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Simple Molecular Architecture Using Alkylamines, α-cyclodextrin and 18-crown-6 in Aqueous Solution

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Alkylamines are able to form complexes with α-cyclodextrin and crown ethers. In the case of complex formation with cyclodextrins, the alkyl group is located inside the cavity of the cyclodextrins, whereas the polar group is positioned outside the cavity in contact with water molecules. Crown ether complexes with alkylammonium ions are formed by ion-dipole interactions between the charged nitrogen atom and the oxygen donor atoms of the crown ether. Formation of 1:1:1 complexes between the alkylammonium ions, 18-crown-6, and α-cyclodextrin is therefore observed. Using calorimetric and potentiometric titrations, each individual reaction step can be measured. The experimental results for each individual reaction step are validated using a thermodynamic cycle. The reactions under study typify the self organization of three different species in solution.

Keywords: Alkylamines; 18-Crown-6; α-Cyclodextrin; Mixed complexes; Calorimetry; Self organisation

INTRODUCTION

Amine compounds, which play an important role in biological processes, have entailed the publishing of many reports on the interactions of amine compounds with macrocyclic host compounds. The most prominent hosts under investigation have been crown ethers [1–9], cryptands [10–12], cyclodextrins [13–18], calixarenes [19–23], and cucurbiturils [24–28]. All these ligands having well-defined binding sites with different sizes are able to form selective complexes with amine compounds by noncovalent interactions. In this respect, the ion-dipole interactions between protonated amino groups and neutral ligands are responsible for the formation of amine complexes with crown ethers and cryptands [1].

The calix[n]arenes and their derivatives have widely been used in molecular recognition of amino species. Their complexes are characterized to a large extent by ion–ion interactions. A proton transfer takes place from each of the hydroxyl group of the neutral ligands to the nitrogen atom of the amine [29–31]. During the complexation of alkylammonium ions with cucurbiturils, ion-dipole as well as hydrophobic interactions enforce the strength of the molecular interactions [24,28].

Due to their particular structure, the cyclodextrins may accommodate within their cavity the hydrophobic part a wide variety of guest molecules in aqueous solutions yielding inclusion complexes [32–34]. In order to better understand the factors involved in multiple recognition mechanism, Liu *et al.* [35] have studied the behaviour of cyclodextrin-crown ether conjugates mediated by alkali metal ions. Additionally, threaded rotaxanes and nanotubular structure involving cyclodextrins have been reported [36–38]. In this respect, the cyclodextrins have been used as components in designing nanoscale structures through self-assembly, a new strategy in chemical synthesis of nanostructures [39,40]. By assembling relatively small molecules into aggregates with well-defined supramolecular entity through noncovalent interactions such as electrostatic and van der Waals forces or hydrophobic effects, π–π staking interactions, metal coordination, or hydrogen bonding, large aggregates have been formed by self-organisation processes [41,42].

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TABLE I Stability constants log K (K in $l\,mol^{-1}$) and thermodynamic values ΔH and TΔS (in kJ/mol) for the complex formation of 18-crown-6 with alkylamine hydrochlorides in aqueous solution at 25°C

Alkylamine	log K[a]	log K[b]	$-\Delta H$[b]	$T\Delta S$[b]
n-$C_2H_5NH_2$·HCl	2.96 ± 0.04	3.07 ± 0.02	0.8 ± 0.2	16.6 ± 0.4
n-$C_3H_7NH_2$·HCl	2.61 ± 0.03	2.52 ± 0.01	1.6 ± 0.1	12.7 ± 0.2
n-$C_4H_9NH_2$·HCl	2.44 ± 0.03	2.42 ± 0.03	2.3 ± 0.4	11.5 ± 0.5
n-$C_5H_{11}NH_2$·HCl	2.42 ± 0.05	2.46 ± 0.04	1.8 ± 0.2	12.2 ± 0.4
n-$C_6H_{13}NH_2$·HCl	2.35 ± 0.02	–[c]	1.5 ± 0.2	11.8 ± 0.4
n-$C_7H_{15}NH_2$·HCl	2.66 ± 0.02	2.51 ± 0.02	2.9 ± 0.3	11.4 ± 0.4
n-$C_8H_{17}NH_2$·HCl	2.10 ± 0.03	–[c]	2.4 ± 0.2	9.5 ± 0.4

[a] from pH-metric tritrations. [b] from calorimetric titrations. [c] heat effect too small or titration curve not suitable for the calculation of stability constants.

Our study addresses some aspects of complex formation between protonated alkylamines, 18-crown-6, and α-cyclodextrin in aqueous solutions by using calorimetric and potentiometric titrations. Formation of ammonium complexes with the crown ether and the inclusion of the alkyl chain within the cavity of α-cyclodextrin is likely to occur, which makes plausible the formation of 1:1:1 complexes between these components.

RESULTS AND DISCUSSION

The stability constants and thermodynamic values for the complex formation between 18-crown-6 and alkylamine hydrochlorides in aqueous solution are summarized in Table I. The values of the stability constants obtained from *pH*-metric and calorimetric titrations are identical within the experimental errors. No influence of the length of the alkyl chain upon the complex stabilities, reaction enthalpies, and entropies is noticed. This is due to ion-dipole interactions that are responsible for the complex formation. Also, the values of the reaction entropies clearly suggest the absence of any influence of the alkyl chain on the sterical demands. Only conformational changes of the crown ether and changes of the solvation during the complex formation are responsible for the observed reaction entropies.

However, by using α-cyclodextrin instead of 18C6 as ligand for the complexation of alkylamine hydrochlorides changes the complexation reaction completely (see Table II). The stability constants measured by two different methods are in good agreement. The values of the reaction enthalpies exhibit monotonic dependence upon the number of methylene groups in the alkyl chain. Obviously, the alkyl chains are located within the cavity of α-CD whereas the ammonium group is located outside. Hydrophobic and van der Waals interactions are responsible for the complex formation [43,44] and the release of water molecules from the cavity [45]. The positively charged amino groups are strongly solvated. These spherically arranged water molecules at the protonated amino group prevent optimal interactions of the alkyl chains inside the cavity.

The complex formation of the protonated amino groups with 18C6 reduces the solvation and changes the sterical arrangement of the solvent molecules around the amino groups. The experimental results for the complex formation of α-CD with the preformed complexes of 18C6 and the alkylamine hydrochlorides are presented in Table III. With the exception of propylamine, all values of the reaction enthalpies significantly increase in presence of the crown ether whose presence at the amino group favored the interactions between the alkyl chain and α-CD. By comparing the values of the reaction entropies for the complex formation of α-CD with the alkylamine hydrochloride (see Table II), and the preformed complex with 18C6 (see Table III), it turns out that in the case of the preformed complex with 18C6 the reaction with α-CD is disfavored by entropic contributions. The sterical requirements for the formation of the 1:1:1 complex are much higher compared with the 1:1 complex (alkylamine hydrochloride:18C6). No explanation for the unusual behaviour of propylamine can be given at the

TABLE II Stability constants log K (K in $l\,mol^{-1}$) and thermodynamic values ΔH and TΔS (in kJ/mol) for the complex formation of α-CD with alkylamine hydrochlorides in aqueous solution at 25°C

Alkylamine	log K[a]	log K[b]	$-\Delta H$[b]	$T\Delta S$[b]
n-$C_3H_7NH_2$·HCl	1.82 ± 0.04[c]	–[d]	0.4 ± 0.1	9.9 ± 0.4
n-$C_4H_9NH_2$·HCl	1.92 ± 0.02[c]	1.83 ± 0.05[c]	0.7 ± 0.4[c]	9.7 ± 0.7[c]
n-$C_5H_{11}NH_2$·HCl	2.14 ± 0.02[c]	2.48 ± 0.02[c]	8.1 ± 0.5[c]	6.0 ± 0.6[c]
n-$C_6H_{13}NH_2$·HCl	2.42 ± 0.02[c]	2.51 ± 0.04[c]	19.5 ± 0.6[c]	−5.2 ± 0.8[c]
n-$C_7H_{15}NH_2$·HCl	2.73 ± 0.01[c]	2.90 ± 0.05[c]	19.7 ± 0.5[c]	−3.2 ± 0.8[c]
n-$C_8H_{17}NH_2$·HCl	3.04 ± 0.15[c]	3.52 ± 0.04[c]	19.3 ± 0.7[c]	0.8 ± 0.8[c]

[a] from pH-metric tritrations. [b] from calorimetric titrations. [c] Reference [50]. [d] heat effect too small or titration curve not suitable for the calculation of stability constants.

TABLE III Stability constants log K (K in $l\,mol^{-1}$) and thermodynamic values ΔH and TΔS (in kJ/mol) for the complex formation of α-CD with the preformed complexes of 18-crown-6 and alkylamine hydrochlorides in aqueous solution at 25°C

Alkylamine complex	log K	−ΔH	TΔS
n-$C_3H_7NH_2$·HCl·18C6	2.57 ± 0.02	0.9 ± 0.2	13.7 ± 0.3
n-$C_4H_9NH_2$·HCl·18C6	2.57 ± 0.01	8.1 ± 0.4	6.5 ± 0.5
n-$C_5H_{11}NH_2$·HCl·18C6	2.50 ± 0.05	14.8 ± 0.8	−0.6 ± 1.1
n-$C_6H_{13}NH_2$·HCl·18C6	2.46 ± 0.05	26.5 ± 2.2	−12.5 ± 2.5
n-$C_7H_{15}NH_2$·HCl·18C6	2.58 ± 0.03	26.5 ± 0.9	−11.8 ± 1.0
n-$C_8H_{17}NH_2$·HCl·18C6	2.55 ± 0.01	37.6 ± 1.2	−23.1 ± 1.2

moment. Thus, the favorable enthalpic contributions are compensated by entropic contributions.

From the comparison of the results given in Tables I and IV, respectively, it is obvious that the complex formation of the protonated amino groups is only slightly affected by the presence of α-CD. In the presence of α-CD, the values of the reaction enthalpy are higher and the values of the reaction entropy lower than in the absence of α-CD. The preformed complex with α-CD reduces the solvation of the protonated amino group. As a result, less energy is necessary to replace part of the solvent molecules during the reaction with 18C6. This leads to higher values for the reaction enthalpies but also to lower values of the reaction entropies.

All individually measured reactions can be arranged in a thermodynamic cycle (see Scheme 1). Using such a cycle, additional reactions may be detected or the accuracy of the experimental results can be evaluated. Without any further reactions, one gets for the stability constants:

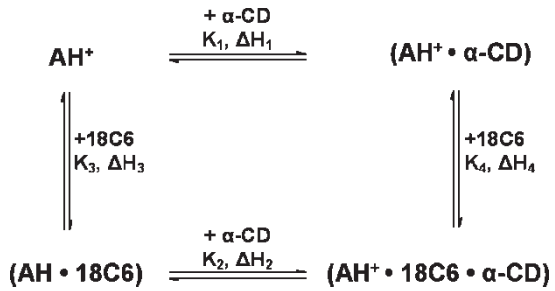
$$\log K_1 + \log K_4 = \log K_3 + \log K_2 \qquad (1)$$

and for the reaction enthalpies:

$$\Delta H_1 + \Delta H_4 = \Delta H_3 + \Delta H_2 \qquad (2)$$

An identical correlation is valid for the reaction entropies, so that Eqs. (1) and (2) can be rearranged:

$$\Delta(\log K) = \log K_1 + \log K_4 - \log K_3 - \log K_2 \qquad (3)$$



SCHEME 1 Thermodynamic cycle for the complexation of protonated alkylamines (AH^+) with 18-crown-6 (18C6) and α-cyclodextrin (α-CD).

TABLE IV Stability constants log K (K in $l\,mol^{-1}$) and thermodynamic values ΔH and TΔS (in kJ/mol) for the complex formation of 18-crown-6 with the preformed complexes of α-CD and alkylamine hydrochlorides in aqueous solution at 25°C

Alkylamine complex	log K	−ΔH	TΔS
n-$C_2H_5NH_2$·HCl·α-CD	–[a]	<0.5	
n-$C_3H_7NH_2$·HCl·α-CD	2.58 ± 0.02	2.0 ± 0.5	12.7 ± 0.5
n-$C_4H_9NH_2$·HCl·α-CD	2.55 ± 0.01	4.0 ± 1.0	10.5 ± 1.1
n-$C_5H_{11}NH_2$·HCl·α-CD	2.52 ± 0.03	7.9 ± 0.1	6.4 ± 0.3
n-$C_6H_{13}NH_2$·HCl·α-CD	2.57 ± 0.13	6.0 ± 0.3	8.6 ± 1.0
n-$C_7H_{15}NH_2$·HCl·α-CD	2.79 ± 0.07	2.8 ± 0.3	13.1 ± 0.7
n-$C_8H_{17}NH_2$·HCl·α-CD	2.47 ± 0.01	3.4 ± 0.5	10.6 ± 0.6

[a] heat effect too small or titration curve not suitable for the calculation of stability constants.

and

$$\Delta(\Delta H) = \Delta H_1 + \Delta H_4 - \Delta H_3 - \Delta H_2 \qquad (4)$$

Ideally, the differences of the thermodynamic data Δ(log K), Δ(ΔH), and Δ(TΔS) should be close to zero. They are summarized in Table V on the basis of the experimental measurements specified in Tables I–IV.

The values of Δ(log K) are indeed quite small. Up to six carbon atoms the values of Δ(ΔH) and Δ(TΔS) are identical within the experimental error. Only in the case of seven and eight carbon atoms the values of Δ(ΔH) and Δ(TΔS) increase. This effect offers a plausible explanation. The formation of aggregates of the protonated alkylamines similar to the formation of micelles is not taken into account in Fig. 1.

The values calculated in Table V also demonstrate the formation of 1:1:1-complexes between protonated alkylamines and the macrocyclic ligands 18-crown-6 and α-cyclodextrin. The reactions between these three different species in solution is a simple example for the self organization of molecules due to specific interactions. Even relative simple molecules can act as building blocks for the construction of nanoscalic structures.

EXPERIMENTAL

Materials

All alkylamines (Fluka) were used without further purification. The hydrochlorides were prepared from

TABLE V Calculated differences of the thermodynamic data for the reaction of alkylamines with α-CD and 18C6, according to Scheme 1, using the experimental data from Tables 1–4

Amines	Δ(log K)	Δ(ΔH)	Δ(TΔS)
n-$C_3H_7NH_2$·HCl	−0.69 ± 0.11	0.1 ± 0.9	−3.8 ± 1.4
n-$C_4H_9NH_2$·HCl	−0.61 ± 0.07	5.7 ± 2.2	2.2 ± 2.8
n-$C_5H_{11}NH_2$·HCl	0.04 ± 0.14	0.6 ± 1.6	0.8 ± 2.4
n-$C_6H_{13}NH_2$·HCl	0.27 ± 0.22	2.5 ± 3.3	4.1 ± 4.7
n-$C_7H_{15}NH_2$·HCl	0.60 ± 0.13	6.9 ± 2.0	10.3 ± 2.9
n-$C_8H_{17}NH_2$·HCl	1.34 ± 0.20	17.3 ± 2.6	24.9 ± 3.0

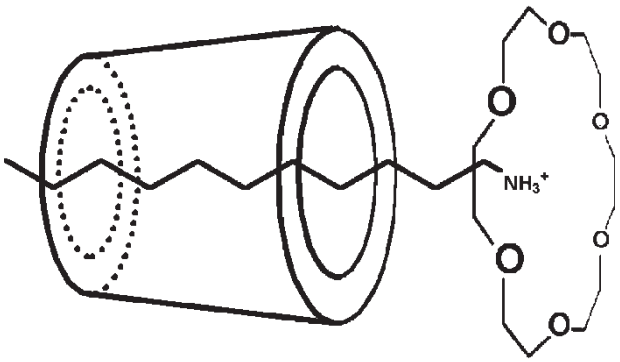


FIGURE 1 Schematic presentation of a 1:1:1 complex between an alkylamine, α-cyclodextrin and 18-crown-6.

solutions of these amines in diethylether after passing gaseous hydrogen chloride. The hydrochlorides were dried in vacuum prior to use. The ligands 18-crown-6 (18C6, Merck) and α-cyclodextrin (α-CD, Wacker) are of the highest purity available. Bidistilled water was used as solvent.

Apparatus and Measurements

Potentiometric titrations were performed using a GLpKa analyser (Sirius Analytical Instruments, Forest Row). The protonation constants and the stability constants were calculated directly from the experimental data using the software package Refinement Pro (Version V1.114, Sirius Analytical Instruments, Forest Row). During the titrations the ionic strength was kept constant with KCl at 0.15 mol/l.

The calorimetric titrations were carried out using a Tronac calorimeter (Model 450). The accuracy of the calorimeter was checked using the reaction of 18C6 with $Ba(ClO_4)_2$ in aqueous solution. The values obtained for the stability constant ($\log K = 3.55 \pm 0.03$) and for the reaction enthalpy ($\Delta H = -31.7 \pm 0.8$ kJ/mol) were in good accordance with the results reported in the literature ($\log K = 3.50 \pm 0.08$; $\Delta H = -31.5 \pm 1.2$ kJ/mol) [46].

Different kinds of calorimetric titrations were performed to study the formation of 1:1 complexes of alkylamine hydrochlorides with the ligands 18C6 or α-CD and the corresponding 1:1:1 complexes:

a) The 1:1 complex formation between the ligands 18C6 or α-CD and the alkylamine hydrochlorides was measured by addition of a ligand solution (0.06–0.08 mol/l) to a solution of the alkylamine hydrochlorides (4×10^{-3}–5×10^{-3} mol/l). The following reaction between the ligand L and the alkylammonium ions A^+ occurred in solution:

$$L + A^+ \leftrightarrow LA^+ \tag{5}$$

b) The formation of 1:1:1-complexes was observed in the following way. A solution of the ligand L_1 (0.06–0.08 mol/l) was titrated into solutions containing the already preformed complexes of the akylammonium ions (4×10^{-3}–5×10^{-3} mol/l with either 18C6 or α-CD. The concentration of the latter ligand L_2 was at least ten times higher compared with the concentration of the ammonium ion. Under these conditions, one of the following reactions may take place:

1. a competitive reaction

$$L_1 + A^+L_2 \leftrightarrow L_1A^+ + L_2 \tag{6}$$

2. or the formation of an amine complex with both ligands

$$L_1 + A^+L_2 \leftrightarrow L_1A^+L_2. \tag{7}$$

From the mathematical evaluation of the experimental titration curves, only the formation of the complex $L_1A^+L_2$ can be verified. Thus, no exchange between both ligands took place. This is not surprising because both ligands interact with different binding sides of the alkylammoium cation.

Generally the heat Q produced during all calorimetric titrations was related to the reaction enthalpy ΔH after correction of all non-chemical heat effects by the following equation:

$$Q = \Delta n^* \Delta H \tag{8}$$

with Δn as the number of moles of the complex formed during the titration. The mathematical treatment of the experimental data is described in detail in the literature [47–49].

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