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Sorption Behavior of Aromatic Compounds in Water on β-Cyclodextrin Polyurethane Resins

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The sorption behavior of aromatic compounds in water on β-cyclodextrin polyurethane resins was evaluated by batch and column procedures. The values of their sorption capacities obtained in the batch experiments were comparable to those of Amberlite XAD-2 and/or -7. In the column experiments, β-H6XDI-P-6.0-M showed a quantitative collection of the aromatic compounds at low concentrations, while Amberlite XAD-7 did not.

Since various organic pollutants exist at relatively low concentrations in water, pre-concentration is generally required before their qualitative and quantitative analyses. For this purpose, commercially available porous polymer sorbents (*i.e.*, Amberlite XAD,[1,2] Tenax GC,[2] Separon,[3] and Hitachi gel[4]) have been widely used. In water, the degree of interaction between solutes and these polymers generally increases with increasing hydrophobicity of the solutes because these polymers are hydrophobic. Therefore, it is difficult for these polymers to sorb specific organic solutes selectively. We have been interested in developing sorbents that can collect the solutes in water selectively.

It is well known that cyclodextrins form stable inclusion complexes with specific organic compounds. The polyurethane resins containing cyclodextrin units as specific sorption sites were prepared by cross-linking β-cyclodextrin with diisocyanates.[5] In gas-solid chromatography these cyclodextrin resins exhibited strong interactions with organic compounds containing π-electrons or heteroatoms. It was found that these cyclodextrin resins interact strongly with benzene vapor in a nitrogen or an air stream and that one of these, β-H6XDI-P-6.0-M, retains the polar volatile organic compounds (*i.e.*, methyl and ethyl alcohols, acetone, and ethyl methyl ketone) more than Amberlite XAD-7 does in the gas stripping experiments.[6]

In the present paper we describe the application of β-cyclodextrin polyurethane resins to sorbents which concentrate aromatic compounds in artificial water samples. The sorption capacities of these resins are compared with that of Amberlite XAD-2 and/or -7 in order to evaluate the possibility of using these cyclodextrin resins as sorbents to collect aromatic compounds dissolved in water.

Experimental

Materials. β-Cyclodextrin polyurethane resins were prepared by cross-linking β-cyclodextrin with diisocyanate (hexamethylene diisocyanate (HDI), 1,3-bis(isocyanatomethyl)benzene (XDI), or 1,3-bis(isocyanatomethyl)cyclohexane (H6XDI)).

Amberlite XAD-2 and -7 resins were obtained from Rohm and Hass (Philadelphia, PA, U. S. A.).

These resins were granulated to particle sizes of 80—100 mesh (for batch method) and 100—200 mesh (for column method), purified by Soxhlet extraction with ethyl alcohol, dried *in vacuo* for 8 h at 80 °C, and then used as sorbents.

The reagents for uptake studies were obtained from Wako (Osaka, Japan) or from Aldrich (U. S. A.) and used without further purification.

Procedure. Sorption capacities of β-cyclodextrin polyurethane resins and Amberlite XAD-2 and -7 were determined by the following batch (static) method. A resin (0.1 g) and 100 ml aqueous solution containing one of the model organic compounds at various concentrations (0.08—1 mM; 1 mM= 10^{-3} mol dm^{-3}) in a 300 ml conical flask with a glass stopper was shaken in a thermostated water bath (25±0.1 °C) for 4 h. The resin was then removed by filtration. The concentration of solute in the filtrate was determined spectrophotometrically (Hitachi Model 340 Recording Spectrophotometer) and from this value the sorption capacity (mmol/g resin) and percent uptake were calculated.

The column (dynamic) experiments were carried out by using a 10 cm×0.52 cm I. D. glass column packed by a slurry packing technique with a sorbent bed volume of 2.1 cm^3. The sample solutions (1 mM) were allowed to pass through the column at a flow-rate of 55.3 ml/h using an Adzuma Model MF-1 microfeeder equipped with a 200 ml cylinder. The absorbance of the effluent was monitored at 254 nm (Atto Model SJ-1541 UV Monitor).

Results and Discussion

Sorption Capacities in Batch System. The sorption capacities of the resins for the disubstituted benzenes (0.2 mM) in the bath system are shown in Table 1. The β-cyclodextrin polyurethane resins (β-H6XDI-P-6.0-M, β-HDI-P-5.5-A, and β-XDI-P-5.8-A; see Ref. 5) have much larger capacities than that of the BDOL-HDI-P-M polyurethane resin. Since it was prepared from 1,4-butanediol and HDI, BDOL-HDI-P-M contains no β-cyclodextrin units. This suggests that the inclusion process by β-cyclodextrin units acts efficiently on the sorption of the solutes on the cyclodextrin resins. The sorption capacities of the cyclodextrin resins decrease in the order β-H6XDI-P-6.0-M>β-XDI-P-5.8-A>β-HDI-P-5.5-A, which indicates that the interaction between the resins and the solutes depends upon the cross-linking diisocyanate, in a way similar to the interaction with the organic vapors.[5] Roughly speaking, the β-cyclodextrin resins take up the solutes as well as the commercially available sorbents, Amberlite XAD-2 and -7, do, except for three dinitrobenzene isomers. It is assumed that dinitrobenzene, much more hydrophobic than the other solutes, is taken up more by the latter resins because their hydrophobicity is stronger than that of the β-cyclodextrin resins.

For each given disubstituted benzene solute, the amount of *o*-, *m*-, or *p*-isomer taken up by each β-cyclodextrin resin decreases in one of three orders: *p*>*m*>*o*

Table 1. Sorption capacities for disubstituted benzenes in water by batch method

Solute[a)]	Sorption capacity/10^{-2} mmol per g resin					
	β-H6XDI-P-6.0-M	β-HDI-P-5.5-A	β-XDI-P-5.8-A	BDOL-HDI-P-M	Amberlite XAD-2	Amberlite XAD-7
o-Nitroaniline	8.6	5.5	7.3	1.2	8.6	13.9
m-	6.4	5.2	5.1	0.8	4.7	11.6
p-	11.6	10.0	9.5	1.2	2.6	11.5
o-Aminobenzoic acid	5.1	2.8	3.7	0.6	0.3	5.8
m-	2.0	1.0	1.5	0.6	0.0	1.4
p-	5.9	4.6	6.0	1.1	0.8	4.8
o-Dinitrobenzene	9.0	5.8	7.1	1.8	14.7	14.9
m-	5.1	3.1	5.3	0.0	15.2	13.4
p-	5.9	4.2	5.8	1.3	13.5	13.7
o-Toluidine	4.6	2.8	4.1	0.3	6.5	5.7
m-	6.4	3.8	5.3	0.1	7.0	6.9
p-	8.1	5.7	7.2	0.0	6.3	6.4
o-Cresol	6.6	5.0	6.5	1.9	4.0	10.0
m-	7.0	5.4	7.1	2.1	3.7	9.2
p-	9.7	7.7	8.6	2.0	4.1	9.7
o-Ethylphenol	10.2	7.7	9.4	2.7	8.4	14.9
m-	11.9	8.9	10.8	2.8	10.3	10.8
p-	14.1	11.3	11.6	1.2	7.7	13.3

a) Concentration of solute: 0.2 mM.

Table 2. Sorption capacities for phenol, aromatic alcohols, and carboxylic acids in water by batch method

Solute[a)]	Sorption capacity/10^{-2} mmol per g resin					
	β-H6XDI-P-6.0-M	β-HDI-P-5.5-A	β-XDI-P-5.8-A	BDOL-HDI-P-M	Amberlite XAD-2	Amberlite XAD-7
Phenol	6.0	5.3	5.5	0.0	2.8	7.5
Benzyl alcohol	4.7	3.3	4.0	0.4	2.9	3.2
2-Phenylethanol	9.5	5.9	6.6	0.0	4.7	6.0
3-Phenyl-1-propanol	13.9	9.4	8.8	0.3	8.6	12.4
Benzoic acid	9.0	6.2	7.5	0.9	2.8	6.9
Phenylacetic acid	7.3	3.6	3.6	0.4	2.0	3.2
3-Phenylpropionic acid	11.4	7.3	6.9	1.4	4.5	9.7
4-Phenylbutyric acid	14.0	11.9	10.3	1.8	9.2	11.0
5-Phenylvaleric acid	16.6	12.3	10.7	3.5	13.5	15.6

a) Concentration of solute: 0.2 mM.

for toluidine, cresol, and ethylphenol; $p>o>m$ for nitroaniline and aminobenzoic acid; $o>p>m$ for dinitrobenzene. It is of great interest that just the same order is observed in the retention of each isomer on the chemically bonded β-cyclodextrin phase.[7)] Except for dinitrobenzene, the *p*-isomers give the largest sorption capacities. This may be reasonably interpreted because the *p*-isomers can enter deep into the cyclodextrin cavity and can participate in the strongest hydrophobic interaction with the cavity. The irregularity of the order for dinitrobenzene is still unexplainable.

Table 2 shows sorption capacities for phenol, aromatic alcohols, and carboxylic acids. Concerning these substances, the β-cyclodextrin resins also have sorption capacities comparable to those of Amberlite XAD-2 or -7. In this case, β-H6XDI-P-6.0-M also exhibits the largest values among these cyclodextrin resins. Therefore, β-H6XDI-P-6.0-M was further investigated.

Effect of Solute Concentration on Sorption Capacities. Percent uptakes (u %) are determined by the equation:

$$u = \left(1 - \frac{\text{concentration of solute in water (filtrate) after sorption}}{\text{initial concentration of solute in water}}\right) \times 100.$$

Figure 1 shows the percent uptakes for phenol, benzyl alcohol, and 3-phenyl-1-propanol in the concentration range of 0.08—1 mM. Phenol is taken up more by Amberlite XAD-7 than by β-H6XDI-P-6.0-M, though slightly, while the reverse is observed for benzyl alcohol and 3-phenyl-1-propanol. The results of similar measurements for three aromatic carboxylic acids are shown in Fig. 2. Compared with Amberlite XAD-7, β-H6XDI-P-6.0-M exhibits the stronger ability to collect these compounds, particularly in the low concentration regions. This phenomenon is presumably attributable to the formation of inclusion complex where the solutes

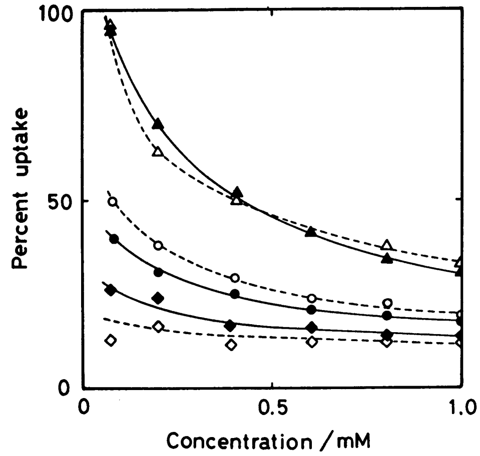

Fig. 1. Uptake of phenol, benzylalcohol, and 3-phenyl-1-propanol in water by β-H6XDI-P-6.0-M (——) and Amberlite XAD-7 (------).

△▲: 3-Phenyl-1-propanol, ○●: phenol, ◇◆: benzyl alcohol.

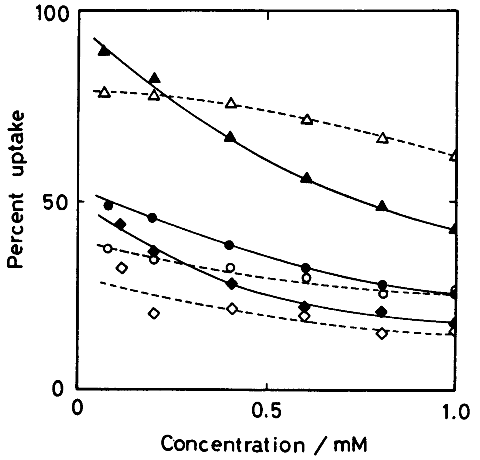

Fig. 2. Uptake of aromatic carboxylic acids in water by β-H6XDI-P-6.0-M (——) and Amberlite XAD-7 (------).

△▲: 5-Phenylvaleric acid, ○●: benzoic acid, ◇◆: phenylacetic acid.

are strongly retained in the β-cyclodextrin cavities. Accordingly, it is expected that the β-H6XDI-P-6.0-M resin will be used as sorbent to collect those compounds in water at trace concentrations.

Sorption Capacities in Column System. In order to achieve practical applications, the breakthrough experiments using the column method were performed, and the breakthrough capacities of the β-cyclodextrin polyurethane resins and Amberlite XAD-7 were compared.

Figure 3 shows the breakthrough curves for phenol (1 mM) on these resins packed separately into 10 cm × 0.52 cm I.D. columns. Ideally, a breakthrough curve should be steep and a solute concentration in an effluent should rise rapidly from zero to that in the influent.[8] The breakthrough curves on the β-cyclodextrin resins are not so steep as the ideal one on Amberlite XAD-7; this is presumably due to slower sorption rates of the solute into the β-cyclodextrin cavities. The breakthrough times for phenol, the points where the tangents of the breakthrough curves intersect the time abscissa, are decreasing in the order β-H6XDI-P-6.0-M>β-XDI-P-5.8-A>β-HDI-P-5.5-A>Amberlite XAD-7>BDOL-HDI-P-M. BDOL-HDI-P-M has only a small breakthrough time. On the other hand, the breakthrough times on the β-cyclodextrin resins are larger than that on Amberlite XAD-7. The β-H6XDI-P-6.0-M resin, which shows the largest breakthrough time of all the three β-cyclodextrin polyurethane resins, was compared in more detail with Amberlite XAD-7.

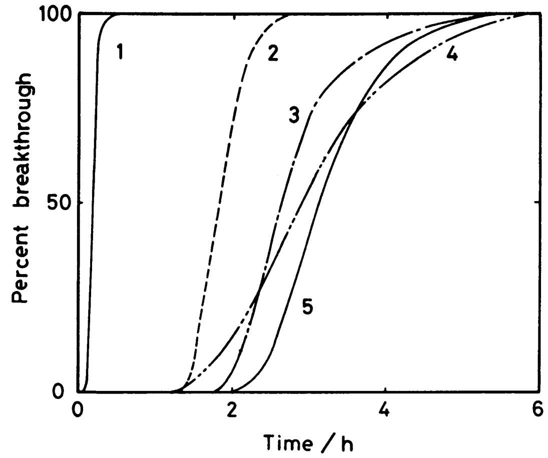

Fig. 3. Breakthrough curves for 1 mM phenol.
1: BDOL-HDI-P-M, 2: Amberlite XAD-7, 3: β-XDI-P-5.8-A, 4: β-HDI-P-5.5-A, 5: β-H6XDI-P-6.0-M.

TABLE 3. BREAKTHROUGH CAPACITIES FOR SEVERAL AROMATIC COMPOUNDS

Solute	Breakthrough capacity/10^{-2} mmol per g resin		
	β-H6XDI-P-6.0-M	BDOL-HDI-P-M	Amberlite XAD-7
p-Nitroaniline	20.0	5.0	44.5
Phenol	13.2	1.7	19.2
p-Cresol	16.2	2.2	41.6
Benzoic acid	10.7	3.6	31.7
Phenylacetic acid	6.6	1.6	23.6

Table 3 shows that the breakthrough capacities (expressed in mmol/g resin) on Amberlite XAD-7 for the aromatic compounds are larger than those on β-H6XDI-P-6.0-M. The weight of β-H6XDI-P-6.0-M and Amberlite XAD-7 per unit bed volume are 0.453 and 0.203 g/ml, respectively; thus there is not much difference in the breakthrough capacities per unit bed volume between β-H6XDI-P-6.0-M and Amberlite XAD-7. In practice, it is of great importance to investigate the sorption behavior of the resins for solutes at lower concentrations than 1 mM.

Each aqueous solution of the four solutes (model concentrations of 0.1, 0.05 or 0.01 mM) was passed at a flow-rate of 55.3 ml/h for 3 h through the column used for the breakthrough studies. The effluent from the column was collected in a graduated cylinder. The concentration of the solute in it was determined spectrophotometrically, and then the percent uptake by β-H6XDI-P-6.0-M or Amberlite XAD-7 was evaluated (Table 4). In the case of Amberlite XAD-7, the percent uptake for benzoic acid decreases with the concentration of the solute. The β-cyclodextrin polyurethane resin, however, shows a perfectly quantitative collection at these low concentrations. The same statement is true for the percent uptake for phenylacetic acid. *p*-Nitroaniline or phenol is perfectly collected on both β-H6XDI-P-6.0-M and Amberlite XAD-7, as shown in Table 4.

TABLE 4. PERCENT UPTAKE BY COLUMN METHOD

Solute	Concentration/mM	Percent uptake	
		β-H6XDI-P-6.0-M	Amberlite XAD-7
p-Nitroaniline	0.10	100	100
	0.05	100	100
	0.01	100	100
Phenol	0.10	100	100
	0.05	100	100
	0.01	100	100
Benzoic acid	0.10	100	93
	0.05	100	89
	0.01	100	63
Phenylacetic acid	0.10	100	89
	0.05	100	77
	0.01	100	67

In this way, it is found that β-H6XDI-P-6.0-M can quantitatively collect the aromatic solutes at low concentrations and is superior to widely used Amberlite XAD-7. In addition, the β-cyclodextrin resins used in this study can be easily regenerated by Soxhlet extraction with ethyl alcohol and the collecting abilities of the resins after several regenerations remain unchanged. These results suggest that the β-cyclodextrin polyurethane resins will be used satisfactorily as sorbents to collect aromatic compounds at low concentrations in water.

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