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SHORT COMMUNICATIONS

# Preparation of Immobilized β-Cyclodextrins by Use of Alkanediol Diglycidyl Ethers as Crosslinking Agents and Their Guest Binding Abilities

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Cyclodextrins (CyDs), cyclic oligomers of 6—8 glucose units, form inclusion complexes with guest compounds. As a result, they exhibit various specific functions.[1-5]

There has been considerable study on the immobilization of CyDs using epichlorohydrin as a crosslinking agent.[1,2] The immobilized CyDs were effectively used as catalysts for selective syntheses[6-10] and as packings for column chromatography.[11,12] Immobilization of CyDs by diisocyanate compounds was also reported.[13]

However, information on the immobilization of CyDs with the use of crosslinking agents other than epichlorohydrin is still scanty. In addition, little is known on the relationship between the kinds of crosslinking agents and the guest binding abilities of the resultant immobilized CyDs.

This paper reports the first successful immobilization of β-CyD using 1,2-ethanediol diglycidyl ether (**Ia**), 1,4-butanediol diglycidyl ether (**Ib**), and 1,6-hexanediol diglycidyl ether (**Ic**) as crosslinking agents. The guest binding abilities of these immobilized β-CyDs on nitrophenols and 2-naphthol in water are determined, and the effects of kinds of crosslinking residues on the abilities are discussed.

## EXPERIMENTAL

Immobilized β-CyDs were prepared as follows. Fifty grams (44 mmol) of β-CyD were sufficiently mixed with 10 $cm^3$ of water in a beaker, and 50 wt% aqueous sodium hydroxide solution (50 $cm^3$) was added to the resultant paste. The mixture was vigorously stirred by mechanical stirrer in the beaker set on a water bath of 50°C, and the crosslinking agent (440 mmol) was dropwise added. Viscosity of the mixture gradually increased, and finally the whole mixture turned into highly viscous mass of color of white to pale yellow. The reaction periods were 0.7, 1.8, 4.0, and 1.3 h for reactions with **Ia**, **Ib**, **Ic**, and epichlorohydrin, respectively. The masses were successively washed with water and acetone, cut to particles of appropriate size (1—3 mm in diameter), and dried *in vacuo* at 90°C for 12 h.

The guest binding abilities of the immobilized β-CyDs were evaluated by incubating 30—200 mg of the immobilized β-CyDs in 10 $cm^3$ of pH 4.0 acetate buffer solutions of nitrophenols and 2-naphthol at 20°C. The charged concentrations ($[G]_0$) of the guest compounds and the ion strength,

respectively, were $1.0 \times 10^{-3}$ and $1.0\,\mathrm{l\,mol^{-1}}$. After 40 h, the concentrations ($X$) of the solutes in the liquid phase were determined by absorption spectroscopy. Completions of the equilibria were confirmed by the fact that the concentrations measured after 60 h incubation were identical with the values at 40 h.

The equilibrium constants ($K$) for the formations of the complexes were calculated by eq 1.

$$K = \frac{[\beta\text{-CyD guest complex}]}{[\text{uncomplexing } \beta\text{-CyD}][\text{uncomplexing guest}]} = \frac{([\mathrm{G}]_0 - X)}{([\beta\text{-CyD}]_0 - [\mathrm{G}]_0 + X)X} \quad (1)$$

## RESULTS AND DISCUSSION

Immobilized β-CyDs were successfully prepared using the alkanediol diglycidyl ethers (**Ia**—**c**) as crosslinking agents. All of them were white beads, and insoluble in water, aqueous alkaline solutions, and organic solvents such as acetone, methanol, benzene, and chloroform.

The molar ratios of the residues derived from the crosslinking agents to the β-CyD residues in the **Ia**-, **Ib**-, **Ic**-, and epichlorohydrin-immobilized β-CyDs are 5.9, 3.8, 4.5, and 3.4, respectively, as shown in the second column in Table I. These values have been determined by the following results of elemental analysis. For **Ia**, C, 49.28% (49.27%) and H, 7.68% (7.62%); for **Ib**, C, 50.14% (50.18%) and H, 7.71% (7.68%); for **Ic**, C, 53.29% (53.33%) and H, 8.29% (8.30%); for epichlorohydrin, C, 47.08% (47.05%) and H, 6.96% (6.84%). Agreement between the observed values and the calculated values, the numbers in the parentheses, is satisfactorily fair.

Table I lists the $K$ values for the complexes of the β-CyD residues in the immobilized β-CyDs with *o*-, *m*-, and *p*-nitrophenols and 2-naphthol at pH 4.0, 20°C. Here, formations of 1 : 1 complexes between guest compounds and β-CyD residues are confirmed by the fact that the $K$ values determined by use of eq 1 are independent of the charged amounts of the immobilized β-CyDs in the ranges of 30—200 mg. Equation 1 was derived under the

**Table I.** Equilibrium constants ($K$) for the formation of complexes between β-CyD residues in immobilized β-CyDs and various guest compounds[a]

| Crosslinking agent[b] | Degree of crosslinking[c] | K/l mol$^{-1}$ | | | |
|---|---|---|---|---|---|
| | | Nitrophenol | | | 2-Naphthol |
| | | *o*- | *m*- | *p*- | |
| **Ia** | 5.9 | 76 | 108 | 119 | 294 |
| **Ib** | 3.8 | 78 | 70 | 108 | 217 |
| **Ic** | 4.5 | 159 | 323 | 313 | 1590 |
| Epichlorohydrin | 3.4 | 119 | 38 | 263 | 526 |

[a] At pH 4.0 (acetate buffer), 20°C.
[b] **Ia**, 1,2-ethanediol diglycidyl ether; **Ib**, 1,4-butanediol diglycidyl ether; **Ic**, 1,6-hexanediol diglycidyl ether.
[c] The molar ratios of the residues derived from the crosslinking agents to the β-CyD residues in the immobilized β-CyD.

assumption of the 1 : 1 complex formation.

The $K$ value ($1301\,mol^{-1}$) in binding of *p*-nitrophenol for the **Ia**-immobilized β-CyD, which was prepared at the charged molar ratio 7 of **Ia** to β-CyD and had a degree of crosslinking of 3.1, was almost identical with that ($1191\,mol^{-1}$) for one with a crosslinking degree of 5.9. This result shows the significant role of β-CyD residues in guest binding by the immobilized β-CyD, since the $K$ values refer to the guest binding ability of the β-CyD residue (see eq 1). The possibility that the differences in the $K$ values in Table I are simply associated with differences in the degree of crosslinking is unlikely.[9]

The $K$ values of the **Ic**-immobilized β-CyD are larger by factors of 2—7 than the corresponding values of the **Ia**- and **Ib**-immobilized β-CyDs for all the guest compounds investigated. Thus, **Ic**-immobilized β-CyD has the largest guest binding abilities. Furthermore, these immobilized β-CyDs exhibit different selectivities in the binding of *o*- *m*-, and *p*-nitrophenols: $K$(*o*-isomer) : $K$(*m*-isomer) : $K$(*p*-isomer) = 0.64 : 0.91 : 1.00 for **1a**; 0.72 : 0.65 : 1.00 for **1b**; 0.51 : 1.03 : 1.00 for **1c**.

The guest binding abilities of the **Ic**-immobilized β-CyD on *o*-nitrophenol, *m*-nitrophenol, and 2-naphthol are 1.3, 8.5, and 3.0 times, respectively, as large as those of the immobilized β-CyD prepared by epichlorohydrin, the crosslinking agent used in almost all immobilizations hitherto made.

These considerable differences in the $K$ values of the four types of the immobilized β-CyDs prepared from different crosslinking agents indicate that the crosslinking residues as well as the β-CyD residues exhibit significant participation in the complex formations between immobilized β-CyDs and guest compounds. Either the magnitude of the interaction between the β-CyD residue and the guest compound or that between the crosslinking residue and the guest compound is highly dependent on the structures of both the guest compounds and crosslinking residues. Thus, the selectivities of the immobilized β-CyDs are significantly different from each other.

In the guest binding by **Ic**-immobilized β-CyD, apolar interactions between the guest compounds and hexamethylene residues in **Ic** are effectively operative in addition to interactions between the guest compounds and cavities of the α-CyD residues. These interactions function cooperatively, giving rise to significant enhancement of guest binding ability. These effects are less important in the guest binding by the **1a**- and **1b**-immobilized β-CyDs, which have shorter methylene carbon chains than the **1c**-immobilized one, and thus the guest binding abilities of them are smaller.

In conclusion, immobilized β-CyDs were prepared by alkanediol diglycidyl ethers as crosslinking agents. The guest binding abilities of the immobilized β-CyDs are highly dependent on the kinds of crosslinking residues.

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## REFERENCES

1. M. L. Bender and M. Komiyama, "Cyclodextrin Chemistry," Springer-Verlag, Berlin, 1978.
2. J. Szejtli, "Cyclodextrins and their Inclusion Complexes," Akadémiai Kiadó, Budapest, 1982.
3. M. Komiyama and H. Hirai, *J. Am. Chem. Soc.*, **105**, 2018 (1983).
4. M. Komiyama and H. Hirai, *J. Am. Chem. Soc.*, **106**, 174 (1984).
5. H. Hirai, *J. Inclusion Phenomena*, **2**, 655 (1984).
6. R. Breslow, H. Kohn, and B. Siegel, *Tetrahedron Lett.*, 1645 (1976).
7. M. Komiyama, I. Sugiura, and H. Hirai, *J. Inclusion Phenomena*, **2**, 823 (1984).
8. M. Komiyama, I. Sugiura, and H. Hirai, *Polym. J.*, **17**, 1225 (1985).
9. M. Komiyama, I. Sugiura, and H. Hirai, *J. Mol. Catal.*, **36**, 271 (1986).
10. M. Komiyama and H. Hirai, *Polym. J.*, **18**, 375 (1986).
11. J. L. Hoffman, *J. Macromol. Sci.-Chem.*, **A7**, 1147 (1973).
12. A. Harada, M. Furue, and S. Nozakura, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 189 (1978).
13. Y. Mizobuchi, M. Tanaka, and T. Shono, *J. Chromatogr.*, **194**, 153 (1980).