ELSEVIER

Thermochimica Acta 346 (2000) 33–36

thermochimica acta

www.elsevier.com/locate/tca

Cucurbituril as host molecule for the complexation of aliphatic alcohols, acids and nitriles in aqueous solution

H.-J. Buschmann*, K. Jansen, E. Schollmeyer

Deutsches Textilforschungszentrum Nord-West e.V., Adlerstr. 1, D-47798 Krefeld, Germany

Received 30 September 1999; received in revised form 17 November 1999; accepted 19 November 1999

Abstract

The complex formation between the macrocyclic ligand cucurbituril and aliphatic alcohols, acids and nitriles has been studied using calorimetric titrations. The polar groups and the number of methylene groups of the guest molecules studied do not influence the stability of the complexes formed. Changes in solvation of the ligand cucurbituril are responsible for the high stability constants. During the complex formation, two solvent molecules are liberated. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Cucurbituril; Calorimetric titrations; Complexes

1. Introduction

During the last two decades, the area of Supramolecular Chemistry established itself as a new important field in chemistry [1–3]. The selective complex formation between host and guest molecules has been studied in detail. The most prominent host molecules upto now are cyclodextrins, crown ethers, cryptands and calixarenes.

Another macrocyclic host molecule is cucurbituril, see Fig. 1. This ligand was first synthesized in 1905 [4]. However, the chemical structure of the molecule was reported at least 76 years later [5]. The name cucurbituril was suggested by Mock due to the tedious name derived from the IUPAC rules for the nomenclature [6]. Cucurbituril is a rigid molecule and possesses a hydrophobic cavity. At each entrance to the cavity, six polar carbonyl groups are located. These conditions are ideal for the complexation of positively charged organic molecules with hydrophobic groups. So the complexation of a large number of different ammonium ions by cucurbituril was examined first [7–11]. However, cucurbituril is also able to bind alkali and alkaline earth cations [12–14]. Some experimental results are known about the complex formation with dye molecules [15] and other neutral aromatic substances [16]. Further results and thermodynamic data for the complexation of uncharged organic molecules by the ligand cucurbituril have not been published upto now. Compared with other macrocyclic ligands, the knowledge about the complexation behavior of cucurbituril is rather small. Thus, we like to report results for the complexation of some aliphatic compounds by cucurbituril.

2. Experimental

The macrocyclic ligand cucurbituril was synthesized from urea, glyoxal and formaldehyde as reported in the literature [4]. The ligand was purified by dis-

* Corresponding author. Fax: +49-2151-843-143.
E-mail address: dtnw@uni-duisburg.de (H.-J. Buschmann).

0040-6031/00/$ – see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(99)00407-4

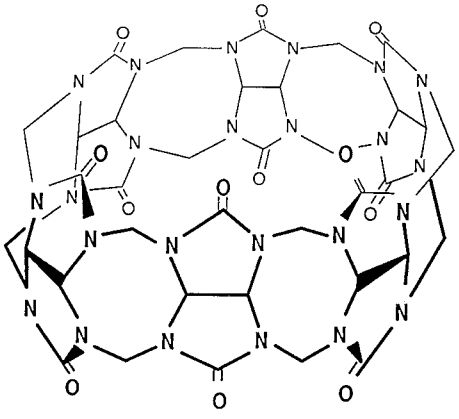

Fig. 1. Structure of cucurbituril.

solution in concentrated hydrochloric acid and by precipitation after dilution with water. The elemental analysis of cucurbituril gave the following results: C, 35.58%; H, 4.48%; N, 27.97% (expected C, 43.38%; H, 3.64%; N, 33.72%). The determined values are in agreement with those already reported [5,6,12]. The differences between the theoretical and experimental values of the elemental analysis are caused by strongly bound water molecules [17]. The ^{1}H NMR spectrum in D_2O/DCl contains only three signals of equal intensity (δ 5.75, δ 5.70, δ 4.46) showing the high symmetry of cucurbituril.

All aliphatic alcohols, carboxylic acids and nitriles were commercial samples (Fluka) and were used without further purification. Due to the low solubility of cucurbituril in aqueous solution, an aqueous solution of formic acid (50 vol %, Merck) was used as solvent.

The stability constants and thermodynamic values were determined by calorimetric titrations using a Tronac Model 458 calorimeter. During a calorimetric titration, a solution of the ligand (0.05–0.08 mol/l) was added to a solution of the guest molecule (3–$6{\cdot}10^{-3}$ mol/l). After corrections of all non-chemical heat effects, the heat Q, produced during titration was related to the reaction enthalpy ΔH by the following equation:

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

with the number of moles Δn of the complex formed. Δn depends upon the stability of the complex formed. The mathematical treatment of the experimental data has already been described in detail [18–20]. The reliability of the results obtained from calorimetric titrations compared with that from potentiometric and conductometric titrations has been demonstrated [21].

^{1}H NMR spectra of pentanoic acid in the absence and presence of equimolar amounts of cucurbituril were recorded using a mixture of D_2O/DCl (20 vol %). As internal standard, the sodium salt of trimethylsilyl tetradeuteropropionic acid were used.

3. Results and discussion

The results for the complexation of aliphatic alcohols, acids and nitriles in aqueous solution by cucurbituril are summarized in Table 1. The stability constants and thermodynamic data for the complexation of all guest molecules are of the same order of magnitude. There are no strong interactions between guest and host molecule. As a result the measured reaction enthalpies were small. Thus, the complex formation is obviously favored by entropic contributions. These results are in agreement with the theory based on hydrophobic interactions [22].

Several individual processes contribute to the reaction entropy:

changes of the solvation of cucurbituril,
changes of the solvation of the guest molecules,

Table 1
Stability constants (log K, K in l/mol) and thermodynamic parameters ΔH and $T\Delta S$ (kJ/mol) for the complex formation of aliphatic alcohols, acids and nitriles with cucurbituril in aqueous formic acid (50 vol %) at 25°C

Guest molecule	log K	$-\Delta H$	$T\Delta S$
Ethanol	2.64±0.08	2.0±0.7	13.0±1.2
1-Propanol	2.61±0.11	2.0±0.9	12.9±1.5
1-Butanol	2.53±0.04	2.9±0.5	11.5±0.7
1-Pentanol	2.73±0.02	1.6±0.1	13.9±0.2
1-Hexanol	2.71±0.03	3.0±0.6	12.4±0.8
1-Heptanol	2.64±0.09	0.7±0.3	14.3±0.8
1-Propionic acid	2.77±0.08	1.4±0.6	14.3±1.0
1-Pentanoic acid	2.70±0.07	1.9±0.4	13.4±0.8
1-Hexanoic acid	2.77±0.04	1.1±0.5	14.6±0.8
1-Heptanoic acid	2.77±0.03	1.5±0.6	14.3±0.7
1-Octanoic acid	2.75±0.03	0.9±0.3	14.7±0.5
1-Nonanoic acid	2.79±0.11	1.3±0.3	14.6±0.4
1-Propane nitrile	2.31±0.06	3.5±0.8	9.7±1.1
1-Hexane nitrile	2.57±0.09	2.6±0.5	12.0±1.0

changes in the ligands internal entropy due to conformational changes,
changes in the internal entropy of the guest molecule due to complex formation,
variation of the number of particles during the complexation and changes in translational entropy.

Since cucurbituril is a very rigid molecule, no conformational changes are expected during complex formation. The most important terms contributing to the reaction entropy are the changes of the solvation of the ligand and guest molecule.

The number of methylene groups of the guest molecules has no influence upon the measured thermodynamic values. This observation indicates that the solvation of the guest molecules has no important influence on the reaction entropies. The dominant contribution to the reaction entropy obviously is the change of solvation of cucurbituril during the complex formation. From thermogravimetric studies it is known that eight water molecules are bound by cucurbituril. Two or three water molecules are more strongly bound compared with the rest [17].

The entropy change for the melting of ice is $T\Delta S_{\text{fusion}}$=6.6 kJ/mol at 298.15 K [23]. Using this value, it is possible to calculate the number of water molecules n liberated during the complex formation:

$$n = \frac{T\Delta S}{T\Delta S_{\text{fusion}}}$$

The values of the reaction entropies given in Table 1 indicate the liberation of two water molecules. Thus, the changes in solvation play an important role for the formation of complexes between cucurbituril and aliphatic alcohols, acids and nitriles.

Amines, diamines, and other compounds containing amino groups form much stronger complexes with cucurbituril than aliphatic alcohols and other guest molecules examined [7–11]. The complexes with all amines are stabilized by strong ion–dipole interactions between the carbonyl groups of cucurbituril and the protonated amino groups. From ^{1}H NMR measure-

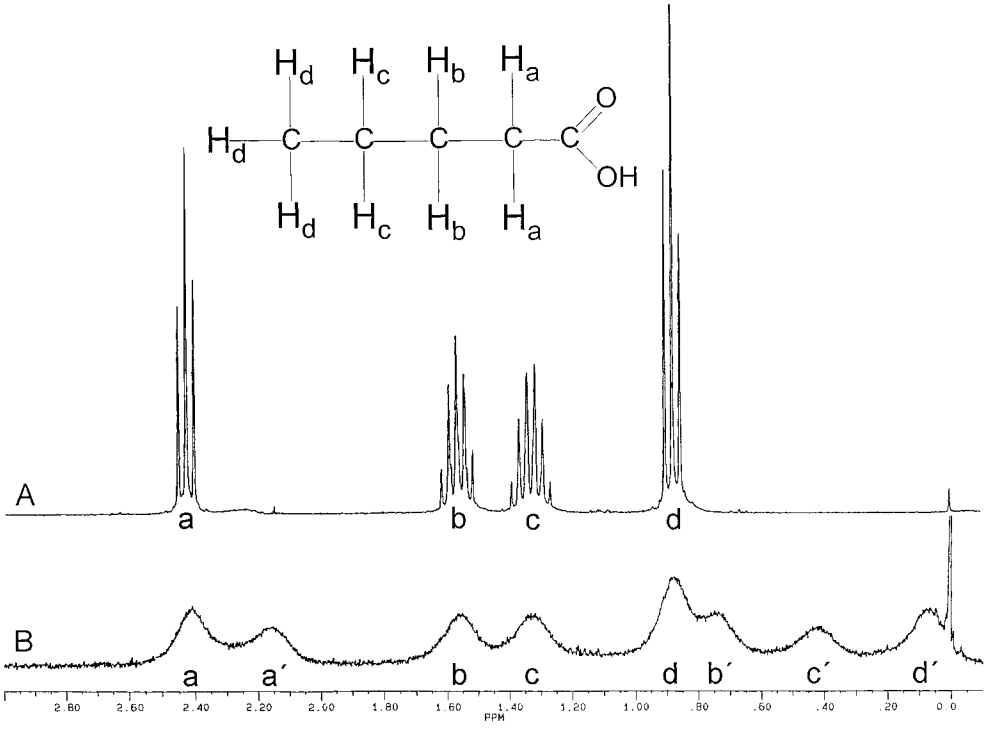

Fig. 2. ^{1}H NMR spectra of pentanoic acid: (a) and in the presence of cucurbituril; (b) in D_2O/DCl with the sodium salt of trimethylsilyl tetradeuteropropionic acid as internal standard.

ments, it is known that these guest molecules are located within the cavity of cucurbituril.

The interpretation of the thermodynamic data for the complexation of aliphatic alcohols, acids and nitriles in aqueous solution is only valid if inclusion complexes are formed. Thus, no hydrophobic interactions between host and guest molecules are possible, if the guest molecule is not located inside the cavity of the host molecule.

In Fig. 2, the ^{1}H NMR spectra of a solution containing pentanoic acid and a mixture of pentanoic acid with cucurbituril is given. Due to the formation of an inclusion complex between cucurbituril and this acid the signals of the methyl and methylene groups are shifted. The observed line broadening further indicates a relative fast exchange between the complexed an uncomplexed pentanoic acid [24]. These results clearly demonstrate the formation of inclusion complexes between the guest molecules examined and cucurbituril.

References

[1] J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.
[2] F. Vögtle, Supramolekulare Chemie, Teubner, Stuttgart, 1989.
[3] V. Balzani, L. De Cola (Eds.), Supramolecular Chemistry, Kluwer Academic Publishers, Dordrecht, 1992.
[4] R. Behrend, E. Meyer, F. Rusche, Liebigs Ann. Chem. 339 (1905) 1.
[5] W.A. Freeman, W.L. Mock, N.-Y. Shih, J. Am. Chem. Soc. 103 (1981) 7367.
[6] N.-Y. Shih, Ph.D. Thesis, University of Illionois at Chicago, 1981.
[7] W.L. Mock, N.-Y. Shih, J. Org. Chem. 48 (1983) 3618.
[8] W.L. Mock, N.-Y. Shih, J. Org. Chem. 51 (1986) 4440.
[9] W.L. Mock, N.-Y. Shih, J. Am. Chem. Soc. 110 (1988) 4706.
[10] C. Meschke, H.-J. Buschmann, E. Schollmeyer, Thermochim. Acta 297 (1997) 43.
[11] H.-J. Buschmann, K. Jansen, E. Schollmeyer, Thermochim. Acta 317 (1998) 95.
[12] H.-J. Buschmann, E. Cleve, E. Schollmeyer, Inorg. Chim. Acta 193 (1992) 93.
[13] R. Hoffmann, W. Knoche, C. Fenn, H.-J. Buschmann, J. Chem. Soc. Faraday Trans. 90 (1994) 1507.
[14] H.-J. Buschmann, K. Jansen, C. Meschke, E. Schollmeyer, J. Solution Chem. 27 (1998) 135.
[15] H.-J. Buschmann, E. Schollmeyer, J. Inclusion Phenom. 29 (1997) 167.
[16] D.A. Dantz, Ö. Otyakmaz, H.-J. Buschmann, E. Schollmeyer, Vom Wasser 91 (1998) 305.
[17] P. Germain, J.M. Létoffé, M.P. Merlin, H.-J. Buschmann, Thermochim. Acta 315 (1998) 87.
[18] J.J. Christensen, J. Ruckman, D.J. Eatough, R.M. Izatt, Thermochim. Acta 3 (1972) 203.
[19] D.J. Eatough, R.M. Izatt, J.J. Christensen, Thermochim. Acta 3 (1972) 219.
[20] D.J. Eatough, R.M. Izatt, J.J. Christensen, Thermochim. Acta 3 (1972) 233.
[21] H.-J. Buschmann, Inorg. Chim. Acta 195 (1992) 51.
[22] A. Ben-Naim, Hydrophobic Interactions, Plenum Press, New York, 1980.
[23] A.A. Bondi, Physical Properties of Molecular Crystals, Liquids and Glass, Wiley, New York, 1968.
[24] H. Strehlow, Rapid Reactions in Solution, VCH, Weinheim, 1992, pp. 143–190.