PREPARATION AND SORPTION BEHAVIOUR OF CYCLODEXTRIN POLY-URETHANE RESINS

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SUMMARY

The interactions between cyclodextrin polyurethane resins and various organic compounds have been estimated by gas–solid chromatography. Cyclodextrin polyurethane resins were obtained by the polymerization of cyclodextrins with diisocyanates in pyridine and/or N,N-dimethylformamide. The cyclodextrin resins exhibit strong interactions with guest molecules containing π-electrons or heteroatoms. The resins can be used to distinguish between the configurations of xylene isomers and pyridine derivatives.

INTRODUCTION

Cyclodextrins are torus-shaped oligosaccharides composed of α-(1,4)-linkages of a number of D(+)-glucopyranose units, where the Greek letter denotes the number of glucose units, *e.g.* α for 6, β for 7, γ for 8, etc. In these compounds the primary hydroxyl groups lie on one side of the torus and the secondary hydroxyl groups on the other side. The cavities which exist in cyclodextrins are slightly "V" shaped, with the secondary hydroxyl side more open than the primary hydroxyl side.

It is well known that cyclodextrins form inclusion complexes with a variety of (guest) compounds and have attracted much interest as models for enzymes. The better the guest fits into the cavity, the more stable is the inclusion complex. Since their cavities are spatially restricted, cyclodextrins exhibit many interesting features such as rate effects, stereospecificity, enantiometric specificity, etc. Many of these have described by Bender and Komiyama[1]. By using this specificity, the epichlorohydrin cross-linked cyclodextrin gels have been used for the chromatographic separation of benzoic acid derivatives[2], nucleic acids[3], mandelic acid derivatives[4], etc.

Solid sorbents, particularly porous organic polymers (*e.g.*, Amberlite XAD-2, Porapak Q, Tenax GC, etc.), have recently been used for concentrating trace organic compounds, because these polymers are hydrophobic in nature and retard the progress of organic compounds through a column. The degree of interaction between organic compounds and these polymers generally increases with increasing boiling point of

the organic compounds. Therefore, these polymers do not sorb various kinds of organic compounds selectively. There is thus a need in environmental analysis to find sorbents that will sorb these compounds selectively.

We have started a study of insoluble porous polymers containing cyclodextrins. In this paper, we describe the preparation and preliminary sorption behaviour of cyclodextrin polyurethane resins cross-linked with diisocyanates.

EXPERIMENTAL

Materials

α- and β-Cyclodextrins were obtained from Hayashibara Biochemical Laboratories (Shimoishii, Okayama, Japan), 1,3-bis(isocyanatomethyl)cyclohexane and 1,3-bis(isocyanatomethyl)benzene from Takeda Chemical Industries (Osaka, Japan); all other chemicals were from Wako (Osaka, Japan).

α- and β-Cyclodextrins were recrystallized from water and dried *in vacuo* at 80°C for 24 h. Diisocyanates were carefully distilled under reduced pressure. Pyridine and N,N-dimethylformamide and n-hexane were dried over potassium hydroxide and calcium hydride, respectively, and distilled before use. Other reagents were used without any purification.

Preparation of cyclodextrin polyurethane resins

β-Cyclodextrin polyurethane resins were prepared by a reaction similar to that of corn starch with phenyl isocyanate in pyridine[5]. β-Cyclodextrin ($8.8 \cdot 10^{-3}$ mol; 10 g) was dissolved in 300 ml of pyridine in a 1000-ml round-bottomed flask at room temperature. Trace amounts of water in this solution was distilled off azeotropically. The volume of pyridine distilled off was 100 ml. (The pyridine solution was cooled to 80°C with constant vigorous stirring.) The calculated amount of the diisocyanate was added. Then, the solution was stirred at 115°C for 4 h. The cyclodextrin polyurethane resin was precipitated from a large excess of methanol or acetone. The resin was purified by thorough Soxhlet extraction and dried *in vacuo* at 80°C for 24 h.

Alternatively, α-cyclodextrin ($8.8 \cdot 10^{-3}$ mol; 8.6 g) or β-cyclodextrin (10 g) was dissolved in 200 ml of N,N-dimethylformamide. (The solution was heated to 50°C for α-cyclodextrin or 80°C for β-cyclodextrin.) The diisocyanate was added without azeotropic distillation. The subsequent treatment was the same as that described above.

The cyclodextrin polyurethane resins thus obtained were granulated to a particle size of 177–250 μm with an agate mortar and sieved. The unreacted hydroxyl groups in the resin particles were silanized with trimethylchlorosilane in n-hexane at 60°C for 4 h.

Apparatus

A Shimadzu Model GC-3BF dual-column gas chromatograph equipped with a flame ionization detector was used. All chromatograms were recorded on a Shimadzu Model R-101 recorder. Chromatographic columns were made of Pyrex glass (80 cm × 3 mm I.D.) unless stated otherwise. Nitrogen was used as the carrier gas at a constant flow-rate of 30 ml/min. The column and detector temperatures were maintained at 150°C or 170°C. The samples were injected with a 1-μl Terumo microsyringe.

Specific surface areas of the resins were estimated by the B.E.T. method; the upper temperature limit was determined thermogravimetrically.

The desorption patterns were measured on a Shimadzu Model ADS-1B sorptograph with automatic temperature-programming equipment connected to a thermal conductivity gas chromatograph, Shimadzu Model GC-3BT.

RESULTS AND DISCUSSION

Physical properties of cyclodextrin polyurethane resins

Table I shows the monomer feed, solvent and precipitant used in the preparation of cyclodextrin polyurethane resins, together with those for butanediol–hexamethylene diisocyanate polyurethane resin.

TABLE I

POLYMERS USED IN THIS STUDY

Solvents: P = pyridine; DMF = N,N-dimethylformamide. Diisocyanates: HDI = hexamethylene diisocyanate; H6XDI = 1,3-bis(isocyanatomethyl)cyclohexane; XDI = 1,3-bis(isocyanatomethyl)-benzene. Precipitants: M = methanol; A = acetone.

Symbol	Feed composition
β-HDI-I-P-5.5-M	
β-HDI-P-5.5-M-Si*	β-Cyclodextrin (10 g; 8.8·10^{-3} mol)–HDI (5.5 g; 3.27·10^{-2} mol)
β-HDI-P-5.5-A	
β-HDI-DMF-5.5-A	
β-HDI-P-18.6-M	β-Cyclodextrin (10 g; 8.8·10^{-3} mol)–HDI (18.6 g; 11.06·10^{-2} mol)
β-HDI-P-18.6-A	
β-H6XDI-P-6.0-M	β-Cyclodextrin (10 g; 8.8·10^{-3} mol)–H6XDI (6.0 g; 3.09·10^{-2} mol)
β-XDI-P-5.8-A	β-Cyclodextrin (10 g; 8.8·10^{-3} mol)–XDI (5.8 g; 3.08·10^{-2} mol)
α-HDI-DMF-5.9-A	α-Cyclodextrin (8.6 g; 8.8·10^{-3} mol)–HDI (5.9 g; 3.5·10^{-2} mol)
α-HDI-DMF-13.3-A	α-Cyclodextrin (8.6 g; 8.8·10^{-3} mol)–HDI (13.3 g; 7.9·10^{-2} mol)
BDOL-HDI-P-M	1,4-Butanediol (BDOL) (8.3 g; 9.2·10^{-2} mol)–HDI (15.5 g; 9.2·10^{-2} mol)

* β-HDI-P-5.5-M was silanized with trimethylchlorosilane.

The physical properties of the resins obtained are listed in Table II. Each cyclodextrin resin has an upper temperature limit of 200–230°C, defined here as the temperature on the thermogravimetric curve where the resin begins to degrade slowly. A rapid weight loss was seen at ca. 250°C. The specific surface area of a resin depends upon the treatment used after precipitation. Consequently, the values in Table II are the average ones for several separate batches of resins.

The number of free hydroxyl groups which did not react with the diisocyanate was calculated from elemental analysis. The hydroxyl groups of cyclodextrins could not be made to react with the diisocyanates.

It is found that porous polyurethane resins containing cyclodextrin units can be prepared which have comparable physical properties to commercial porous polymers.

Retention behaviour of cyclodextrin polyurethane resins

The interactions of cyclodextrin polyurethane resins with typical organic com-
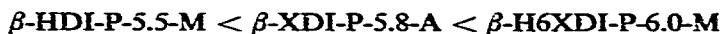
TABLE II

PHYSICAL PROPERTIES OF CYCLODEXTRIN POLYURETHANE RESINS

Adsorbent	Temperature limit (°C)	Surface area (m²/g)	OH Residues per cyclodextrin molecule
β-HDI-P-5.5-M	200	170	14.4
β-HDI-P-5.5-M-Si	200	150	—
β-HDI-P-5.5-A	200	260	13.5
β-HDI-DMF-5.5-A	200	170	13.5
β-HDI-P-18.6-M	200	420	4.4
β-HDI-P-18.6-A	200	350	4.8
β-H6XDI-P-6.0-M	230	250	15.5
β-XDI-P-5.8-A	210	170	14.6
α-HDI-DMF-5.9-A	230	180	10.1
α-HDI-DMF-13.3-A	230	280	0.9
BDOL-HDI-P-M	250	160	—

pounds (adsorbates) were estimated from retention times measured by gas chromatography.

First, five adsorbates with similar boiling points were injected on columns packed with β-cyclodextrin resins prepared using different diisocyanates in order to minimize the vapour pressure effect of adsorbates on their retention times. These β-cyclodextrin resins exhibit similar interactions as shown in Table III: the interaction with benzene or methyl ethyl ketone is strong and that with cyclohexane is the weakest. The strong interaction seems to proceed through the π-electrons of the adsorbates. Silylation of hydroxyl groups in the resin does not affect the interactions with the adsorbates. The absolute interaction with benzene, for example, is strongly dependent upon the cross-linking diisocyanate and increases in the order:

$$\beta\text{-HDI-P-5.5-M} < \beta\text{-XDI-P-5.8-A} < \beta\text{-H6XDI-P-6.0-M}$$

The cyclodextrin resins obtained from hexamethylene diisocyanate seem to reflect most the effect of cyclodextrin units because of the presence of the linear

TABLE III

RETENTION TIMES (RELATIVE TO BENZENE) OF ADSORBATES WITH SIMILAR BOILING POINTS ON β-CYCLODEXTRIN POLYURETHANE RESINS

Carrier gas: nitrogen, 30 ml/min. Column temperature: 170°C. Actual retention times (min) are given in parentheses.

Adsorbate	β-HDI-P-5.5-M	β-HDI-P-5.5-M-Si	β-H6XDI-P-6.0-M	β-XDI-P-5.8-A
Benzene	1.00 (28.76)	1.00 (22.32)	1.00 (101.00)	1.00 (88.85)
Cyclohexane	0.13	0.15	0.18	0.16
Ethanol	0.31	0.32	0.25	0.23
Methyl ethyl ketone	0.81	0.60	0.88	0.85
Methyl propionate	0.54	0.37	0.36	0.72

methylene linkages. Thus, the interactions of resins from β-cyclodextrin and hexamethylene diisocyanate with various adsorbates were investigated. The relative retention times are shown in Table IV together with those on BDOL-HDI-P-M and on Tenax GC. The interactions of the cyclodextrin resins are very weak with the aliphatic hydrocarbons and extraordinarily strong with pyridine, compared with the other classes of adsorbates. p-Xylene is retained more strongly than the m- and o-isomers. The retention behaviours of the xylene isomers and the pyridine derivatives are discussed later in this paper. The precipitants have little effect on the absolute values of the retention times. However, the use of N,N-dimethylformamide as solvent instead of pyridine results in a large decrease in the absolute retention times and a variation of elution order. This seems to reflect the difference in the porosity of the resin to the solvent[6,7]. The retention times of benzene, for example, increase with increasing cyclodextrin content in the resins. Neither BDOL-HDI-P-M nor Tenax GC interacts strongly with benzene, compared with the other adsorbates with similar

TABLE IV

RETENTION TIMES (RELATIVE TO BENZENE) ON CYCLODEXTRIN POLYURETHANE RESINS

Carrier gas: nitrogen, 30 ml/min. Column temperature: 150°C. Actual retention times (min) are given in parentheses. Column length of β-HDI-P-18-6-M and Tenax GC is 120 cm.

Adsorbate	β-HDI-P-5.5-M	β-HDI-P-5.5-A	β-HDI-DMF-5.5-A	β-HDI-P-18.6-M	β-HDI-P-18.6-A	BDOL-HDI-P-M	Tenax GC
Hexane	0.07	0.04	0.04	0.12	0.06	0.47	0.44
Heptane	0.10	0.09	0.06	0.12	0.06	0.53	0.72
Octane	0.18	0.15	0.10	0.20	0.07	0.61	1.62
Methanol	0.09	0.12	0.36	0.29	0.19	0.96	0.16
Ethanol	0.29	0.35	0.78	0.57	0.50	1.07	0.21
Propanol	1.16	1.33	1.96	1.80	1.67	1.44	0.35
Butanol	3.37	—	4.63	4.14	4.00	2.08	0.66
Acetone	0.37	—	0.67	0.37	0.54	0.80	0.25
Methyl ethyl ketone	0.84	1.03	1.24	1.10	1.02	1.01	0.55
Methyl propyl ketone	1.80	—	2.02	1.71	1.81	1.29	1.06
Methyl butyl ketone	*	—	3.64	2.70	3.46	1.82	2.09
Methyl propionate	0.57	0.69	0.85	0.64	0.63	0.89	0.64
Methyl butyrate	1.36	—	1.49	1.07	1.16	1.10	1.30
Methyl valerate	3.40	—	2.93	1.47	2.05	1.49	2.88
Ethyl propionate	1.06	—	1.11	0.75	0.84	0.99	1.04
Cyclohexane	0.08	0.05	0.05	0.27	0.04	0.59	0.75
Benzene	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	(70.36)	(60.52)	(16.68)	(24.42)	(22.80)	(1.52)	(4.25)
Toluene	1.46	—	1.20	1.12	1.26	—	1.96
o-Xylene	*	—	0.60	2.17	1.58	2.35	5.12
m-Xylene	*	—	1.08	2.00	1.48	1.91	4.38
p-Xylene	*	—	1.87	2.65	1.95	1.87	4.34
Pyridine	*	—	9.00	6.80	5.36	3.16	1.94

* This peak is too broad.

boiling points. Therefore, it is reasonable that the β-cyclodextrin units in the resins result in the strong interactions with the adsorbates.

It is of interest to investigate the polyurethane resins containing α-cyclodextrin whose cavity diameter is smaller than that of β-cyclodextrin. Table V shows the retention times on the polyurethane resins of α- and β-cyclodextrins prepared in N,N-dimethylformamide. The difference in the cavity diameter between α- and β-cyclodextrins is reflected in the retention behaviours of adsorbates. Bulky adsorbates such as the aromatic ones interact with β-HDI-DMF-5.5-A more strongly than with α-HDI-DMF-A; most adsorbates with a linear group, such as aliphatic hydrocarbons, esters and ketones, exhibit the opposite trend. This behaviour may be explained on the basis that the adsorbates with a linear group are less bulky and fit better into the α-cyclodextrin cavity than the aromatic adsorbates.

TABLE V

RETENTION TIMES (RELATIVE TO BENZENE) ON CYCLODEXTRIN POLYURETHANE RESINS

Carrier gas: nitrogen, 30 ml/min. Column temperature: 150°C. Actual retention time (min) are given in parentheses.

Adsorbate	β-HDI-DMF-5.5-A	α-HDI-DMF-5.9-A	α-HDI-DMF-13.3-A
Hexane	0.04	0.16	0.27
Heptane	0.06	0.24	0.33
Octane	0.10	0.29	0.45
Methanol	0.36	0.53	1.06
Ethanol	0.78	0.83	1.53
Propanol	1.96	2.03	2.80
Butanol	4.63	6.01	6.23
Acetone	0.67	0.71	0.98
Methyl ethyl ketone	1.24	1.61	1.65
Methyl propyl ketone	2.02	5.44	3.32
Methyl butyl ketone	3.64	11.68	6.58
Diethyl ketone	1.75	6.09	2.97
Methyl propionate	0.85	1.84	1.20
Methyl butyrate	1.49	6.43	2.51
Methyl valerate	2.93	—	5.61
Ethyl propionate	1.11	6.80	1.90
Cyclohexane	0.05	0.07	0.12
Benzene	1.00	1.00	1.00
	(16.68)	(6.59)	(4.16)
Toluene	1.20	2.73	1.96
o-Xylene	0.60	0.89	2.62
m-Xylene	1.08	2.22	2.77
p-Xylene	1.87	6.53	3.41
Pyridine	9.00	7.23	6.80

Table VI shows the retention times of the aromatic adsorbates on the cyclodextrin resins from hexamethylene diisocyanate at the column temperature of 170°C. On the resins of BDOL-HDI-P-M and Tenax GC containing no cyclodextrin units, the xylene isomers are eluted in the order of the p-, m- and o-isomers, as shown in Table IV. This order parallels that of the boiling points of the isomers. The m- and

TABLE VI

RETENTION TIMES (RELATIVE TO BENZENE) OF AROMATIC ADSORBATES ON CYCLODEXTRIN POLYURETHANE RESINS

Carrier gas: nitrogen, 30 ml/min. Column temperature: 170°C. Actual retention times (min) are given in parentheses.

Adsorbate	β-HDI-P-5.5-M	β-HDI-DMF-5.5-A	β-HDI-P-5.5-M-Si	α-HDI-DMF-5.9-A
Benzene	1.00 (28.76)	1.00 (7.25)	1.00 (22.32)	1.00 (3.88)
Toluene	1.19	1.11	1.00	1.25
o-Xylene	1.59	1.00	1.32	1.53
m-Xylene	1.42	1.09	1.10	2.20
p-Xylene	2.07	1.49	1.55	4.93

o-isomers interact with the β-cyclodextrin resins almost to the same extents, considering their boiling points. The o-isomer interacts the least with the α-cyclodextrin resin. The p-isomer is eluted last on the resins containing α- or β-cyclodextrin. This effect of the structure of xylene isomers may be reasonably interpreted as follows. p-Xylene can enter deep into the cavity of β-cyclodextrin with one of the methyl groups first, but the benzene ring of m- or o-xylene cannot enter so deeply because of the steric hindrance of the methyl groups. As seen from the retention times of benzene, the smaller cavity of α-cyclodextrin is unable to interact with a benzene ring as strongly as the β-cyclodextrin cavity. The entrances of the cross-linked cyclodextrins are more rigid and more crowded than of native cyclodextrins. Therefore, the α-cyclodextrin resin interacts more strongly with a less bulky isomer and with the three xylene isomers to different extents.

As shown in Tables IV and V, pyridine gives very long retention times on the cyclodextrin resins. This is also true for tetrahydrofuran and 1,4-dioxan. This fact suggests a strong hydrogen-bonding interaction between the heteroatoms and the polyurethane resins in addition to the hydrophobic guest–host interaction. The retention behaviours of pyridine derivatives, picolines and lutidines, on the resins were therefore investigated. The results in Table VII may be interpreted as follows. If we consider that the pyridine ring of a picoline enters the β-cyclodextrin cavity deeply like benzene or pyridine, the introduction of a methyl group into the pyridine ring will cause the position of the nitrogen atom in the cavity to change. The nitrogen atom of α-picoline is included inside the cavity and greatly shielded from the hydrogen-bonding interaction. γ-Picoline, on the other hand, interacts in the same way as pyridine. In the case of the α-cyclodextrin cavity, the pyridine rings are not able to enter the cavity deeply. All the nitrogen atoms of pyridine and picolines are situated in similar environments. They are, therefore, eluted in the order of increasing boiling point.

A similar argument is presumably true for the retention behaviours of lutidine isomers. The nitrogen atom of 2,6-lutidine cannot participate in hydrogen-bonding and 2,6-lutidine cannot enter deep into the β-cyclodextrin cavity, because of the introduction of two methyl groups at the 2- and 6-positions. Consequently, 2,6-lutidine is eluted faster on the β-cyclodextrin resins than any of the other pyridine derivatives discussed. 2,5-Lutidine is able to enter the β-cyclodextrin cavity as deeply

TABLE VII

RETENTION TIMES (RELATIVE TO PYRIDINE) OF PYRIDINE DERIVATIVES ON CYCLODEXTRIN POLYURETHANE RESINS

Carrier gas: nitrogen, 30 ml/min. Column temperature: 170°C. Actual retention times (min) are given in parentheses.

Adsorbate	β-HDI-P-5.5-M	β-HDI-DMF-5.5-A	α-HDI-DMF-5.9-A
Pyridine	1.00	1.00	1.00
	(142.09)	(48.95)	(19.36)
α-Picoline	0.90	0.93	1.49
β-Picoline	1.60	1.55	2.76
γ-Picoline	2.19	1.84	2.33
2,3-Lutidine	1.94	1.65	2.37
2,4-Lutidine	1.74	1.65	2.33
2,5-Lutidine	1.73	1.62	3.68
2,6-Lutidine	0.58	0.67	1.13

as p-xylene, and its hydrophobic guest–host interaction is the strongest. The interaction due to hydrogen-bonding, however, is reduced considerably, for the nitrogen atom is situated inside the cavity. 2,5-Lutidine is thus eluted faster than the 2,4- or 2,3-isomer (Table VII). All the isomers cannot enter into the cavity of α-cyclodextrin so deeply as into that of β-cyclodextrin, as the cavity of the former is smaller and more crowded as mentioned above. Except for 2,6-lutidine, these isomers have almost equal hydrogen-bonding effects. 2,5-Lutidine with the least bulky structure is eluted last. The cyclodextrin polyurethane resins thus have the ability to distinguish between the configurations of picoline and lutidine isomers.

In order to confirm the strong interactions of the cyclodextrin cavities in the resins with guest molecules containing π-electrons and/or heteroatoms, the desorption patterns for benzene were measured by means of the temperature-programmed des-
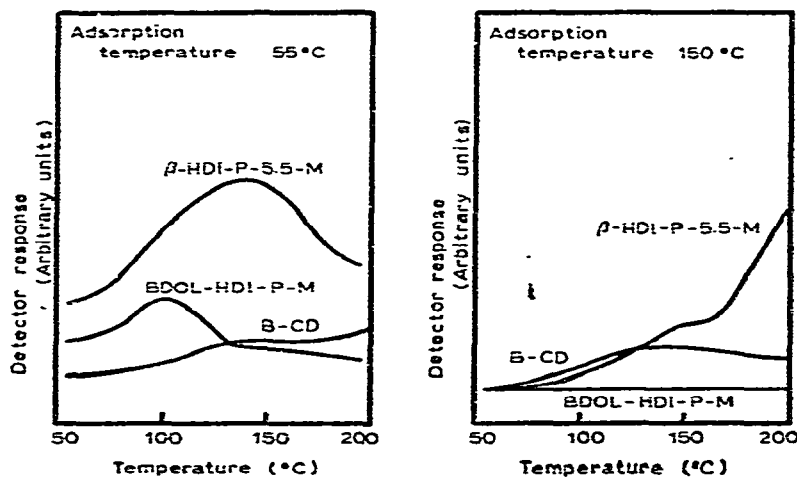

Fig. 1. Desorption patterns for benzene. Particle size, 60–80 mesh. Programmed at 3.1°C/min. Carrier gas, helium.

orption method (Fig. 1). At the adsorption temperature of 55°C, β-HDI-P-5.5-M and native β-cyclodextrin exhibit the peak of benzene at 140°C, while BDOL-HDI-P-M has it at 110°C. At the adsorption temperature of 150°C, the desorption peaks on β-HDI-P-5.5-M and native β-cyclodextrin appear above 200°C; on the other hand, BDOL-HDI-P-M shows no peak at all. These results strongly suggest that the cyclodextrin cavities in the resins take part in interactions with guest molecules.

This preliminary study of cyclodextrin polyurethane resins was carried out to investigate the specific interactions between the resins and organic compounds for the purpose of using these resins for selective concentration of organic compounds. The cyclodextrin resins prepared here strongly interact with guest molecules containing heteroatoms and can be used to distinguish between the configurations of the guest molecules. The results obtained indicate the possibility of using the cyclodextrin polyurethane resins as adsorbents that can selectively adsorb organic compounds in the gas phase.

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