

Inclusion Complexation of Volatile Chlorinated Hydrocarbons in Aqueous Solutions of Branched Cyclodextrins

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Abstract. The inclusion complexation of five volatile chlorinated hydrocarbons, i.e., chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, and monochlorobenzene, with branched cyclodextrins (CDs) such as monoglucosyl- α -CD and monomaltosyl- β -CD in aqueous solutions was examined. Their inclusion complexes were found to be very water soluble and the solubilities of the chlorinated hydrocarbons in aqueous solutions increased almost linearly or gradually with increasing concentration of the branched CDs. The amounts of the chlorinated hydrocarbons included in the branched CDs were well related to their molecular size and shape. In addition, the viability of application to pollution prevention is discussed.

Key words: Branched cyclodextrins, volatile chlorinated hydrocarbons, inclusion complexation.

1. Introduction

In a previous paper [1] we demonstrated that branched α -cyclodextrins (CDs) were very effective reagents for selective liquid-liquid extraction of xylene isomers and ethylbenzene since their inclusion complexes did not precipitate. Branched CDs, which are now commercially available, were developed in order to enhance the water solubilities of CDs and their inclusion complexes [2–4].

In this study we have examined the inclusion complexation of five typical volatile chlorinated hydrocarbons, i.e., chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, and monochlorobenzene, in aqueous solutions of branched CDs. No further detailed research has been reported on the inclusion complexation of halogenated hydrocarbons by branched CDs since the solubilization of tetrachloroethane, etc. in water through inclusion by monoglucosyl- α -CD was reported about ten years ago [2].

This study is also interesting from the viewpoint of pollution prevention. Volatile chlorinated hydrocarbons such as trichloroethylene 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 [5]. In a recent symposium, the use of CDs to reduce environmental

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pollution was emphasized [6]. It is well known that CDs have a strong affinity for halogenated hydrocarbons and easily form inclusion complexes, which are usually insoluble in water [7]. The solid complexes are also produced when chlorinated hydrocarbons in the gas phase come into contact with aqueous solutions of CDs [8]. Such processes have been suggested for trapping halogenated hydrocarbons and preventing their emission to the environment, and some equipment has been proposed [8, 9]. Aqueous solutions of CDs were used and one of the difficulties consists in handling the solid complexes, which are usually very fine and sticky. In order to retard the production of insoluble complexes, highly-soluble CD derivatives were used or some additives were employed to enhance the solubility of CDs. The solubilities of the complexes with chlorinated hydrocarbons could not, however, be significantly improved [9]. Thus the use of branched CDs is explored in this paper.

2. Experimental

2.1. REAGENTS

Chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, monochlorobenzene, benzene, toluene, and diethyl ether were purchased from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan). They were all guaranteed reagents and used without further purification. G- α -CD (6-O- α -D-glucosyl- α -CD) and M- β -CD (6-O- α -maltosyl- β -CD) were supplied by Ensuiko Sugar Refining Co., Ltd. (Yokohama, Japan). The impurities in the branched CDs are less than 1.5%. Distilled and deionized water was used.

2.2. PROCEDURE OF INCLUSION COMPLEXATION

A branched CD was dissolved in water, to which a chlorinated hydrocarbon was added. In most cases, 1.0–1.5 g of a chlorinated hydrocarbon was added to 5 mL of aqueous solutions of a branched CD. The mixture was vigorously stirred in a thermostated bath. The reaction product was then placed in a glass tube and centrifuged at 3000 rpm for 5 min. It separated into two transparent liquid layers: one phase is the chlorinated hydrocarbon and the other is the aqueous phase containing CD and chlorinated hydrocarbon-CD inclusion complex. 3 mL of the CD 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 hydrocarbon and benzene were almost completely extracted into the ether layer. The ether solution was then subjected to gas chromatographic analysis.

2.3. CHROMATOGRAPHIC MEASUREMENT OF CHLORINATED HYDROCARBONS

Chlorinated hydrocarbons were determined with a GC-9A gas chromatograph (Shimadzu Corporation, Japan) with a fused-silica wall coated capillary column (50 m \times 0.25 mm I.D.) using OV-1 as the liquid phase under the following conditions: carrier gas, He; flow rate, 0.6 mL/min; injection port temperature 250°C; sample size, 2–5 μ L; splitting ratio, 1 : 50, flame ionization detector. The column temperature was held at 35°C for chloroform (retention time, 10.7 min for chloroform and 13.2 min for benzene), at 50°C for trichloroethylene (11.9 min for trichloroethylene and 10.2 min for benzene), and at 60°C for tetrachloroethylene and monochlorobenzene (16.7 min and 19.0 min, respectively, and 8.8 min for benzene). For analysis of carbon tetrachloride, toluene was used as the internal standard instead of benzene, since the chromatographic peak of carbon tetrachloride was not separated completely from that of benzene. The retention times were 10.4 min for carbon tetrachloride and 16.7 min for toluene at 50°C, respectively.

3. Results and Discussion

Figure 1 shows that the solution of trichloroethylene in a 0.10 M aqueous solution of M- β -CD became almost saturated in 1 min. For the other chlorinated compounds, it took only a few minutes to reach a saturated level of dissolution, indicating that the inclusion complex formation proceeds rather fast.

As can be seen from Figure 2, the amount of trichloroethylene dissolved at a temperature above 35°C was smaller than that at 30°C. Furthermore, the higher the temperature of the aqueous solution, the smaller the amount of dissolved trichloroethylene. This reflects the general fact that the formation of the CD complex is exothermic. On the other hand, at a temperature below 15°C, the solid inclusion complex deposited in some cases.

Figures 3 and 4 show the solubility isotherms of five chlorinated hydrocarbons in aqueous solutions of branched CDs. The solubilities of chlorinated hydrocarbons increased almost linearly or gradually with increasing concentration of the branched CD. Deposition of solid inclusion complex was not observed in the range of CD concentrations given in Figures 3 and 4. At higher concentration, for example, solid products did not deposit in any system of the five chlorinated hydrocarbons with 0.2 M G- α -CD. On the other hand, in 0.2 M solutions of M- β -CD, no solid product was seen in the cases of chloroform, trichloroethylene, and tetrachloroethylene, while in the case of carbon tetrachloride the reaction product was gelified and in the case of monochlorobenzene a trace amount of white solid was produced. Thus, whether or not the deposition of solids happens depends on the combination of chlorinated hydrocarbons and the concentration of branched CDs.

The slope in Table I, i.e., the solubility increase in moles/mole cyclodextrin [8], can be correlated with the molar ratio of guest species to CD of the inclusion complex. A 1 : 1 (CD : guest) complex is considered to be formed in the G- α -

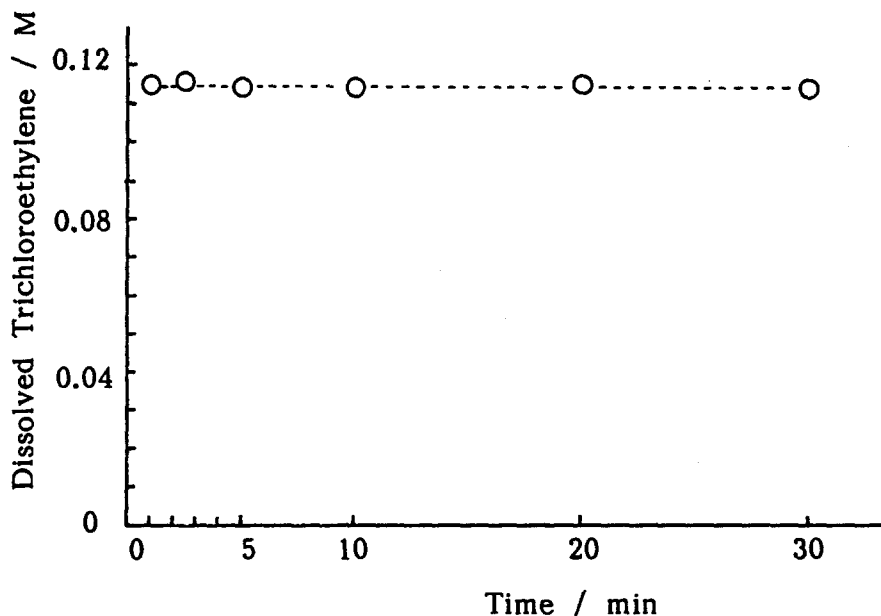


Fig. 1. Relation between stirring time and the amount of trichloroethylene dissolved in a 0.10 M aqueous solution of M- β -CD at 25°C.

TABLE I. Values of the slope obtained from straight line fitting of data in Figures 3 and 4.

	G- α -CD	M- β -CD
Chloroform	0.90	1.33
Carbon tetrachloride	0.47	0.94
Trichloroethylene	0.50	1.07
Tetrachloroethylene	0.21 ^a	0.84
Monochlorobenzene	0.40	0.78

^a Four data points from 0.04–0.10 M were used for calculation.

CD-chloroform system, with 2 : 1 complexes in the G- α -CD-trichloroethylene, G- α -CD-carbon tetrachloride, and G- α -CD-monochlorobenzene systems. In the latter three systems, a 1 : 1 complex also may be formed but a 2 : 1 complex seems to be dominant. In the case of tetrachloroethylene, the complex in which more than three CD molecules include one tetrachloroethylene molecule is assumed to be formed. On the other hand, a 2 : 3 (CD : guest) complex as well as a 1 : 1 complex seems to be formed in the M- β -CD-chloroform system. With the four other compounds and M- β -CD, the 1 : 1 complex seems to be formed mainly.

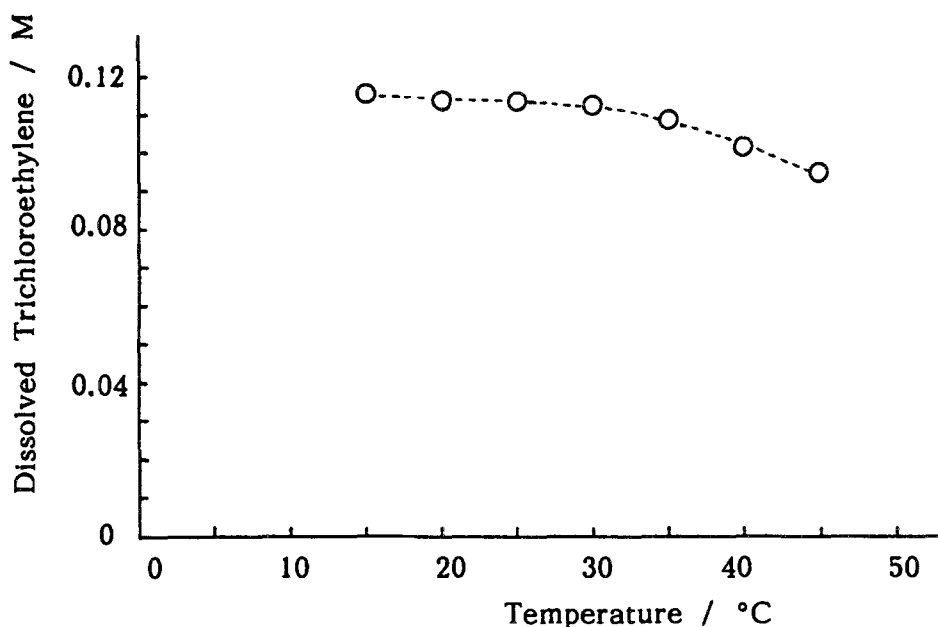


Fig. 2. Effect of temperature on the amount of trichloroethylene dissolved in a 0.10 M aqueous solution of M- β -CD.

The amount of chlorinated hydrocarbons included has a good correlation with their molecular size and shape. This situation is clearly seen by the use of Corey–Pauling–Koltun (CPK) molecular models. A chloroform molecule just fits the cavity of the α -CD molecule. Therefore, α -CD should form a 1 : 1 inclusion complex with chloroform. Only half of a molecule of carbon tetrachloride can be accommodated in the cavity of α -CD, and the cavity formed by two α -CD molecules with a head-to-head structure can include a carbon tetrachloride molecule completely. The explanation holds also in the case of trichloroethylene. On the other hand, a tetrachloroethylene molecule, which is a little bulkier than a trichloroethylene molecule, is difficult to be included by two α -CD molecules. As for monochlorobenzene, the slope of Figure 3 indicates that a 2 : 1 complex is mainly formed, although the CPK molecular model shows that a monochlorobenzene molecule can be included almost completely in the cavity of α -CD.

On the other hand, the cavity of β -CD can accommodate more than one chloroform molecule. In the cases of the four other compounds, a molecule can be almost completely included in the cavity of β -CD to form a 1 : 1 complex.

There are a few differences between the abovementioned molar ratios of branched CD to guest and those reported for the complexes of unsubstituted CDs. The molar ratio of 1 : 1 was reported for the α -CD-monochlorobenzene and the β -

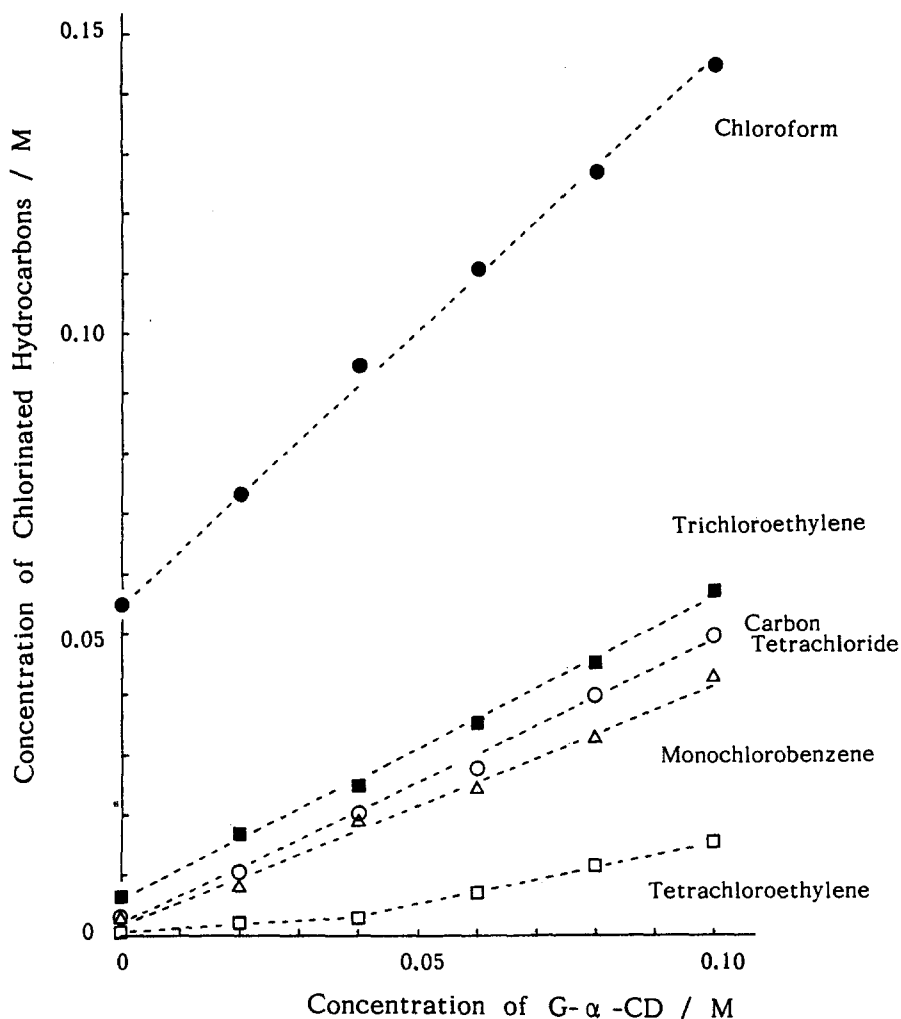


Fig. 3. Solubility isotherms of five chlorinated hydrocarbons in aqueous solutions of G- α -CD at 25°C.

CD-chloroform complexes and a 1 : 0.42 ratio for the β -CD-monochlorobenzene complex [8, 9]. It has not yet been clarified why such differences occurred [10].

The branched CDs seem to have the possibility of being used as effective absorbents of chlorinated hydrocarbons.

As examined above, the aqueous solutions of branched CDs can dissolve and absorb the volatile chlorinated hydrocarbons very effectively since the inclusion complexes are so water-soluble. For comparison, we carried out an experiment mixing aqueous solutions of unsubstituted α -CD or β -CD with sufficient amounts of the five chlorinated hydrocarbons at 25°C for 30–60 min. When the production

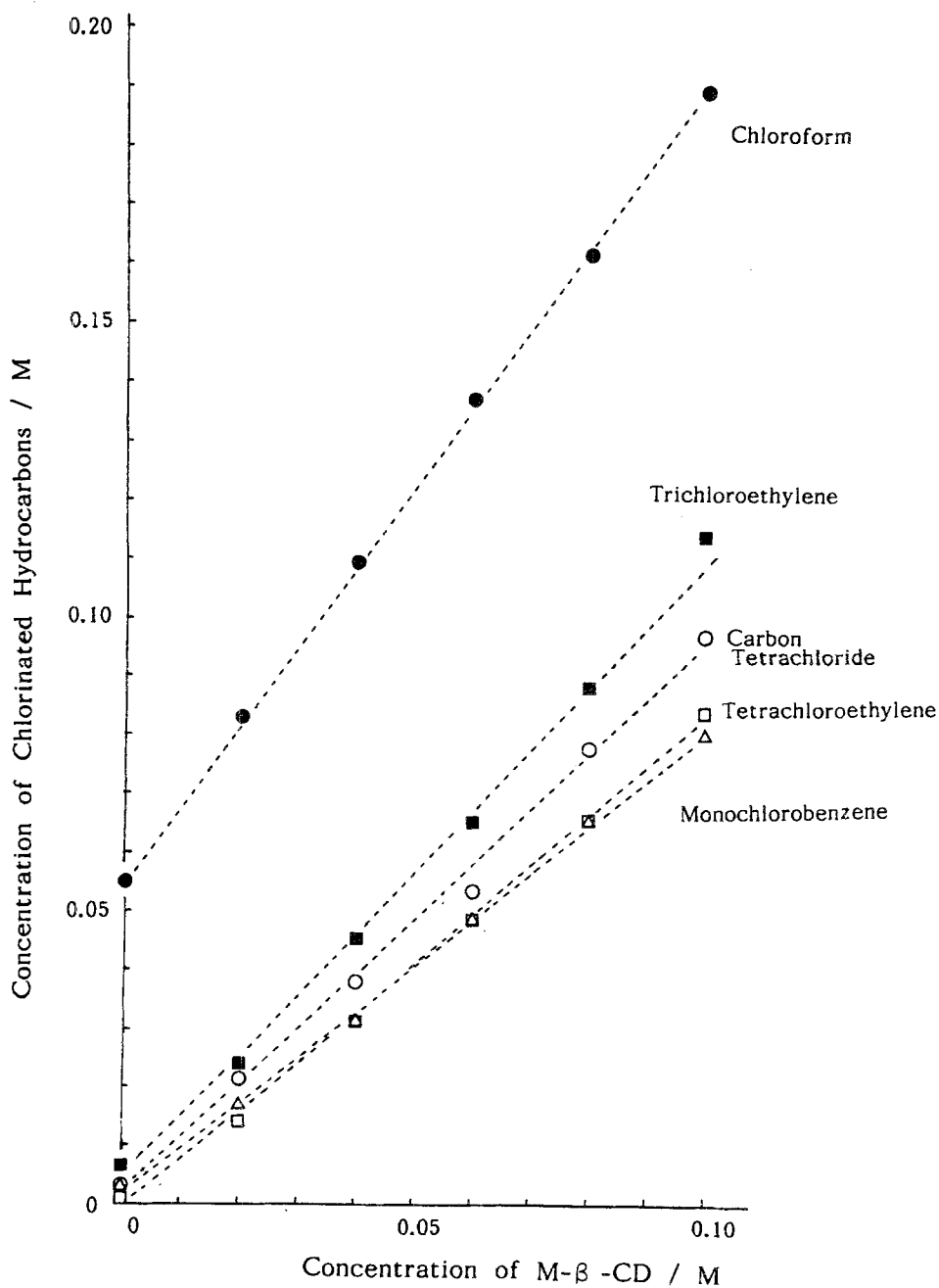


Fig. 4. Solubility isotherms of five chlorinated hydrocarbons in aqueous solutions of M-β-CD at 25°C.

of white solid was observed, the concentrations of α -CD were 0.025 M for chloroform, 0.005 M for carbon tetrachloride, 0.01 M for trichloroethylene, 0.015 M for tetrachloroethylene, and 0.02 M for monochlorobenzene, respectively. In the case of β -CD, they were 0.002 M for chloroform and carbon tetrachloride, and 0.001 M for trichloroethylene, tetrachloroethylene, and monochlorobenzene, respectively [11].

The examination of the temperature dependency of inclusion indicates that it is advisable to carry out the dissolution of chlorinated hydrocarbons at a temperature between 20–30°C.

We tested the release of trichloroethylene dissolved in a 0.1 M β -CD solution. CD inclusion complexes were reported to dissociate in water at 60–70°C [12]. The solution was kept in a thermostated bath at 60°C for 5 min and then it was subjected to GC analysis. No trichloroethylene was detected, which indicates that trichloroethylene was completely released from the CD solution. After the guest release, the M- β -CD solution was able to include trichloroethylene again. Thus we can release and recover chlorinated hydrocarbons without consuming much energy and use the CD solution repeatedly.

In addition, we ascertained that almost the same results were obtained using the other branched α -CDs such as diglucosyl- α -CD, maltosyl- α -CD, and their mixtures, instead of highly purified G- α -CD. And it was just the same with branched β -CDs. For practical applications, therefore, we do not need to use expensive, pure branched CDs but can use cheap mixtures.

The use of branched CDs has some other advantages: (i) since the branched CDs can be used in much higher concentration than unsubstituted CDs, the solvent volume can be lowered. (ii) Since they are not toxic [13] and do not cause environmental pollution, we can use them without anxiety. These facts as well as the results of this study indicate that branched CDs can be very useful in trapping chlorinated hydrocarbons.

Notes and References

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4. Tetrachloroethane, lemon oil, etc., which form insoluble complexes with α -CD, became very water soluble through inclusion by monoglucosyl- α -CD (G- α -CD) [2]. The water solubility of G- α -CD (0.80 M at 25°C) is more than four times that of α -CD and that of monomaltosyl- β -CD (1.04 M at 25°C) is about sixty times that of β -CD [3].
5. About 20 halogenated organic compounds were included in 189 substances regulated by the 1990 Clean Air Act of the United States. The five compounds treated in this study are all listed in the 1990 Clean Air Act.
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10. Branched CDs have glucosyl or maltosyl units in the primary hydroxyl groups of the narrow rims joined through 1,6- α linkages and their wider rims undergo no modification. Their inclusion characteristics, therefore, are expected to be very similar to those of unsubstituted CDs.
11. The results are slightly different from those of Ref. 7. But the general trend was almost the same. The difference should be attributed to the experimental methods.
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13. Branched CDs have been mainly applied to foods. For example, see *Jpn. Fudo Saiensu* **27**, 66 (1988) (*Chem. Abstr.* **109**, 36663b (1988)).