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Concentration of Indole in Coal Tar Using α-Cyclodextrin as the Host for Inclusion Complexation

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Abstract. Inclusion complexation by α-cyclodextrin (α-CD) was utilized to develop a novel method of extracting indole in coal tar. An aqueous solution of α-CD and a sample oil containing indole was stirred to form a solid α-CD–indole complex. Both model and real sample oils were tested. Composition changes of the sample oils accompanied by the inclusion process were measured with capillary gas chromatography. α-CD was found to have the remarkable characteristic of concentrating indole selectively even in a complicated mixture.

Key words. α-Cyclodextrin, indole, coal tar, concentration, separation.

1. Introduction

α-Cyclodextrin (α-CD) is composed of six α-1,4-linked D(+)-glucopyranoses and its cavity can accommodate various organic compounds to form inclusion complexes. α-CD, as well as β- and γ-CDs, has been attracting much attention because of their use in inclusion complexation and catalysis [1]. The characteristic of inclusion complexation has been applied to the separation and analysis of mixtures. Recently CDs (β-CD in particular) have been used as CD-bonded polymers [2] or mobile phase components in reversed-phase systems [3]. However, their applications have been limited only to simple systems consisting of a few kinds of components, e.g. positional isomers of disubstituted benzene derivatives or optical isomers. To our knowledge, there is no report applying CD to the separation of useful compounds in complicated samples such as coal tar and petroleum oil, comprising many kinds of components. Our study is the first example of the use of α-CD for concentrating indole in coal tar. Indole is valuable as a material in perfumery, tryptophan synthesis, drugs manufacture, etc., and this attempt will present a novel method of extracting indole in coal tar. The idea of this study is based on the very high formation constant of the α-CD–indole complex [4].

2. Experimental

2.1. MODEL AND REAL SAMPLE OILS INCLUDING INDOLE

A model sample oil comprising seven constituents was prepared by reference to a textbook. The composition is listed in Table I.

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Table I. Composition changes accompanied by inclusion complexation of model sample oil

	Model sample oil	1st inclusion complexes	2nd inclusion complexes	3rd inclusion complexes	Cf. boiling point (°C)
Indole	6.0%[a]	20.3	42.8	57.0	254
Quinoline	9.3	11.1	11.1	7.7	238
Isoquinoline	6.1	6.2	7.2	6.4	243.3
2-Methylnaphthalene	45.3	32.2	15.5	6.1	243.1
Quinaldine	6.2	13.2	21.6	22.1	246.6
1-Methylnaphthalene	15.1	8.5	0.4	0	244.4
Biphenyl	12.0	8.5	1.4	0.7	255.9

[a] Weight percentage.

Real sample oil was fractionated from coal tar (provided by NKK Corporation) using a distillation apparatus of the spinning band column type. The 240–270°C fraction was subjected to the inclusion reaction.

2.2. INCLUSION COMPLEXATION

The sample oil (1 g) was added to 20 mL of 10 wt% aqueous solution of α-CD. It was vigorously agitated with a magnetic stirrer for 90 min in a thermostated bath at 25°C, when solid-state substances deposited. Then the reaction product was centrifuged for 5 min at 2500 rpm and filtered with a membrane filter (pore size: 0.4 μm), washed with water and toluene and dried with acetone. Thus we obtained white precipitates of inclusion complexes, in which indole was concentrated. To further concentrate indole, we dissociated the inclusion complexes in 10 mL of hot water (CD inclusion compounds were reported to dissociate in water at 60–70°C [5]) and repeated the inclusion process, i.e. stirring in a thermostated bath and followed by filtration.

2.3. MEASUREMENT OF COMPOSITION CHANGES

The change of indole concentration accompanied by the inclusion process was measured with a GC-9A gas chromatograph (Shimadzu, Kyoto, Japan) with a fused-silica wall-coated capillary column (50 m × 0.25 mm I.D.) using OV-1 as the liquid phase. The sample solution for the GC measurement was prepared by dissociating the inclusion complexes in hot water and extracting with diethyl ether. The measurement conditions were as follows: carrier gas, He; flow rate, 0.6 mL/min; injection port temperature, 300°C; sample size, 0.4–1.0 μL; splitting ratio, 1 : 50; flame ionization detector; column temperature, 150°C for 25 min, then increased at 5°/min to 250°C.

3. Results and Discussion

The composition changes of the model sample oil accompanied by inclusion complexation are listed in Table I. The major components of the model sample oil, i.e. 1-methylnaphthalene, 2-methylnaphthalene and biphenyl, were excluded to a great extent. They are hydrocarbons that consist of only carbon and hydrogen atoms. On the other hand, the rest of the components of the model sample oil contain nitrogen atoms, which should form hydrogen bonds with hydroxyl groups of α-CD. In the case of indole, however, the hydrogen atoms of the N—H groups must form hydrogen bonds with the oxygen atoms of α-CD [6]. Consequently,

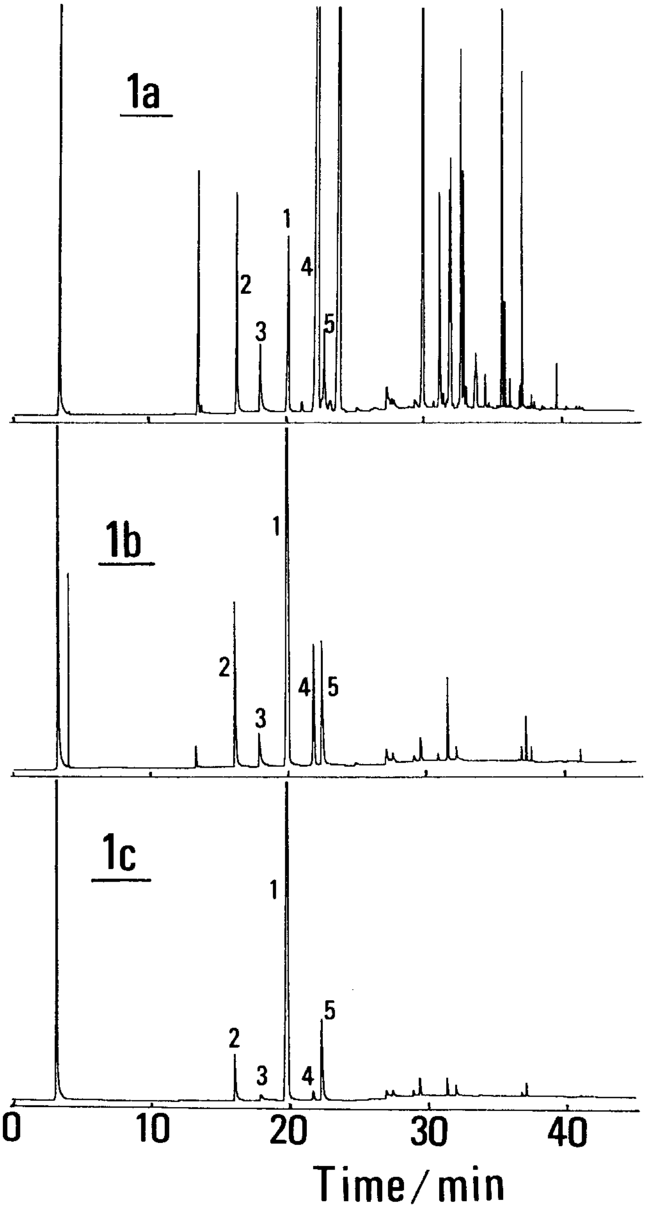

Fig. 1. Chromatograms of the real sample oil (*a*), of the extracted components from the 1st inclusion complexes (*b*) and of those from the 2nd complexes (*c*). Each sample was diluted with diethyl ether. Assigned peaks: **1** Indole, **2** Quinoline, **3** Isoquinoline, **4** 2-Methylnaphthalene, **5** Quinaldine.

indole and other heterocyclic nitrogen compounds should have a stronger interaction with the host lattice of α-CD than the usual hydrocarbons. This seems to lead to the very easy separation of indole from the usual hydrocarbons despite their similar molecular size and shape. The separation was certainly easy according to the preliminary work where indole and a kind of hydrocarbon, i.e. 1-methylnaphthalene, 2-methylnaphthalene or biphenyl, were used. It was remarkable that indole and biphenyl whose boiling points are so close were easily separated by the inclusion process.

On the other hand it was not very easy to separate indole and other heterocyclic nitrogen compounds. The degree of difficulty in exclusion was as follows: quinaldine $\gg$ quinoline $>$ isoquinoline. The order obtained from the experiment using the model sample oil was in agreement with the difficulty of separating indole selectively in a simple system of two components, i.e. indole and each heterocyclic nitrogen compound. Since quinaldine (= 2-methylquinoline) has a methyl group adjacent to its nitrogen atom, it is seemingly difficult for quinaldine to form stable hydrogen bonds with α-CD compared with quinoline and isoquinoline. But the experimental fact suggests that quinaldine forms a more stable complex with α-CD rather than quinoline and isoquinoline. A detailed structural study of the inclusion complex will be necessary in order to find an explanation.

Figure 1 shows the chromatograms of the real sample oil fractionated from coal tar (a), of the extracted components from the first inclusion complexes (b) and of those from the second complexes (c), respectively. The composition changes of some main components are listed in Table II. We obtained a result corresponding to the abovementioned case of the model sample oil. The result indicates that α-CD is very effective for the concentration of indole even in a complicated real sample oil. It should be noted that so many kinds of hydrocarbons in the real sample oil were excluded through inclusion complexation by α-CD, although it did not seem easy to exclude the heterocyclic nitrogen compounds except indole through only one inclusion process. However, it seems possible to exclude them and concentrate indole by repeating the inclusion process. In conclusion, it has been shown here that inclusion complexation by α-CD could be applied to the extraction of indole in coal tar.

We are now investigating the association constants for complex formation between α-CD and the various compounds in coal tar and the structural relationship between them. Furthermore, we are planning to use α-CD-bonded polymers instead of simple α-CD.

Table II. Composition changes accompanied by inclusion complexation of real sample oil

	Real sample oil	1st inclusion complexes	2nd inclusion complexes
Indole	3.5%[a]	49.9	75.8
Quinoline	3.4	10.8	4.5
Isoquinoline	1.3	2.5	0.3
2-Methylnaphthalene	25.4	10.2	1.2
Quinaldine	2.0	10.8	10.2
Others	64.4	15.8	8.0

[a] Percentage of each chromatographic peak area.

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