

Short communication

# Competitive immobilization of multiple component chlorinated solvents by cyclodextrin derivatives

Jung-Seok Yang<sup>a</sup>, Kitae Baek<sup>b</sup>, Tae-Soon Kwon<sup>a</sup>, Ji-Won Yang<sup>a,\*</sup>

<sup>a</sup> Department of Chemical and Biomolecular Engineering, KAIST, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

<sup>b</sup> Department of Environmental Engineering, Kumoh National Institute of Technology, 1 Yangho-dong, Gumi, Gyeongbuk 730-701, Republic of Korea

Received 7 September 2005; received in revised form 6 April 2006; accepted 11 April 2006

Available online 25 April 2006

## Abstract

Immobilization of chlorinated solvents with hydropropyl and methyl cyclodextrins (CDs) was observed by head-space analysis to obtain the stability constants in single and multiple component systems. In each single component system, the highest stability constant was  $0.299 \text{ mM}^{-1}$  for perchloroethylene (PCE) by methyl- $\beta$ -cyclodextrin (M- $\beta$ -CD),  $0.136 \text{ mM}^{-1}$  for trichloroethylene (TCE) by M- $\beta$ -CD,  $0.106 \text{ mM}^{-1}$  for *cis*-dichloroethylene (*cis*-DCE) by hydropropyl- $\alpha$ -cyclodextrin, and  $0.090 \text{ mM}^{-1}$  for *trans*-dichloroethylene (*trans*-DCE) by M- $\beta$ -CD. When HP- $\beta$ -CD and M- $\beta$ -CD were used, the stability constants of PCE and TCE increased and those of DCEs decreased in a multiple component system. Differences in stability constants of single and multiple component systems thus should be important parameters when cyclodextrins are applied to solubilization of multiple chlorinated solvents.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Inclusion; Perchloroethylene; Remediation; Solubilization; Stability constant; Trichloroethylene

## 1. Introduction

Chlorinated solvents have been listed as major organic contaminants in soil and water. Used in dry-cleaning and degreasing operation, these chemicals are commonly found in the environment as a result of accident spillage or poor disposal practices. These compounds are known to cause health problems such as liver and kidney disorders and are suspected carcinogens. Once released into the environment, chlorinated solvents persist in the subsurface via formation of dense nonaqueous phase liquid (DNAPL) pools at the bottom of aquifers because of their low aqueous solubility and high density [1–4].

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 capacity to significantly increase the apparent solubility of low polarity organic contaminants such as aromatic hydrocarbons [5], polycyclic aromatic hydrocarbons [6,7], chlorinated solvents [3,4,8,9], herbicides [10], pesticides [11], phenols [12,13], and various organics [2,14,15].

The majority of studies, that have been performed for the solubilization of chlorinated solvents by cyclodextrins, are limited to single contaminant [4,15]. In real fields, however, most of contaminated soil and groundwater are polluted with multiple component DNAPLs [1,2]. Thus, the purpose of this study was to investigate the immobilization of single and multiple component chlorinated solvents by cyclodextrin derivatives, which was analyzed with respect to stability constants.

## 2. Materials and methods

### 2.1. Materials

Cyclodextrins (2-hydropropyl- $\alpha$ -cyclodextrin (HP- $\alpha$ -CD), 2-hydropropyl- $\beta$ -cyclodextrin (HP- $\beta$ -CD), 2-hydropropyl- $\gamma$ -cyclodextrin (HP- $\gamma$ -CD), and randomized methyl- $\beta$ -cyclodextrin (M- $\beta$ -CD)) and chlorinated solvents (perchloroethylene (PCE) and trichloroethylene (TCE)) were purchased from Aldrich Chemical Company (Milwaukee, WI, USA). Dichloroethylenes (*trans*-dichloroethylene (*trans*-DCE) and *cis*-dichloroethylene (*cis*-DCE)) were purchased from TCI (Tokyo, Japan). The physical properties of CDs and chlorinated solvents are summarized in Tables 1 and 2, respectively. The

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

Table 1  
Selected physical properties of cyclodextrin derivatives [16]

Cyclodextrin	Substitution	MW	Cavity volume (nm <sup>3</sup> )
HP- $\alpha$ -CD	0.6	1180	0.174
HP- $\beta$ -CD	0.6	1380	0.262
HP- $\gamma$ -CD	0.6	1576	0.427
M- $\beta$ -CD	1.8	1312	0.262

Table 2  
Selected physicochemical properties of chlorinated solvents<sup>a</sup>

Name	PCE	TCE	<i>trans</i> -DCE	<i>cis</i> -DCE
Formula	C <sub>2</sub> Cl <sub>4</sub>	C <sub>2</sub> HCl <sub>3</sub>	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>
Molecular weight (g/mol)	165.83	131.39	96.95	96.95
Liquid density (g/cm <sup>3</sup> )	1.613	1.4578	1.2649	1.2444
Molecular volume (nm <sup>3</sup> ) <sup>b</sup>	0.170	0.150	0.127	0.129
Henry's constant <sup>c</sup>	0.699	0.417	0.386	0.186

<sup>a</sup> All values are at 25 °C.

<sup>b</sup> Calculated from liquid density and molecular weight.

<sup>c</sup> Measured for this work and is dimensionless.

water used in this study was purified by EASYpure water purification system (Barnstead, USA) and had an initial resistivity of 18.3 M $\Omega$  cm. All chemicals were used without further purification.

## 2.2. Methods

Immobilization of chlorinated solvents in CDs was determined by head-space analysis in a batch system [3,9,11,14] that 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 (from 0.5 to 5 wt%) and chlorinated solvents was shaken for 5 h at 25 °C in order to achieve phase equilibrium. In preliminary test, 5 h was enough to reach equilibrium. One hundred microliters of head space was sampled with a gas tight syringe and immediately injected into the gas chromatograph (GC 6890 series II, Hewlett Packard) coupled with a flame ionization detector (FID). A HP-5 (Hewlett-Packard, 30 m  $\times$  0.25 mm) chromatographic capillary column was used. The GC settings were programmed as the following: injector temperature, 250 °C; initial column temperature, 40 °C for 4 min; then ramped to 190 °C at a rate of 20 °C/min; detector temperature, 280 °C.

## 2.3. Theory

The amount of chlorinated solvents immobilized into cyclodextrins was obtained by following equation:

$$M_{CD-S} = M_{S-I} - M_{S-aq} - M_{S-v} \quad (1)$$

where  $M_{CD-S}$ ,  $M_{S-I}$ ,  $M_{S-aq}$ , and  $M_{S-v}$  are the moles of chlorinated solvents immobilized in the CD, initial moles added to the vial, in the aqueous phase, and in the vapor phase, respectively. The chlorinated solvent concentration in the vapor phase was determined by GC and that in the aqueous phase was calculated by

Henry's law:

$$C_{S-aq} = H \times C_{S-v} \quad (2)$$

where  $C_{S-aq}$ ,  $C_{S-v}$ , and  $H$  represent the concentration of chlorinated solvents in aqueous phase, in vapor phase, and dimensionless Henry's constant for chlorinated solvents, respectively.

The immobilization of chlorinated solvents by cyclodextrins is described as the formation of 1:1 inclusion complexes [10,15]:



where  $S$  is the uncomplexed chlorinated solvents,  $CD$  the uncomplexed cyclodextrins, and  $CD-S$  is the complexed solutes in the aqueous phase. The stability constants ( $K_s$ , mM<sup>-1</sup>) of the complex can be determined by

$$K_s = \frac{C_{CD-S}}{C_{S-aq} \times C_{CD}} \quad (4)$$

where  $C_{CD}$  is the concentration of uncomplexed cyclodextrins in aqueous phase.

## 3. Results and discussion

Fig. 1 shows the stability constants for PCE, TCE, *trans*-DCE, and *cis*-DCE in HP- $\alpha$ -CD, HP- $\beta$ -CD, HP- $\gamma$ -CD, and M- $\beta$ -CD in single component (Fig. 1A) and multiple component (Fig. 1B) systems. For PCE, the stability constants in HP- $\beta$ -CD and M- $\beta$ -CD were 0.279 and 0.299 mM<sup>-1</sup>, respectively. Stability constants in HP- $\alpha$ -CD and HP- $\gamma$ -CD were very low (0.030 and 0.056) compared to HP- $\beta$ -CD and M- $\beta$ -CD. For TCE, stability constants in HP- $\alpha$ -CD, HP- $\beta$ -CD, and M- $\beta$ -CD were similar as 0.136, 0.119, and 0.136, respectively. Stability constants in DCEs in HP- $\alpha$ -CD were the highest value among the tested CDs. Stability constants in the M- $\beta$ -CD were higher than those in the HP- $\beta$ -CD for all chlorinated solvents.

Immobilization mechanism of chlorinated solvents in cyclodextrin can be described by the capture of chlorinated solvents into the cavity of cyclodextrins. The main parameter of immobilization mechanism is the size or volume of cavity and chlorinated solvents. The molecular volume calculated from density and molecular weight of PCE is 0.170 nm<sup>3</sup>. The cavity volumes of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD are 0.174, 0.262, and 0.427 nm<sup>3</sup>. Because the cavity of  $\alpha$ -CD is similar to molecular volume of PCE,  $\alpha$ -CD cannot easily capture PCE and stability constant of PCE in HP- $\alpha$ -CD was very small. In contrast, the cavity volume of  $\beta$ -CDs is appropriate to capture PCE. In the case of  $\gamma$ -CD, PCE can easily go out of cavity and binding strength between cavity molecules of  $\gamma$ -CD and PCE was very weak because the cavity volume is too big. So, the stability constant of PCE in HP- $\gamma$ -CD was lower than that in HP- $\beta$ -CD. The molecular volume of TCE is small (0.150 nm<sup>3</sup>) compared to PCE. Therefore, the stability constants of TCE in both,  $\alpha$ - and  $\beta$ -CDs, were high and similar because the cavity volume of CDs was proper to capture TCE. With same reason in PCE, the stabil-

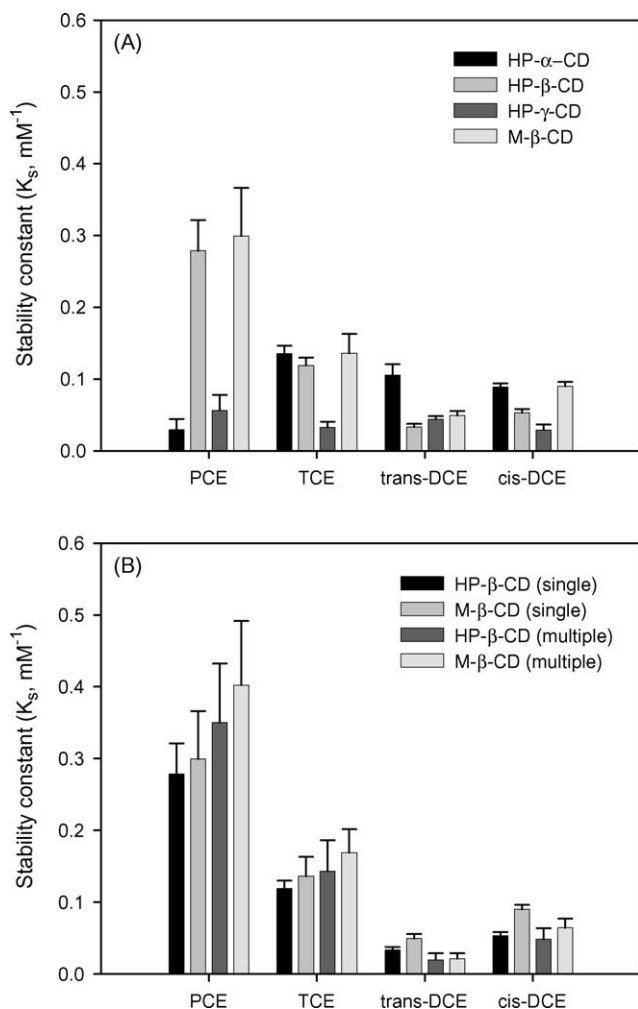


Fig. 1. Stability constants of (A) single component and (B) multiple component chlorinated solvents with similar volumes in cyclodextrins.

ity constant of TCE in HP- $\gamma$ -CD was low. Because volumes of DCEs were smaller than those of  $\beta$ - and  $\gamma$ -CDs, the stability constant of DCEs in  $\alpha$ -CD had the highest value. From the results, we concluded that the optimum cavity volume of CDs was the range between 1.1 and 2 times of contaminant molecular volume.

In the presence of multiple components of chlorinated solvents, stability constants of PCE in HP- $\beta$ -CD and M- $\beta$ -CD increased from 0.279 to 0.350 and 0.299 to 0.402, respectively. Stability constants of TCE also increased from 0.119 to 0.143 and 0.136 to 0.169, respectively. But, stability constants of *trans*-DCE in HP- $\beta$ -CD and M- $\beta$ -CD decreased from 0.033 to 0.020 and 0.049 to 0.021, respectively, and stability constants of *cis*-DCE decreased also from 0.053 to 0.049 and 0.090 to 0.064, respectively. It means that PCE and TCE are more suitable to complex with  $\beta$ -CDs than DCEs because of the molecular volume of PCE and TCE. So, cavities of  $\beta$ -CDs occupied originally by DCEs are replaced by TCE or PCE. To calculate the solubilization of chlorinated solvents, stability constants in single component were used. However, difference of stability constants between single component and multiple components should be considered for accurate estimation.

## 4. Conclusions

The stability constants of chlorinated solvent in cyclodextrins were obtained by head-space analysis in single and multiple component systems. Stability constant of PCE at  $\beta$ -CDs was the highest and that of TCE and DCEs at  $\alpha$ -CDs was the highest. In a multiple component system, stability constants of PCE and TCE increased and those of DCEs decreased. To apply cyclodextrins to remediate real sites contaminated by chlorinated solvents, CDs mixed with  $\alpha$  and  $\beta$  types are more suitable in mixed contaminant system and the difference of stability constants between single and multiple component systems should be considered.

## Acknowledgments

This research was partially supported by a grant (M1-0412-00-0001) from Korea Ministry of Science and Technology through National Research Laboratory program and by a grant from KOSEF through Advanced Environmental Monitoring Research Center (ADEMRC) at Gwangju Institute of Science and Technology (GIST).

## References

- [1] J.E. Mccray, M.L. Brusseau, Cyclodextrin-enhanced in situ flushing of multiple-component immiscible organic liquid contamination at the field scale: mass removal effectiveness, *Environ. Sci. Technol.* 32 (1998) 1285–1293.
- [2] J.E. Mccray, M.L. Brusseau, Cyclodextrin-enhanced in situ flushing of multiple-component immiscible organic liquid contamination at the field scale: analysis of dissolution behavior, *Environ. Sci. Technol.* 33 (1999) 89–95.
- [3] T. Shimotori, W.A. Arnold, Measurement and estimation of Henry's law constants of chlorinated ethylenes in aqueous surfactant solutions, *J. Chem. Eng. Data* 48 (2003) 253–261.
- [4] S. Shirin, E. Buncel, G.W. vanLoon, The use of  $\beta$ -cyclodextrins to enhance the aqueous solubility of trichloroethylene and perchloroethylene and their removal from soil organic matter: effect of substituents, *Can. J. Chem.* 81 (2003) 45–52.
- [5] S. Tanada, N. Nakamura, N. Kawasaki, Y. Torii, S. Kitayama, Removal of aromatic hydrocarbon compounds by hydroxypropyl-cyclodextrin, *J. Colloid Interface Sci.* 217 (1999) 417–419.
- [6] S.-O. Ko, M.A. Schlautman, E.R. Carraway, Partitioning of hydrophobic organic compounds to hydroxypropyl- $\beta$ -cyclodextrin: experimental studies and model predictions for surfactant-enhanced remediation applications, *Environ. Sci. Technol.* 33 (1999) 2765–2770.
- [7] X. Wang, M.L. Brusseau, Cyclopentanol-enhanced solubilization of polycyclic aromatic hydrocarbons by cyclodextrins, *Environ. Sci. Technol.* 29 (1995) 2346–2351.
- [8] N. Kashiyama, T.B. Boving, Hindered gas-phase partitioning of trichloroethylene from aqueous cyclodextrin systems: implications for treatment and analysis, *Environ. Sci. Technol.* 38 (2004) 4439–4444.
- [9] L.M. Vane, E.L. Giroux, Henry's law constants and micellar partitioning of volatile organic compounds in surfactant solutions, *J. Chem. Eng. Data* 45 (2000) 38–47.
- [10] J. Villaverde, J.I. Pérez-Martínez, C. Maqueda, J.M. Ginés, E. Morillo, Inclusion complexes of  $\alpha$ - and  $\gamma$ -cyclodextrins and the herbicide norflurazon: I. Preparation and characterisation. II. Enhanced solubilisation and removal from soils, *Chemosphere* 60 (2005) 656–664.
- [11] S. Ishiwata, M. Kamiya, Structural study on inclusion complexes of cyclodextrins with organophosphorus pesticides by use of rotational strength analysis method, *Chemosphere* 41 (2000) 701–704.

- [12] V. Chatain, K. Hanna, C. de Brauer, R. Bayard, P. Germain, Enhanced solubilization of arsenic and 2,3,4,6-tetrachlorophenol from soils by a cyclodextrin derivative, *Chemosphere* 57 (2004) 197–206.
- [13] K. Hanna, C. de Brauer, P. Germain, Solubilization of the neutral and charged forms of 2,4,6-trichlorophenol by  $\beta$ -cyclodextrin, methyl- $\beta$ -cyclodextrin and hydroxypropyl- $\beta$ -cyclodextrin in water, *J. Hazard. Mater.* 100 (2003) 109–116.
- [14] K. Baek, J.-S. Yang, J.-W. Yang, Immobilization behavior of methyl *tert*-butyl ether by cyclodextrins, *J. Hazard. Mater.* 105 (2003) 169–177.
- [15] X. Wang, M.L. Brusseau, Solubilization of some low-polarity organic compounds by hydroxypropyl- $\beta$ -cyclodextrin, *Environ. Sci. Technol.* 27 (1993) 2821–2825.
- [16] J. Szejtli, Introduction and general overview of cyclodextrin chemistry, *Chem. Rev.* 98 (1998) 1743–1753.