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COMPLEX FORMATION BETWEEN CROWN ETHERS AND UREA AND SOME GUANIDINIUM DERIVATIVES IN METHANOL

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Abstract

The complexation of urea and some guanidinium derivatives by the ligands 15-crown-5, 18-crown-6, benzo-18-crown-6 and diaza-18-crown-6 in methanol has been studied by means of calorimetric titrations. The complex formation is mainly favored by entropic contributions. The number of solvent molecules released during the complex formation is responsible for the stability of the complexes formed.

Keywords: calorimetry, complex formation, crown ethers, guanidinium derivatives

Introduction

The guanidinium group plays an important role in biological systems because this group is able to bind anions [1]. In synthetic receptors the guanidinium group and its derivatives are used as building blocks for selective anion receptors [2–4]. The positive charge of the guanidinium ion is delocalized at all three nitrogen atoms by resonance. Thus, this organic cation is very stable in solution. However, up to now nothing is known about the complex formation between crown ethers and guanidinium derivatives in solution.

The interactions between crown ethers and different cations are well documented in the literature [5–7]. These ligands also form complexes with the ammonium ion and substituted ammonium ions in solution [5–8]. Recently, the complexation of amino acids with crown ethers and cryptands has been reported [9–11]. Even unprotonated amines form complexes with crown ethers in different solvents [12, 13]. The uncharged amines show much weaker interactions compared with the corresponding ammonium ions.

The complex formation between crown ethers and guanidinium derivatives is studied by calorimetric titrations. These organic ions are strongly solvated in aqueous solution and therefore methanol is used as solvent.

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Experimental

The ligands (Fig. 1) 15-crown-5 (15C5, Merck), 18-crown-6 (18C6, Merck), benzo-18-crown-6 (B18C6, Merck) and 1,10-diaza-18-crown-6 (22, Merck) are used without further purification.

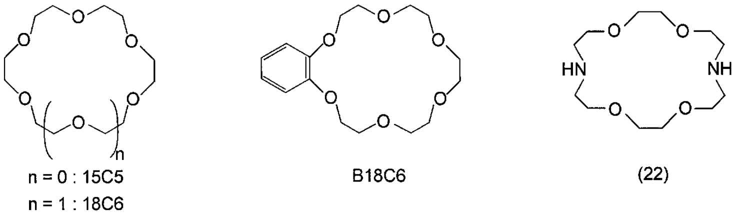

Fig. 1 Chemical structures of the ligands used

All guest molecules urea (G1), guanidine hydrochloride (G2), 1,1,3,3-tetramethylguanidine hydrochloride (G3), benzamidine hydrochloride (G4), and 1,5,7-triazabicyclo[4,4,0]-dec-5-ene (G5) are commercially available (all Fluka). The tetraphenylborates of the organic cations are prepared as follows. An aqueous sodium tetraphenylborate solution is added to acidified solutions of the neutral guests (G3, G5) or to solutions of the hydrochlorides (G2, G4). The organic tetraphenylborate salts precipitate. They are filtered off and washed with water. They are recrystallized from a water-methanol mixture. Their chemical structures are given in Fig. 2. The tetraphenylborate salts are used to ensure the complete dissociation of the organic salts in methanol.

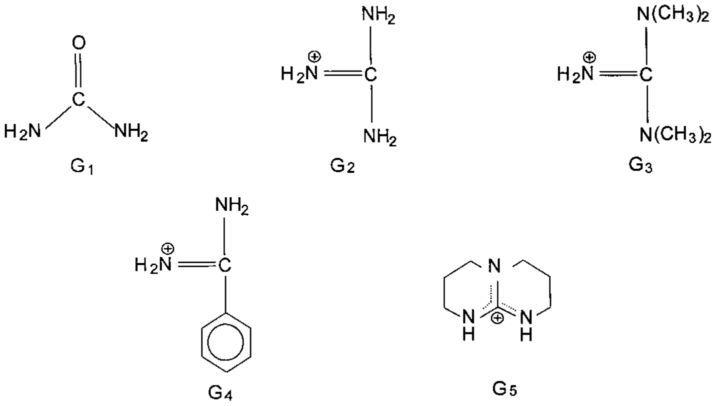

Fig. 2 Chemical structures of the different guest molecules or their cations examined in this work

The calorimetric titrations are performed using a Tronac calorimeter (Model 450). A solution of the ligands (0.06–0.08 mol l^{-1}) is added continuously to a solution of the guest molecules ($4\cdot10^{-3}$–$5\cdot10^{-3}$ mol l^{-1}). After correction of all non-chemical heat effects the heat Q produced during titration is related to the reaction enthalpy ΔH by the following equation

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

with Δn as the number of moles of the complex formed. The mathematical treatment of the experimental data is described in detail in the literature [14–16]. The reliability of the stability constants obtained from calorimetric measurements is known [17].

Results and discussion

The stability constants and the thermodynamic data for the complexation of urea and some guanidinium derivatives by some crown ethers in methanol are summarized in Table 1. All values of the reaction enthalpies are of the same order of magnitude. The size of the crown ethers does not influence the values of the reaction enthalpies. Obviously not all ether donor atoms of the crown ethers are involved in the complex formation. This is in accordance with the values obtained for B18C6 because the benzo groups reduce the basicity of the attached oxygen donor atoms. However, the values of the reaction enthalpies for the complex formation with 18C6 and B18C6 are nearly identical. The reaction enthalpies do not significantly influence the stabilities of the complexes formed.

Table 1 Stability constants (log$K$, K in l mol^{-1}) and thermodynamic parameters ΔH and $T\Delta S$ (in kJ mol^{-1}) for the complexation of urea and some guanidinium derivatives by different crown ethers in methanol at 25°C

Ligand	Value	G1	G2	G3	G4	G5
15C5	log$K$	2.46	3.70	2.55	3.23	2.80
	$-\Delta H$	1.6	1.8	0.6	0.9	0.7
	$T\Delta S$	12.4	19.2	13.9	17.5	15.2
18C6	log$K$	2.47	4.27	>5	3.80	4.05
	$-\Delta H$	1.0	3.0	1.0	5.5	2.3
	$T\Delta S$	13.0	21.3		16.1	20.7
B18C6	log$K$	–[a]	3.57	3.96	3.83	3.74
	$-\Delta H$	–	2.9	1.2	5.6	2.7
	$T\Delta S$	–	17.4	21.3	16.2	18.6
(22)	log$K$	2.54	2.53	–[b]	–[b]	–[b]
	$-\Delta H$	2.8	6.6	–	–	–
	$T\Delta S$	11.6	7.8	–	–	–

[a] Not calculable from the curves
[b] No 1:1 stoichiometry

The driving force for the complex formation is the reaction entropy. From the individual values of the reaction entropies no further information can be obtained. Comparing the reaction entropies of one ligand and different guest molecules it becomes possible to get some further information. Under these circumstances the entropic contributions from the desolvation and deformation of the ligand during complex formation should nearly be constant. As a result the differences of the reaction entropies between two guest molecules are caused mainly by changes of the solvation of both guests. Taking into account the entropy of fusion of methanol at 298.1 K ($T\Delta S_{\text{fusion}}$=4.1 (kJ mol^{-1}) [18] it becomes possible to calculate the difference between the number of solvent molecules liberated during complex formation from the guest molecules. This is shown for example for the complexation of the guest molecules G2 and Gl by the ligand 15C5:

$$n = \frac{[T\Delta S_{\text{G2}} - T\Delta S_{\text{G1}}]}{T\Delta S_{\text{fusion}}} = 1.7$$

During the complex formation of the guest molecules G2 and G1 with 15C5 nearly two more solvent molecules are set free from the guest molecule G2 than from G1. The values of *n* obtained in this way for the other guest molecules and also for their complexation with 18C6 are summarized in Table 2.

Table 2 Difference between the reaction entropy at 25°C for the complexation of urea (G1) and the other guanidinium derivatives by 15C5 and 18C6 in methanol and the corresponding number of solvent molecules *n* (mol l^{-1}) liberated during the complexation

Ligand	Guest molecules	$\Delta(T\Delta S)$	*n*
15C5	G2-G1	6.8	1.7
	G3-G1	1.5	0.4
	G4-G1	5.1	1.2
	G5-G1	2.8	0.7
18C6	G2-G1	8.3	2.0
	G3-G1	–	–
	G4-G1	3.1	0.8
	G5-G1	7.7	1.9

Comparing the results for the ligands 15C5 and 18C6 one finds that in the case of 18C6 in most cases few more solvent molecules are liberated during complex formation. The most important factor for the complex formation are the changes of solvation of the guest molecules and of their complexes during the reaction.

Substituting two oxygen donor atoms of the ligand 18C6 by two nitrogen atoms changes the complexation reactions completely. Unfortunately no stability constants and thermodynamic data can be calculated from the experimental data in the case of G3, G4 and G5. Thus no detailed discussion in the case of the ligand (22) is possible. Similar observations have been reported in the case of the reaction of amino acids with the ligand (22) [11]. Further investigations are necessary to understand the role of nitrogen donor atoms of aza crown ethers upon the complex formation with guanidinium derivatives.

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