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Selective Liquid–Liquid Extraction of Xylene Isomers and Ethylbenzene through Inclusion by Branched α-Cyclodextrins

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Abstract. Branched α-cyclodextrins (CDs) such as glucosyl-α-CD(G-α-CD) were found to be very effective reagents for selective liquid-liquid extraction of xylene isomers and ethylbenzene since their inclusion complexes did not precipitate and handling of solids was not necessary. Reaction temperatures higher than room temperature did not increase the yield. The inclusion complexation proceeded fast. The liquid-liquid extraction process was found to be energy-saving and not time-consuming.

Key words. Branched α-cyclodextrin, glucosyl-α-cyclodextrin, xylene isomers, ethylbenzene, liquid-liquid extraction

1. Introduction

Cyclodextrins (CDs) have the structure of a doughnut-shaped ring and can accommodate various kinds of organic compounds in their cavities to form inclusion complexes [1]. Their selectivity in the formation of inclusion complexes depends chiefly upon the size and shape of the guest species. Thus CDs have been used to separate some useful organic compounds [1–3].

A separation method for xylene isomers and ethylbenzene using α-CD was presented about twenty years ago [4]. It was also well known that clathration with Werner type complexes such as $Ni(4\text{-Methylpyridine})_4(SCN)_2$ was useful for separating xylene isomers [5]. To our knowledge, however, these methods have not yet been carried out commercially. One of the main reasons is the difficulty of handling the solid inclusion complexes [3, 6]. In particular, the precipitates of the CD complexes are so fine and sticky that the procedure of separating them from the solution phase is very troublesome.

Recently the effectiveness of γ-CD-modified solvent extraction for large polynuclear aromatic hydrocarbons was demonstrated [7]. The method, however, does not seem to be suitable for separating xylene isomers and ethylbenzene.

In this study we have found that the branched CDs such as glucosyl-α-CD(G-α-CD) and maltosyl-α-CD(M-α-CD) have great advantages for the separation of xylene isomers and ethylbenzene. Since G-α-CD or M-α-CD has a glucosyl or maltosyl unit joined through a 1,6-α linkage and its broader rim undergoes no modification, the inclusion selectivity to guest species is not considered to be very different from that of α-CD. The branched CDs were produced in order to enhance the solubility of CDs. For example, at 25°C, the solubility of G-α-CD in water is about four times that of α-CD and that of G-β-CD is about fifty times that

of β-CD [8]. The solubility enhancement confers some great advantages. One is that in the method using the branched CDs the process of solid–liquid separation is not necessary since the CD–xylene or CD–ethylbenzene complex does not precipitate. The merit seems to be greatest because it makes the whole system of separation very simple, even facile. Another advantage is that branched CDs can be used in higher concentration than simple CDs, so that an improvement of reactivity and yield should be expected and solvent volume should be reduced.

The use of the branched CDs such as G-α-CD in foods has been widely examined [9], while the application to the separation of useful organic compounds in petroleum oil and coal tar has hardly ever been studied.

Although there are several methods of separating xylene isomers, e.g. using zeolites [10] or HF-BF_3 [11], which have been commercially established, we think that the method reported here has the potential to become another effective separation process.

2. Experimental

2.1. REAGENTS

All the chemicals used were guaranteed reagents. *o*-, *m*-, and *p*-xylenes, xylene mixture, ethylbenzene, toluene and diethyl ether were purchased from Wako Pure Chemical Industries, Ltd. and α-CD from Tokyo Kasei Kogyo Co., Ltd. G-α-CD and M-α-CD were supplied by Ensuiko Sugar Refining Co., Ltd. They contain less than 1.5% impurities. Distilled and deionized water was used.

2.2. PROCEDURE OF INCLUSION EXTRACTION

Branched CD was dissolved into water, to which guest species were added. It was vigorously stirred in a thermostated bath. No solids deposited. After stirring the solution it was left undisturbed for a few minutes, whereupon it separated into two layers: the upper was the organic phase of the guest species and the lower was the CD aqueous solution in which guest species were selectively extracted by inclusion complexation. To recover the included oil components, it was sufficient to shake the CD solution with diethyl ether for a few minutes. This procedure ensured that all the included oil components were transferred to the ether phase. Although we tried a second extraction from the aqueous phase, only a trace amount of guest species was detected by GC measurement. Diethyl ether was evaporated easily and the extracted oil remained.

In the case of α-CD, the white, solid inclusion complex was filtered with a membrane filter (pore size: 0.4 μm), and washed with acetone. The solids were placed in a desiccator over silica gel and dried under reduced pressure (1 Torr) for 2 h at room temperature before weighing.

2.3. CHROMATOGRAPHIC MEASUREMENT OF OIL COMPONENTS

The oil components were determined with a GC-9A gas chromatograph (Shimadzu, Kyoto, Japan) using a stainless steel (SUS) WCOT capillary column

(60 m × 0.25 mm I.D.) with SPX-1 as the liquid phase. The measurement conditions were as follows: carrier gas, He; flow rate, 0.6 mL/min; injection port temperature, 300°C; sample size, 0.2–5.0 μL; splitting ratio, 1 : 50; flame ionization detector; column temperature, 50°C for 1 min, increasing at 5°/min to 100°C and then holding at that temperature. Under these conditions, the retention times were 17.2 min for toluene, 23.7 min for ethylbenzene, 26.3 min for *m*-xylene, 26.8 min for *p*-xylene and 31.0 min for *o*-xylene, respectively.

After the inclusion reaction the solution easily separated into two layers, as mentioned above. But in order to make the phase separation more complete, a part of the aqueous layer was taken in a glass tube and centrifuged at 3000 rpm for 5 min. The CD solution in the lower part of the glass tube was taken, weighed, and toluene was added as internal standard. It was transferred to a separatory funnel, with water and diethyl ether added, and shaken for a few minutes. Then the included oil components and toluene were extracted into the diethyl ether layer. The ether solution was subjected to GC measurement. In the case of α-CD, the dried complex solids were weighed and toluene was added. The subsequent procedure was the same as described above.

The following test was performed in order to certify the precision of this analysis. Xylene mixture and toluene were weighed and added to a G-α-CD aqueous solution. Diethyl ether was added and, after shaking for a few minutes, the ether phase was subjected to determination by GC. The analytical result was 0.01064($\pm$0.00006) g ($n = 3$) for 0.01068 g of weighed xylene mixture.

3. Results and Discussion

We carried out a preliminary examination to see whether there was any noticeable difference in the inclusion characteristics among α-CD, G-α-CD and M-α-CD. The result is listed in Table I. The selectivity of inclusion towards *p*-xylene and other guest species was observed to have almost the same trend among the CDs. Regarding the yield of guest species, α-CD gave a slightly better yield than G-α-CD and M-α-CD. As can be seen from this preliminary examination, G-α-CD and M-α-CD showed very similar characteristics of inclusion. Therefore, using only G-α-CD, we investigated the liquid–liquid extraction of xylene isomers and ethyl-

Table I. Composition and yield of oil extracted by α-CD, G-α-CD and M-α-CD

Component	Source Oil	Extracted Oil α-CD	G-α-CD	M-α-CD
Ethylbenzene	17.1 wt%	21.9	21.7	21.6
m-Xylene	43.3	9.4	14.4	15.5
p-Xylene	18.5	63.4	60.1	59.6
o-Xylene	20.5	5.3	3.8	3.0
Yield		27.5%	21.5	22.9

The concentrations of α-CD, G-α-CD and M-α-CD were 0.103 mol/L H_2O, respectively. The amount of source oil (xylene mixture purchased from Wako; see text) was three tenths of the weight of water. Stirring time: 2 h. Temperature: 25°C. Yield means percentage of CD-included guest species.

Table II. Inclusion selectivity to two kinds of guest species

	Source Oil	Extracted Oil
Ethylbenzene–*o*-Xylene	50.0 : 50.0	87.8 : 12.2
Ethylbenzene–*m*-Xylene	50.0 : 50.0	74.1 : 25.9
Ethylbenzene–*p*-Xylene	50.0 : 50.0	33.6 : 66.4
o-Xylene–*m*-Xylene	50.0 : 50.0	22.0 : 78.0
o-Xylene–*p*-Xylene	50.0 : 50.0	7.3 : 92.7
m-Xylene–*p*-Xylene	50.0 : 50.0	10.8 : 82.9

Each value is given as mass ratio.
The concentration of G-α-CD was 0.103 mol/L H_2O. The amount of the source oil was three tenths of the weight of water. Stirring time: 5 min. Temperature: 25°C.

benzene in further detail. Another reason why we chose G-α-CD was that we were able to examine a wider range of CD concentration using G-α-CD rather than M-α-CD [8].

The order of inclusion selectivity was as follows: *p*-xylene > ethylbenzene > *m*-xylene > *o*-xylene which was confirmed by examining all the combinations of two components. The results are listed in Table II. As is already known, the order corresponds to how well the guest molecule is packed in the cavity of CD.

Figure 1 shows that the yield became greater with increasing concentration of G-α-CD. In practice, however, its concentration should be kept somewhat lower than the upper limit of solubility in order to carry out liquid–liquid extraction without depositing solid matter.

As can be seen from Table III, compared with the yields at 25°C, those at 35°C were almost the same and those at 45°C were slightly lower: a high reaction temperature did not bring about any increase in the yield of the inclusion complex. It is well known that temperature affects the stability of some CD complexes [7]. Therefore

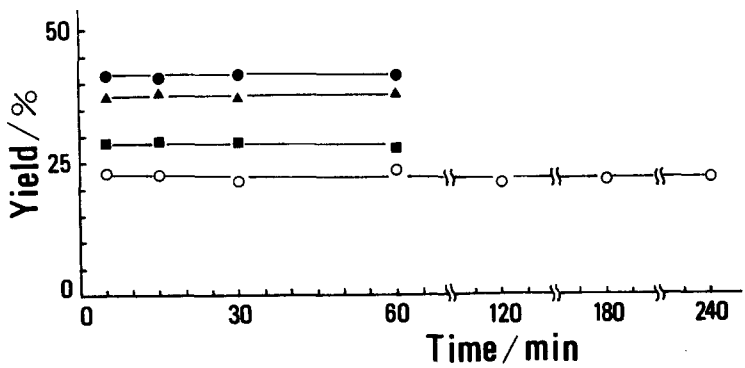

Fig. 1. Effect of G-α-CD concentration on the yield of inclusion complex. G-α-CD concentrations were (a) 0.103 mol/L H_2O(○), (a) x2(■), (a) x4(▲) and (a) x6(●), respectively. The amount of xylene mixture was three tenths of the weight of water. Temperature: 25°C. As for the meaning of yield, see Table I.

Table III. Effect of temperature on yield of inclusion complex

Temperature	Yield at Each Stirring Time		
	5 min	15 min	30 min
25°C	28.6%	29.0	28.6
35°C	29.3	29.4	29.2
45°C	27.3	27.4	27.6

The concentration of G-α-CD was 0.206 mol/L H_2O. The amount of xylene mixture was three tenths of the weight of water.

the extraction process can be satisfactorily performed at room temperature, which is considered to be one of the merits of this method in the light of the need to save energy.

Figure 1 and Table III show that the yield at 5 min was almost the same as yields obtained after longer times. This indicates that the reaction of G-α-CD – xylene

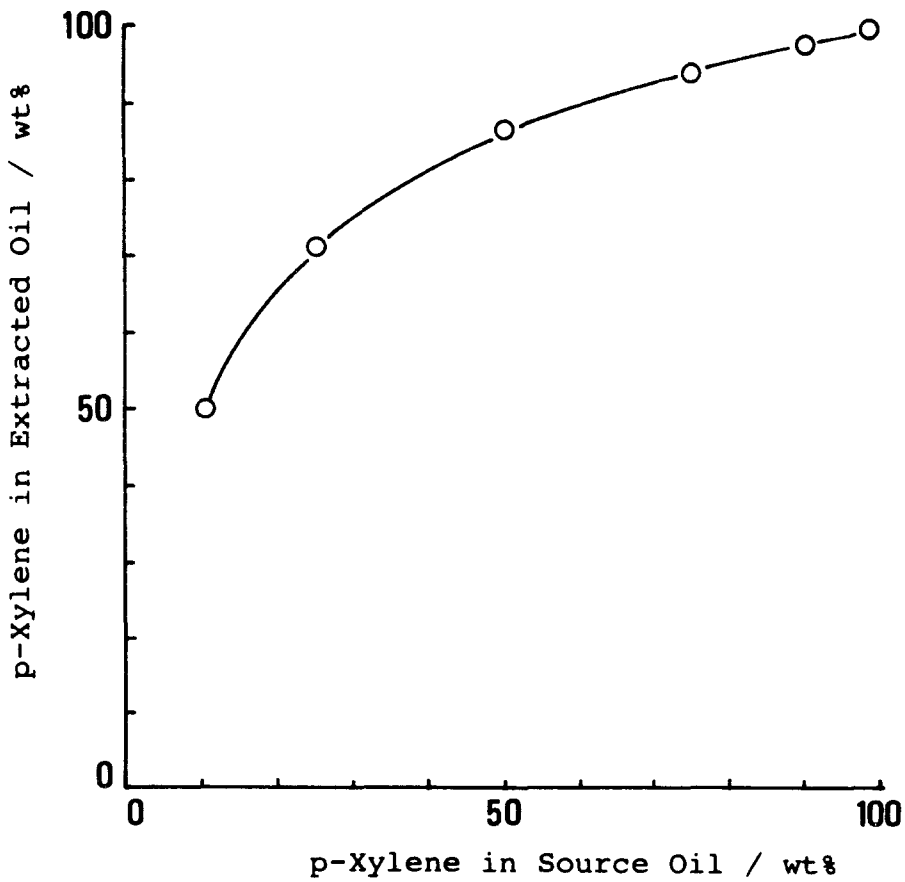

Fig. 2. Relationship between the composition of source oil of *m*- and *p*-xylene mixture and that of extracted oil. G-α-CD concentration: 0.103 mol/L H_2O. The total molar amount of *m*- and *p*-xylene mixture was twenty times that of G-α-CD. Stirring time: 30 min. Temperature: 25°C.

Table IV. Composition change in repetition of inclusion extraction

Component	Source Oil	Extracted Oil 1st	2nd
Ethylbenzene	16.5%	21.4%	5.3%
m-Xylene	43.9	16.3	0.4
p-Xylene	18.9	59.6	94.3
o-Xylene	20.7	2.7	0

Each value is given in percentage of GC peak area.
It was almost parallel to the value in weight percentage.
The concentration of G-α-CD was 0.206 mol/L H_2O.
The amount of source oil (xylene mixture) was six tenths of the weight of water in the first extraction. The extracted oil obtained from the first extraction was used for the second extraction. The amount was three tenths of the weight of water. Stirring time: 2 h. Temperature: 25°C.

complex formation proceeded very rapidly. A short reaction time, like 5 min, is thus sufficient for one extraction process.

The curve of Figure 2 gives us the information on what percentage of *p*-xylene would be obtained from the starting mixture of *p*-xylene and *m*-xylene containing a certain percentage of *p*-xylene. When we started with a 1:9 mixture of *m*- and *p*-xylenes, we were able to obtain the extracted oil in which *p*-xylene was concentrated up to 98%. Even when the ratio of *p*-xylene to *m*-xylene was 1:9, *p*-xylene was selectively concentrated to 50% through one process of inclusion complexation by G-α-CD.

According to Table IV, the concentration of *p*-xylene was effected by the repetition of inclusion complexation. Although we spent 2 hr stirring in this case, several minutes is enough (see Figure 1).

4. Conclusion

In conclusion, it was demonstrated that selective liquid–liquid extraction of xylene isomers and ethylbenzene is possible by the use of branched CDs. Room temperature is suitable for the inclusion complexation and the included components can easily be released, which is very advantageous in the light of energy saving. The inclusion complexation seems to proceed very rapidly and the procedure of solid–liquid separation is not necessary. This is also favorable since the whole procedure is not time consuming. In addition, the branched CDs can be used repeatedly. These facts indicate that the method presented here has the potential to become an effective way of separating xylene isomers and ethylbenzene.

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