

Solubilisation of chlorinated solvents by cyclodextrin derivatives A study by static headspace gas chromatography and molecular modelling

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Abstract

The capacity of α -cyclodextrin (α -CD) and four β -cyclodextrins (β -CDs) in reducing the volatility of volatile organic compounds (VOCs) and particularly carbon tetrachloride (CT), chloroform (TCM) and dichloromethane (DCM) is investigated by using static headspace gas chromatography (HSGC). The experiments allowed the determination of Henry's law constant (H_c) in absence and in presence of cyclodextrins (CDs). The use of CDs may lead to a reduction of 95% of the Henry's law constant for some VOCs. The association constants of the inclusion complexes formed between CDs and the three guests are determined using a new method involving an algorithmic treatment bringing the shortening of experimental time required for the determination of the stability constant. The complementarities of the host and the guest are investigated by molecular modelling. The complexation energies obtained are in good agreement with the experimental formation constants. Furthermore, this study shows the effectiveness of CDs in trapping pollutants and reducing their volatility in the viewpoint of pollution prevention.

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1. Introduction

Volatile organic compounds (VOCs) are widely used in industry as solvents, dry-cleaning agents, degreasers, and intermediates in the production of plastics, synthetic resins or pharmaceuticals [1]. From an environmental point of view, it is necessary to limit and control their emissions because they affect the change of climate, the growth and decay of plants, and the health of human beings and all animals [2].

New regulations regarding volatile organic compounds emissions demand more efficient and less costly technologies [3]. Many techniques are available to control VOCs emission (destruction based and recovery based) with some advantages and limitations. Absorption is used to remove VOCs from gas streams by contacting the contaminated air with a liquid solvent

with high removal efficiency. Any soluble VOCs will transfer to the liquid phase. But among the most common VOCs (chlorinated or aromatic hydrocarbons), there is a majority of poorly hydrosoluble compounds, thus a solubilizing additive is needed.

Cyclodextrins (CDs) are a family of cyclic oligosaccharides that are composed of α -1,4-linked glucopyranose subunits [4–6]. CDs are produced from starch by enzymatic degradation. The most common CDs are of three types: α -cyclodextrin (α -CD), β -cyclodextrin (β -CD) and γ -cyclodextrin (γ -CD), referred to as first generation or parent CDs. α -, β - and γ -CD are composed of six, seven and eight glucosyl units, respectively. Of the parent cyclodextrins, β -CD is the most accessible, the lowest-priced and generally the most useful (see Fig. 1) [7]. Chemically modified β -CDs with higher solubility than the first generation are commercially available.

CDs have a low-polarity cavity in which organic compounds of appropriate shape and size can form inclusion complexes [8]. From a microscopical point of view, since each guest molecule is individually surrounded by a CD, the molecule is micro-

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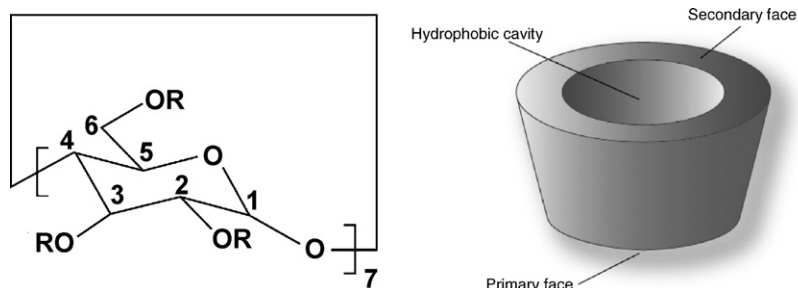


Fig. 1. Chemical structure of β -CDs: if R=H: β -CD; R=CH₂-CHOH-CH₃: HPBCD (0.8 OH group modified per glucopyranose unit); R=CH₃: CRYSMEB (0.7 OH groups modified per glucopyranose unit) and RAMEB (1.8 OH groups modified per glucopyranose unit).

encapsulated. This unique property provides CDs with a capacity to significantly increase the apparent solubility of low-polarity organic compounds [9]. As a consequence, they can play a major role in environmental science in terms of solubilisation of organic contaminants, enrichment and removal of organic pollutants and heavy metals from soil, water and atmosphere [10–14]. CDs can immobilize VOCs into the cavity in the aqueous phase [15–17]. In this way, they are expected to improve the transfer between gaseous and aqueous phase during the absorption process.

We use static headspace gas chromatography (HSGC) to investigate the effect of α -CD, β -CD, hydroxypropyl- β -cyclodextrin (HPBCD) methylated- β -cyclodextrin (CRYSMEB) and randomly-methylated- β -cyclodextrin (RAMEB) on three chlorinated hydrocarbons: carbon tetrachloride (CT), chloroform (TCM) and dichloromethane (DCM) used as solvents and extractants in various manufacturing and laboratory procedures [18]. Finally, molecular modelling is applied to the β -CD complexes in order to understand the factors governing the inclusion compounds stability.

2. Experimental

2.1. Materials

Carbon tetrachloride, chloroform and dichloromethane (Aldrich) all of analytical reagent grade were used as received. Distilled deionised water was used throughout this work. β -CD, HPBCD and CRYSMEB were kindly donated from Roquette Frères (Lestrem, France), α -CD and RAMEB were purchased from Wacker-Chimie (Lyon, France).

2.2. Static headspace

Headspace sampling is employed with gas chromatography (GC) in numerous fields and with a variety of applications [19,20]. A headspace sample is in principle a gas sample which has been previously in contact with a liquid or solid sample from which volatile compounds were released into the gas with subsequent analysis by gas chromatography. Headspace gas chromatography is therefore a technique of gas extraction and can be carried out comparable to a solvent extraction as a one-step extraction (static or equilibrium headspace) or as a continuous extraction (dynamic headspace) [21]. Measurements were con-

ducted with a Varian Genesis headspace autosampler. Sample solutions of 10 mL containing various concentrations of pollutant (10–100 ppm) were introduced into 22 mL headspace vials and sealed using silicone septa and aluminium foil. The vials were then thermostated at 30 ± 0.1 °C. After the equilibrium was established (30 min), 1 mL of vapor from the above solution was drawn out from the vial using a gas-tight syringe and injected directly in the chromatographic column via a transfer line. This sample was then analyzed by gas chromatography (Perkin-Elmer Autosystem XL) equipped with a flame-ionization detector using a DB624 column. The GC settings were programmed as following: detector temperature, 280 °C; column temperature, 60 °C during 8 min.

2.2.1. Vapour–liquid equilibria studies

Accurate vapour–liquid equilibria (VLE) experimental data are essential for the design of absorption tower. Henry's law is used to describe the distribution of a volatile contaminant between the aqueous and gas phase. There are two forms of Henry's law constant. One form is the dimensionless Henry's law constant (H_c), sometimes called the gas–liquid partition coefficient, which is described as the ratio of a compound's concentration in gas phase (C_g ; mol L⁻¹) and that in aqueous phase (C_{aq} ; mol L⁻¹) at equilibrium:

$$H_c = C_g / C_{aq} \quad (1)$$

A number of methods to determine Henry's constant have been presented in the literature [22–24]. In this study, we use the phase ratio variation (PRV) for the determination of H_c in absence and in the presence of CD. This method is based on the following equation:

$$C_{aq,0}/A = 1/\alpha(V_g/V_{aq} + 1/H_c) \quad (2)$$

where $C_{aq,0}$ is the initial chemical concentration in the prepared liquid solution (mg mL⁻¹), V_{aq} the liquid sample volume added into the vial (mL), V_g the headspace gas volume in the vial (mL), A the integrated area counts of GC peak for a given sample, and α is a specific parameter of the headspace defined by $A = \alpha C_g$. Eq. (2) can be used to determine Henry's constant of VOCs by using various gas–liquid volume ratios in the headspace vials during the experiments. Linear regression of $C_{aq,0}/A$ against V_g/V_{aq} gives the slope and intercept. Henry's constant is calculated as $H_c = \text{slope}/\text{intercept}$ [24,25].

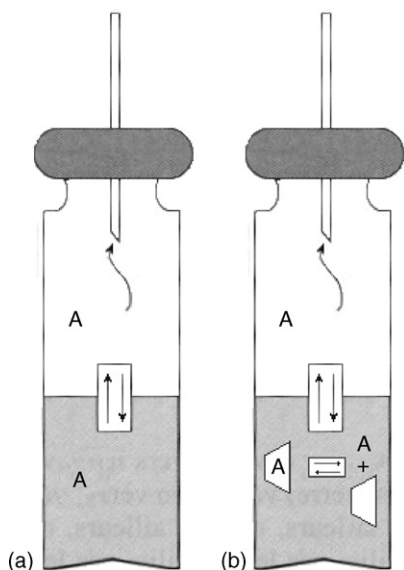


Fig. 2. : Illustration of the equilibrium for a VOC (A) between aqueous and gas phase in the absence (a) and in the presence of CD (b).

However, the presence of chemical agents in solution is expected to impact H_c [26,27]. This is because the addition of chemical agents can change the solubility of hydrophobic compounds, for example, by forming chemical inclusion complexes in the case of CD (see Fig. 2).

2.2.2. Formation constants

There are few references in literature in which HSGC is used for determining stability constants of different compounds with CDs [28–33] and especially for VOCs [15–17]. The stability constants for the inclusion of VOCs with α -CD, β -CD, HPBCD, CRYSMEB and RAMEB in aqueous solution were determined at 30 °C.

The VOC/CD system is characterised by a titration method. Different concentrations of CD are used while the initial concentration of the VOC is constant. Assuming that 1:1 complexes are formed, the calculation of formation constant K_f is developed as follows:



$$K_f = [\text{VOC/CD}]/[\text{VOC}][\text{CD}] = [\text{VOC/CD}]/([\text{VOC}]_T - [\text{VOC/CD}])([\text{CD}]_T - [\text{VOC/CD}]) \quad (4)$$

$$[\text{VOC/CD}] = -1/2\sqrt{[(1/K_f + [\text{CD}]_T + [\text{VOC}]_T)^2 - 4[\text{CD}]_T[\text{VOC}]_T]} + 1/2(1/K_f + [\text{CD}]_T + [\text{VOC}]_T) \quad (5)$$

where K_f and T stand for formation constant and total, respectively. For a given value of K_f $[\text{VOC/CD}]$ is known. An algorithmic treatment developed in our laboratory is used to calculate the formation constant K_f from the experimental data [34]. Only one concentration of VOC in water is needed. Indeed, the conventional static headspace gas chromatography methods require the calibration curves to evaluate the concentration of free guest in the presence of CD. The method developed by Wu et al. [33] is based on the following equation:

$$[\text{CD}] = [\text{CD}]_T(A_0 - A)/K' \quad (6)$$

where A_0 is the peak area of the VOC in water, A the peak area in the presence of CD and K' the slope of the calibration curve. A_0/A versus $[\text{CD}]$ plots give a straight line, the slope of which corresponds to K_f .

Another method developed by Saito et al. [28] is based on Eq. (7):

$$[\text{COV}] = [\text{COV}]_T/1 + K_f[\text{CD}] \quad (7)$$

The concentration of the CD is constant while different concentrations of VOC are used. It is assumed that $[\text{CD}]_T$ is equal to $[\text{CD}]$.

In this study we compare the results obtained with these two methods with our algorithmic treatment of the experimental data. This must bring the shortening of experimental time required for the determination of the stability constant.

2.3. Molecular modelling

The docking of each chlorinated species into the CD cavity was studied by the use of the BOSS 4.2 software [35,36]. The z matrix of β -CD was written on the basis of a non-distorted monomeric β -CD with C_7 symmetry. Such a conformation has been chosen since the C_7 symmetry corresponds to the average structure of β -CD, even if this average is consecutive to successive structures, which are more or less distorted. In order to take into account electrostatic interactions between each cavity, atomic charges have been estimated on the basis of the electrostatic potentials at the ab initio 6.31G* (Spartan software: PC Spartan Pro 1.0.8, Wavefunction Inc.). The relative orientation between host and guest was defined by the use of four dummy atoms, virtually linked to the carbon atom of the guest and to one interglucosidic oxygen of the host. The six intermolecular coordinates, and thus the substrate inclusion, were then simulated by applying a Monte Carlo search based on two distances, one angle and three dihedrals. During the search, the CD host is kept rigid, while the guest freedom is freely allowed. Indeed and contrary to the structure of the studied guests, the CD conformation is controlled by many geometric parameters so that random variations may be observed during the search if the CD geometry is not locked: since such exploration of the conformational space of the CD is not exhaustive, but has a considerable influence on

the energetic parameter, comparison from one guest to another may be biased if no constraint is applied to the CD cavity. In each study, 100 000 successive generated structures were considered. Each structure was optimised with the conjugated gradient as minimisation algorithm (convergence: 0.01 kcal mol⁻¹), with a dielectric constant fixed to 78.3 in order to simulate the electrostatic influence of water. The conformer identification was done with the following parameters: RMS criteria, 10.0 Å; internuclear distance criteria 40.0 Å²; energetic criteria, 1 kcal mol⁻¹. The stabilisation energy (ΔE , kcal mol⁻¹) is expressed as the energetic difference between complexed form and free species.

3. Results and discussions

Full equilibrium of the chemical solute between liquid and gas phases is required for the determination of Henry's constant. For the chemicals tested, the equilibrium time was 30 min. Linear response of the GC detector to the chemical concentration range tested is another requirement for the successful application of the method. For all compounds, we verify that the GC detector responds linearly. The correlation coefficients are all better than 0.998.

The determination of the Henry's law constants were done with five different values of V_{aq} (2, 3, 5, 7 and 10 mL) for the three VOCs at 30 °C in water and in aqueous solutions of various CDs concentrations. The measured dimensionless Henry's constants are listed in Table 1.

These values are in good agreement with the one found in literature: 1.823, 0.223 and 0.129 for CCl_4 , $CHCl_3$ and CH_2Cl_2 , respectively, at 34.6 °C [22].

The results indicate that, at a given temperature, H_c decreases with increasing CD concentration. β -CD as a limited solubility (18.5 g L^{-1}) so the use of modified β -CDs with higher solubility is of great interest in order to reduce the Henry's law constant of the VOCs. Our data have demonstrated that the volatility of CCl_4 could be greatly reduced in presence of β -CDs, in comparison with α -CD. This behaviour should be directly linked to the formation of inclusion complex between the β -CD and CCl_4 , by improving the apparent solubility of CCl_4 . The minimum requirement for inclusion complex formation is the size compatibility between the host and guest molecules. According to Nishimura et al. [37], the CCl_4 molecule could be suitably accommodated in the β -CD cavity assuming a 1:1 association, whereas it would be only partly included in the α -CD. Indeed, our computer molecular modelling shows that the CCl_4 fits tightly in the β -CD cavity (see Fig. 5).

On the other hand, no association could have been measured between CCl_4 and γ -CD (result not presented), since the cavity is too large for this guest to be fitted in. Moreover the reduction of the Henry's law constant increases versus the concentration of CDs. Hence, the use of RAMEB at a concentration of 0.05 mol L^{-1} leads to a reduction of volatility up to 95%. This reduction is linked to the number of chlorine atoms bonded to the carbon atom.

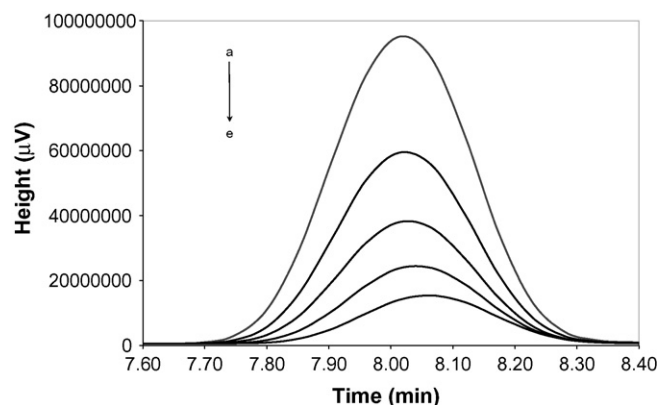


Fig. 3. Representation of the variation of the chromatogram of CCl_4 10 ppm: (a) with various concentrations of RAMEB: 5 mM (b), 10 mM (c), 20 mM (d) and 35 mM (e).

Table 2
Formation constants (M^{-1}) at 30 °C determine by the algorithmic treatment

	α -CD	β -CD	HPBCD	CRYSMEB	RAMEB
CH_2Cl_2	21 (28) ^a	9	10	9	12
$CHCl_3$	34 (42) ^a	60 (24) ^a	61	55	93
CCl_4	40 (42) ^a	164 (150) ^a	218	215	238

^a Data obtained by Nishimura et al. [37].

3.1. Formation constants

Determinations of the formation constant were done with four CDs concentration (35, 20, 10 and 5 mM for HPBCD, CRYSMEB and RAMEB and 7, 4, 2 and 1 mM for α - and β -CD). The effect of an increased concentration of CD on the chromatographic peak of CT is shown in Fig. 3 in the case of RAMEB.

The obtained variations are in agreement with the 1:1 host–guest ratio. The formation constants are calculated by an algorithmic procedure [34] and are reported in Table 2.

They are few values in the literature for the complexation of volatile chlorinated hydrocarbons. Nishimura et al. [37] study the association of CT, TCM and DCM with α -, β - and γ -CD by using the volatilisation rate of guest from aqueous into gaseous phase. Their data (in brackets) are given for comparison with the one obtained in the present study. In their study Nishimura et al. did not observe complexation between DCM and β -CD. Lantz

Table 1
Henry's law constants of H_c (dimensionless) DCM, TCM and CT at 30 °C in water and in aqueous solution of CDs at various concentrations

	H_2O	[CD] (mol L^{-1})	α -CD	β -CD	HPBCD	CRYSMEB	RAMEB
CH_2Cl_2	0.127	0.01	0.104	0.107	0.105	0.105	0.105
		0.05	–	–	0.090	0.089	0.081
$CHCl_3$	0.210	0.01	0.162	0.143	0.140	0.143	0.115
		0.05	–	–	0.048	0.046	0.033
CCl_4	1.600	0.01	1.168	0.560	0.496	0.500	0.430
		0.05	–	–	0.144	0.145	0.080

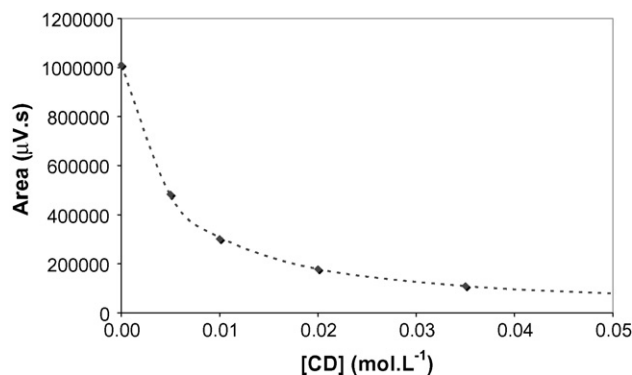


Fig. 4. Representation of the experimental point (♦) obtained for CT and RAMEB compare with theoretical titration curve (–) for a 1:1 complex ($K_f = 238 \text{ M}^{-1}$) with the algorithmic treatment.

Table 3
Comparison of the formation constants (M^{-1}) obtained for CT by different methods at 30°C

Method	Algorithmic treatment	Wu et al.	Saito et al.
β -CD	164	170	199
HPBCD	218	222	243
RAMEB	238	233	288

et al. [17] find an association constant of 30 M^{-1} for DCM with HPBCD.

One can notice from Table 2 that CT and TCM are better recognized than DCM. Hence, the more chlorine atoms present in the molecule, the more efficient is the molecular recognition. Modified β -CDs have more affinities for the three VOCs in comparison with the parent one.

The experimental data obtained for CT and RAMEB are given in Fig. 4 with the theoretical curve for a 1:1 complex with a formation constant of 238 M^{-1} . As one can see, the experimental points fit well with the theoretical curve.

We compare our results with the two other methods only in the case of CT. As we can see on Table 3, the values of the formation constant are closed for the two first methods. This can be due to the fact that no assumptions are done in these methods and that the same data (the peak area of VOCs in presence of different CDs concentrations) are used. However, our method needs only one value of VOC in water. In the method developed by Saito et al. it is assumed that $[\text{CD}]_T$ is equal

to $[\text{CD}]$, this can explain the small differences with the other two data.

3.2. Molecular modelling

In order to understand the mechanisms controlling the stability of the three chlorinated complexes, we have realised a molecular mechanics study on the inclusion compounds. The docking has been performed with a Monte Carlo procedure which samples all the intermolecular coordinates. The corresponding most stable structures are described in Fig. 5.

As observed and as could be expected, the filling of the cavity increases with the number of chlorine atoms, giving rise to greater van der Waals interactions for CT ($11.7 \text{ kcal mol}^{-1}$), than for TCM ($8.8 \text{ kcal mol}^{-1}$) or for DCM ($7.3 \text{ kcal mol}^{-1}$). Moreover, such interactions are the main factor explaining the complexation energy (respectively -11.7 , -9.9 and $-8.0 \text{ kcal mol}^{-1}$ for CT, TCM and DCM). Besides, there is a perfect correlation between the experimental formation constants and these simulated stabilisation energies (correlation coefficient equal to 0.984). Hence, we may affirm that the recognition is mainly based on the steric complementarity between the species. Within this framework, the weak empty space observed between the β -CD cavity and the CT suggests that this CD is more adapted to such substrate than α -CD and γ -CD, whose cavities will be, respectively, too small and too broad. The influence of the steric complementarity also explains the greater stability observed for the modified β -CDs HPBCD, CRYSMEB and RAMEB, since hydroxypropylation and methylation extend the cavity, thus increasing van der Waals interactions with the included substrate.

4. Conclusions

This work shows that HSGC is a method of choice to investigate the effect of CDs on air–water partitioning of some VOCs. Inclusion complexes between CT, TCM, DCM and α -CD, β -CD, HPBCD, CRYSMEB and RAMEB are formed, which make the volatility of the guest (H_c) decrease. The solubilisation capacity of CDs depends on the host–guest complementarity (K_f), but also on the solubility of CDs. Our method permits the calculation of formation constants with a good accuracy even for small formation constant. The most stable structure for the β -CD complexes predicted by the docking study shows that the recognition

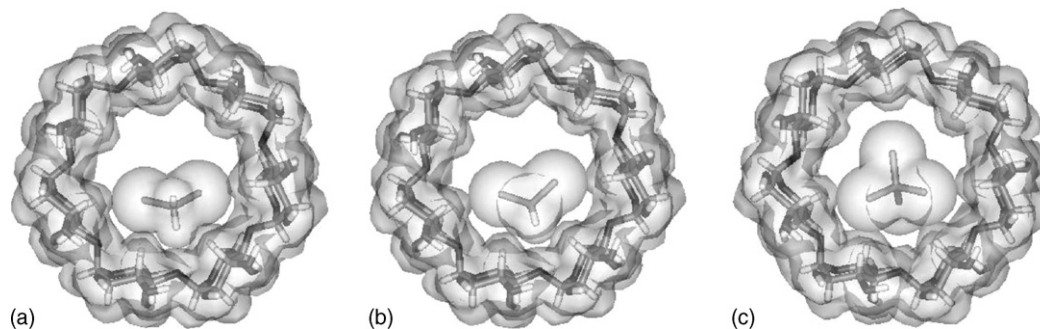


Fig. 5. Most stable structures for the β -CD complexes of DCM (a), TCM (b) and CT (c), as predicted by the docking study.

is mainly based on the steric complementarity between host and guest. The complexation energies obtained are in good agreement with the experimental formation constant. To apply CD in remediate gaseous effluent contaminated by chlorinated solvents, the use of β -CDs is more appropriate than α -CD. Study of the capacity of CDs to trap VOCs in a dynamic way is actually under investigation.

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