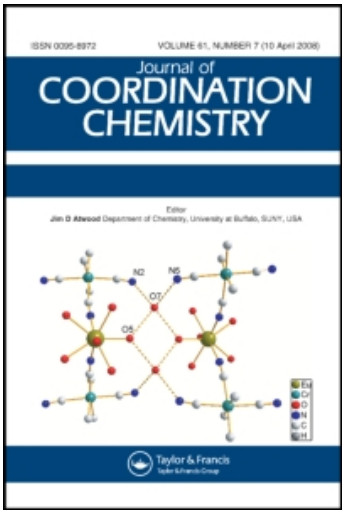

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Guest-Binding and Catalytic Properties of Immobilized β-Cyclodextrins

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GUEST-BINDING AND CATALYTIC PROPERTIES OF IMMOBILIZED β-CYCLODEXTRINS

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Cyclodextrins[1](CyDs), cyclic oligomers of 6-8 glucose units, form inclusion complexes with guest compounds and have been used as catalyst for the selective syntheses.[2] Previously, immobilization of CyD with epichlorohydrin as crosslinking agent have been described.[3-4] Here, we report the first successful immobilization of β-CyD using various crosslinking agents. The guest binding abilities and the catalytic abilities of these immobilized β-CyDs are shown.

Immobilized β-CyDs were prepared by dropwise addition of the crosslinking agents to the aqueous sodium hydroxide solutions of β-CyD. The resultant high viscous masses were washed with water and then with acetone, and were dried. The guest binding abilities of the immobilized β-CyDs were evaluated by incubating them in buffer solutions of guest compounds. The concentrations of the guests in the liquid phase were determined by absorption

spectroscopy.

Selective carboxylation of phenol[2,4] was achieved by adding carbon tetrachloride to the alkaline solution of phenol in the presence of the immobilized β-CyD and copper powder as cocatalyst. The product analysis was made by HPLC.

The immobilized β-CyDs were obtained as white to pale yellow beads of diameter 1-3mm. They were insoluble in water, methanol, ethanol, acetone, and chloroform. The degrees of crosslinking (molar ratios of the residues derived from the crosslinking agents to the β-CyD residues), determined by elemental analysis, were 3-6.

TABLEs 1 and 2 list the equilibrium constants K for the 1:1 complex formation between the β-CyD residues in the immobilized β-CyDs with o-, m-, and p-nitrophenols (TABLE 1) and with 2-naphthol (TABLE 2) at 20°C. The 1:1 complex formation is confirmed by independence of K values from the charged amount of the immobilized β-CyDs in the ranges of 30-200mg.

As shown in TABLEs 1 and 2, the K values highly depend on the crosslinking agents. This dependence indicates that the crosslinking residues play an important role in complex formation. The K values at pH 4 are larger than those at pH 9 or 10. The guest compounds exist as neutral molecules at pH 4 whereas they exist as anion at pH 9 or 10. For the 1,6-hexanediol diglycidyl ether-immobilized β-CyD (TABLE 1, A;n=6), the K value (897) with o-nitrophenol at pH 4 is 179 times as large as that (5) at pH 9. This result shows predominance of the apolar interaction for the guest binding by the immobilized β-CyD. The immobilization promotes the hydrophobic character of the β-CyD cavity due to "capping" by the apolar crosslinking residues, and in addition the direct apolar interaction between the guest compound and the crosslinking residues can be operative there. The K values at pH 4 are larger than the values for epichlorohydrin-immobilized β-CyD by factor of 1.6-9.2.

TABLE 1 Equilibrium constants (K) at 20°C of complex formation with nitrophenols for the immobilized β-CyD prepared by use of various crosslinking agents

Crosslinking agent		Degree of crosslinking[a]	(K)[b] (l/mol) o pH4	o pH9	m pH4	m pH9	p pH4	p pH9
A[c]	n=2	4.5	432	11	115	42	142	143
	n=4	4.6	294	28	87	57	112	112
	n=6	4.5	897	5	268	57	262	58
B[d]	n=4	3.6	594	13	200	80	311	344
epichlorohydrin		3.9	215	34	151	38	161	257

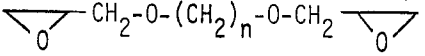
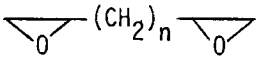
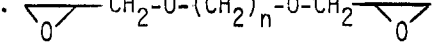
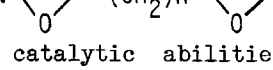
a. Molar ratio of crosslinking residue to β-CyD
b. o,m,and p, : o-,m-,and p-nitrophenol
c. 
d. 

TABLE 2 Equilibrium constants (K) at 20°C of complex formation with 2-naphthol for the immobilized β-CyD prepared by use of various crosslinking agents

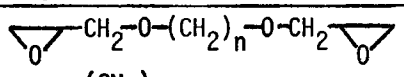
Crosslinking agent		Degree of crosslinking[a]	K (l/mol) pH4	pH10
A[b]	n=2	4.5	339	269
	n=4	4.6	324	100
	n=6	4.5	1460	883
B[c]	n=4	3.6	686	1095
epichlorohydrin		3.9	159	211

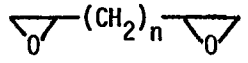
a. Molar ratio of crosslinking residues to β-CyD
b. 
c. 

The catalytic abilities of the immobilized β-CyDs for the carboxylation of phenol are shown in TABLE 3. With the immobilized β-CyD prepared by use of 1,2-ethanediol diglycidyl ether (A;n=2), 1,4-butanediol diglycidyl ether (A;n=4), 1,3-butadiene diepoxide (B;n=0), 1,7-octadiene diepoxide (B;n=4), and epichlorohydrin as catalyst, the selectivity for the formation of 4-hydroxybenzoic acid is virtually 100 %, and the yields are high.

TABLE 3 Selective synthesis of 4-hydroxybenzoic acid using the immobilized β-CyD catalysts

Crosslinking agent		Yield (mole %) 4-hydroxy-benzoic acid	Yield (mole %) 2-hydroxy-benzoic acid	Selectivity for 4-hydroxy-benzoic acid (%)
A[a]	n = 2	48	0	100
	n = 4	32	0	100
	n = 6	37	6	86
B[b]	n = 0	25	0	100
	n = 4	59	2	97
epichlorohydrine		42	1	98
without catalyst		15	12	56

a. 

b. 

In their absence, however, the selectivity and the yield are only 56 % and 15 mole%, respectively. Thus selective synthesis is successfully achieved by use of these immobilized β-CyD catalysts. Rather low selectivity for the 1,6-hexanediol diglycidyl ether immobilized β-CyD (A;n=6) is probably associated with steric hindrance by crosslinking residues in the catalyst.

In conclusion, immobilized β-CyDs are successfully prepared by use of various crosslinking agents. The guest binding abilities of these immobilized β-CyDs are highly dependent on the crosslinking residues. These immobilized β-CyDs exhibit selective catalysis in the para-carboxylation of phenol.

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