# CAPTURE OF VOLATILE CHLORINATED HYDROCARBONS BY AQUEOUS SOLUTIONS OF BRANCHED CYCLODEXTRINS

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## ABSTRACT

The use of aqueous solutions of branched cyclodextrins was examined in order to develop an effective method of capturing toxic volatile chlorinated hydrocarbons such as trichloroethylene and monochlorobenzene. From the experiments in which trichloroethylene diluted with nitrogen gas came into contact with aqueous solutions of branched cyclodextrin mixtures, it was found that absorption could be performed without the formation of inclusion complex solids, which should simplify the whole process of absorption and recovery.

## 1. INTRODUCTION

Volatile chlorinated hydrocarbons have been widely used as solvents, detergents, agents for chemical synthesis, etc. Since they are toxic and cause environmental pollution, the control of their emission from industrial sources is mandatory.

It is well known that cyclodextrins(CDs) have a strong affinity for halogenated hydrocarbons and easily form inclusion complexes, which are usually insoluble in water[1]. The use of aqueous CD solutions to recover the vapors of such organic compounds was reported more than ten years ago[2]. One of the difficulties consists in handling the solid inclusion complexes, which are usually very fine and sticky. In order to retard the production of insoluble complexes, some additives such as cetyl-trimethyl ammonium bromide were employed or the use of highly-soluble CD derivatives were examined.

We have been studying the application of branched CDs to the capture of volatile halogenated hydrocarbons[3]. Branched CDs, which are now commercially available, have high water solubilities and their inclusion complexes, too. In this study, we examined the solubilities of four volatile chlorinated hydrocarbons in aqueous solutions of branched CD mixtures and the absorption of trichloroethylene diluted with nitrogen gas into the CD solutions.

*Journal of Inclusion Phenomena and Molecular Recognition in Chemistry* **25**: 221–224, 1996.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Branched CD mixtures were obtained from Ensuiko Sugar Refining Co., Ltd.( Yokohama, Japan ). Glucosyl-α-CD mixture( G-α-CD mixture ) contains 45% monoglucosyl-α-CD( 6-*O*-α-D-glucosyl-α-CD ), 34% diglucosyl-α-CD and other. Maltosyl-β-CD mixture( M-β-CD mixture ) contains 43% monomaltosyl-β-CD( 6-*O*-α-maltosyl-β-CD ), 44% dimaltosyl-β-CD, 9% trimaltosyl-β-CD and other. Carbon tetrachloride, trichloroethylene, tetrachloroethylene, monochlorobenzene, benzene, and diethyl ether were purchased from Wako Pure Chemical Industries, Ltd.( Tokyo, Japan ). They were all guaranteed reagents and used without further purification. Distilled and deionized water was used.

### 2.2. Methods

**MEASUREMENT OF SOLUBILITIES OF CHLORINATED HYDROCARBONS IN AQUEOUS SOLUTIONS OF BRANCHED CD MIXTURES** A branched CD mixture was dissolved in water. 1.0 g of a chlorinated hydrocarbon was added to 5 mL of an aqueous solution of branched CD mixture. Then it was vigorously stirred in a thermostated bath. The reaction product was then placed in a glass tube and centrifuged at 3,000 rpm for 5 min. It separated into two transparent liquid layers, i.e., the chlorinated hydrocarbon phase and the aqueous phase containing CD and chlorinated hydrocarbon-CD inclusion complex. 3 mL of the aqueous solution was taken with a pipette and benzene was added as internal standard for analysis. It was transferred to a separatory funnel, with water and diethyl ether added, and shaken for a few minutes. The included chlorinated

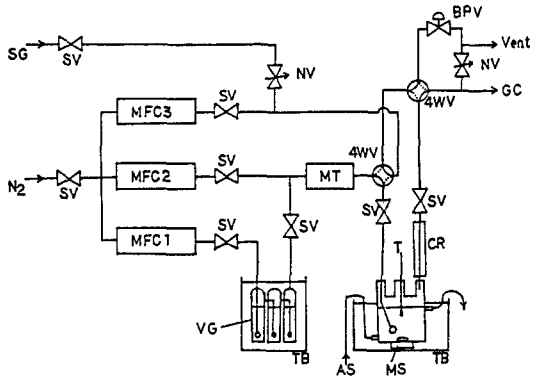


Fig. 1 Apparatus for Absorption Experiment
MFC: Mass flow controller, SV: Stop valve, NV: Needle valve, SG: Standard gas, 4WV: Four way valve, BPV: Back pressure valve, VG: Chlorinated hydrocarbon vaporizer, AS: Absorbing solution, MS: Magnetic stirrer, CR: Reflux condenser, T: Thermometer, TB: Thermostated bath, MT: Gas mixing tube, GC: Gas chromatograph

hydrocarbon and benzene was almost completely extracted into the ether layer. The ether solution was then subjected to gas chromatographic analysis.

**ABSORPTION OF TRICHLOROETHYLENE GAS IN A CONTINUOUS FLOW SYSTEM** The experimental apparatus used for gas absorption is illustrated in Figure 1. As shown in the figure, the concentration of trichloroethylene gas was changed by controlling the flow of $N_2$ via mass flow controllers 1 and 2. Then the diluted trichloroethylene gas was introduced into the aqueous solution of M-β-CD mixture. Fresh aqueous solution of the CD was continuously supplied. The concentration of trichloroethylene was measured every 3 min by GC. For comparison, a similar experiment was carried out using pure water in place of M-β-CD mixture solution.

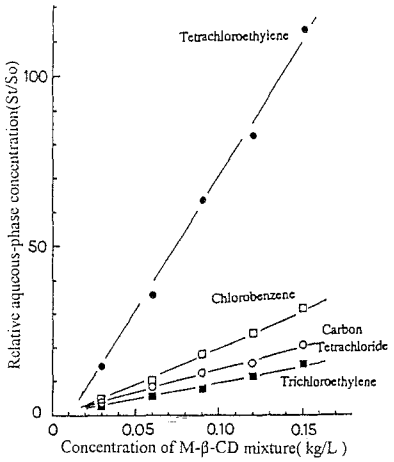


Fig. 2 Solubilities of Chlorinated Hydrocarbons in Aqueous Solutions of M-β-CD mixture ( See text as for St and So. )

## 3. RESULTS AND DISCUSSION

### 3.1. Solubilities and partition coefficients

As can be seen in Figure 2, the solubilities of four chlorinated hydrocarbons increased almost linearly with increasing concentration of branched cyclodextrin mixture. The data were analyzed according to a linear partition model[4] expressed as follows;

$$S_t / S_0 = 1 + K_{CW} X_{CD}$$

where St is the total aqueous-phase concentration of a chlorinated hydrocarbon, $S_0$ is the aqueous solubility of the chlorinated hydrocarbon, $K_{CW}$ is the partition coefficient of the chlorinated hydrocarbon between cyclodextrin and water, and $X_{CD}$ is the concentration of

TABLE 1. Values of partition coefficient( log Kcw )

| | G-α-CD mixture | Monoglucosyl -α-CD | M-β-CD mixture | Monomaltosyl-β-CD |
|---|---|---|---|---|
| Carbon tetrachloride | 1.95 ( 0.999 ) | 2.14 ( 0.997 ) | 2.12 ( 0.998 ) | 2.33 ( 0.998 ) |
| Trichloroethylene | 1.72 ( 0.999 ) | 1.84 ( 0.999 ) | 1.98 ( 0.992 ) | 2.06 ( 0.998 ) |
| Tetrachloroethylene | 2.13 ( 0.984 ) | 2.22 ( 0.968 ) | 2.88 ( 0.995 ) | 2.86 ( 0.999 ) |
| Chlorobenzene | 2.07 ( 0.999 ) | 2.10 ( 0.996 ) | 2.35 ( 0.999 ) | 2.28 ( 0.999 ) |

Values of correlation coefficient for least-squares fitting are shown in parentheses.

cyclodextrin(kg/L). Table 1 shows that the Kcw values in the system using branched CD mixtures are not very different from those in the system using highly purified branched CDs. This indicates that branched CD mixtures have an inclusion characteristic almost equivalent to that of highly purified branched CDs. This is significant from a viewpoint of practical use since branched CD mixtures are much cheaper than highly purified branched CDs. Thus a branched CD mixture was used in the following absorption experiment.

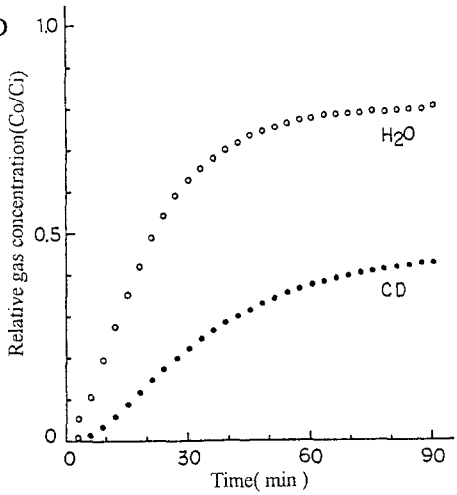


Fig. 3 Concentration Change of Trichloroethylene Gas after Contact with M-β-CD Mixture Solution or Pure Water ( Ci and Co mean concentrations of trichloroethylene before and after contact with absorbent, respectively.)

### 3.2. Absorption in a continuous flow system

A preliminary result is shown in Figure 3. 3,000 ppm trichloroethylene gas diluted with $N_2$ was bubbled through 600 mL of 0.1 kg/L branched β-CD mixture solution at 25°C( GHSV: 10 $h^{-1}$ ) while 0.1 kg/L branched CD mixture solution was continuously provided( LHSV: 1 $h^{-1}$ ). Production of solid compounds was not observed in this experiment. From the comparison between the CD solution system and the $H_2O$ system, it is clear that trichloroethylene gas was absorbed in the aqueous solution of branched CD mixture. It is expected that more effective absorption can be performed by optimizing the experimental conditions such as concentration of CD, flow rate of absorbing solution, the way of contacting gas with absorbing solution, etc. By the way, the branched CD mixture solution used for the absorption of trichloroethylene was heated to 70°C. Then the chlorinated hydrocarbon included by CD was released and the CD solution could be used to absorb trichloroethylene again.

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