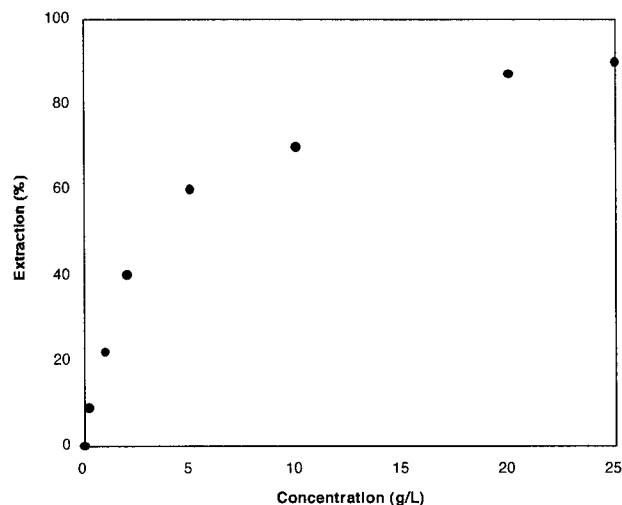


Figure 8 Extraction efficiency of the Ca^{2+} ion as a function of the BA-m monomer concentration in CH_2Cl_2 .

ions studied shows little variation as a function of the ion size. Thus, we propose that the ion extraction mechanism for the ionophore is due to a molecular assembly of host and guest compounds, rather than specific sizes of cage-like structures of cyclic compounds, such as calixarene and cyclodextrin. Yamagishi et al.¹³ proposed that the ionic affinity of the cavity which is present in the molecular assembly can be based on the pseudocyclic conformation. In this study, it is presumed that the assemblies of the benzoxazine oligomers may be flexible, thus the ion extraction can be performed efficiently with various metal ions but the selectivity is not obvious.

Generally, host compounds will provide a specific cavity for guest molecules depending on its molecular assembly structure. In this study, the ionophore was varied to investigate the guest responsive structure due to the assembly formation of the BA-m monomer and oligomers. Alkali, alkaline earth, and transition metal ion (Ni) are used for the observation of ion extraction. Six kinds of metallic ions were used to observe the ion extraction ability of the BA-m monomer. It is expected that there will be an appropriate ion size that fits the cavity of the ionophore if the configuration of the ionophore is fixed. As shown in Figures 5–7, among alkali and alkali earth ions, lithium and potassium ions tend to show slightly higher ion extraction efficiencies than other ions. It should be noted that the size of the potassium ion is twice the size of the lithium ion, whereas the ion extraction percentages are similar. This is

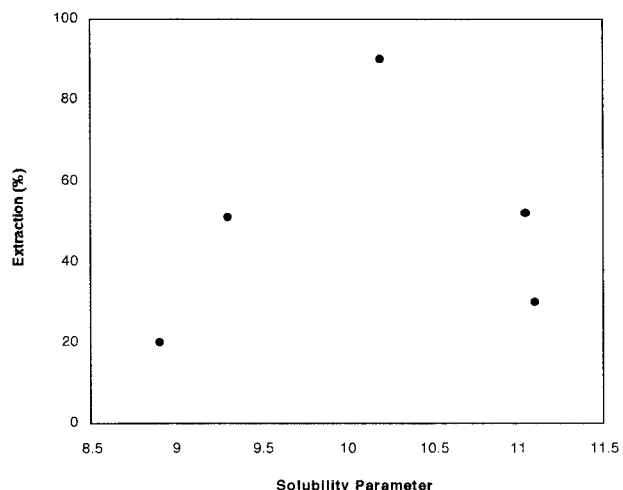


Figure 9 Percent extraction of Ca^{2+} ion by varying solubility parameter of the organic phase when BA-m monomer concentration is 2 g/L.

yet another indication of ion entrapment by the molecular assembly rather than the cavity of fixed size and shape. Miyata et al.¹⁷ reported that when the host molecule acts as a flexible structure for the guest, various types of guest molecules will be allowed in the cavity, as seen in the case of the cholic acid molecular assembly system. Accordingly, the various observations stated above indicate that the BA-m monomer and oligomers provide the guest responsive structure, while the inclusion phenomenon with the low size selectivity takes place.

It is well known that the inclusion phenomenon is related to the interaction of the host and guest molecules. When the host concentration is in excess of the guest molecules, a greater amount of guests will be included in the host compound. It is found that in the case of CHCl_3 and CH_2Cl_2 , when the ionophore (both the BA-m oligomers shown in Figures 2–4, and the BA-m monomer shown in Figures 5–7) concentrations are increased by 100 times from 0.200 to 20.0 g/L, the ion extraction efficiencies are increased only by 60%. In the case of a toluene organic phase, in which the ion extraction percentages are relatively low, the relationship of the ionophore concentration and ion extraction ability is not significant, ranging from 10 to 30%.

The organic phase in a liquid-liquid system plays an important role in the ion extraction step. Tsurubou et al.¹⁵ reported that the host guest assembly can be controlled by the surrounding organic solvent molecules in the liquid-liquid

phase system. Thomas et al.¹⁶ reported that size of the solvent affects the ion transfer across the liquid-liquid phase because of the hydrodynamic continuum effect. The ion extraction selectivity can be established when the appropriate solvent is applied under a certain hydrodynamic continuum atmosphere. In the present work, methylene chloride, chloroform and toluene, which differ in molecular size, clarify the factor of organic phase in the interaction between ionophore and metal ions.

It can be concluded that benzoxazines act as an ionophore to form the ion complexes whereas the organic solvent molecules provide the preferable assembly in the host-guest formation.¹⁶ The solubility parameter of the BA-m monomer, $\delta = 9.99$, is much closer to that of CH_2Cl_2 than to that of toluene. Therefore, the ion entrapment efficiency was suspected to be influenced by the benzoxazine monomer-solvent interaction. This can be examined by varying the solubility parameter of organic phase. As shown in Figure 9, when BA-m monomer is used as an ionophore, the percent extraction is high when the solubility parameter of the organic phase is close to that of the BA-m monomer. To quantitatively evaluate the effect of the interaction, the Flory-Huggins χ_{ab} parameter as defined below was calculated.

$$\chi_{ab} = 0.34 + V_r (\delta_a - \delta_b)^2/RT$$

where V is the molar volume of the solvent; δ , the solubility parameter; R , gas constant; and T , temperature.

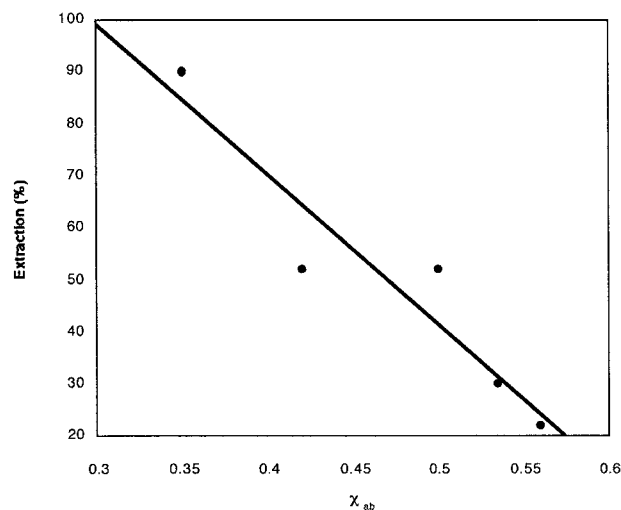


Figure 10 Extraction efficiency of the Ca^{2+} ion in various solvents. The extraction efficiency is plotted against the Flory-Huggins χ_{ab} parameter of the BA-m monomer/solvent system.

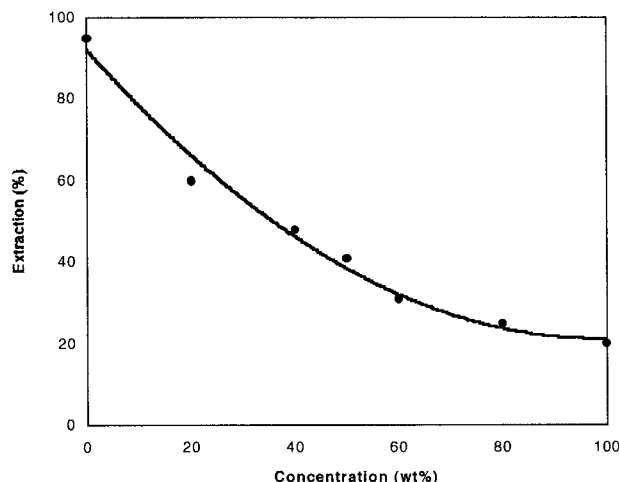


Figure 11 Extraction efficiency of the Ca^{2+} ion in CH_2Cl_2 /toluene mixtures. The extraction efficiency is plotted against the concentration of toluene in the mixtures.

The observed ion entrapment efficiency was plotted as a function of the χ_{ab} parameter of the system as shown in Figure 10. An excellent correlation is observed in which the smaller the χ_{ab} parameter, the greater the ion entrapment. It indicates that the solvation of the benzoxazine monomer is related to the ion entrapment efficiency. This supports that the molecular assembly enhancement by organic solvent molecules plays an important role in ion entrapment.

To study the relationship of the solubility parameter and the ion interaction with the ionophore, the solubility parameter was changed by systematically varying the composition of CH_2Cl_2 and toluene mixtures. Assuming that the Flory-Huggins χ_{ab} parameter can be averaged for the mixture system, the ion entrapment efficiency is again plotted as a function of the toluene concentration as shown in Figure 11. Here, it is found that the ion extraction efficiency is decreased when the solubility parameter is varied by the composition of toluene. Similar to Figure 10, where various solvents are used to vary the χ_{ab} parameter, it is observed that the smaller the χ_{ab} parameter (the lower the concentration of toluene), the higher the ion entrapment efficiency. Accordingly, the solubility of the benzoxazine systems is an important parameter for influencing the ion entrapment efficiency.

Calixarenes, crown-ether, and cyclodextrin are well known inclusion compounds and some practical applications are established. The ion extraction ability of 18-crown-6, calix[4]arene,

calix[6]arene, and calix[8]arene for the calcium, lithium, and sodium ions¹⁸ is compared with that of benzoxazine monomer as shown in Figure 12. To compare the ion extraction ability to the mentioned ionophores, experiments were performed under the same conditions as those reported in the literature. The concentration of the benzoxazine monomer was $2.7 \times 10^{-3}\text{M}$, which is also the same as the ionophore concentration reported in the cited reference.

The preliminary study shows that, in the case of lithium and calcium, the ion extraction is in the range of 20–50% for the calixarenes and crown-ether, whereas the extraction efficiency of the benzoxazine is quite high at nearly 80%. The high ion extraction ability of benzoxazines suggests that the benzoxazine can be an effective ionophore based on each phenolic-like repeat unit structure combined with the local structure of the assembly under the preferable condition of the organic phase.

CONCLUSIONS

Benzoxazine, BA-m monomer, and its oligomer perform as an ionophore to show a significant ion interaction among alkali and alkaline earth ions in the liquid-liquid phase. The ion extraction

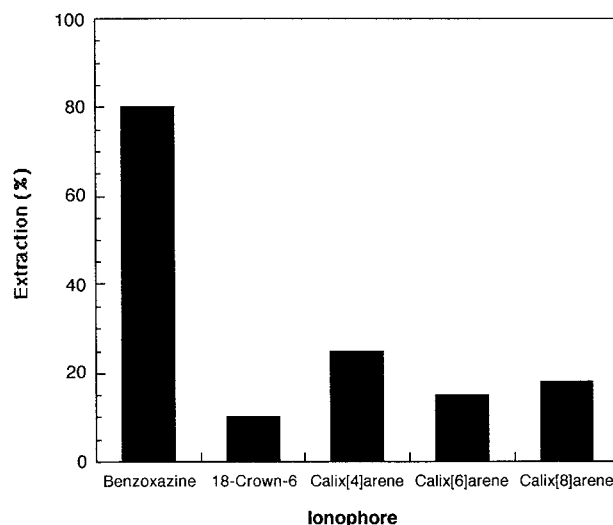


Figure 12 Comparison of the extraction efficiency of lithium picrate of the BA-m monomer with the published results on calix[4]arenes, calix[6]arenes, calix[8]arenes, and 18-crown-6 ether.¹³ The ionophore concentration of all the systems was $2.7 \times 10^{-3}\text{M}$ in CH_2Cl_2 as the organic solvent.

study clarifies that benzoxazines entrap all types of ions studied but shows little selectivity for ion size. The ion entrapment is found to proceed via molecular assembly formation under the preferable structure provided by the organic phase molecule in the liquid-liquid system. The ion entrapment efficiency shows a good correlation with the Flory-Huggins c_{ab} parameter of the benzoxazine/organic solvent system studied.

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