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Note

Sorption behaviour of several organic compounds on 6-deoxycyclodextrin polyurethane resins

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Many kinds of porous polymer beads have been used as column packings for collecting organic compounds in air or water and/or separating them chromatographically; Amberlite XAD resins are typical examples[1–3]. These and related resins have energetically homogeneous sorption sites and no specific ones. In order to increase the selectivity of resins for organic compounds, we prepared polyurethane resins containing cyclodextrins as specific sorption sites[4]. These cyclodextrin resins exhibited interesting, selective sorption behaviour considered to be based on the formation of inclusion compounds[4–6].

It is of great interest to investigate the sorption behaviour of polyurethane resins containing 6-deoxycyclodextrins whose primary hydroxyl groups are all deoxygenated, because such chemical modification may affect the interaction of the resins with organic sorbates. The sorption behaviour of several model organic compounds on such resins is briefly described here.

EXPERIMENTAL

The materials used were as described previously[4].

Preparation of 6-deoxycyclodextrin polyurethane resins

6-Deoxy-α- or -β-cyclodextrin[7] (10.0 g) was dissolved in 150 ml pyridine in a 500-ml three-necked flask at room temperature. One third of the pyridine was distilled off to remove trace amounts of water. The calculated amount of HDI or H6XDI (see Table I) was added, and the solution was stirred at 115°C for 6 h under nitrogen. The 6-deoxycyclodextrin polyurethane resin was precipitated from a large excess of acetone. It was purified by thorough Soxhlet extraction with acetone and then with water, and dried *in vacuo* at 80°C for 24 h. The resin thus obtained was granulated to particle sizes of 60–80 and 100–200 mesh with an agate mortar and sieved.

Apparatus

A Shimadzu Model GC-3BF gas chromatograph equipped with a flame ionization detector was used. A glass column (80 cm × 3 mm I.D.) was packed with the resin particles (60–80 mesh). The nitrogen flow-rate was 30 ml/min. The detector and column temperatures were maintained at 150°C.

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An Atto Model SF-0396-57 pump and an Mitsumi Model SF-1205 UV monitor (at 254 nm) were used for liquid chromatographic and breakthrough studies. The resin particles (100–200 mesh) were packed in a glass column (5.2 mm I.D.) to form a 40 cm long bed for the former studies and a 10 cm long-bed for the latter.

RESULTS AND DISCUSSION

Table I shows the isocyanate/hydroxyl ratio in the monomer feed and the physical properties of 6-deoxycyclodextrin polyurethane resins.

TABLE I

PHYSICAL PROPERTIES OF 6-DEOXYCYCLODEXTRIN POLYURETHANE RESINS

6-D-α = 6-Deoxy-α-cyclodextrin; 6-D-β = 6-deoxy-β-cyclodextrin; HDI = hexamethylene diisocyanate; H6XDI = 1,3-bis(isocyanatomethyl)cyclohexane.

Resin	*NCO/OH in feed*	*Cyclodextrin content* (%, w/w)*	*Temperature limit** (°C)*	*Surface area*** (m^2/g)*
6-D-β-HDI	1.20	53.2	220	7
6-D-α-HDI	1.20	46.8	220	11
6-D-β-H6XDI	0.57	57.7	220	30

* Calculated from elemental analysis.
** Determined thermogravimetrically.
*** Estimated by the BET method.

Fig. 1 is a typical gas chromatogram of a mixture of five organic compounds with similar boiling points. It is apparent that these five compounds can be well separated on the 6-D-β-HDI column more efficiently than on the β-HDI column. This mixture was also chromatographed on four other columns. The peaks of benzene and

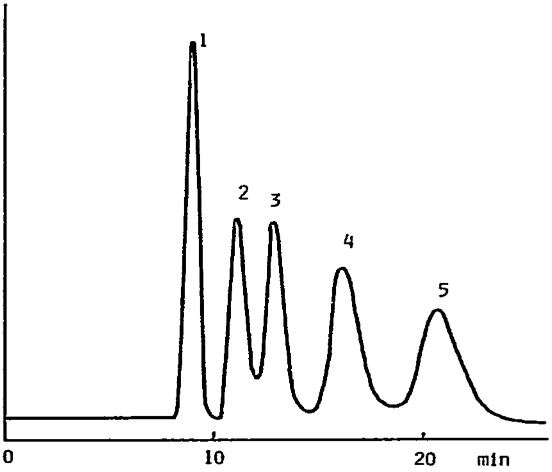

Fig. 1. Gas chromatogram of five organic compounds with similar boiling points on 6-D-β-HDI. Peaks: 1 = cyclohexane; 2 = ethanol; 3 = methyl propionate; 4 = benzene; 5 = methyl ethyl ketone.

cyclohexane overlap on the columns packed with Porapak Q (80 cm at 150°C) or 10% SE-30 (2 m at 45°C). Cyclohexane, methyl ethyl ketone and methyl propionate cannot be separated on 10% dinonyl phthalate (DNP) (1.5 m at 60°C). The PEG HT column exhibits much poorer resolution.

The gas chromatographic retention times of several organic compounds on the polyurethane resins are given in Table II. The retention times of octane and cyclohexane on 6-D-β-HDI are more than ten times larger than those on β-HDI prepared by cross-linking unmodified β-cyclodextrin with hexamethylene diisocyanate. The deoxygenation at the primary hydroxyl groups of the β-cyclodextrin units results in a significant increase in the interaction of the resin with octane and cyclohexane, which may be due to the increase in hydrophobicity at the cyclodextrin torus. Both 6-D-β-HDI and β-HDI exhibit similar retention behaviour for the other compounds in Tabel II. 6-D-β-H6XDI interacts with the organic compounds slightly more strongly, compared with 6-D-β-HDI. All the compounds studied interact with 6-D-α-HDI much more weakly than with 6-D-β-HDI.

TABLE II

RETENTION TIMES (RELATIVE TO BENZENE) ON 6-DEOXYCYCLODEXTRIN POLYURETHANE RESINS

Actual retention times (min) are given in parentheses.

Compound	*6-D-β-HDI*	*6-D-α-HDI*	*6-D-β-H6XDI*	*β-HDI*
Octane	1.03	0.70	2.41	0.07
Ethanol	0.68	1.84	1.25	0.50
Methyl ethyl ketone	1.24	2.04	1.82	1.02
Methyl propionate	0.79	1.31	1.31	0.63
Cyclohexane	0.56	0.12	0.39	0.04
Benzene	1.00 (16.03)	1.00 (4.89)	1.00 (19.69)	1.00 (22.80)
Pyridine	5.19	9.43	7.82	5.36

The interactions of 6-deoxycyclodextrin polyurethane resins with four disubstituted benzene derivatives in water were estimated from retention volumes measured by liquid chromatography (Table III). A liquid chromatogram of a mixture of *o*-, *m*- and *p*-iodoaniline isomers is shown in Fig. 2 together with that of the three dinitrobenzene isomers on 6-D-β-HDI. A complete baseline separation of the three iodoaniline isomers is obtained, while the *ortho*- and *meta*-isomers of dinitrobenzene or nitroaniline cannot be separated. Compared with *o*-, *m*- and *p*-cresol, the isomers of nitroaniline, dinitrobenzene or iodoaniline are retained more strongly: especially the *para*-isomers have large retention volumes. The three isomers of cresol, however, exhibit nearly equal retentions and cannot be separated. Because 6-D-β-H6XDI interacts with dinitrobenzene and iodoaniline very strongly, 60% aqueous ethanol is used as eluent instead of 40% aqueous ethanol in this case.

Each zone of the solutes placed on columns containing the 6-deoxycyclodextrin polyurethane resins scarcely moves when eluted with pure water. This indicates the possibility of using these resins as sorbents to collect aromatic compounds in water. The breakthrough capacities for the *para*-isomers of nitroaniline, cresol and

TABLE III

RETENTION VOLUMES ON 6-DEOXYCYCLODEXTRIN POLYURETHANE RESINS

Eluent: ethanol–water (40:60); flow-rate 25.5 ml/h.

Solute	*Retention volume (ml)*		
	6-D-β-HDI	*6-D-α-HDI*	*6-D-β-H6XDI*
Nitroaniline			
o-	76.9	63.3	84.3
m-	74.2	62.4	85.7
p-	142.0	75.2	187.0
Dinitrobenzene			
o-	74.3	63.9	27.2*
m-	59.4	65.0	26.5*
p-	108.5	129.2	46.4*
Iodoaniline			
o-	86.7	88.9	30.2*
m-	125.3	108.4	36.6*
p-	171.8	101.1	45.9*
Cresol			
o-	48.4	49.7	62.4
m-	42.6	46.7	56.5
p-	46.4	45.6	60.6

* Eluent: ethanol–water (60:40).

dinitrobenzene on 6-deoxycyclodextrin resins are shown in Table IV, together with those on BDOL-HDI prepared from 1,4-butanediol and hexamethylene diisocyanate. It is clear that the 6-deoxycyclodextrin units in the resins participate in the uptake of the solutes. Both 6-D-β-HDI and 6-D-β-H6XDI give larger breakthrough capacities than 6-D-α-HDI and BDOL-HDI. 6-D-β-HDI is superior to 6-D-β-H6XDI because the breakthrough profiles on the former are well-defined S-shaped curves which rise steeply.

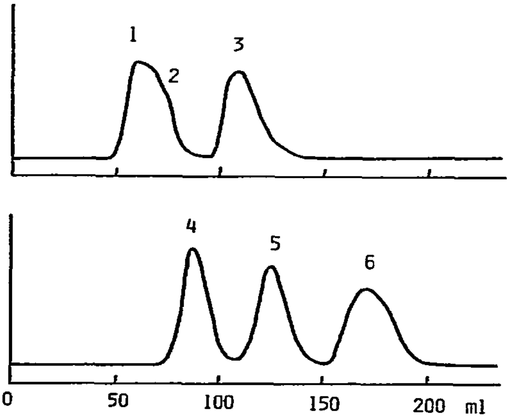

Fig. 2. Liquid chromatograms of dinitrobenzene and iodoaniline isomers on 6-D-β-HDI. Peaks: 1 = *m*-dinitrobenzene; 2 = *o*-dinitrobenzene; 3 = *p*-dinitrobenzene; 4 = *o*-iodoaniline; 5 = *m*-iodoaniline; 6 = *p*-iodoaniline.

TABLE IV

BREAKTHROUGH CAPACITIES ON 6-DEOXYCYCLODEXTRIN POLYURETHANE RESINS

Flow-rate of the sample aqueous solution: 80 ml/h.

Resin	*Breakthrough capacity (mg/g)*		
	p-Nitroaniline, 0.8 mM	*p-Cresol, 0.8 mM*	*p-Dinitrobenzene, 0.4 mM*
6-D-β-HDI	45.3	17.4	18.2
6-D-α-HDI	17.0	6.5	9.9
6-D-β-H6XDI	38.8	18.0	16.0
BDOL-HDI	4.9	2.2	1.5

From the results obtained it is expected that the 6-deoxycyclodextrin polyurethane resins will be used as column packing materials to separate and collect organic compounds.

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