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Cucurbituril and β-Cyclodextrin as Hosts for the Complexation of Organic Dyes

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Abstract. The complexation of neutral organic molecules by cucurbituril and β-cyclodextrin in formic acid was studied by means of spectrophotometric titrations. In the case of β-cyclodextrin the composition of the solvent has almost no influence upon the stability of the complexes formed. This situation is completely different for cucurbituril. Due to its interactions with protons the measured stability constants of the complexes formed with organic molecules increase with decreasing acid concentration. At low acid concentrations cucurbituril forms more stable complexes with organic molecules than β-cyclodextrin.

Key words: Cucurbituril, β-cyclodextrin, dye molecules, complex formation.

1. Introduction

The formation of complexes with β-cyclodextrin is well known [1–4]. Many other synthetic host molecules which are able to encapsulate organic molecules are known [5, 6]. The interior of the cavities of the host molecules shows a hydrophobic character [7]. Thus hydrophobic interactions are mainly responsible for the complex formation between these ligands and organic molecules [8].

The structure of the host molecule cucurbituril, see Figure 1, has been known for some years [9]. Two review articles on cucurbituril have been published recently [10, 11]. This host molecule also possesses a hydrophobic cavity for the inclusion of suitable guest molecules. Thus, the complexation of a large number of different amines and diamines [12] and even the reaction between two complexed amines was observed [13]. This ligand forms insoluble complexes with dye molecules which are too big to be encapsulated completely within the cavity [14–17]. However, with one exception [18], nothing is known about the complex formation between cucurbituril and dye molecules in solution.

The formation of dye complexes with different host molecules has been studied by means of NMR spectroscopy [5, 19], UV-VIS spectroscopy [20–22] and other experimental techniques [5, 22].

Since cucurbituril is soluble in formic acid [12] the complex formation of cucurbituril and β-cyclodextrin was studied in this solvent, together with the influence of the solvent composition upon complex formation.

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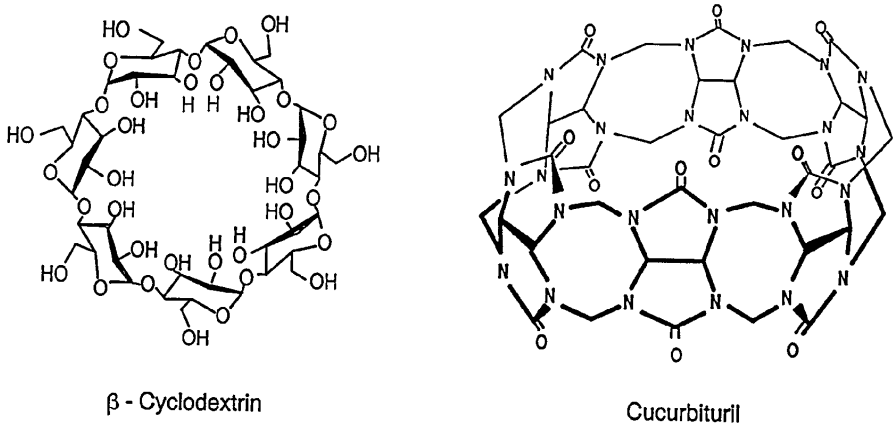

Figure 1. Chemical structures of the host molecules cucurbituril and β-cyclodextrin.

2. Experimental

The cucurbituril host molecule was synthesized according to the procedure described in the literature [23, 24]. The pure host was obtained after several recrystallizations from acidic solution. Cucurbituril was characterized using fast-atom bombardment mass spectral analysis, elemental analysis and ^{1}H- and ^{13}C-NMR spectroscopy [25]. β-cyclodextrin was used as purchased (Wacker) without further purification. The chemical structures of both ligands are given in Figure 1.

The guest molecules 4-methylbenzylamine (Fluka), 1,4-phenylene diamine (Fluka), methyl orange, orange II and orange IV (all Fluka) were also used without further purification. The dyes direct orange 39 and direct orange 40 (Bayer AG) were purified by column chromatography. For the chemical structures of the dye molecules see Figure 2.

Mixtures (by volume) of bidistilled water and formic acid (Fluka) were used as solvent.

All spectra were recorded using a Hewlett Packard Spectrophotometer Model 8452A. For each guest molecule the extinction of solutions containing the pure guest was measured as a function of its concentration. A solution with an identical concentration of formic acid was used as reference. In this way the concentration range of the guest molecules was determined in which no aggregation took place. The complex stabilities were measured at guest concentrations below the concentration at which dimerization occurs [26, 27]. At this concentration no aggregation was observed even in 40% formic acid. Variable amounts of the host molecules were added to these dye solutions (1–4 $\times$ 10^{-5} mol dm^{-3}). The change in the absorbance due to complex formation with β-cyclodextrin or cucurbituril was observed. The complex formation between methyl orange and cucurbituril could only be studied in aqueous solutions containing 40 or 30% formic acid. At lower acid concentrations insoluble complexes of this dye molecule with cucurbituril are

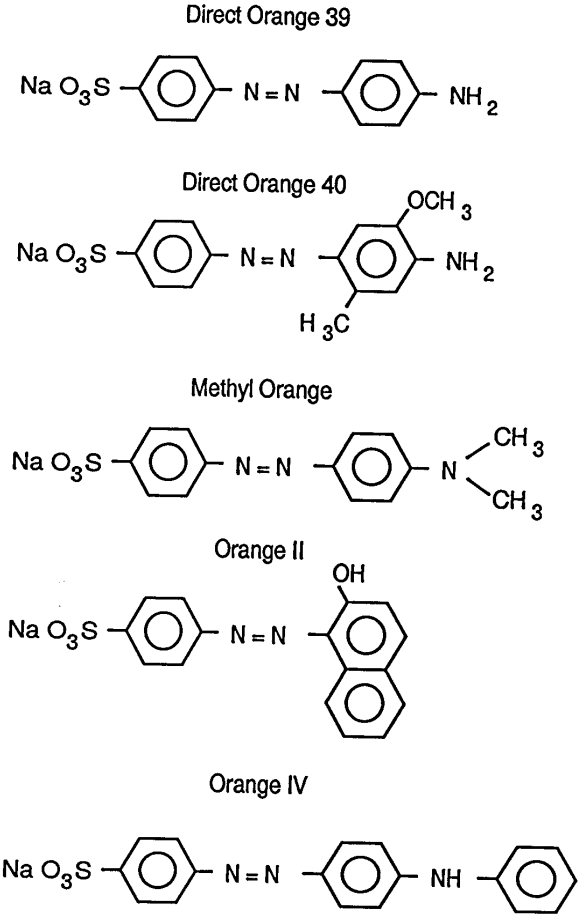

Figure 2. Chemical structures of dye molecules used in this work.

formed, as has already been reported in the literature for complexes of other dyes with cucurbituril [14–17, 23]. Up to now all attempts to prepare crystalline dye complexes with cucurbituril were unsuccessful.

The complex formation between a guest molecule G and a host molecule H can be described by the following equation:

$$\mathrm{G} + \mathrm{H} \rightleftharpoons \mathrm{GH}.$$

The stability constant K is defined by

$$K = \frac{[\mathrm{GH}]}{[\mathrm{G}][\mathrm{H}]}. \tag{1}$$

If no other species are present in solution and only the guest molecule and the complex formed absorb at a given wavelength the measured absorbance E at a constant optical path length d can be expressed by the following equation:

$$E/d = \epsilon_1[\mathrm{G}] + \epsilon_2[\mathrm{GH}], \tag{2}$$

with the molar extinction coefficients of the guest ϵ_1, of the complex formed ϵ_2, and the molar concentrations of the guest [G] and of the complex [GH]. The concentration of the complex formed in solution depends on the stability constant. The unknown parameters K and ϵ_2 were fitted to the experimental data using a non-linear regression analysis.

At low concentrations of formic acid the solubility of cucurbituril is not high enough to reach even the equivalent point during the spectrophotometric titrations. In those cases the extinction coefficients of the corresponding complexes at higher acid concentrations were used to calculate the stability constants. Due to the fact that the guest molecules are partly located inside the cavity of cucurbituril and β-cyclodextrin the solvent composition should have only a minor effect upon the extinction coefficients of the complexed molecules. This assumption could be verified in all cases where a two-parameter fit was possible using Equation (2). For example, the following extinction coefficients ϵ_2 at 278 nm for the complex of the dye orange IV with cucurbituril were calculated using Equation (2):

$$\epsilon_2 = 29\,950 \text{ L mol}^{-1} \text{ cm}^{-1} \quad (30\% \text{ formic acid})$$

and

$$\epsilon_2 = 30\,220 \text{ L mol}^{-1} \text{ cm}^{-1} \quad (40\% \text{ formic acid}).$$

For comparison the stabilities of the complexes formed with β-cyclodextrin as host molecule were determined in 40% formic acid as solvent. Only in the case of the guest molecule methyl orange was the influence of the solvent composition upon the complex stability measured.

3. Results and Discussion

The absorbance of a solution containing the dye molecule orange IV as a function of the concentration of cucurbituril at different acid concentrations is shown in Figure 3. With increasing concentration of the host an increase of the absorbance at a constant wavelength is observed. These experimental measurements allow the calculation of the unknown extinction coefficient of the complex formed and of the stability constant. Similar observations are made for β-cyclodextrin as host. The calculated stability constants for complexes of different guest molecules with β-cyclodextrin or cucurbituril are summarized in Table I.

With a few exceptions, the stability constants of the complexes between the guest molecules examined and β-cyclodextrin or cucurbituril as hosts are of the same

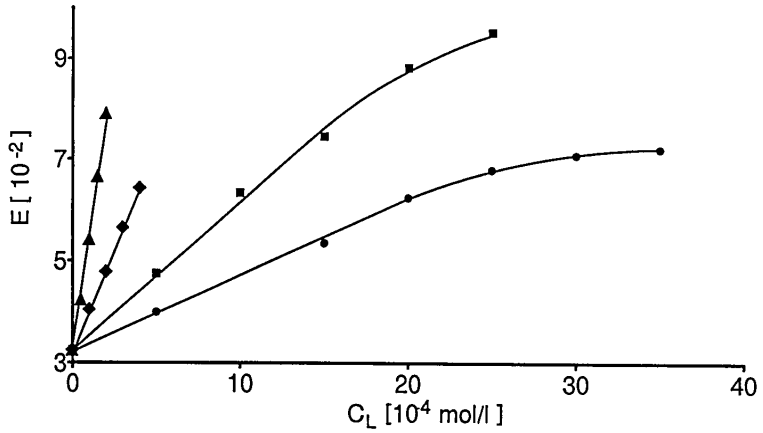

Figure 3. The absorbance E at 278 nm of a solution of the dye orange IV (1×10^{-5} mol/l) as a function of the concentration of cucurbituril at 25 °C and different formic acid concentrations (▲, 10%; ♦, 20%; ■, 30%; ●, 40%).

Table I. Stability constants K (dm^3 mol^{-1}) for the complexation of some organic guests by β-cyclodextrin and cucurbituril in aqueous 40% formic acid at 25 °C.

	β-cyclodextrin log K	Cucurbituril log K
4-methylbenzylamine	2.08	2.67[a]
		2.58[b]
		2.44[b]
1,4-phenylene diamine	1.14	2.58
Methyl orange	1.84	1.76
Direct orange 39	1.99	1.93
Direct orange 40	2.10	1.80
Orange II	1.59	1.61
Orange IV	2.64	2.06

[a]From Ref. [12].
[b]From Ref. [33].

order of magnitude. One would expect that the interactions between a protonated amino group and the carbonyl donor atoms of cucurbituril should result in the formation of stronger complexes than with β-cyclodextrin because it is known that the ammonium ion forms a strong complex with cucurbituril in aqueous solution [12, 25]. The small differences between the stabilities of the dye complexes formed with both hosts demonstrate that hydrophobic interactions between the hosts and dye molecules are mainly responsible for the complex formation. Only in the case of the small guest molecules 4-methylbenzylamine and 1,4-phenylene diamine do the

Table II. Stability constants K (dm^3 mol^{-1}) for the complexation of methyl orange with β-cyclodextrin at different concentrations of formic acid [vol.-%] in aqueous solutions at 25 °C.

Formic acid	0	10	20	30	40
log K	2.43[a]	2.47	2.46	2.33	1.84
	2.36[b]				
	2.48[c]				
	2.57[d]				
	2.48[e]				

[a]From Ref. [28]. [b]From Ref. [29]. [c]From Ref. [30]. [d]From Ref. [31]. [e]From Ref. [32].

Table III. Stability constants K (dm^3 mol^{-1}) for the complex formation of dyes with cucurbituril at 25 °C at different concentrations of formic acid [vol.-%].

Formic acid dye	10	15	20	25	30	40
Direct orange 39	3.02	2.80	2.32	2.22	1.99	1.93
Direct orange 40	3.17		2.53		2.16	1.80
orange II	2.83				1.86	1.61
orange IV	2.97		2.49		2.16	2.06
Methyl orange					2.24	1.76

interactions between the amino groups and the donor atoms of cucurbituril result in an increase of the stability of the complexes formed compared with β-cyclodextrin.

The solvent composition influences the stability of the complexes of methylorange and β-cyclodextrin only at a very high formic acid concentration (Table II). All values of the stability constant measured at concentrations of formic acid below 40% are within the range of the values given in the literature for pure water as solvent [28–32].

In contrast the complex formation with cucurbituril is more influenced by the concentration of formic acid (Table III). With decreasing concentration of the acid the measured complex stabilities increase. These results are not surprising because it is known that cucurbituril forms strong complexes with protons [20]. Thus, both protons and guest molecules compete to form complexes with cucurbituril.

4. Conclusions

Cucurbituril and β-cyclodextrin are rigid molecules with hydrophobic cavities. They are able to form inclusion complexes with organic molecules in aqueous formic acid solutions. The values of the stability constants of the complexes formed with both ligands are comparable at high concentrations of formic acid. At low acid concentrations the complexes formed with cucurbituril are more stable when compared with β-cyclodextrin.

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