ORIGINAL ARTICLE

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-, γCD) as well as of some industrial βCD derivatives (RAMEB, HPBCD, AcβCD) measured by UV photometry. From the phase solubility diagrams the complex association constants were determined. The βCD derivatives increased the solubility of individual monoaromatic compounds, depending on the structure of the guest molecule. We have found that RAMEB (randomly methylated βCD) and AcβCD (partially acetylated βCD) 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-cylodextrin
CD	Cyclodextrin
HPBCD	Hydroxypropyl β-cyclodextrin
HPLC	High Performance Liquid Chromatography
K	Complex association constant
RAMEB	Randomly methylated β-cyclodextrin

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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.

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 αCD 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 αCDs the precipitation of the inclusion complexes could be avoided without a loss in selectivity [5, 6].

When a BTEX mixture was extracted with the αCD and its derivatives two types of extracts were obtained: a suspension of solid inclusion complexes in case of neutral aqueous solution of αCD with an enhanced p-xylene concentration and a clear solution of complexes in case of αCD 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 αCD are of lower stability than the p-xylene complexes [8].

The para-isomer was preferably included by branched αCDs and the ortho-isomer by branched βCDs [9]. Branched αCDs showed higher inclusion selectivity than branched βCD, but the yield with the βCD derivative was higher. The inclusion selectivity of branched βCDs to these guest species was in the following order: o-xylene >> 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 αCD 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 (HPβCD 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 (HPβCD, DS = 2.7 and AcβCD, 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 µl) of the selected BTEX compound to 5 ml aqueous solutions of various CD concentrations in the range of 0–5% (βCD 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% HPβCD, RAMEB or AcβCD 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 × 0.25 mm × 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 µl) 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	AcβCD	HPβCD	αCD	βCD	γCD
Benzene	221	332	121	n.d.	48	n.d.
	(110[a])	(334[a])	(99[a], 142)	(20[a], 17[d])	(111[a], 120[d])	(8.8[a], 12[d])
Toluene	911	597	287	n.d.	n.d.	n.d.
	(144[a])	(508[a])	(170[a], 156)	(29[a], 33[d])	(172[a], 140[d])	(33[a], 20[d])
Ethylbenzene	846	748	435	n.d.	n.d.	n.d.
	(320[a])	(1202[a])	(248[a])	(131[a], 110[d])	(289[a], 330[d])	(125[a], 36[d])
o-xylene	488	590	305	32	56	n.d.
	(225[a])	(669[a])	(170[a], 289[b])	(9.7[a], 16[c], 22[d])	(184[a], 210[c], 300[d])	(57[a], 34[d])
m-xylene	383	442	210	75	27	n.d.
	(216[a])	(518[a])	(167[a], 238[b])	(36[a], 32[c], 40[d])	(100[a], 120[c], 160[d])	(18[a], 27[d])
p-xylene	581	827	353	n.d.	29	n.d.
	(300[a])	(821[a])	(236[a], 376[b])	(132[a], 56[c], 72[d])	(218[a], 230[c], 240[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% AcβCD	8.09	25.46	11.28	12.04	34.21	8.93
5% HPβCD	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 γCD) as well as of some industrial βCD 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:

RAMEB $\sim$ AcβCD > HPβCD > αCD > βCD > γCD

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:

p-xylene $\sim$ ethyl benzene > o-xylene $\sim$ m-xylene $\sim$ toluene > > benzene.

There are some exceptions, like the extreme K value for toluene/RAMEB and for ethylbenzene/AcβCD system. The absolute values of the solubility, however,
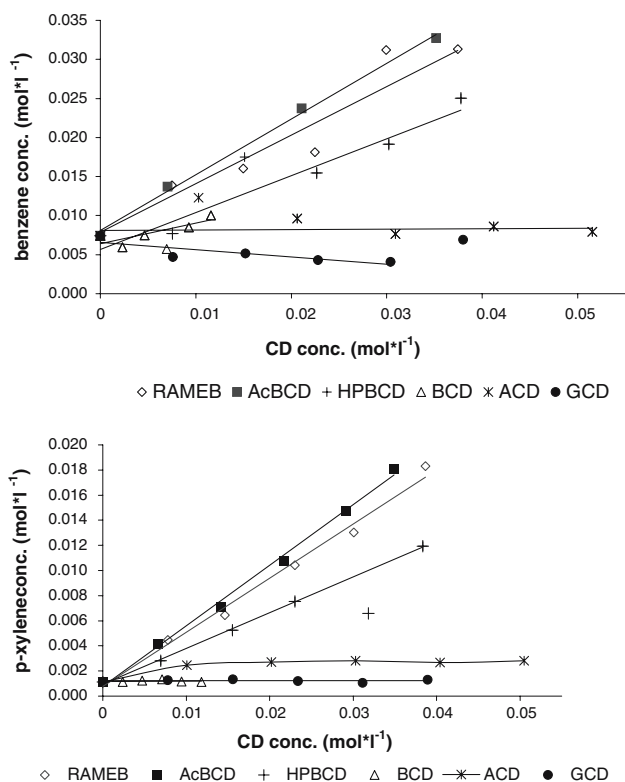
Fig. 1 Phase solubility diagrams of benzene (top) and p-xylene (bottom) in aqueous CD solutions

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 αCDs [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 αCD, which made possible the separation of
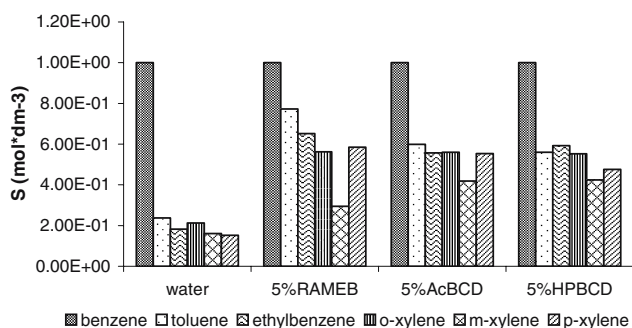

Fig. 2 The solubility of BTEX compounds in aqueous solutions of βCD derivatives (5%) normalized to the solubility of benzene

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):

$$\text{ethyl benzene} \geq \text{p-xylene} \geq \text{o-xylene}$$
$$\sim \text{m-xylene} \sim \text{toluene} > \text{benzene}.$$

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, AcβCD and HPβCD, 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

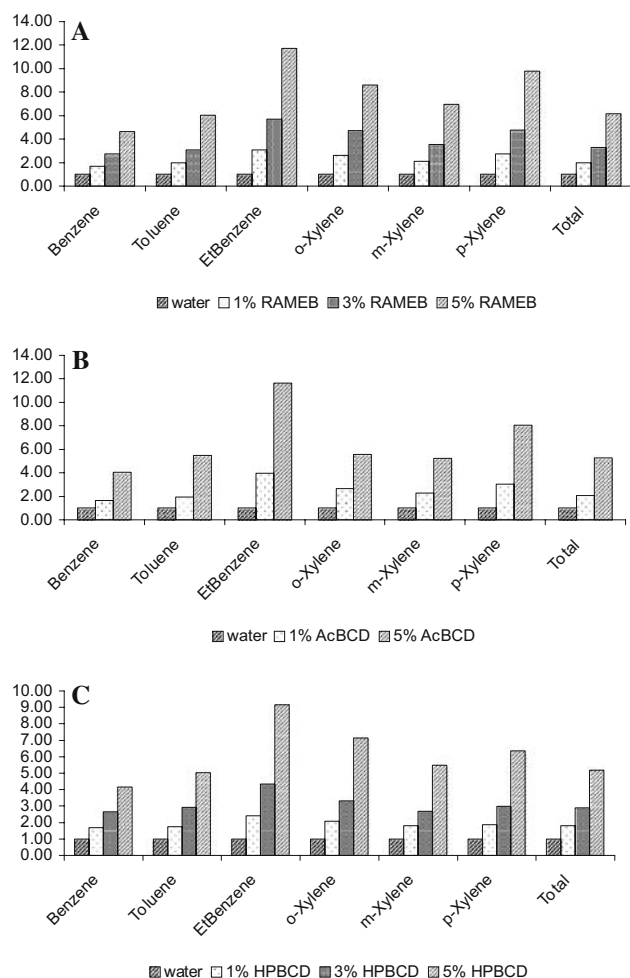|	mg BTEX/5 ml aqueous phase
Water	1.85
5% RAMEB	11.87
5% AcβCD	9.41
5% HPβCD	7.68

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

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.

References

1. Sybilska, D., Koscielski, T.: β-cyclodextrin as a selective agent for the separation of o-, m- and p-xylene and ethylbenzene mixtures in gas-liquid chromatography. J. Chromatogr. **261**, 357–362 (1983)
2. Kim, M., Way, J. D., Baldwin, R. M.: Liquid chromatographic separation of xylene isomers on α-cyclodextrin bonded phases. Korean J. Chem. Eng. **19**, 876–879 (2002)
3. Debowski, J., Sybilska, D.: Separation of isomeric alkylbenzenes in reversed-phase high-performance liquid chromatography through α- and β-cyclodextrin inclusion complexes. J. Chromatogr. **353**, 409–416 (1986)
4. Gerhold, C. G., Broughton, D. B.: Clathrate separation process for xylenes. US 3456028 (1969)
5. Uemasu, I., Takagi, Y., Chiwa, M.: Removal of xylene isomers or ethylbenzene from xylene mixtures by selective complexation with α-cyclodextrin. JP 89–240807 (1989), DE 4029489 (1991), US 5200517 (1993)
6. Uemasu, I.: Selective liquid-liquid extraction of xylene isomers and ethylbenzene through inclusion by branched α-cyclodextrins. J. Inclusion Phenom. Mol. Recognit. Chem. **13**, 1–7 (1992)
7. Uemasu, I., Kushiyama, S.: Cyclodextrin: Inclusion selectivity of α-cyclodextrin and its derivatives to mixture of benzene, toluene and xylene isomers. Basic Res. Mark., Int. Cyclodextrin Symp., 10th, 359–363. Wacker Biochem Corp.: Adrian, Mich. (2000)
8. Sanemasa, I., Akamine, Y.: Association of benzene and alkylbenzenes with cyclodextrins in aqueous medium. Bull. Chem. Soc. Jpn. **60**, 2059–2066 (1987)
9. Uemasu, I., Takahashi, H.: Use of branched β-cyclodextrins as separating agents for liquid-liquid extraction of mixed xylenes. Sekiyu Gakkaishi **36**(3), 210–214 (1993), (Chem. Abstr. 119:81261)
10. Uemasu, I., Takahashi, H., Hara, K.: Continuous separation process using aqueous solutions of branched cyclodextrins. 12th Intern. CD Symp., May 16–19, 2004, Montpellier, France, P-132
11. Tick, G. R., Lourenso, F., Wood, A. L., Brusseau, M. L.: Pilot-scale demonstration of cyclodextrin as a solubility-enhancement agent for remediation of a tetrachloroethene-contaminated aquifer. Env. Sci. Techn. **37**, 5829–5834 (2005)
12. Molnar, M., Leitgib, L., Gruiz, K., Fenyvesi, E., Szaniszlo, N., Szejtli, J., Fava, F.: Enhanced biodegradation of transformer oil in soils with cyclodextrin – from the laboratory to the field. Biodegradation **16**, 159–168 (2005)
13. Higuchi, T., Connors, K. A.: Phase-solubility techniques. Adv. Anal. Chem. Instrum. **4**, 117 (1965)
14. Szaniszlo, N., Fenyvesi, E., Balla, J.: Structure-stability study of cyclodextrin complexes with selected volatile hydrocarbon contaminants of soils. J. Incl. Phenom. Macrocycl. Chem. **53**(3), 241–248 (2005)
15. Misawa, K., Saito, Y., Hashizaki, K., Taguchi, H., Ogawa, N., Ueda, H.: Stability constants for 1:1 complexes formed between 2-hydroxypropyl-beta-cyclodextrin with an average substitution degree of 4.4 and benzene and alkylbenzenes as guests by modified static head-space gas chromatography

method. J. Incl. Phenom. Macrocycl. Chem. **53**, 237–240 (2005)

16. Poh, B. L., Chow, Y. M.: Transport method for determining the association constants of complexes formed between aromatic hydrocarbons and α- and β-cyclodextrin in water. J. Inclusion Phenom. Mol. Recognit. Chem. **14**, 85–90 (1992)

17. Loftsson, T., Masson, M., Brewster, M. E.: Self-association of cyclodextrins and cyclodextrin complexes. J. Pharm. Sci. **93**, 1091–1099 (2004)

18. Fenyvesi, E.: Selective extraction of BTEX compounds with aqueous CD solutions. Cyclodextrin News **19**, 152–155 (2004)