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Complexation of Volatile Organic Molecules from the Gas Phase with Cucurbituril and β -Cyclodextrin

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The first results about the complexing ability of the supramolecular ligand cucurbituril with different volatile organic molecules from the gas phase are presented. The behaviour of cucurbituril is similar to that of β -cyclodextrin. The capacity of both ligands was determined with toluene. Columns filled with β -cyclodextrin and cucurbituril have a capacity of 0.50 and 0.42 mol toluene per mol ligand, respectively. The extraction of volatile molecules is not limited to toluene, also several other organic molecules are complexed from the gas phase. The fluorescence spectra of the solid naphthalene and aniline complexes with cucurbituril and β -cyclodextrin are presented. Comparing the differential scanning calorimetry (DSC) curves of cucurbituril, the cucurbituril toluene complex and silica gel with adsorbed toluene shows that a complexation and no adsorption takes place.

Keywords: Cucurbituril, cyclodextrin, complexes, gas phase

INTRODUCTION

The complex formation between macrocyclic and macrobicyclic ligands with suitable guests in solution has been described in numerous articles [1–4]. The solvation of the ligands and guests plays an important role for the stability

of the complexes formed. However, also complexation reactions of these ligands in heterogeneous systems are known. So it is possible *e.g.* to extract cations from aqueous solution to an organic solvent using crown ethers or cryptands [5,6]. The extraction equilibrium is mainly influenced by the anion. Also extraction processes between solid ligands and dissolved guest molecules take place. Cations can be separated from solutions using polymeric bound ligands [7–9]. Halogenated organic molecules are removed from the aqueous phase using calixarenes [10]. Only few examples for complexation reactions between gaseous molecules and solid ligands have been reported. For a long time, solid cyclodextrins have been used in gas chromatography for the separation of various compounds [11]. The retention times were found to differ due to the complexation. So even different isomeric molecules can be detected. A further analytical application is the preconcentration of volatile polycyclic aromatic hydrocarbons (PAH) with β -cyclodextrin [12]. Some macrocyclic ligands are used as selective complexation agents in gas sensors. Crown

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ether complexes [13, 14], cyclodextrins [15, 16] and calixarenes [17] are suitable host-molecules for the detection of aromatic halogenated hydrocarbons and organic solvents. In the case of the complexation of gaseous neutral molecules by host molecules only interactions like the molecule dimension and the possible hydrophobic or hydrophilic interactions between guest and host are important [18].

The complexation abilities of the supramolecular host molecule β -cyclodextrin with different neutral volatile organic molecules have been described [11,12]. The ligands β -cyclodextrin and cucurbituril have similar properties. Both ligands have a rigid structure and a hydrophobic cavity. Up to now nothing is known about the complexation ability of cucurbituril for molecules from the gas phase. So this paper presents the first results on the extraction of organic molecules from air using solid cucurbituril.

EXPERIMENTAL

The macrocyclic ligand cucurbituril was synthesized as described in the literature [19]. The ligand was recrystallized several times by adding distilled water into a solution of cucurbituril in concentrated hydrochloric acid. The elemental analysis of the ligand is in accordance with those reported in the literature [20–22].

Toluene, xylene, naphthalene, 1-hexanol, aniline, 2-chlorophenol, 1,2-dichlorobenzene, 3-methylphenol, pentylamine, hexane (all Fluka) and silica gel (Kieselgel 100, 35–70 mesh ASTM, Merck) were used without further purification. Before the complexation experiments cucurbituril and β -cyclodextrin (Wacker) were dried at 150 °C for 4 hours.

The complexation of organic molecules from the gas phase by cucurbituril and β -cyclodextrin was studied as follows: air and vapor of the organic substances were passed through a column filled with the solid ligand. The columns

were plugged up with glass wool at both ends. The air flow rate through the columns was 100 ml/min. The reaction time was two hours. The adsorption of toluene on the surface of silica gel was performed in the same manner. The determination of the complexed molecules in the column was carried out after extracting the ligands with acetone. The extracts were analysed using gas chromatography/mass spectrometry analysis (Hewlett-Packard, GC 5890 series II and MSD 5972 series).

The fluorescence spectra of naphthalene and aniline are obtained by measuring the solid column material using 275 nm and 230 nm as excitation wavelength, respectively (Fluorescence Spectrometer LS-3B, Perkin-Elmer). In the case of the naphthalene complex with β -cyclodextrin the column material was mixed with pure β -cyclodextrin due to the high amount of complexed naphthalene which leads to an overrange of the fluorescence signal.

The differential scanning calorimetry curves (DSC) of the pure ligands and the corresponding complexes were recorded using TA-Instrument DSC TA 2000.

RESULTS AND DISCUSSION

The structures of β -cyclodextrin and cucurbituril are shown in Figure 1. β -Cyclodextrin and cucurbituril have an approximate inner cavity diameter of 0.65 nm [23] and 0.55 nm [21], respectively. The cavities of both molecules are hydrophobic. These properties enable both supramolecular molecules to incorporate guest molecules based on size and hydrophobicity. Due to the complexation of volatile organic molecules from the gas phase the weight of columns filled with solid β -cyclodextrin or cucurbituril increases. The increasing weight allows the determination of the ligand capacity for volatile organic molecules. This is shown in Figure 2. Under the given experimental conditions the maximum capacity of β -cyclodextrin

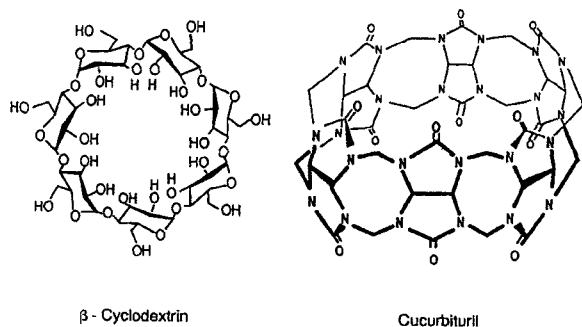


FIGURE 1 Chemical structures of β -cyclodextrin and cucurbituril.

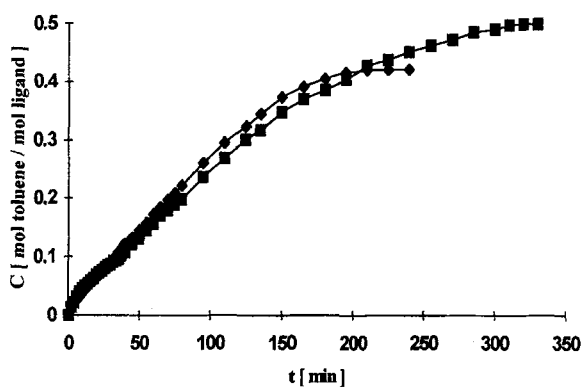


FIGURE 2 Load C versus the time of exposure of columns with cucurbituril (\blacklozenge) and β -cyclodextrin (\blacksquare) for the complexation of toluene from the gas phase.

and cucurbituril is 0.50 and 0.42 mol toluene per mol ligand, respectively. In both cases not all ligand molecules are accessible to toluene. The weight of the cucurbituril filled column increases faster than that of a column with β -cyclodextrin. This observation may be explained by differences of the complex stability.

The complexation of volatile organic molecules by β -cyclodextrin and cucurbituril is not limited to toluene, also several other compounds are bound from the gaseous phase. A list of the examined compounds is given in Table I. Aromatic molecules with different substituents at the benzene ring form complexes with both ligands. The influence of the substituents upon

TABLE I Selected organic substances complexed from the gas phase by cucurbituril and β -cyclodextrin (+, detectable complex formation; -, no detectable complex formation)

Substance	cucurbituril	β -cyclodextrin
toluene	+	+
xylene	+	+
naphthaline	+	+
aniline	+	+
2-chlorophenol	+	+
1,2-dichlorobenzene	+	+
3-methylphenol	+	+
1-hexanol	+	+
hexane	-	-
pentylamine	+	+

the complex formation will be investigated subsequently. Even aliphatic compounds can be separated from the gas phase which is shown by the complexation of pentylamine and hexanol.

The formed complexes with naphthaline and aniline show fluorescence emissions. The spectra of the naphthalene complex with solid cucurbituril and β -cyclodextrin are presented in Figure 3. The much higher fluorescence signal of the β -cyclodextrin complex than the signal of the cucurbituril complex shows the high affinity of naphthalene for β -cyclodextrin. This is explained by the different cavity dimensions of the supramolecular ligands. Naphthalene fits better into the larger cavity of β -cyclodextrin than into cucurbituril. The different intensities of the fluorescence signal between the cucurbituril complex and the β -cyclodextrin complex is not observed with aniline. In this case the signal intensity of both complexes is similar.

The difference between complexation and adsorption of organic molecules is examined by comparing the cucurbituril toluene complex and silicagel with adsorbed toluene on its surface. Silicagel also shows a high affinity for toluene. Pumping an air-toluene mixture through a column it is possible to achieve a capacity of 0.38 g toluene/g silicagel. Under the same conditions the value of 0.039 g toluene/g cucurbituril is much smaller. The adsorption of toluene on silica gel leads to a much higher capacity than it is possible for a host-guest

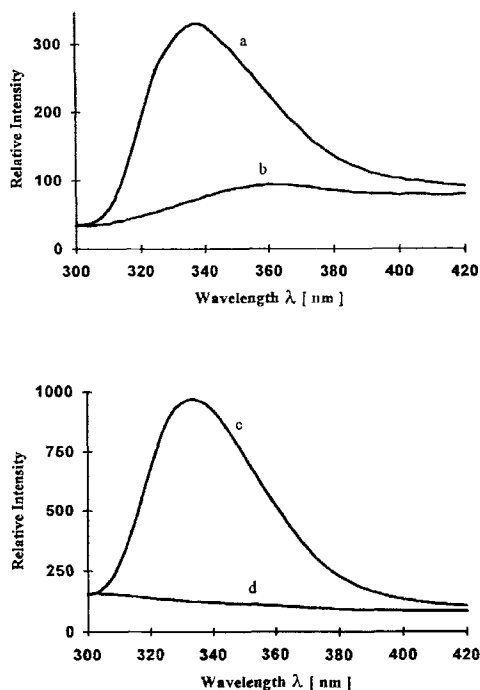


FIGURE 3 Fluorescence spectra (excitation wavelength 275 nm) of the naphthalene cucurbituril complex (a), cucurbituril (b), naphthalene β -cyclodextrin complex (c) and β -cyclodextrin (d).

complexation with cucurbituril. Therefore, the two column materials show a different behaviour in the DSC analysis. This is shown in Figure 4. Heating silicagel with adsorbed toluene a peak three degrees above the boiling point of toluene (111°C) is observed. The adsorbed toluene desorbes from the surface of the silicagel. In contrast no peak can be detected at the DSC spectra of the cucurbituril complex at the same temperature. The decomplexation of toluene from the cucurbituril complex starts at about 125°C. This indicates that strong interactions between cucurbituril and toluene take place.

CONCLUSION

The first results obtained by using cucurbituril as a ligand for the complexation of organic molecules from the gas phase show that cucur-

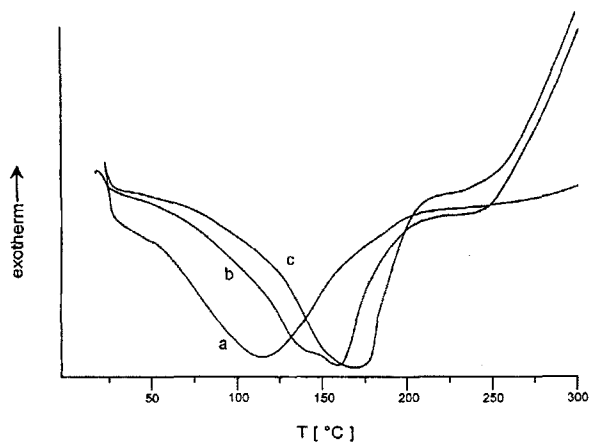


FIGURE 4 Differential scanning calorimetry curves of silicagel with adsorbed toluene on its surface (a), cucurbituril toluene complex (b) and cucurbituril (c).

bituril and β -cyclodextrin have similar properties. The complexation of volatile organic molecules is significant and suggests a potential use for the separation of organic molecules from the gas phase. However, more work is necessary to get quantitative results about the factors influencing the formation of complexes between cucurbituril and volatile organic molecules.

Acknowledgement

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