

VOC trapping by new crosslinked cyclodextrin polymers

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Abstract The first results about the trapping ability of new cyclodextrin polymers towards Volatile Organic Compounds (VOCs) from the gas phase and from water are presented. These polymers have been prepared by using a low methylated- β -cyclodextrin (CRYSMEB) and epichlorohydrin (EP) as a crosslinking agent. Several polymers with various EP/CRYSMEB ratio were synthesized. Polymerization was also conducted in the presence of a guest as template. The adsorption capacities of the obtained polymers towards toluene as a model aromatic compound have been investigated by static headspace gas chromatography (HSGC). First results showed that polymers seem to be efficient absorbents for toluene with values closed to CRYSMEB.

Keywords Cyclodextrin polymer · CRYSMEB · Epichlorohydrin · Adsorption · Volatile organic compounds

Abbreviations

β -CD	β -Cyclodextrin
CDs	Cyclodextrins
CRYSMEB	Low methylated- β -cyclodextrin
DS	Degree of substitution
EP	Epichlorohydrin
SHGC	Static headspace gas chromatography
VOCs	Volatile organic compounds

Introduction

Volatile Organic Compounds (VOCs) in effluent gas from industries have been known as the most hazardous materials which affect public health and welfare owing to their toxicity potential, carcinogenicity and stability [1]. Recently emission control of VOCs has become a major concern in air pollution prevention. Therefore, there is a need to develop technologies that can remove toxic pollutants found in gaseous effluent. There are many techniques available to control VOCs emission (destruction based and recovery based) with many advantages and limitations. Adsorption is a procedure of choice for treating industrial effluents, and a useful tool for protecting the environment. In particular, adsorption on natural polymers and their derivatives are known to remove pollutants from water [2]. Adsorption is used to remove VOCs from gas streams by contacting the contaminated air with a liquid solvent. Any soluble VOCs will transfer to the liquid phase. In the case of hydrophobic VOCs, water cannot be used and other kinds of absorbents are required. Cyclodextrins (CDs) are potentially useful sorbents for the sorption of aromatic hydrocarbons from the gas phase and water.

CDs have a low-polarity cavity in which organic compounds of appropriate shape and size can form inclusion complexes [3, 4]. This unique property provides CDs with a capacity to significantly increase the apparent solubility of low polarity organic compounds [5]. 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 [6–11]. Because they are water soluble, simple CDs cannot be used to either separate or eliminate specific components in aqueous media. A

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feasible solution is to incorporate CDs into polymeric structures. There has been considerable interest in the preparation and application of crosslinked CDs polymers. Polymers with β -cyclodextrin (β -CD) have been extensively studied in different fields such as analytical chemistry [12, 13], pharmaceutical and food industries [14–16] and waste water treatment [2, 17, 18]. One of the first and most frequently used crosslinkers is epichlorohydrin (EP). EP can react with the hydroxyl groups of CDs in basic media to yields ethers. Although it is considered to hazardous environmental pollutant and potential carcinogen, EP is widely used in chemical industries as intermediates for synthesis of many products (epoxy-resins, glycerine, polyurethane foam, surfactants, lubricants, drugs, etc.) [2]. α -, β -, and γ -cyclodextrin epichlorohydrin polymer products have been synthesized [19]. To the best of our knowledge, no polymers were prepared using CRYSMEB, a crystallised partially methylated β -CD with a DS = 4.9. Methyl groups are mainly located on the secondary rim of this β -CD derivative. Previous studies have underlined the inclusion capacities of CRYSMEB with VOCs and aroma component [10, 20, 21]. In this work, soluble and insoluble crosslinked EP/CRYSMEB polymers have been synthesized with or without guest as template. In fact, the ability to selectively recognize a target molecule in a vast pool of similar molecules is essential to biological and chemical processes. Molecular imprinting is a technique that introduces molecular memory in polymers and increases the accessibility and selectivity towards the guest molecules [22].

The capacities of the synthesized polymers to trap toluene, an aromatic VOC widely used as a solvent (paints and coatings, gums, resins, rubber), from the gas phase and from water have been investigated by static headspace gas chromatography (SHGC).

Materials and methods

Chemical

Toluene, sodium hydroxide and epichlorohydrin (Aldrich) of analytical reagent grade were used as received. CRYSMEB (DS = 4.9) were provided from Roquette Frères (Lestrem, France). Distilled deionised water was used throughout this work.

Synthesis

The polymerization of CRYSMEB with epichlorohydrin was carried out in aqueous media. Sodium hydroxide (5 g) and water (15 g) were mixed together in a flask, while the mixture was heated under stirring at 60 °C. CRYSMEB

was added slowly to the solution. Once the CRYSMEB dissolved, epichlorohydrin was added dropwise to the stirred solution at the rate of about 2 mL per every 15 min. After addition, the reaction mixture was kept at 60 °C for 4 h except for P2 (T = 90 °C) and for P3 (t = 3 h). Polymer precipitation was realised with ethanol. In some cases, toluene was introduced as template before the beginning of the polymerization step and kept under stirring with CRYSMEB during 20 min. The experimental conditions are summarized in Table 1.

Static headspace gas chromatography

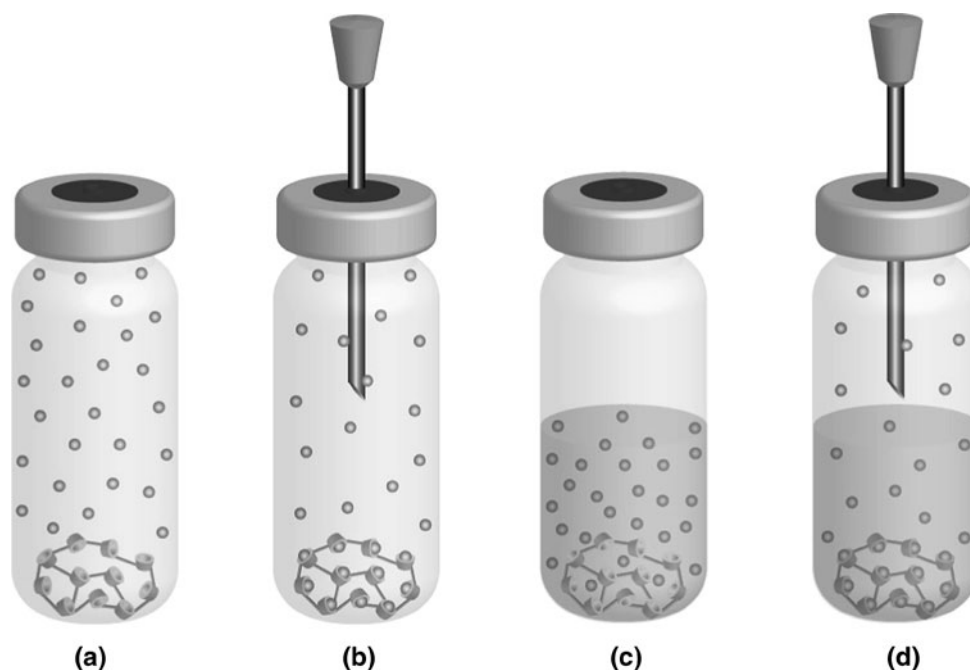
Headspace sampling is employed with gas chromatography (GC) in numerous fields and with a variety of applications [23, 24]. A headspace sample is in principle a gas sample which has been previously in contact with a liquid or solid sample from which volatile compounds were released into the gas with 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) [25].

Measurements were conducted with a Agilent headspace autosampler under solid support or aqueous media. The oven-dried adsorbents were weighed in glass vials of 22 mL in volume. For studies under aqueous media 10 mL of distilled deionised water were added in the vial. After addition of the sorbate with a microsyringe, the vial was sealed using silicone septa and aluminium foil. The vials were then thermostated at 30 ± 0.1 °C. After the equilibrium was established (24 h), 1 mL of vapour 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 (Fig. 1).

Table 1 Experimental conditions for the synthesis of polymers

Polymer	Imprinting	EP/CD	Guest/host	Soluble	Insoluble
1	–	3/1	–	+	–
2	–	5/1	–	+	+
3	–	5/1	–	+	+
4	–	10/1	–	+	+
5	–	15/1	–	+	+
6	–	24/1	–	+	+
7	–	40/1	–	–	+
8	+	40/1	2/1	–	+
9	+	40/1	3/1	–	+
10	+	40/1	4/1	–	+
11	+	40/1	1/4	–	+
12	+	40/1	1/2	–	+

Fig. 1 Illustration of the sorption experiment: addition of the sorbate in gaseous phase (a) or in water (c) and after equilibrium (b) and (d)



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 follows: detector temperature, 280 °C; column temperature, 80 °C during 6 min. The obtained chromatograms allow quantitative analysis of the vapour above each sample. Blank experiments (without sorbents) were used to account for sorption losses.

Results and discussion

A preliminary study concerning temperature, EP/CRYSMEB ratio and reaction time parameters was investigated to find the best conditions for polymerization. The results were closed to those described in the literature for β -CDs [26, 27]. The reaction was carried out in basic aqueous media to deprotonate the hydroxyl groups of CRYSMEB. Reaction between epichlorohydrin and CRYSMEB couldn't be managed, in such a way that different polymer reticulation could be get. Nevertheless, methyl groups on CRYSMEB avoid the formation of intralink between hydroxyl groups and epichlorohydrin.

Polymers were precipitated with ethanol and washed with water or organic solvents. Soluble polymers were dialysed during one night to remove all impurities (Spectra/Por® Dialysis membrane, MWCO: 1000).

Depending on the temperature, the gel point can be reached [26]. At low temperature, polymers were obtained under soluble form without any trace of insoluble forms. Gel point phenomena was around 60–65 °C, leading to

simultaneous formation of insoluble and soluble polymers.

The same procedure was employed with toluene as a template. No significant modifications were observed after polymerization, soluble and insoluble polymers were obtained as well. Toluene could be easily removed by drying in oven under vacuum.

Retention of toluene by cyclodextrin polymers

In solution, the presence of chemical agents is known to impact the vapour–liquid equilibrium [28]. In fact, the presence of CDs in aqueous solution involves a decrease of the Henry's law constant of VOCs by forming inclusion complexes [10]. Very few studies on the inclusion of VOCs into CDs have been undertaken in the gaseous phase [29–31]. It was found that the adsorption abilities of β -CD for adsorbing aromatic hydrocarbons from the gas phase and water have a similar trend [31].

In this study, we determine the capacities of our new CRYSMEB polymers to trap toluene from gas phase and water. In both cases, the percentage of retention (r) of the studied VOC by the different adsorbents is expressed as follows:

$$r(\%) = \left(1 - \frac{A_{CD}}{A_0}\right) \quad (1)$$

with A_0 and A_{CD} the peak area of the VOC in the absence and in the presence of CD respectively.

The percentage of retention was determined at 30 °C for a 5 ppm solution of the VOC and a weight of 30 mg for

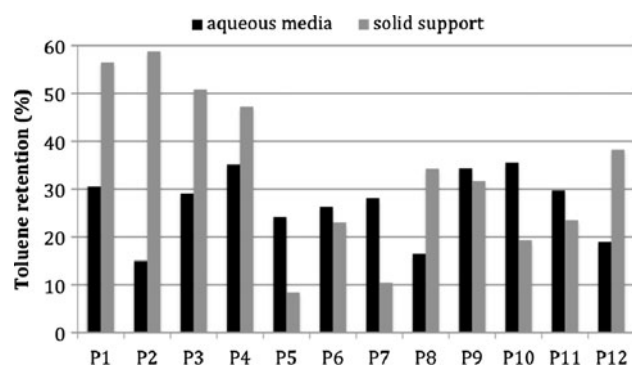


Fig. 2 Toluene retention from gas phase and water by the different polymers

CD polymers. For each adsorbent, measurements were done in triplicate. The results obtained for different polymers are presented in Fig. 2.

In aqueous media, the results are similar with an average value of 27%, no significant difference being observed between insoluble and soluble polymers.

Comparatively, in solid phase, the best results were obtained for small EP/CRYSMEB ratio, which may be due to a better accessibility of the CD cavity. Nevertheless, soluble and insoluble polymers should be used in fine powder for the reproducibility of the results. Difference between the results in aqueous media and solid support could be due to a better accessibility of toluene for cyclodextrins in gaseous phase.

Insoluble imprinted polymers (P9, P10, P11) trapped more efficiently toluene than insoluble polymers (P7) in gas phase and in water, showing that polymerization in presence of toluene limits the lock of CD cavities. For imprinted polymers, the complexed cyclodextrin concentrations during the synthesis are similar whatever the guest/host ratio (for ratio superior to unity), as may be estimated by means of the formation constant value between CRYSMEB and toluene [10]. This could explain the small effect of these ratios during trapping assays.

No attempts were run with soluble imprinted polymers to confirm the real importance of imprinting.

Conclusion

Novel water soluble and insoluble CRYSMEB polymers crosslinked with epichlorohydrin were synthesized. In these polymers, the ability of cyclodextrin cavities to make inclusion complexes with model pollutants has been probed by static headspace gas chromatography. To the best of our knowledge, it was the first report of VOC trapping by CD polymers from gaseous phase. The obtained results are promising for the use of CD polymers for organic

pollutants remediation. Further investigations are underway to characterize polymers and to study the dynamic VOC trapping.

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