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Sorption Behavior of Low Molecular Weight Organic Vapors on β-Cyclodextrin Polyurethane Resins

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The sorption behavior of low molecular weight organic vapors on β-cyclodextrin polyurethane resins was estimated from desorption or breakthrough experiments and compared with that on the commercially available resins. Temperature-programmed desorption patterns show that the β-cyclodextrin resins interact strongly with benzene vapor in a nitrogen or air stream. This strong interaction presumably results from the hydrophobic interaction of benzene with the β-cyclodextrin cavity. From the breakthrough experiments using the gas stripping method, it was found that the resin prepared by reacting β-cyclodextrin with 1,3-bis(isocyanatomethyl)cyclohexane, β-H6XDI-P-6.0-M, retains the polar volatile organic compounds more than Amberlite XAD-7 does.

Because of the relatively low concentrations of organic contaminants in ambient air or in water, most methods for the measurement of these contaminants require a concentration step before the actual analysis.[1–3] Several commercially available porous polymer beads (*i. e.*, Tenax GC,[4,5] Porapak Q,[6] and Amberlite XAD-2[7]) and graphitized carbon black[8] are used widely to collect organic contaminants. The polarity of monomers brings about some selectivity[9] in sorbing organic compounds to the porous polymer beads: the more polar the monomer is, the more strongly the polymer beads interact with polar organic compounds. A series of the Amberlite XAD resins, for example, are capable of collecting a variety of organic compounds. The Amberlite XAD resins and related ones are hydrophobic in nature and have energetically homogeneous sorption sites. Therefore, the selectivity of these resins in collecting organic compounds cannot be expected to be strong. In order to strengthen the selectivity mentioned above, it is necessary to introduce specific sorption sites into a resin.

We are interested in finding organic sorbents that will be able to collect organic compounds in environments selectively. It is well known that cyclodextrins form stable inclusion complexes with specific organic compounds. The polyurethane resins containing cyclodextrin units were prepared by cross-linking cyclodextrins with diisocyanates.[10] The interactions of these polyurethane resins with low molecular weight organic vapors were investigated by gas chromatography in a dry nitrogen carrier gas. It was found that the cyclodextrin resins exhibit large retention times for the compounds containing π-electrons or hetero atoms (such as benzene, pyridine, and ethyl methyl ketone).

In this work, the preliminary sorption behavior of β-cyclodextrin polyurethane resins is investigated and compared with that of Porapak Q, Tenax GC, or Amberlite XAD-7 in order to evaluate the possibility of using these cyclodextrin resins as sorbents to collect organic vapors. The isothermal and temperature-programmed desorption patterns and the breakthrough times were studied for several low molecular weight organic compounds.

Experimental

Materials. β-Cyclodextrin was obtained from Hayashibara Biochemical Laboratories, 1,3-bis(isocyanatomethyl)cyclohexane and 1,3-bis(isocyanatomethyl)benzene from Takeda Chemical Industries, and all other chemicals from Wako.

The preparation of β-cyclodextrin polyurethane resins was described in detail in our previous paper.[10] The β-cyclodextrin polyurethane resins obtained were granulated to a particle size of 177—250 μm with an agate mortar, sieved, and used as sorbents.

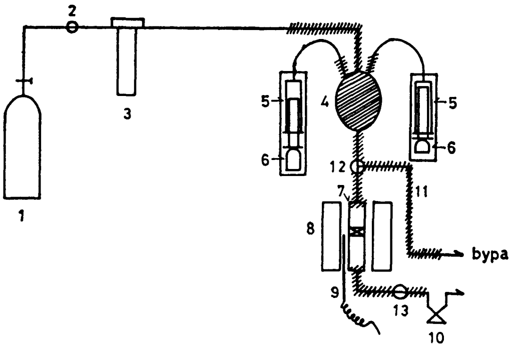

Fig. 1. Apparatus for adsorption behavior studies.
1: Nitrogen gas cylinder, 2: bellows valve, 3: flow meter, 4: mixing vessel, 5: syringe, 6: syringe drive, 7: adsorption tube, 8: furnace, 9: thermocouple, 10: gas sampler, 11: heater, 12: 3-way cock, 13: 2-way cock.

Apparatus. The apparatus utilized for the studies of adsorption behavior of the resins is shown schematically in Fig. 1. This apparatus was constructed in our laboratory and equipped with an automatic temperature-programming device. The nitrogen stream flowing through the path was controlled to 100 ml/min by a bellows valve. The flow rate was measured with an orifice flow meter. One or two adsorbates (model organic compounds) were introduced into an adsorption tube at a known, continuous, reproducible rate using one or more syringe pumps (Adzuma Model MF-2). As the adsorbate(s) vaporized from the syringe tip(s) inserted into the mixing vessel (60 ml) heated with a heater, it was swept into the flowing nitrogen stream. Thus, a constant stream containing the gaseous adsorbate(s) with a constant concentration was provided; the stream was introduced into the glass adsorption tube (25×2 cm i.d.) with a sintered glass filter. Each resin (*ca.* 2 g) was dry-packed into the tube and preconditioned at 180 °C for 1 h in a pure nitrogen stream at 100 ml/min. The nitrogen gas containing the adsorbate(s) was collected in a gas sampler (1.2—1.5 ml), and the concentration of adsorbate(s) was determined by gas chromatography with a thermal conductivity detector (Shimadzu Model

GC-3BT gas chromatograph). The chromatographic column packed with Porapak Q (2 m×3 mm i.d.) or with 10% DNP on Chromosorb W (3 m×3 mm i.d.) was used.

After the resin in the tube was equilibrated with the adsorbate(s)-nitrogen mixture at 102 °C, the asdorbate(s) vapor was completely removed from the mixing vessel through a 3-way cock (by-pass). Then, the 3-way cock was positioned again so that the pure nitrogen stream (at 100 ml/min) passed through the adsorption tube, and the adsorbate(s) taken up by the resin was desorbed at 102 °C for 2 h. Then, the desorption temperature was programmed at 3.1 °C/min to 170 °C. The desorbed adsorbate(s)-nitrogen mixture was periodically collected in a gas sampler and analyzed by gas chromatography.

The measurements of breakthrough time were carried out by replacing nitrogen gas cylinder in Fig. 1 with an air bag containing the adsorbate(s) and by directly introducing the sample gas in the air bag with a pump into a FID (flame ionization detector in a Shimadzu Model GC-3BF gas chromatograph) through the adsorption tube. The sample-air flow rate was 20 ml/min and the resin weight in the tube was 1 g.

The total adsorption capacities of adsorbates on the resins were measured with a Shimadzu Model ADS-1B sorptograph with the automatic temperature-programming device connected to a Shimadzu Model GC-3BT gas chromatograph.

All chromatograms were recorded on a Shimadzu Model R-101 recorder; peak areas were measured by a Shimadzu Chromatopac E-1A integrator.

Results and Discussion

Preliminary Uptake Studies. Initially, the total amounts of organic vapors taken up by the resins were estimated from the desorption peak area measured with the sorptograph. As listed in Table 1, the β-cyclodextrin polyurethane resin, β-HDI-P-5.5-M, gives larger uptake values for the organic vapors than the polyurethane resin containing no cyclodextrin units, BDOL-HDI-P-M, does. This result suggests that the β-cyclodextrin units in the resin interact strongly with the organic vapors.

The amount of benzene vapor taken up by each resin was compared. Porapak Q has the greatest uptake of benzene at 55 °C. On the other hand, at 150 °C Porapak Q takes up less than the resins containing β-cyclodextrin units do. The uptake amount of benzene for the β-cyclodextrin resin at 55 °C varies apparently with the diisocyanate used. The amount of benzene taken up by each β-cyclodextrin resin decreases with increasing adsorption temperature and reaches a constant, nearly equal value at 150 °C; this result strongly suggests that the β-cyclodextrin cavities in the resins take part in the adsorption of benzene molecules.

Sorption Behavior of β-Cyclodextrin Polyurethane Resins for Benzene Vapor. As one approach to the actual application of the β-cyclodextrin resins, it is of value to investigate their sorption behavior for one given organic vapor (benzene in this work) co-existing with another one. The resin was equilibrated with the 0.004% benzene–0.055% cyclohexane–nitrogen flow at 102 °C. After benzene and cyclohexane which had been taken up were desorbed for 2 h by the pure nitrogen stream at the same temperature, the desorption temperature was programmed at 3.1 °C/min to 170 °C. Figure 2 shows the temperature-programmed desorption patterns thus obtained. The amount of benzene desorbed is larger than that of cyclohexane. Considering that there is a much lower concentration of benzene than of cyclohexane in the benzene–cyclohexane–nitrogen flow, we interpret these results as indicating that the β-cyclodextrin resins collect the benzene vapor much better than the cyclohexane one. β-XDI-P-5.8-A gives desorption patterns different from those on either β-HDI-P-5.5-A or β-H6XDI-P-6.0-M; this is presumably due to the lower thermal stability of β-XDI-P-5.8-A. Thermally, the β-H6XDI-P-6.0-M resin is the most stable of the three β-cyclodextrin resins. Therefore,

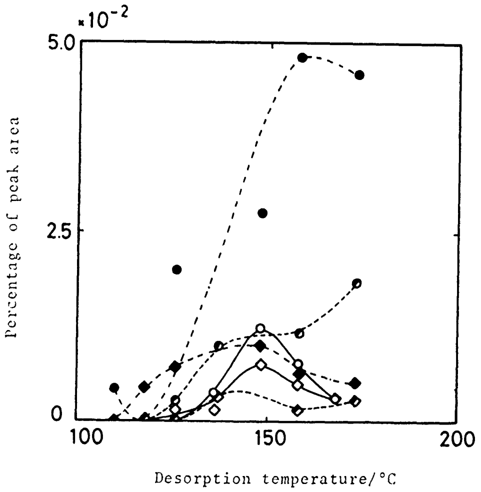

Fig. 2. Desorption of benzene and cyclohexane on β-cyclodextrin polyurethane resins.
——: β-HDI-P-5.5-A, —·—: β-H6XDI-P-6.0-M, ----: β-XDI-P-5.8-A.
○●◐: Benzene, ◇◆⬖: cyclohexane.
0.004% benzene–0.055% cyclohexane–N_2.

Table 1. Total adsorption capacities for organic vapors

Resin	mg Benzene/g Resin		mg Cyclohexane/g Resin		mg Ethyl alcohol/g Resin	
	55 °C	150 °C	55 °C	150 °C	55 °C	150 °C
β-HDI-P-5.5-M	107	30	68	40	111	48
β-H6XDI-P-6.0-M	72	32				
β-XDI-P-5.8-A	58	27				
BDOL-HDI-P-M	48	5	38	1	21	0.5
Tenax GC	59	1				
Porapak Q	213	18				

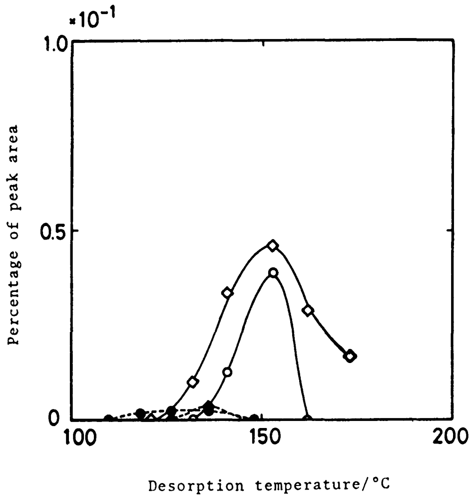

Fig. 3. Desorption of benzene and ethyl methyl ketone on β-H6XDI-P-6.0-M and Porapak Q.
——: β-H6XDI-P-6.0-M, ----: Posapak Q. ○●: Benzene, ◇◆: ethyl methyl ketone.
0.013% benzene–0.12% ethyl methyl ketone–N_2 (β-H6XDI-P-6.0-M), 0.016% benzene–0.074% ethyl methyl ketone–N_2 (Porapak Q).

β-H6XDI-P-6.0-M was investigated in further experiments.

Figure 3 shows the temperature-programmed desorption peaks of benzene and ethyl methyl ketone on both β-H6XDI-P-6.0-M and Porapak Q. β-H6XDI-P-6.0-M gives large peaks of benzene and ethyl methyl ketone. Considering the concentrations of both adsorbates, the benzene peak area is very large compared with that of ethyl methyl ketone. On the other hand, Porapak Q gives only small peaks of both adsorbates; BDOL-HDI-P-M shows no desorption peaks at all in the temperature-programmed experiments.

It is interesting to investigate whether one adsorbate on the resin is replaced by the other or not. Figure 4 clearly shows that ethyl methyl ketone on β-H6XDI-P-6.0-M is replaced by benzene. First, the 0.16% ethyl methyl ketone–nitrogen flow was passed for 1 h through the tube containing the resin to saturate the adsorption sites completely with ethyl methyl ketone; next, the 0.006% benzene–0.06% ethyl methyl ketone–nitrogen flow was passed for 3 h. A large desorption peak of benzene appears when the desorption temperature is programmed at 3.1 °C/min from 102 °C. Similarly, the 0.08% benzene–nitrogen flow was passed for 1 h and then the 0.5% benzene–0.05% ethyl methyl ketone–nitrogen flow was passed for 3 h. The desorption peak of ethyl methyl ketone is minute in comparison with that of benzene.

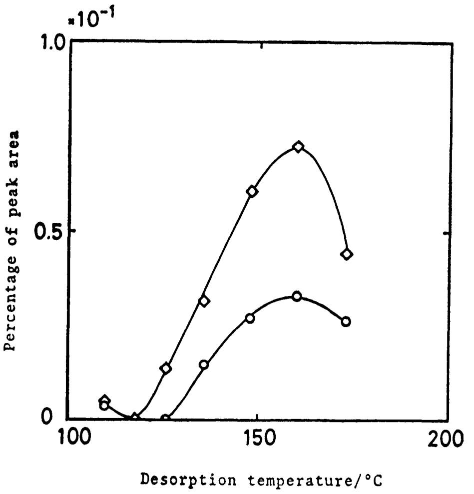

Fig. 4. Replacement of ethyl methyl ketone with benzene on β-H6XDI-P-6.0-M.
○: Benzene, ◇: ethyl methyl ketone.
Adsorption system: 0.16% ethyl methyl ketone–N_2 (1 h), 0.06% ethyl methyl ketone–0.006% benzene–N_2 (3 h).

These results strongly suggest that the β-cyclodextrin polyurethane resin is selectively adsorptive for benzene vapor. Both desorption peaks have the maxima at *ca.* 150 °C; this result supports the contention that the cyclodextrin cavities in the resin take part in the interaction with the adsorbate molecules, as described previously.[10]

Breakthrough Studies. All the experiments cited to this point were carried out with samples prepared by introducing one or two organic compounds into a dry nitrogen flow. Practical samples, however, will contain many different compounds including water. It is thus especially important to study the effect of co-existing water.

First, the 0.4% benzene–air stream containing 0.4% ethyl methyl ketone or 1.76% water as a concomitant was used to obtain the breakthrough profiles for β-H6XDI-P-6.0-M. Co-existing water or ethyl methyl ketone does not affect the breakthrough time (26 min). In the case of 0.4% ethyl methyl ketone–air stream, the breakthrough time is 66 min. It decreases to 45 min, when 0.04% benzene is added to the 0.4% ethyl methyl ketone–air stream. This result is reasonably interpreted as follows. Ethyl methyl ketone is adsorbed on the β-cyclodextrin resin by both the hydrophobic and hydrogen-bonding interactions, while benzene is taken up almost by the hydrophobic one. This is supported by the fact that BDOL-HDI-P-M interacts strongly with the compounds capable of forming hydrogen-bonding.[10] The decrease in the breakthrough time with increasing benzene concentration in the ethyl methyl ketone–air stream seems to result from the strong, selective occupation of the hydrophobic adsorption sites by benzene.

Second, the mixing vessel in Fig. 1 was replaced with a gas stripping vessel in order to perform the breakthrough experiments by a gas stripping method; this is generally a highly sensitive method for collecting volatile organic compounds in water.[11] A stream of nitrogen at 50 ml/min stripped 150 ml of sample solution at 25 °C. After the concentration of stripped organic compound in the gas coming out of the vessel reached a constant value, the sorption tube containing 2 g of a resin was connected to the stripping vessel, and the breakthrough curve was obtained by flame ionization gas chromatography. The breakthrough profiles were well-defined S-shaped curves.

Table 2 shows the breakthrough times on β-H6XDI-

Table 2. Breakthrough times (min) on β-H6XDI-P-6.0-M and Amberlite XAD-7

Compound	β-H6XDI-P-6.0-M		Amberlite XAD-7	
	50 °C	100 °C	50 °C	100 °C
Methyl alcohol[a]	32	5	7.5	0.8
Ethyl alcohol[a]	123	17	28	3
Acetone[b]	70	19	39	3.6
Ethyl methyl ketone[b]	121	53	103	12
Benzene[c]	12	10.5	72	9
Water[d]	30	5	5	0

Concentration of solute: a) 4 ml/l. b) 1 ml/l. c) 0.1 ml/l. d) Measured by gas chromatography with a thermal conductivity detector.

P-6.0-M and Amberlite XAD-7 at sorption temperatures of 50 and 100 °C. At both temperatures, β-H6XDI-P-6.0-M gives a larger breakthrough time for each polar solute expect for benzene than XAD-7 does, while the reverse is observed for nonpolar benzene at 50 °C. The greater retention of the polar compounds on β-H6XDI-P-6.0-M presumably results from the much stronger affinity of this resin for water: the distribution of the polar compounds into the water layer retained on β-H6XDI-P-6.0-M plays an important role in their greater retention, compared with the XAD-7 resin. It is unusual that benzene breakthrough on β-H6XDI-P-6.0-M varies little with the sorption temperature in the range of 50—100 °C. Supposedly, a large amount of water on the resin surface also brings about the small breakthrough time of 12 min for benzene at 50 °C: nonpolar benzene must penetrate through the water layer to reach the hydrophobic sorption site of the resin. Amberlite XAD-7, on the other hand, is hydrophobic in nature and retains much less water than β-H6XDI-P-6.0-M does. Therefore, nonpolar benzene is taken up more strongly by the XAD-7 resin.

In summary, it is found from this preliminary work that the β-cyclodextrin polyurethane resins exhibit a strong interaction with benzene vapor in the nitrogen or air stream. Also, in the gas stripping method, the β-H6XDI-P-6.0-M resin retains the polar volatile organic compounds more greatly than Amberlite XAD-7 (used widely to collect them) does; this results indicates the possibility of using the β-cyclodextrin polyurethane resins as sorbents to collect polar volatile organic compounds.

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