

# Removal of Organic Pollutants from Water via Molecular Inclusion within a Cavitand

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**Abstract.** The molecular inclusion chemistry of cavitands provides a useful way for the removal of organic pollutants from water. A wide range of lipophilic organic compounds, present at trace level in water, are efficiently extracted by cavitand **1**, which can be easily reactivated and reused.

**Key words.** Cavitands, molecular inclusion, partition coefficient between octanol and water, organic pollutants, wastewater treatment.

## 1. Introduction

The problem of water contamination has already reached a critical level in several countries and the need for effective treatment of both municipal and industrial wastewater is well known. Treatment Technology utilize physical, chemical and biological methods [1]. Selection depends primarily on the type of pollutants and the effluent-discharge criteria. Treatment of the organic material, especially at trace level, is normally carried out by membrane separation, chemical treatment and adsorption [2].

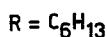
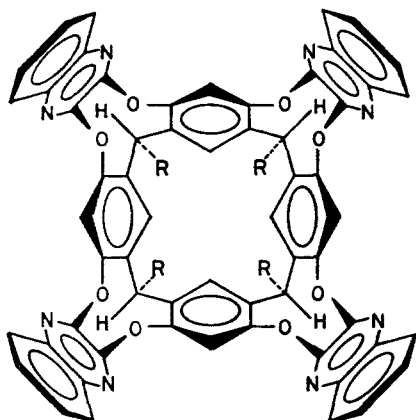
During the course of our studies on the complexation properties of macrocycles towards neutral organic molecules we realized that molecular inclusion chemistry could be a valuable answer to the wastewater treatment problem [3]. Among many different host macrocycles studied so far, cavitands, synthetic organic compounds with enforced concave surfaces of molecular dimensions [4], seemed particularly suitable for this purpose.

Cavitand **1** presents a 7.2 Å wide and 8.3 Å deep lipophilic cavity with a strong tendency to engulf organic compounds [5, 6]. Several 1:1 cavitates were isolated and characterized by <sup>1</sup>H-NMR and elemental analyses. Thermogravimetric analyses show the high thermal stability of such complexes. In most cases dissociation occurs at temperatures well above the boiling point of the guest component, which indicates that guests are tightly included in the host cavity (Table I).

Here we report that the water-insoluble, empty cavitand **1**, obtained by heating any cavitare above 260°C, is able to remove a wide variety of organic pollutants from water via molecular inclusion.

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Table I. Dissociation temperatures of 1⊂guest complexes,<sup>a</sup> compared with the boiling points of the pure guests. The values of  $T_{\text{diss}}$  are obtained from thermogravimetric analyses.

Guest	b.p. (°C)	$T_{\text{diss}}$ (°C)	$\Delta T$ (°C)
DMF	153	200	47
Acetone	56	140	84
Ethyl acetate	76	185	109
CH <sub>2</sub> Cl <sub>2</sub>	40	154	114
CHCl <sub>3</sub>	61	209	148
CCl <sub>4</sub>	77	262	185
C <sub>6</sub> H <sub>5</sub> —NCO	165	195	30
C <sub>6</sub> H <sub>5</sub> —CN	188	220	32
C <sub>6</sub> H <sub>5</sub> —Cl	132	212	80
C <sub>6</sub> H <sub>6</sub>	80	169	89
C <sub>6</sub> H <sub>5</sub> —CH <sub>3</sub>	111	201	90
C <sub>6</sub> H <sub>5</sub> —F	85	215	130

<sup>a</sup>1 decomposes at  $T > 400^\circ\text{C}$ .

## 2. Experimental

ACS grade reagents were used without further purification. Analytical TLC was conducted on precoated Merck silica gel 60 plates. NMR spectra were recorded on a Bruker AM-300 spectrometer. Mass spectra were recorded on a Finnigan MAT 8400 spectrometer, using the DCI technique. Elemental analyses were performed by the microanalytical laboratory of the Donegani Institute. Thermogravimetric analyses were performed using a Perkin-Elmer TGA-7. Solid phase extraction of the micropollutants was conducted on C<sub>18</sub> silica gel columns (Bakerbond spe 6 ml; J. T.

Baker). GLC analyses were carried out with a Carlo-Erba Mega 5300 instrument, equipped with NPD, FID and ECD detectors.

Cavitand **1** was prepared by reacting the macrocyclic octol forming the bottom part of the cavity [7] with four equivalents of 2,3-dichloroquinoxaline under basic conditions [5]. Here we report a procedure for a multigram scale preparation of **1**.

*r*-9,*c*-11,*c*-13,*c*-15-Tetrahexyl-7,17:8, 16-dimetheno-9*H*,11*H*,13*H*,15*H*-quinoxalino-[2''',3''':2'',3'''] [1,4]benzodioxonino[10''',9''':5,6]quinoxalino[2',3':2',3']quinoxalino[2'',3'':2'',3'''] [1,4]dioxonino[6'',5'':9',10''] [1,4]benzodioxonino[6',5':9,10] [1,4]benzodioxonino[2,3-*b*]quinoxaline(**1**)

To a solution, stirred under argon, of 66.01 g (80 mmol) of octol [7] and 75.95 g (366 mmol) of 2,3-dichloroquinoxaline in 1300 mL of dry DMSO, 63.75 g (461 mmol) of potassium carbonate were added. The suspension was stirred at 50°C for 72 h, monitoring the consumption of 2,3-dichloroquinoxaline by TLC (eluant 7:3 hexane/ethyl acetate). The suspension was then poured into water (1300 mL) and acidified with 70 mL of concentrated hydrochloric acid. The precipitate formed was filtered and washed to neutrality with water. The crude precipitate (110 g) was crystallized twice with 9:1 ethyl acetate/chloroform (3000 mL for each crystallization batch) giving 52.1 g (49% yield) of pure **1** as white crystals. More product can be obtained from the remaining crude by column chromatography (silica gel, eluant 7:3 hexane/ethyl acetate).

The solvent trapped into the cavity was removed by heating the crystals of **1** at 260°C for four hours under vacuum ( $1 \times 10^{-2}$  mm Hg).

Before being used in water treatment tests, empty **1** was passed through a 200 mesh sieve, in order to obtain a uniform powder with a large surface area.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.92 (12H, *t*,  $\text{CH}_3$ ,  $J = 6.7$  Hz), 1.23–1.47 [32H, *m*,  $(\text{CH}_2)_4$ ], 2.26 (8H, *m*,  $\text{CH}_2\alpha$ ), 5.52 (4H, *t*,  $\text{CH}$ ,  $J = 7.9$  Hz), 7.20 (4H, *s*, Ar—H), 7.45–7.50 (8H, *m*, AA' part of the quinoxaline AA'BB' system), 7.77–7.82 (8H, *m*, BB' part of the quinoxaline AA'BB' system), 8.13 (4H, *s*, Ar—H).

*DCI-MS* (isobutane),  $m/z$  1328 ( $\text{M}^-$ , 100%).

*Anal. Calcd.* for  $\text{C}_{84}\text{H}_{80}\text{N}_8\text{O}_8$ : C, 75.88; H, 6.06; N 8.43. *Found*: C, 75.80; H 6.11; N 8.40.

#### *Preparation of 1 ⊂ Toluene cavitate (typical procedure)*

Toluene (0.14 g, 1.5 mmol) was added to a stirred solution of **1** (0.5 g, 0.38 mmol) in 1000 mL of acetone at room temperature. After a few minutes a white solid began to precipitate. The suspension was stirred for 30 min, then filtered, the solid collected and dried under reduced pressure ( $5 \times 10^{-2}$  mmHg) at 50°C until constant weight. A portion of the solid was dissolved in  $\text{CDCl}_3$ , and submitted to  $^1\text{H-NMR}$  analysis. A 1:1 ratio between **1** and toluene was determined by careful integration of selected peaks. A dissociation temperature of 201°C was measured by thermogravimetric analysis with a weight loss of 6.40% (calculated value for the 1:1 complex: 6.48%).

*Anal. Calcd.* for  $\text{C}_{84}\text{H}_{80}\text{N}_8\text{O}_8 \cdot \text{C}_7\text{H}_8$ : C, 76.88; H, 6.24; N 7.88. *Found*: C, 76.85; H 6.24; N 7.80.

Working water solutions contaminated with organic materials were prepared by diluting with water aliquots of standard solutions of pollutants in *n*-propanol, a solvent which is not complexed by **1**. Water treatment tests were carried out by dispersing the desired quantity of **1** in a known volume of contaminated water in a sealed glass reactor. Every test was made at three different scale volumes: 0.1, 1 and 10 L. Blank tests without **1**, from which the initial concentration of pollutants  $[M]_0$  was determined, were conducted in parallel to the treatment tests, in each case using the same mother solution. In this way any possible loss of organic material due to sample handling was taken into account. After the desired treatment time, the aqueous suspension was filtered through a 40–60  $\mu$  Buchner funnel. The recovered solid, reactivated under vacuum ( $1 \times 10^{-2}$  mmHg) at 260°C for four hours, was ready for a new cycle without any detectable loss of activity. The residual concentration of pollutants, both in the treated and blank solutions, was determined via standard quantitative analyses.

The following analytical methods have been set up in order to evaluate the complexing performances of cavitands:

- determination of aromatic amines and aromatic derivatives containing nitrogen: the method is based on a solid phase extraction with a  $C_{18}$  derivatized silica gel column, followed by capillary gas-chromatographic analysis with a nitrogen-phosphorus detector (NPD).
- determination of halogenated aromatic solvents: the method is based on a solid phase extraction with a  $C_{18}$  derivatized silica gel column, followed by capillary gas-chromatographic analysis with an electron capture detector (ECD).
- determination of naphthalene: the method is based on a solid phase extraction with a  $C_{18}$  derivatized silica gel column, followed by capillary gas-chromatographic analysis with a flame ionization detector (FID).
- determination of chlorobenzene: the method is based on capillary gas-chromatographic analysis and flame ionization detection, according to the head-space procedure.
- determination of halogenated aliphatic solvents: the method is based on capillary gas-chromatographic analysis and electron capture detection according to the head-space procedure.

### 3. Results and Discussion

Table II reports examples of three classes of organic compounds efficiently removed after treatment with **1**: chlorinated hydrocarbons, aromatic hydrocarbon derivatives, aromatic amines. The cavitand concentration in water was  $1 \text{ g L}^{-1}$ ; a concentration of  $0.2 \text{ g L}^{-1}$  caused an average 25% decrease of complexing efficiency, while no substantial increase was found at higher concentrations. The extracting power is not affected by the concentration of the pollutants: very small variations were detected in the range  $1\text{--}100 \mu\text{g L}^{-1}$ . The residence time of **1** in water is an extremely important factor for the extracting efficiency: over 70% of the compounds reported in Table II were extracted by at least 50% after 30 min, by 75% after 165 min and by 90% after 960 min.

A substantial increase in complexing efficiency was found using ultrasonic instead of mechanical stirring (Table III). Ultrasound provided a better dispersion of the

Table II. Cavittand I ( $1.0 \text{ g L}^{-1}$ ) extracting efficiency of some organic compounds (mechanical stirring). In brackets are reported the percentage extracted.  $[M]_0$  = initial concentration in  $\mu\text{g L}^{-1}$ ;  $[M]^n$  = residual concentration in  $\mu\text{g L}^{-1}$  after  $n$  min;  $\log P_{\text{oct}}$  = partition coefficient between octanol and water.

Compound	$[M]_0$	$[M]^{30}$	$[M]^{165}$	$[M]^{960}$	$\log P_{\text{oct}}$
Dichloromethane	26.7	3.2 (88)			
Chloroform	29.8	23.5 (21)		4.8 (84)	1.97
Carbon tetrachloride	31.0	10.2 (67)		2.5 (92)	2.64
Trichlorofluoromethane	31.5	1.4 (96)			
1,1,2,2-Tetrachloroethane	8.0	0.4 (95)		0.4 (95)	2.39
Pentachloroethane	8.0	0.2 (97)		0.2 (97)	2.89
1,1-Dichloroethylene	25.0	12.7 (49)		1.5 (94)	
Trichloroethylene	29.3	12.0 (59)		1.8 (94)	2.42
Tetrachloroethylene	32.6	5.3 (84)		1.0 (97)	2.88
Benzene	87.9		23.0 (74)		2.13
Toluene	86.7		15.0 (83)		2.69
<i>m</i> -Xylene	86.4		11.5 (87)		3.20
Ethylbenzene	86.7		7.5 (91)		3.15
Styrene	90.7		6.0 (93)		
Naphthalene	89.7	5.2 (94)	3.2 (96)	4.5 (95)	3.37
Benzonitrile	100.5		25.0 (75)		1.56
Fluorobenzene	102.6		28.0 (73)		2.27
Chlorobenzene	93.6	7.2 (92)	4.7 (95)	3.6 (96)	2.84
1,2-Dichlorobenzene	102.5	13.5 (87)	5.1 (95)	7.4 (93)	3.38
1,2,4-Trichlorobenzene	99.6	7.6 (92)	4.4 (96)	3.9 (96)	4.04
1,3,5-Trichlorobenzene	97.8	14.1 (86)	8.9 (91)	8.1 (92)	4.08
Nitrobenzene	94.9	24.1 (75)	3.6 (96)	0.5 (99)	1.85
2-Chloronitrobenzene	114.0	48.5 (58)	10.5 (91)	2.2 (98)	2.24
3-Chloronitrobenzene	89.9	24.1 (73)	14.6 (84)	15.4 (83)	2.46
4-Chloronitrobenzene	124.5	18.4 (85)	6.3 (95)	3.1 (97)	2.39
2,5-Dichloronitrobenzene	91.7	11.0 (88)	2.0 (98)	0.9 (99)	2.90
3,4-Dichloronitrobenzene	102.5	11.2 (89)	4.5 (96)	1.5 (98)	3.12
Pentachloronitrobenzene	108.4	4.0 (96)	2.5 (98)	4.5 (96)	4.18
Aniline	91.5	42.9 (53)	49.0 (46)	31.1 (66)	0.98
2-Chloroaniline	99.8	51.1 (49)	28.3 (72)	12.0 (88)	1.90
3-Chloroaniline	85.2	49.8 (42)	27.5 (68)	18.1 (79)	1.88
4-Chloroaniline	103.5	52.6 (49)	47.4 (54)	7.3 (93)	1.83
2,3-Dichloroaniline	89.7	32.4 (64)	11.5 (87)	6.0 (93)	2.78
3,4-Dichloroaniline	101.4	40.1 (60)	32.4 (68)	28.5 (72)	2.69
3,5-Dichloroaniline	103.6	39.6 (62)	12.3 (88)	7.3 (93)	2.90
5-Chloro-2-methylaniline	85.8	38.8 (55)	14.2 (83)	7.1 (92)	
2-Nitroaniline	94.2	77.0 (18)	24.6 (74)	9.7 (90)	1.44
3-Nitroaniline	95.4	51.8 (46)	38.8 (59)	29.7 (69)	1.37
4-Nitroaniline	102.0	51.8 (49)	23.9 (77)	2.7 (97)	1.39
2-Chloro-4-nitroaniline	98.2	50.2 (49)	11.5 (88)	3.0 (97)	
4-Chloro-2-nitroaniline	93.1	44.7 (52)	10.7 (88)	3.5 (96)	2.72
2,6-Dichloro-4-nitroaniline	82.5	26.8 (67)	12.3 (85)	4.2 (95)	
2-Methoxyaniline	104.6	53.9 (48)	54.5 (48)	58.6 (44)	0.95
4-Chloro-2-methoxyaniline	97.3	52.5 (46)	16.6 (83)	6.7 (93)	

Table III. Effect of mechanical stirring (200 rpm) versus ultrasound (48 KHz frequency) on the extracting efficiency of cavitand **1** ( $1.0 \text{ g L}^{-1}$ ). In brackets are reported the percentage extracted.  $[M]_0$  = initial concentration in  $\mu\text{g L}^{-1}$ ;  $[M]^n$  = residual concentration in  $\mu\text{g L}^{-1}$  after  $n$  min.

Compound	$[M]_0$	$[M]^{30}$ mechanical	$[M]^{30}$ ultrasound
2-Methylaniline	11.4	7.1 (38)	4.7 (59)
2,6-Diethylaniline	9.0	2.4 (73)	0.9 (90)
4-Chloroaniline	11.0	5.8 (47)	4.1 (63)
2,6-Dichloroaniline	9.3	2.3 (75)	1.6 (83)
3,4-Dichloroaniline	11.2	3.1 (72)	2.7 (76)
2,6-Dichloro-4-nitroaniline	8.2	1.9 (77)	1.2 (85)

solid in water and a larger contact area between the particles of **1** and the aqueous solution, thus increasing the probability of contact between host and guest.

The driving force for complexation is the hydrophobicity of the organic pollutants, which prefer the lipophilic cavity of **1** to water solvation. Aromatic amines are less efficiently removed from water with respect to the other, more lipophilic, aromatic derivatives.

For a given molecule the partition coefficient between octanol and water is a quantitative measure of its hydrophobicity [8]. In our case we noticed that the compounds extracted by at least 50% have a  $\log P_{\text{oct}} \geq 0.95$ . The threshold value for complexation is about 0.7 (i.e. ethyl acetate:  $\log P_{\text{oct}} = 0.73$ ; only 17% extracted). However there is no direct correlation between partition coefficient and extracting power, which means that other interactions still play a role. For instance *meta* substitution in aromatic derivatives depress complexation with respect to *ortho* and *para* substitution, even if the partition coefficients are comparable (Table II).

#### 4. Conclusion

Through molecular inclusion chemistry, a new, extremely efficient and versatile adsorbing agent has been developed, capable of extracting at the same time a wide variety of organic pollutants from water up to the ppb level. Besides, the capability of cavitand **1** to remove a given compound from water can be predicted on the basis of the partition coefficient between octanol and water of the latter.

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