

Can cyclodextrins really improve the selectivity of extraction of BTEX compounds?

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Abstract Solubility of BTEX compounds was determined in aqueous solutions of natural CDs (α -, β -, γ CD) as well as of some industrial β CD derivatives (RAMEB, HPBCD, Ac β CD) measured by UV photometry. From the phase solubility diagrams the complex association constants were determined. The β CD derivatives increased the solubility of individual monoaromatic compounds, depending on the structure of the guest molecule. We have found that RAMEB (randomly methylated β CD) and Ac β CD (partially acetylated β CD) are the most effective solubilizers while the effect of natural CDs is not significant because the complexes precipitate from the solutions. Extraction experiments were performed to see how the complexation of components influences the extraction using a mixture modeling the composition of these pollutants in soil. We have found that although the soluble CD derivatives are not as selective as expected based on complex association constants, they increased the efficacy of extraction by 4–6 times. The reason of the low selectivity is that the concentration ratio of certain BTEX compounds in CD solutions is smaller than in water. CD derivatives seem to have an equalizing effect: the solubility of the least

soluble p-xylene is improved in the highest extent, but that of benzene the least. This result, however, is an advantage in the application of these CD derivatives in soil remediation (the availability of each BTEX compounds will be enhanced).

Keywords Benzene · Xylene · Complex association constant · Solubility · Cyclodextrin derivatives · Soil remediation

List of abbreviations

BTEX	Mixtures of benzene, toluene, ethyl benzene and xylenes
AcBCD	Acetyl β -cyclodextrin
CD	Cyclodextrin
HPBCD	Hydroxypropyl β -cyclodextrin
HPLC	High Performance Liquid Chromatography
K	Complex association constant
RAMEB	Randomly methylated β -cyclodextrin

Introduction

In the literature mixtures of benzene, toluene, ethyl benzene and xylenes (BTEX compounds) have been frequently used as model compounds to prove the selectivity of inclusion complex formation. On the other hand, these compounds are widespread contaminants of soil and groundwater, which can be removed by extraction (soil washing) or bioremediation from the contaminated soil. These technologies can be intensified by using CDs to improve the aqueous solubility of BTEX compounds.

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These compounds, especially ethyl benzene and xylenes have very similar structure and properties therefore their separation on the usual stationary phases is not possible. On CD-containing stationary phases, however, baseline separation can be achieved in gas chromatography [1]. The separation in HPLC can be attained either by CD-modified stationary phases [2] or by using CD in the eluent [3].

For the separation in preparative scale liquid-liquid extraction using CD solutions has been proposed and studied.

The selective extraction of p-xylene from a mixture containing also ethylbenzene, o- and m-xylene and other C8 aromatic hydrocarbons using the complex formation with α CD was patented as early as in 1969 [4]. In this multistage extraction process p-xylene was recovered from the complex precipitated.

Using the well soluble branched α CDs the precipitation of the inclusion complexes could be avoided without a loss in selectivity [5, 6].

When a BTEX mixture was extracted with the α CD and its derivatives two types of extracts were obtained: a suspension of solid inclusion complexes in case of neutral aqueous solution of α CD with an enhanced p-xylene concentration and a clear solution of complexes in case of α CD solubilized by either derivatization or by increasing the pH. These latter solutions contained enhanced concentration of benzene explained by the higher stability of the benzene complexes compared to the complexes of the other BTEX compounds [7]. According to the literature, however, the benzene complexes with CDs, even with α CD are of lower stability than the p-xylene complexes [8].

The para-isomer was preferably included by branched α CDs and the ortho-isomer by branched β CDs [9]. Branched α CDs showed higher inclusion selectivity than branched β CD, but the yield with the β CD derivative was higher. The inclusion selectivity of branched β CDs to these guest species was in the following order: o-xylene \gg p-xylene > ethylbenzene > m-xylene.

An apparatus has been developed for large scale continuous separation of isomers [10]. The process is based on the extraction of selected components by aqueous CD solution and by hexane from the aqueous solution of the complex. Using this apparatus with 10w% glucosyl α CD an 83.8:16.2 ratio of p-xylene : m-xylene was obtained from the equimolar mixture.

The aim of the present study was to understand if there is really a selectivity in the complex formation of the BTEX compounds, these typical soil contaminants with the CDs, especially with those soluble CD

derivatives (HP β CD and RAMEB), which are preferably used for remediation of contaminated soil [11, 12].

Experimental

BTEX compounds of gas chromatography grade were applied (Merck and Aldrich). The natural cyclodextrins (α -, β -, γ -CD) and randomly methylated β -cyclodextrin (RAMEB, DS = 13.6) were purchased from Wacker Chemie, Germany; hydroxypropyl and acetyl β -cyclodextrin (HP β CD, DS = 2.7 and Ac β CD, DS = 7.2, respectively) are the products of Cyclolab Ltd, Hungary.

Determination of association constants

The solubility isotherms were measured by adding fixed amount (100 μ l) of the selected BTEX compound to 5 ml aqueous solutions of various CD concentrations in the range of 0–5% (β CD 0–1.5%) and stirred for 24 h in sealed vials. The obtained emulsions or suspensions were centrifuged (10 min, 5000 min^{-1}) and the clear aqueous solutions were measured by UV photometry after proper dilution with 50% aqueous ethanol. HP 8452A Diode Array Spectrophotometer was used to measure the concentration. The first linear section of the isotherms was used for the calculation of the complex association constants using the equation of Higuchi and Connors [13].

Extraction experiments

A BTEX mixture (0.5 ml) with the composition given in Table 2 was extracted with 5 ml water, or aqueous CD solutions containing 0–5% HP β CD, RAMEB or Ac β CD by stirring at room temperature for 24 h. The two phases were separated by centrifuging.

The separated organic phase diluted in hexane was measured by gas chromatography using Shimadzu, GC-17A equipment and Alpha dex (30 m \times 0.25 mm \times 0.25 mm) fused silica capillary column. Chromatographic conditions: carrier gas: helium, temperature of injector and detector: 250°C, oven temperature program: 50°C for 25 min, increased to 200°C at 40°C/min, hold for 5 min, split 200:1.

The aqueous phase (30 μ l) was pipetted to 5 ml water in 19.5 ml headspace vials. The vials were thermostated at 90°C for 40 min prior to analysis. Vapor sample (1 ml) was injected to the gas chromatograph and was measured under the same

Table 1 Association constant values (K , M^{-1}) calculated from the phase solubility diagrams and found in the literature (the latter in parenthesis)

	RAMEB	Ac β CD	HP β CD	α CD	β CD	γ CD
Benzene	221 (110 ^a)	332 (334 ^a)	121 (99 ^a , 142)	n.d. (20 ^a , 17 ^d)	48 (111 ^a , 120 ^d)	n.d. (8.8 ^a , 12 ^d)
Toluene	911 (144 ^a)	597 (508 ^a)	287 (170 ^a , 156)	n.d. (29 ^a , 33 ^d)	n.d. (172 ^a , 140 ^d)	n.d. (33 ^a , 20 ^d)
Ethylbenzene	846 (320 ^a)	748 (1202 ^a)	435 (248 ^a)	n.d. (131 ^a , 110 ^d)	n.d. (289 ^a , 330 ^d)	n.d. (125 ^a , 36 ^d)
o-xylene	488 (225 ^a)	590 (669 ^a)	305 (170 ^a , 289 ^b)	32 (9.7 ^a , 16 ^c , 22 ^d)	56 (184 ^a , 210 ^c , 300 ^d)	n.d. (57 ^a , 34 ^d)
m-xylene	383 (216 ^a)	442 (518 ^a)	210 (167 ^a , 238 ^b)	75 (36 ^a , 32 ^c , 40 ^d)	27 (100 ^a , 120 ^c , 160 ^d)	n.d. (18 ^a , 27 ^d)
p-xylene	581 (300 ^a)	827 (821 ^a)	353 (236 ^a , 376 ^b)	n.d. (132 ^a , 56 ^c , 72 ^d)	29 (218 ^a , 230 ^c , 240 ^d)	n.d. (32 ^a , 7.9 ^d)

n.d. not determined because the shape of the isotherm

^a by static head space gas chromatography, ref. [14]

^b by modified static head space gas chromatography, ref. [15]

^c by transport method, ref. [16]

^d by volatilization method, ref. [4]

Table 2 Composition of the BTEX mixture (w/w%) before and after the extraction

	Benzene	Toluene	Ethyl benzene	o-xylene	m-xylene	p-xylene
Before	11.09	26.98	10.91	11.06	31.06	8.90
After extraction with water	9.14	26.36	11.07	11.59	33.06	8.78
5% RAMEB	8.49	26.21	11.09	11.84	33.61	8.76
5% Ac β CD	8.09	25.46	11.28	12.04	34.21	8.93
5% HP β CD	8.70	26.37	10.94	11.67	33.42	8.90

conditions as given above, except that the split ratio was decreased to 100:1.

Results and discussion

The solubility of BTEX compounds in water and in aqueous solutions of natural CDs (α -, β - and γ CD) as well as of some industrial β CD derivatives were measured and the isotherms recorded. A_L type isotherms were obtained for the CD derivatives involved in the study. All the 3 natural CDs show B_s type isotherms with the aromatic hydrocarbons studied: the complexes precipitated. Two examples are shown in Fig. 1: the phase solubility curves of benzene and p-xylene. These two compounds are the two extremes: benzene with the lowest, p-xylene with the highest solubility enhancement in CD solutions.

The complex association constant values calculated from the phase solubility diagrams are listed in Table 1.

Comparing the data with those published in the literature obtained by different methods we can see good correspondence for a certain set of data and high difference for the other group. In this group the values

calculated in the present work are always higher than those published. It can be probably explained by the aggregation of complexes in aqueous solutions which results in overestimation of the complexed fraction typical in phase solubility studies [17].

The order of the association constants (K), which are proportional with the solubility enhancement in the CD solution related to plain aqueous solution without CD, is as follows:

$$\text{RAMEB} \sim \text{Ac}\beta\text{CD} > \text{HP}\beta\text{CD} > \alpha\text{CD} > \beta\text{CD} > \gamma\text{CD}$$

Using the soluble CD derivatives the highest enhancement of solubility was achieved for p-xylene followed by ethyl benzene showing that the selected CD derivatives have high affinity to these compounds forming complexes of high stability. The association constant values follow roughly the order below:

$$\begin{aligned} \text{p-xylene} &\sim \text{ethyl benzene} > \text{o-xylene} \sim \text{m-xylene} \\ &\sim \text{toluene} > > \text{benzene}. \end{aligned}$$

There are some exceptions, like the extreme K value for toluene/RAMEB and for ethylbenzene/Ac β CD system. The absolute values of the solubility, however,

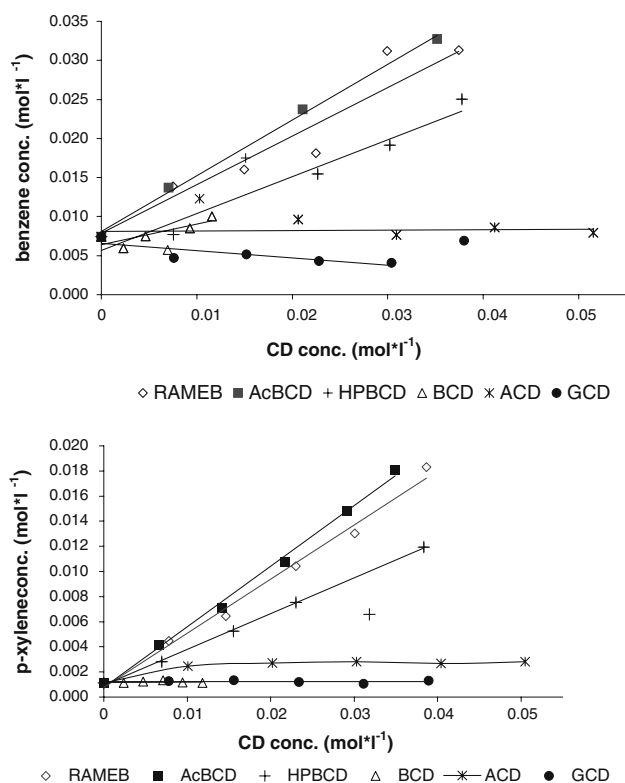


Fig. 1 Phase solubility diagrams of benzene (top) and p-xylene (bottom) in aqueous CD solutions

follow a different order (Fig. 2): in spite of the lower complex stability benzene keeps its leading position in aqueous solutions of each CD studied [18]. This can explain the high benzene concentrations in the aqueous extracts of BTEX mixture similarly to the results obtained earlier by using α CDs [7].

Both the organic phase and the aqueous phase were analyzed for the individual BTEX compounds by gas chromatography using Alpha dex (Restec) column containing α CD, which made possible the separation of

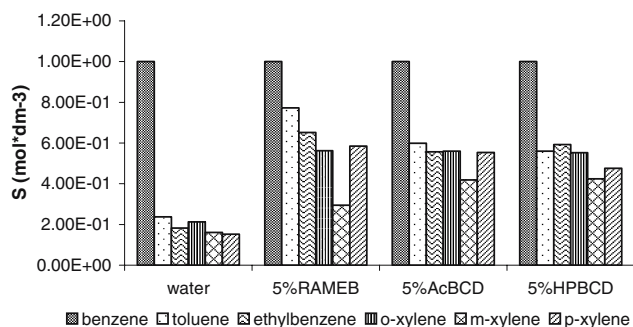
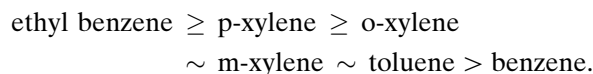


Fig. 2 The solubility of BTEX compounds in aqueous solutions of β CD derivatives (5%) normalized to the solubility of benzene

two otherwise non-separating compounds: p-xylene and ethyl benzene.

On the effect of extraction slight changes (within the experimental error) were observed in the composition of the BTEX mixture, only the benzene content decreased significantly (Table 2) in accordance with its high solubility in aqueous solutions (with or without CD), and the content of the least soluble m-xylene increased.

The composition of the aqueous phase was very similar for the three CD derivatives involved in this study. To demonstrate the differences the concentrations were related to those obtained by the extraction with the pure water. The order of the enhancement of the BTEX concentrations in CD solutions compared to water as extractant was more or less similar to that obtained for the association constants (see above):



The highest enhancement was achieved for ethyl benzene (11.7, 11.6 and 9.2 fold enhancement in concentration compared to that obtained in the aqueous extract without CD for RAMEB, Ac β CD and HP β CD, respectively), the lowest for benzene (4.6-, 4.1- and 4.1-fold enhancements, respectively). These results do not correlate with the K values.

On the other hand, there was a remarkable increase in the efficiency of the extraction when the solutions of the CD derivatives were used (Table 3). Not less than 4–6 fold more BTEX compounds were extracted with 5% CD solutions than with water (Fig. 3).

Conclusions

Only a slight selectivity was observed when BTEX mixture was extracted by aqueous solutions of the CD derivatives. It can be concluded that not the complex stability expressed by the association constants (calculated from the solubility enhancement) is the most important factor in the extraction, but the solubility of the complexes seems to be determinant.

Table 3 Efficacy of the extraction

	mg BTEX/5 ml aqueous phase
Water	1.85
5% RAMEB	11.87
5% Ac β CD	9.41
5% HP β CD	7.68

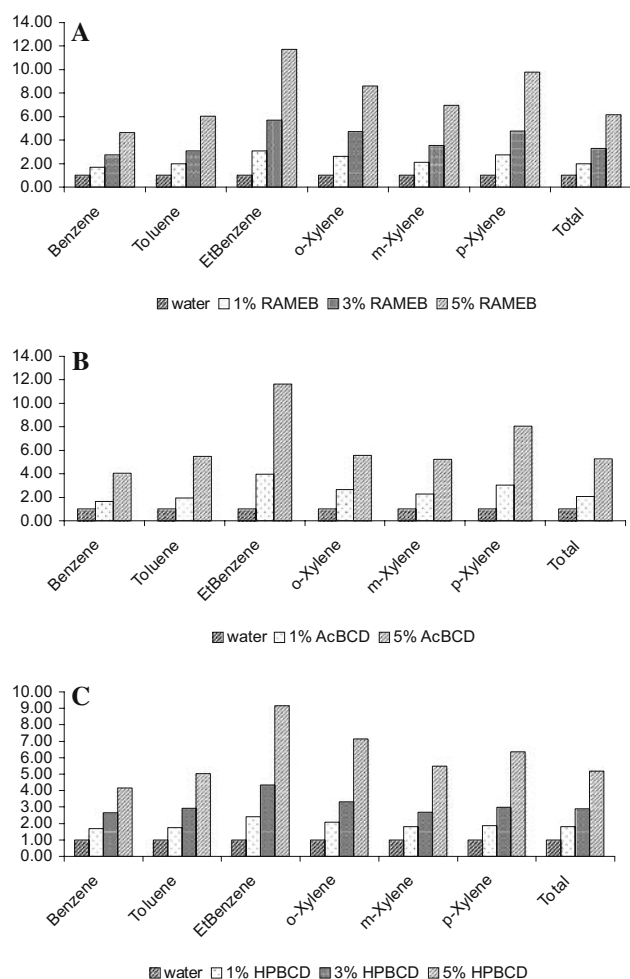


Fig. 3 Concentration of BTEX compounds in the aqueous extracts related to the concentration in the extract obtained with pure water. **(A)** RAMEB; **(B)** Ac β CD; and **(C)** HP β CD

Concerning the application of the CD derivatives for soil remediation it is of high importance that the CDs do not dissolve only certain BTEX compounds, but solubilize them all. The CD complexation has an equalizing effect on the solubility of these compounds: the lower the intrinsic solubility the higher is the solubility enhancement achieved by these CD derivatives. The CD derivatives involved in this study meet the requirement of a soil remediation additive as they improve the availability of all the BTEX compounds.

The low selectivity but high efficiency make the application of these CD derivatives favorable in soil washing and remediation technologies, since CDs should improve the solubility and with this the (bio)availability of all the organic pollutants present in the soil.

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