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The formation of cucurbituril complexes with amino acids and amino alcohols in aqueous formic acid studied by calorimetric titrations

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Abstract

The complex formation between cucurbituril and some amino acids and amino alcohols was studied by means of calorimetric titrations in aqueous formic acid (50% v/v). In the case of amino acids no influence of the number of methylene groups upon the stability constants could be observed. The complex formation is favoured by enthalpic and entropic contributions. During complex formation water molecules bound to carboxylic groups are set free. The situation changes completely in the case of amino alcohols. Reaction enthalpies and entropies are influenced by the number of methylene groups. The amino alcohol with three methylene groups forms the most stable complex. With increasing number of methylene groups the stability of the complexes formed decreases. For this decrease only entropic factors are responsible. © 1998 Elsevier Science B.V.

Keywords: Cucurbituril; Complexes; Stability; Amino acids; Amino alcohols

1. Introduction

The complex formation of the macrocyclic ligand cucurbituril (see Fig. 1) with inorganic and organic molecules was reported for the first time by Behrend et al. in 1904 [1]. At this time the molecular structure of this ligand was unknown. Only few years before, in 1894, Fischer postulated the lock and key principle for the action of enzymes [2]. It took a long time before this principle was rediscovered in the area of biochemistry and later in supramolecular chemistry.

Other macrocyclic ligands similar with cucurbituril are the cyclodextrins. They were first described in the literature in 1891 by Villiers [3]. However, it took a rather long time until the ability of cyclodextrins to form inclusion complexes was discovered by Pringsheim and Lichtenstein in 1916 [4]. So Behrend was the first one who reported the formation of inclusion compounds between a synthetic host molecule and organic guest molecules. Without knowledge of the structure of the host molecule he really could say nothing about the complexes formed. However, he described the formation of complexes between cucurbituril and salts and indicator dyes.

The chemical structure of cucurbituril was reported by Freeman et al. [5] and Freeman [6]. Mock and Shih investigated the complex formation between cucurbituril and amines and diamines quantitatively [7,8]. In the meantime, more results about the reaction of cucurbituril with cations [9–11], ammonium ions [12] and dye molecules [13] have been reported in

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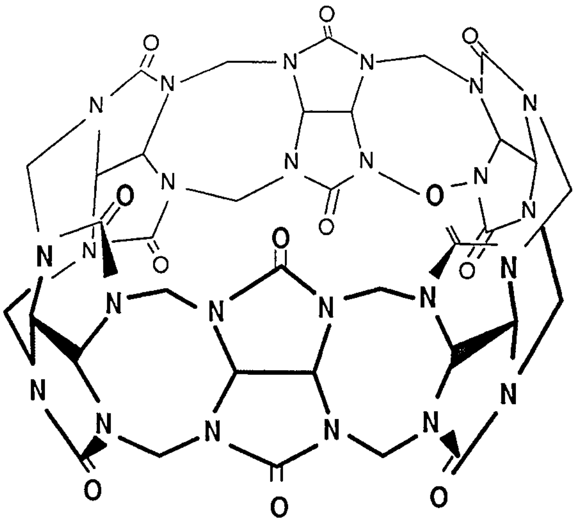

Fig. 1. Chemical structure of cucurbituril.

the literature. However, compared with other macrocyclic ligands like crown ethers, cryptands and cyclodextrins, only few quantitative results are known about the complex formation of cucurbituril with organic molecules [[4–16]].

In this paper the results for the complexation of aliphatic amino acids, amino alcohols and few other amino compounds by cucurbituril are reported.

2. Experimental

The amino compounds: 2-amino ethanoic acid, 3-amino propanoic acid, 4-amino butyric acid, 5-amino pentanoic acid, 6-amino hexanoic acid, 8-amino octanoic acid, 11-amino undecanoic acid, 2-amino ethanol, 3-amino propanol, 4-amino butanol, 5-amino pentanol, 6-aminohexanol, 3-amino propanenitrile, 4-methylbenzylamine and urea (all Fluka) were of the highest purity commercially available. They were used without further purification.

The ligand cucurbituril was synthesized, purified and characterized as described in the literature [1,9]. Aqueous formic acid (50 vol %, Merck) was used as solvent.

Table 1
Stability constants log K (K l mol^{-1}) and thermodynamic values ΔH and $T\Delta S$ (kJ mol^{-1}) for the complexation of some amino compounds by cucurbituril in aqueous formic acid (50% v/v) at 25°C

Amino compound	$-(CH_2)_n-$	log K	$-\Delta H$	$T\Delta S$
4-methylbenzyl amine	—	2.70±0.08 2.67[a] 3.08[b]	5.1±0.3	10.2±0.8
n-hexylamine	6	3.83[c]	22.1[c]	0.9[c]
1,6-diamino hexane	6	6.44[a]	29.6[c]	8.9[c]
2-amino ethanoic acid	1	3.67±0.06	13.1±0.5	7.8±0.8
3-amino propanoic acid	2	3.37±0.08	8.5±0.3	10.7±0.7
4-amino butyric acid	3	3.40±0.07	8.6±0.6	10.7±1.0
5-amino pentanoic acid	4	3.59±0.01	9.9±0.1	10.5±0.1
6-amino hexanoic acid	5	3.57±0.01	12.0±0.4	8.4±0.4
8-amino octanoic acid	7	3.27±0.06	12.2±0.3	6.4±0.7
11-amino undecanoic acid	10	1.93±0.08	5.2±0.5	5.8±0.7
2-amino ethanol	2	2.58±0.08	5.0±1.2	9.7±1.6
3-amino propanol	3	3.59±0.07	5.3±0.3	15.1±0.7
4-amino butanol	4	3.34±0.06	14.3±0.5	4.7±0.9
5-amino pentanol	5	2.84±0.04	24.2±1.8	−8.1±2.0
6-amino hexanol	6	2.27±0.03	52.5±2.2	−39.5±2.3
3-amino propannitrile	2	2.64±0.03	4.6±0.7	10.4±0.9
Urea	—	1.66±0.08	10.5±0.4	−1.1±0.9

[a] Ref. [8]
[b] Ref. [10]
[c] Ref. [12]

Calorimetric titrations using a Tronac Model 450 calorimeter were performed to obtain stability constants and reaction enthalpies for the complex formation between cucurbituril and the amino compounds. The ligand solution (0.03–0.04 mol/l) was added continuously into a solution of the amino compounds (2–$4 \cdot 10^{-3}$ mol/l). After corrections of all non-chemical heat effects the heat Q produced during titration is related to the reaction enthalpy ΔH by the following equation:

$$Q = \Delta n \cdot \Delta H$$

with the number of moles Δn of the complex formed. Δn depends upon the stability of the complex. The mathematical treatment of the experimental data has been described in the literature in detail [17–19]. The reliability of the results obtained from calorimetric titrations has already been demonstrated [20].

3. Discussion and results

Stability constants and thermodynamic parameters for the complexation of amino compounds by the ligand cucurbituril in aqueous formic acid are summarized in Table 1. Under these experimental conditions the amino groups are completely protonated. Stability constants of the complex between cucurbituril and 4-methylbenzylamine agree very well with results reported in the literature [8,10].

In the case of the amino acids all stability constants are of the same order of magnitude. Compared with 1,6-diamino hexane the complex formation of amino acids is less favoured by enthalpic contributions. The values of the reaction entropies, however, are comparable for the complexation of 1,6-diamino hexane and amino acids. No influence of the number of methylene groups upon reaction enthalpies and entropies can be observed. The positive values of the reaction entropies can only be explained if the carboxylic groups of the molecules interact with water molecules already bound by cucurbituril. It is known that cucurbituril shows strong interactions with water molecules [21]. Thus, the water molecules in contact with the uncomplexed amino acids are set free during complex formation. As a result the entropic contributions for complexation of the amino acids are constant. Only for 8-amino octanoic acid and 11-amino undecanoic acid the values of the reaction entropies decrease. Both molecules are too long to fit completely into the cavity of cucurbituril. So the carboxylic groups are located outside the cavity.

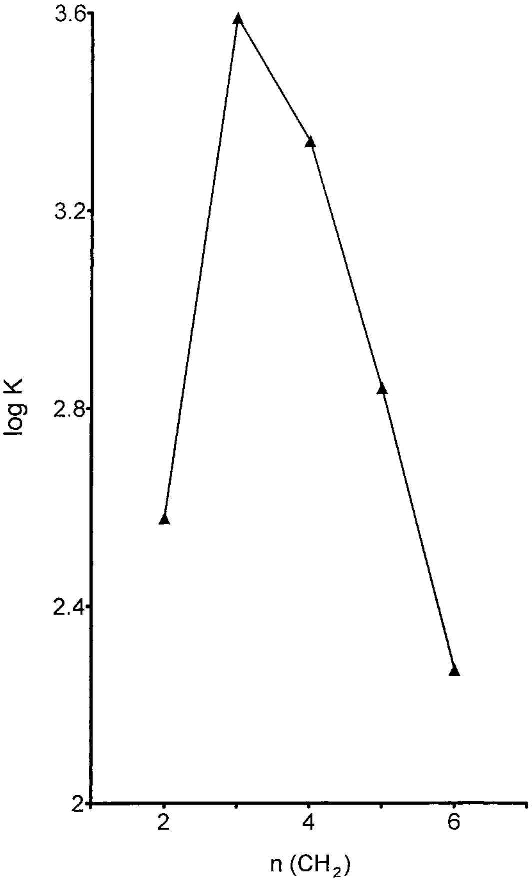

Fig. 2. Stability constants K (log K, K l mol^{-1}) for complex formation between amino alcohols and cucurbituril as a function of the number of methylene groups of amino alcohols in aqueous formic acid (50% v/v) at 25°C.

Amino alcohols behave quite differently compared with amino acids. The stability of the complexes formed depends upon the number of the methylene groups, see Fig. 2. Amino alcohol with three methylene groups forms the most stable complex of all amino alcohols. In contrast the values of reaction enthalpies increase with the number of methylene groups and the values of reaction entropies decrease. Hydrophobic interactions between the alkyl chains and cucurbituril may be responsible for changes of reaction enthalpies.

Hydroxyl groups have weaker interactions with water molecules than carboxylic groups. As a result, they have to arrange themselves within the cavity of cucurbituril. Therefore, the sterical requirements increase with increasing chain length.

The complexation behaviour of 3-amino propanenitrile is somewhat between an amino acid and an amino alcohol. However, at the moment there are not enough results to discuss this complexation in detail.

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