

## CYCLODEXTRINS: A POTENTIAL ABSORBENT FOR VOC ABATEMENT

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### ABSTRACT

The capacity of cyclodextrins in trapping VOCs is studied. Cyclodextrins (CDs) are a family of cyclic oligosaccharides that are composed of  $\alpha$ -1,4-linked glucopyranose subunits. The most notable feature of cyclodextrins is their ability to form inclusion complexes (host-guest complexes) in solution with a very wide range of solid, liquid and gaseous compounds by a phenomenon of molecular complexation. Inclusion in cyclodextrins exerts a profound effect on the physicochemical properties of guest molecules as they are temporarily locked within the host cavity giving rise to beneficial modifications of guest molecules. Cyclodextrins are non toxic compounds.

Volatile Organic Compounds (VOCs) are among the most common air pollutants emitted from chemical, petrochemical, and allied industries. VOCs are one of the main sources of photochemical reaction in the atmosphere leading to various environmental hazards; on the other hand, these VOCs have good commercial value. There are many techniques available to control VOCs emission (destruction based and recovery based) with many advantages and limitations. Absorption is one of the recovery techniques with a removal efficiency of 95 to 98% but its applications are limited to hydrosoluble VOCs.

The measurements of vapour liquid equilibrium (VLE) data in absence or in the presence of cyclodextrins were done. These data are needed to perform the design of an absorber for process application. The determination of Henry's law constant ( $H_c$ ) was achieved with a static headspace coupled with a gas chromatography (HS-GC). Moreover this technique permits us to calculate the association constant in the aqueous medium between the volatile solute and different cyclodextrins. The use of cyclodextrins may lead to a reduction of 95% of the Henry's law constant for some VOCs.

Dynamical studies were done by using impinger filled with an aqueous solution of cyclodextrin. By contacting a contaminated air with this solution, we observed the transfer of the VOCs from the gaseous phase to the liquid phase. These results show that by using cyclodextrins as liquid solvent, absorption can be used for the removal of a large variety of VOCs from gaseous effluents. The test in an absorber tower are also performed.

**KEYWORDS:** VOCs, cyclodextrins, absorption, vapour-liquid equilibria, Henry's law constant.

### 1. INTRODUCTION

Volatile Organic Compounds (VOCs) include most solvent thinners, degreasers, cleaners, lubricants, and liquid fuels. VOCs are the common air pollutants emitted by the chemical and petrochemical industries. Control of VOCs emission is a major concern of the industries commitment towards the environment. From an environmental point of view, it is necessary to limit and control vapour emissions because they affect the change of climate, the growth and decay of plants, and the health of human beings and all animals. New regulations regarding volatile organic compounds (VOCs) emissions demand more efficient and less costly technologies. There are many techniques available to control VOCs emission (destruction

based and recovery based) with many advantages and limitations. Absorption is used to remove VOCs from gas streams by contacting the contaminated air with a liquid solvent with a removal efficiency of 95 to 98%. Any soluble VOCs will transfer to the liquid phase. But among the most common VOCs (tetrachloroethane, methyl chloride, aromatic hydrocarbons...), there is a majority of poorly hydrosoluble compounds [1]. Many materials such as active carbons and active carbon fibers are presently studied with the aim to reduce pollutant emissions from gaseous or aqueous media. Cyclodextrin (CD) is also expected as one of them.

Cyclodextrins (CDs) are a family of cyclic oligosaccharides that are composed of  $\alpha$ -1,4-linked glucopyranose subunits [2]. Cyclodextrins are produced from starch by enzymatic degradation. The most common cyclodextrins are of three types :  $\alpha$ -cyclodextrin,  $\beta$ -cyclodextrin and  $\gamma$ -cyclodextrin, referred to as first generation or parent cyclodextrins.  $\alpha$ -,  $\beta$ - and  $\gamma$ -cyclodextrins are composed of six, seven and eight glycosyl units, respectively.  $\beta$ -Cyclodextrin is the most accessible, the lowest-priced and generally the most useful (see figure 1). Chemically modified  $\beta$ -cyclodextrins with higher solubility than the parent one are commercially available.

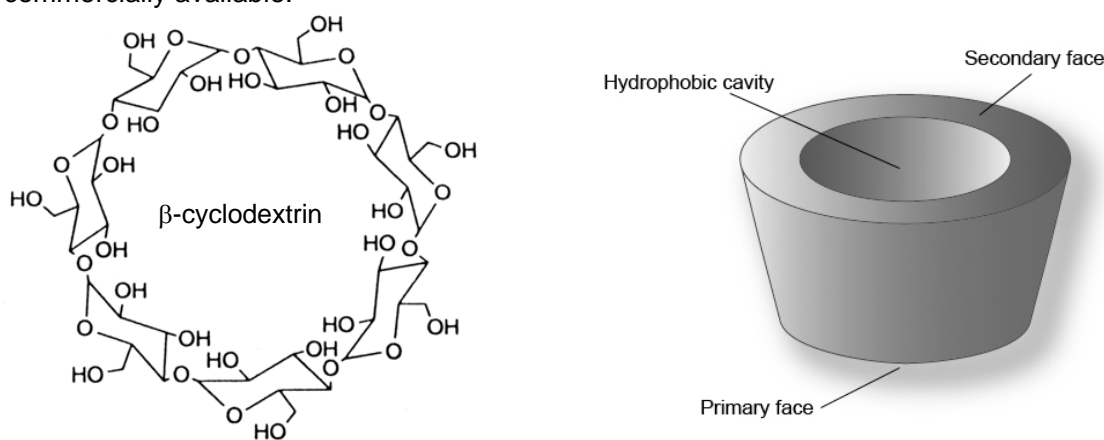


Figure 1. Chemical structure of  $\beta$ -cyclodextrin

These macrocyclic carbohydrates with apolar internal cavities can form complexes with a large variety of compounds (host-guest complexes). Since each guest molecule is individually surrounded by a cyclodextrin the molecule is micro-encapsulated from a microscopical point of view. This can lead to advantageous changes in the chemical and physical properties of the guest molecules :

- Stabilisation of light- or oxygen-sensitive substances,
- Modification of the chemical reactivity of guest molecules,
- Fixation of very volatile substances,
- Solubilisation of many normally water-insoluble compounds...

Cyclodextrins 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 [3].

Even if it is known that CD can reduce volatility of VOCs, very few studies have been reported on the inclusion complexation of these compounds. The aim of this work is to investigate the effect of cyclodextrins on air-water partitioning of some VOCs and to show the effectiveness of cyclodextrins in trapping these pollutants and reducing their volatility in the viewpoint of pollution prevention.

## 2. STATIC HEADSPACE STUDY

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 (HS-GC) is thus 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) [4].

The experiments were conducted using 22 ml glass vial filled with 10 ml of liquid samples of known concentration, a Genesis headspace autosampler and a Perkin Elmer Autosystem XL gas chromatography (GC). The GC was equipped with a capillary column (DB-624) and a flame ionization detector (FID). The temperature of the GC oven depends on the compound. After the equilibrium was established (30 mn), 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.

### 2.1. Vapor-Liquid Equilibria studies

Accurate vapor-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 the 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<sup>-1</sup>) and that in aqueous phase ( $C_{aq}$ ; mol l<sup>-1</sup>) at equilibrium :

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

A number of methods to determine Henry's constant have been presented in the literature. In this study, we use the phase ratio variation (PRV), based on the following equation :

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

where  $C_{aq,0}$  is the initial chemical concentration in the prepared liquid solution (mg ml<sup>-1</sup>),  $V_{aq}$  is the liquid sample volume added into the vial (mL),  $V_g$  is the headspace gas volume in the vial (ml),  $A$  is the integrated area counts of GC peak for a given sample, and  $\alpha$  is a specific parameter of the headspace defined by  $A = \alpha C_g$ . Equation 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  $H_c = \text{slope}/\text{intercept}$ .

However, the presence of chemical agents in solution is expected to impact  $H_c$  [5]. 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 cyclodextrin (see Figure 2).

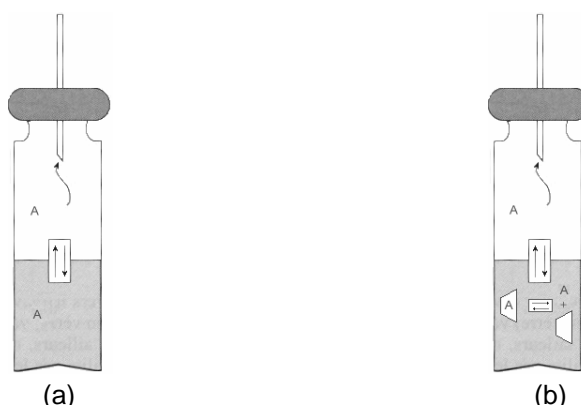


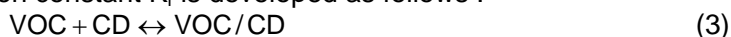
Figure 2. Illustration of the equilibrium for a VOC (A) between aqueous and gas phase in absence (a) and in the presence of cyclodextrin (b)

### 2.2. Formation constants

The stability constants for the inclusion of VOCs with  $\beta$ -cyclodextrin ( $\beta$ CD), hydroxypropyl- $\beta$ -cyclodextrin (HPBCD) and randomly-methylated- $\beta$ -cyclodextrin (RAMEB) in aqueous solution were determined at 30°C by a solubility method [6].  $\beta$ CD and HPBCD was a kind gift from

Roquette Frères (Lestrem, France), RAMEB were purchased from Wacker-Chimie (Lyon, France).

The VOC/CD system is characterised by a titration method. Different concentrations of cyclodextrin are used while the concentration of the VOC is constant. For a 1:1 molar ratio complex the calculation of formation constant  $K_f$  is developed as follows :



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

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

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 [7].

### 3. DYNAMICAL STUDY

In order to simulate the process existing in an absorption tower, we developed an experimental setting. A stable source of VOC is obtained by using a syringe pump. After equilibrium, the gaseous VOC is introduced in an aqueous solution of cyclodextrin by the way of an impinger. Variation of the concentration of VOC is followed by using a total hydrocarbon analyser (see Figure 3).

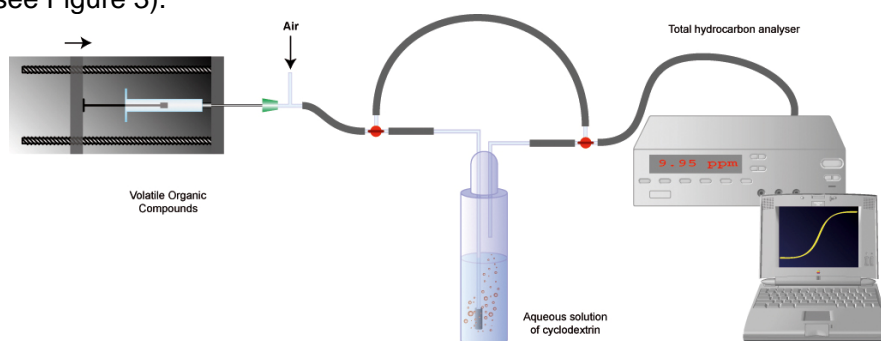


Figure 3. Experimental setting for the study of dynamical absorption

### 4. RESULTS

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. Results are presented for two VOCs: carbon tetrachloride (representative of halogenated hydrocarbon) and toluene (for aromatic compounds) at 30°C.

#### 4.1. Henry's Law Constant

The Henry's law constants for the VOCs in water and in solutions of various cyclodextrin's concentrations are shown in Table 1.

The results indicate that, at a given temperature,  $H_C$  decreases with increasing cyclodextrin concentration.  $\beta$ CD as a limited solubility (18.5 g l<sup>-1</sup>) so the use of modified  $\beta$ -cyclodextrins with higher solubility is of great interest in order to reduce the Henry's constant of the VOCs.

#### 4.2. Formation Constants

The stability of the inclusion complexes depends primarily on hydrophobic interactions and on size and shape considerations. The formation constant describes the stability of the inclusion complexes formed between cyclodextrins and guests. As we can see on Table 2, modified cyclodextrins have more affinities for the two VOCs.

Table 1. Henry's law constants

	$H_c$ (dimensionless)				
	Water	[CD] $\text{mol l}^{-1}$	$\beta\text{CD}$	HPBCD	RAMEB
Carbon tetrachloride	1.600	0.01	0.560	0.456	0.430
		0.05	-	0.144	0.080
Toluene	0.268	0.01	0.086	0.107	0.090
		0.05	-	0.031	0.025

Table 2. Formation constants ( $M^{-1}$ )

$K_f$ ( $M^{-1}$ )	$\beta\text{CD}$	HPBCD	RAMEB
Carbon tetrachloride	164	218	238
Toluene	142	163	171

#### 4.3. Absorption of toluene

We use 250 mL of an aqueous solution of cyclodextrin to trap toluene (600 ppm). All the studied cyclodextrins are more efficient than water. The capacity of a given cyclodextrin increases by increasing concentration. We choose HPBCD because this cyclodextrin is commercially available as an aqueous solution (40%). This cyclodextrin is actually tested at a pilot scale.

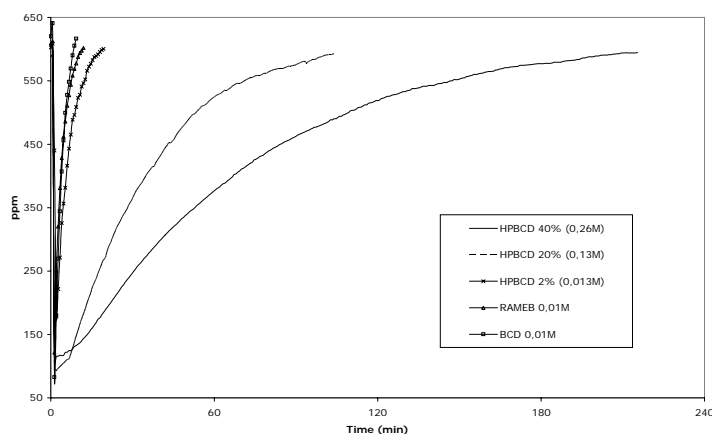


Figure 4. Absorption of toluene in an aqueous solution of cyclodextrin

## 5. CONCLUSIONS

Headspace gas chromatography has been used to study the solubilisation of VOCs by cyclodextrins. As we can see, the solubilisation capacity of cyclodextrins depends on the host-guest complementarity ( $K_f$ ) but also on the solubility of cyclodextrin. Thus, the use of high water solubility cyclodextrins, like sulfobutylether- $\beta$ -cyclodextrin (SBE), should confer great advantages in a possible industrial application for the removal of VOC from polluted air.

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