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Immobilization behavior of methyl *tert*-butyl ether by cyclodextrins

Kitae Baek, Jung-Seok Yang, Ji-Won Yang*

National Research Laboratory for Environmental Remediation, Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, South Korea

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Abstract

The immobilization behavior of methyl *tert*-butyl ether (MTBE) by various cyclodextrins (CDs) was studied. Although it has a low hydrophobic character and high polarity compared to other organics, MTBE was effectively immobilized by CDs. The immobilization isotherm was a type of Freundlich isotherm. The immobilization capacity of β-CDs was the largest of the natural CDs. The initial apparent association constant for MTBE–CD complex follows the order: γ = β > methyl-β > hydroxypropyl β > α. The difference in these constants is related to the size of MTBE and CDs. The size of β- and γ-CD is large enough to encapsulate MTBE molecule into the cavity, which that of α-CD is too small to encapsulate MTBE.

Keywords: MTBE; Cyclodextrin; Inclusion; Immobilization

1. Introduction

The presence of methyl *tert*-butyl ether (MTBE) in groundwater and drinking water has become a significant environmental issue mainly due to its taste. As MTBE is highly soluble in water and does practically not adsorb to soil particles due to its low hydrophobicity, it is readily transported into groundwater and surface water systems. MTBE has a low taste and odor threshold value and is tentatively classified by the US EPA as a possible human carcinogen [1]. MTBE is not removed by conventional treatment methods such as air stripping, carbon adsorption and aerobic biodegradation as effectively as they do for other volatile organic compound (VOC) contaminants [2–4].

* Corresponding author. Tel.: +82-42-869-3924; fax: +82-42-869-3910.
E-mail address: jwyang@kaist.ac.kr (J.-W. Yang).

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Cyclodextrins (CDs) have a low-polarity cavity in which organic compounds of appropriate shape and size can form inclusion complexes. This unique property provides CDs with a capacity to significantly increase the apparent solubility of low polarity organic contaminants such as polyaromatic hydrocarbons, herbicides, pesticides, iodine, and various organics [5–10]. For VOCs with relative high water solubility such as benzene and MTBE, however, CDs can immobilize the VOCs into the cavity in the aqueous phase.

In this study, the feasibility of natural and chemically modified CDs for the immobilization of MTBE from water into CD cavity was investigated.

2. Materials and methods

2.1. Materials

Analytical grade MTBE (>99% of purity) was purchased from Aldrich. Three different types of natural CDs (α-, β-, and γ-CD) and chemically modified CDs (hydroxypropyl β-CD and methyl-β-CD) (>99% of purity) were purchased from Tokyo Chemical Industry (Japan). The characteristics of α-, β- and γ-CD are summarized in Table 1.

Headspace analysis using solid-phase microextraction (SPME) is a useful tool for measuring the concentration of MTBE in the aqueous phase [11–14]. For this procedure, SPME holder and fiber coated with poly(dimethylsiloxane) (PDMS) and carboxen (30 μm film thickness) were purchased from Supelco (Bellefonte, USA). MTBE analysis was performed by a gas chromatograph (GC 6890 series II, Hewlett-Packard) coupled to a flame ionization detector (FID).

2.2. Methods

The extraction was performed in an open-top screw cap vial (20 ml) equipped with a teflon-coated silicon septum. A 10 ml sample containing the desired amount of CDs and MTBE was shaken for 2 h at 25 °C in order to achieve phase equilibrium. After a 10 min headspace extraction, the SPME fiber was removed from the vial and immediately inserted into the GC injector. Desorption of MTBE from SPME fiber was performed within 3 min at 250 °C (GC injector temperature).

The chromatographic capillary column was a HP1 (30 m × 0.25 mm) with 0.2 μm film thickness. The injector program was as follows: injector temperature, 250 °C, from 40 to 130 °C at a rate of 10 °C/min, and the detector temperature, 250 °C.

Table 1
Physicochemical properties of cyclodextrins [20]

	α-Cyclodextrin	β-Cyclodextrin	γ-Cyclodextrin
Molecular weight	972	1135	1297
Glucose monomers	6	7	8
Internal cavity diameter (nm)	0.5	0.6	0.8
Water molecules in cavity	6	11	17
Water solubility (g/100 ml: 25 °C)	14.2	1.85	23.2

2.3. Theory

In the headspace analysis, calibration standards (MTBE–water) and samples (MTBE–water–CDs) with known amount of MTBE, CD and water are prepared. The amount of MTBE immobilized in CD is obtained from a mass balance.

$$m_{\text{MTBE–CD}} = m_{\text{MTBE–i}} - m_{\text{MTBE–aq}} - m_{\text{MTBE–va}} \tag{1}$$

where $m_{\text{MTMB–CD}}$, $m_{\text{MTMB–i}}$, $m_{\text{MTMB–aq}}$, $m_{\text{MTMB–va}}$ are the moles of MTBE immobilized in the CD, initial added to the vial, in the aqueous phase and in the vapor phase, respectively. The moles in the aqueous phase and in the vapor phase are related by Henry's law assuming that the partitioning of MTBE between the water and vapor phases is unaffected by the presence of the cyclodextrin. The dimensionless Henry's constant for MTBE was 0.12 at 25 °C [3].

The immobilization isotherms are presented as the MTBE moles immobilized in CDs per moles of CDs in the aqueous phase versus the free MTBE concentration in the aqueous phase (i.e. equilibrium concentration of MTBE in aqueous phase).

$$\frac{m_{\text{MTBE–CD}}}{m_{\text{CD}}} = K_{\text{F}} M_{\text{MTBE–aq}}^{1/n} \tag{2}$$

where K_{F}, m_{CD} and $M_{\text{MTBE–aq}}$ are immobilization capacity of MTBE in CD, moles of total CDs, and equilibrium concentration of MTBE in the aqueous phase, respectively.

Using the solubility isotherms, the apparent association constants (K_{a}) were calculated assuming a 1:1 complex stoichiometry. The following equation was employed.

$$\text{CD} + \text{MTBE} \Leftrightarrow \text{MTBE} - \text{CD} \qquad K_{\text{a}} = \frac{M_{\text{MTBE–CD}}}{M_{\text{CD–f}} \times M_{\text{MTBE–aq}}} \tag{3}$$

where $M_{\text{MTBE–aq}}$, $\text{M}_{\text{CD–f}}$, and $M_{\text{MTBE–aq}}$ are concentration of MTBE–CD complex, free CD concentration, and free MTBE concentration in aqueous phase, respectively.

3. Results and discussion

3.1. Calibration

The concentration of MTBE in deionized water was determined using headspace SPME analysis. The characteristics of MTBE extraction/adsorption on the PDMS/Carboxen fiber showed a non-linear calibration up to 1000 mg/l MTBE. The GC peak area was proportional to the log scale of MTBE concentration and showed a good correlation ($r^2 = 0.9987$, data not shown).

3.2. Immobilization isotherms of MTBE

The immobilization of MTBE in various CDs solutions can be regarded as a measure of their MTBE-binding capacity under the utilized experimental conditions. Figs. 1–3 show the immobilization of MTBE into α-, β-, and γ-CD, respectively. Sorption isotherms can

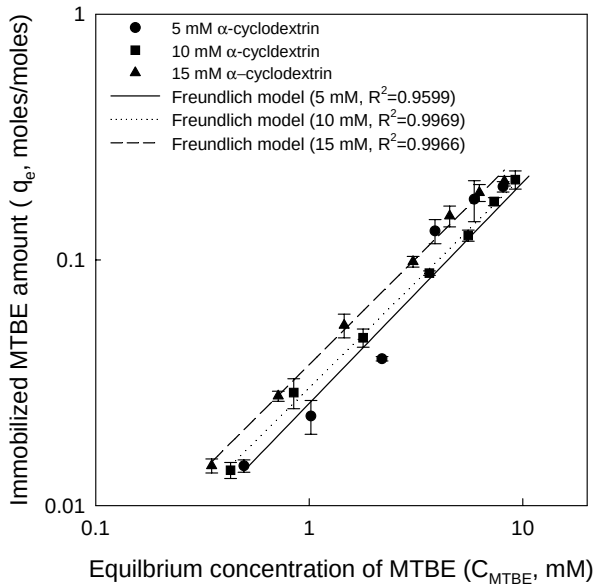

Fig. 1. Immobilization isotherms of α-cyclodextrin for MTBE. At the each concentration of cyclodextrins, immobilization of MTBE was investigated up to the concentration of MTBE of 1000 mg/l.

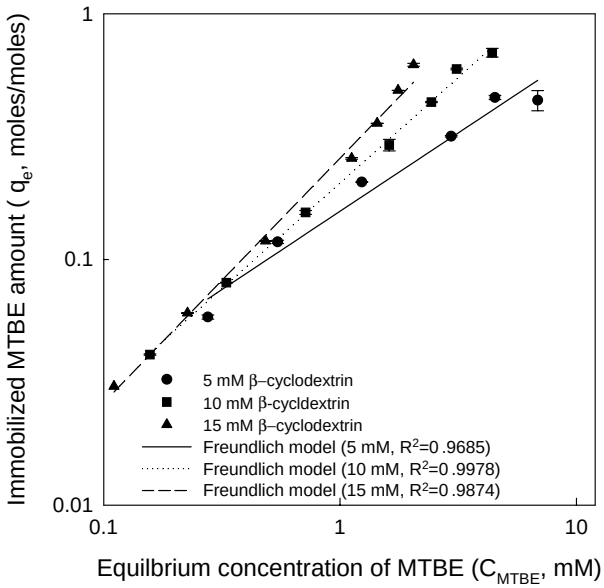

Fig. 2. Immobilization isotherm of β-cyclodextrin for MTBE. At the each concentration of cyclodextrins, immobilization of MTBE was investigated up to the concentration of MTBE of 1000 mg/l.

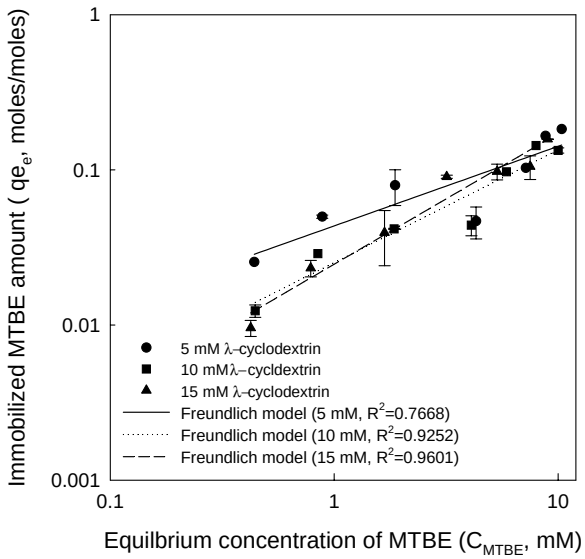

Fig. 3. Immobilization isotherm of γ-cyclodextrin for MTBE. At the each concentration of cyclodextrins, immobilization of MTBE was investigated up to the concentration of MTBE of 1000 mg/l.

be used to express the immobilization isotherms because the immobilization behavior of MTBE into CDs is analogous to the sorption phenomenon of MTBE on CDs. The data have been plotted according to the Freundlich isotherm (Figs. 1–3). The immobilization capacity increased remarkably with increasing MTBE equilibrium concentration, and the relationship between the sorption capacity and the equilibrium concentration could be expressed with the Freundlich equation described according to the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where q_e is the adsorption capacity (mol/mol) and C_e the equilibrium concentration (mM). The results and the correlation coefficients from plotting $\log q_e$ versus $\log C_e$ and calculating K_F and $1/n$ as Freundlich parameters are summarized in Table 2.

The isotherms for the sorption of 4-nonylphenol on β-CD polymer and the sorption with silica-supported methacryloyl-β-CD as a sorbent for *p*-nitrophenol, pentachlorophenol and (2,4-dichlorophenoxyl) acetic acid were also described by Freundlich equation [15–18]. The sorption isotherm of MTBE by polymeric resins was expressed by Freundlich equation [1,19]. Each isotherm had a similar value of $1/n$ except CD concentration of 5 mM, indicating that each curve had a similar shape as shown in Figs. 1–3.

The value of $1/n$ for immobilization of MTBE onto CD was approximately unity. This means that the relationship between immobilization capacity and equilibrium concentration of MTBE is almost linear. On the other hand, the K_F values were quite different. This result means that the immobilization capacity of each CD is quite different. The magnitude of the immobilization capacity was low compared to other low-polarity materials such as

Table 2
Parameters of MTBE for Freundlich isotherms models of the various cyclodextrins

$\log q_e = \log K_F + 1/n \log C_e$	Concentration of cyclodextrins (mM)		
	5	10	15
α-Cyclodextrin			
K_F	0.0261	0.0302	0.0375
$1/n$	1.024	0.8613	0.8664
R^2	0.9599	0.9969	0.9966
β-Cyclodextrin			
K_F	0.1510	0.2045	0.2580
$1/n$	0.6370	0.8594	0.9947
R^2	0.9685	0.9978	0.9874
γ-Cyclodextrin			
K_F	0.0435	0.0252	0.0246
$1/n$	0.5127	1.3763	0.8423
R^2	0.7668	0.9252	0.9601

Where C_e is MTBE concentration in the aqueous phase at the equilibrium (mM); q_e the immobilized MTBE amount (moles of MTBE/moles of cyclodextrin); $1/n$ the intensity of the immobilization according to the theories; K_F the Freundlich constant which means immobilization capacity of cyclodextrin for MTBE.

nonylphenol, benzene, toluene and xylene because of the comparably low hydrophobicity and high polarity of MTBE [7]. The immobilization isotherms revealed that β-CD had the highest immobilization capacity; however, the solubility of β-CD is low (16.3 mM).

To study immobilization isotherms of MTBE according to the concentration of β-CD, two different types of chemically modified β-CD, methyl-β-CD and hydroxypropyl β-CD, were investigated (Fig. 4). The factors affecting immobilization or inclusion of organics with low-polarity into CD are molecular size and hydrophobicity of organics [7,17]. The apparent association constants calculated using our experimental results are listed in Table 3.

The association constants, K_a, were calculated from the initial slope (to 0.5 wt.% concentration of each CD). K_a was variable in this study. The initial association constant for CD–MTBE system was lower than other organics such as benzene, toluene, xylene and iodine because the hydrophobicity of MTBE was lower and the polarity was greater than other organics. As the hydrophobicity (alkyl chain length or 1-octanol–water partitioning coefficient) increased, the immobilization capacity represented by the Freundlich isotherm

Table 3
Apparent association constant of MTBE with various cyclodextrins assuming 1:1 stoichiometry

	Apparent association constant (M^{-1})
α-Cyclodextrin	125
β-Cyclodextrin	359
γ-Cyclodextrin	360
Methyl β-cyclodextrin	313
Hydroxypropyl β-cyclodextrin	223

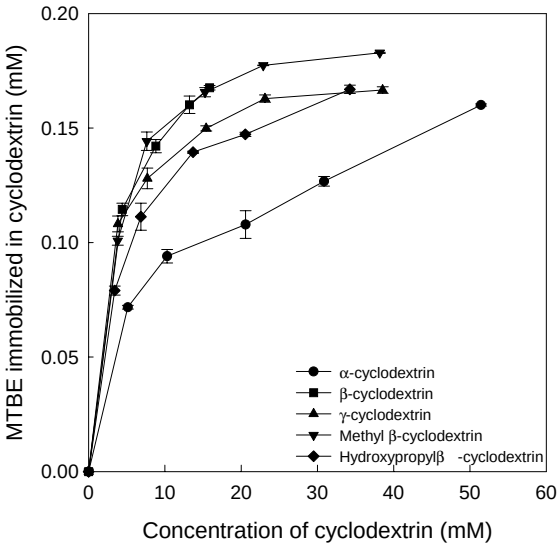

Fig. 4. Immobilization of MTBE as a function of cyclodextrins concentration. The immobilization for MTBE was investigated to the concentrations of 5.0 wt.% for each cyclodextrin except β-cyclodextrin, for which was used to the solubility (1.8 wt.%). All experiments were done with the same initial MTBE concentration.

and association constants increased [17]. However, the increase in alkyl chain length caused the increase in molecular size, which decreased the immobilization or inclusion of organics into CD. The order of initial immobilization association constants among different CDs were $\gamma = \beta >$ methyl $\beta >$ hydroxypropyl $\beta > \alpha$. The highest constant was obtained from the β and γ-CD. It was approximately three times higher than that obtained for α-CD.

The magnitude of the association constant can be explained by the size of MTBE and CDs. The molecule size of MTBE is 0.53 nm in length and 0.43 nm in width. The cavity of α-CD is 0.5 nm in diameter and 0.8 nm in depth. As shown in Fig. 5, inclusion is not

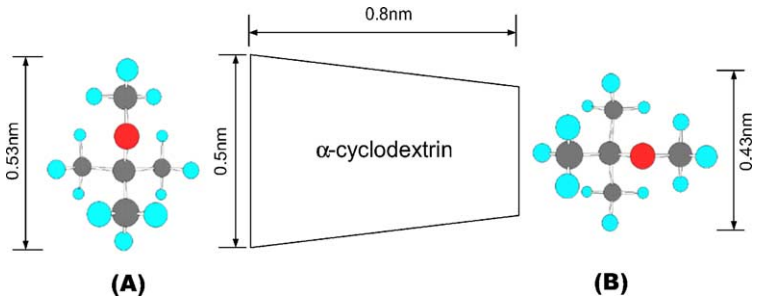

Fig. 5. Orientation of MTBE relative to the cavity of α-cyclodextrin. Two different orientation for inclusion of MTBE-α-cyclodextrin can be considerable: (A) no inclusion; (B) inclusion.

possible in case (A), since the length of MTBE is larger than the diameter of the α-CD cavity. In case (B), however, due to the smaller width of MTBE in orientation relative to the α-CD cavity, MTBE can be successfully encapsulated into the cavity. This is why the association constant of α-CD is the lowest compared to other CDs. While β- and γ-CD with the diameter cavity of 0.6 and 0.8 nm, respectively, show similar association constant because both Fig. 5A and B are possible. For chemically modified β-CDs, both figures are possible, but the association constant was lower than β-CD because of the steric hindrance of substitution by methyl and hydroxypropyl groups.

4. Conclusions

The immobilization isotherms of MTBE into CDs closely followed the Freundlich sorption isotherms. The immobilization capacity for MTBE was lower than other hydrophobic organics due to the lower hydrophobicity of MTBE. Among other CDs tested in this study, β-CD had the highest immobilization capacity. The association constant of the MTBE–CD complex was calculated assuming 1:1 stoichiometry. β-CD and γ-CD showed similar values of association constant because of the comparable size for immobilization of MTBE. Insoluble cyclodextrin polymers suggested by Crini and Morcellet [20] and Crini et al. [21] can be used for the removal of MTBE from subsurface water or groundwater.

Acknowledgements

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