ELSEVIER

Thermochimica Acta 261 (1995) 1–5

thermochimica acta

Solvent influence upon complex formation between crown ethers and unprotonated amines

H.-J. Buschmann[a,*], G. Wenz[a], E. Schollmeyer[a], Lucia Mutihac[b]

[a] *Deutsches Textilforschungszentrum Nord-West e.V., Frankenring 2, D-47798 Krefeld, Germany*
[b] *Department of Analytical Chemistry, Faculty of Chemistry, University of Bucharest, 13 Carol 1, Bucharest Romania*

Received 23 February 1995; accepted 20 March 1995

Abstract

The complexation reactions of some primary and secondary amines with crown ethers have been studied by means of calorimetric titrations. Thus, the stability constants and values of the reaction enthalpies and entropies were obtained. The values of the stability constants are nearly identical in all solvents examined. However, the values of the reaction enthalpies and entropies are influenced by solvation effects. In non-polar solvents such as toluene, cyclohexane, and carbon tetrachloride, complex formation with the amines is only favoured by entropic contributions. The values of the reaction enthalpies are rather small and nearly identical in these solvents.

Keywords: Amines; Complexes; Crown ethers; Solvation; Titration calorimeter

1. Introduction

In biological systems the amino group plays an important role, due to its ability to form hydrogen bonds[1]. The understanding of selective recognition of amines is of fundamental interest, mainly in view of mimicking natural biological systems.

The interactions between synthetic receptors, such as crown ethers and cryptands, and ammonium ions or amino acids have been studied [2–8]. The influence of different substituents upon the basicity of amines is known from protonation reactions in the gas phase [9] and in solution [10, 11]. Few results concerning the influence of the solvent upon the complex formation between ammonium ions and crown ethers have been

---

* Corresponding author.

SSDI 0040-6031(95)02384-4

reported [12]. The number of hydrogen bonds formed between the ammonium ions and crown ethers is generally considered as the dominant factor for the stabilities of the complexes formed. However, for a better understanding of the factors influencing the molecular recognition of amines more experimental results are needed. Therefore the interactions between uncharged primary and secondary amines with several crown ethers in different solvents have been studied.

2. Experimental

The crown ethers 15-crown-5 (15C5, Merck), 18-crown-6 (18C6, Merck), benzo-18-crown-6 (B18C6, Merck) and the amines *n*-butylamine (n-BA, Sigma), *n*-dibutylamine (n-DbA, Fluka), benzylamine (BeA, Fluka) and *N*-methylbenzylamine (N-MbeA, Fluka) were used without further purification. The chemical structures of the crown ethers are given in Fig. 1.

As solvents, anhydrous methanol (Merck, max. 0.01% H_2O), propylene carbonate (Merck, H_2O content less than 0.1%), acetonitrile (Merck, H_2O content less than 0.3%), toluene (Fluka, H_2O content less than 0.005%), cyclohexane (Fluka, H_2O content less than 0.005%) and CCl_4 (Fluka, H_2O content less than 0.001%) were used.

All calorimetric titrations were performed using a Tronac calorimeter (Model 450). During titration a solution of the ligand (0.06–0.08 M) was added continuously into a solution of the amine ($4–6 \times 10^{-3}$ M). Only in the solvents cyclohexane and CCl_4 higher concentrations of the crown ether (0.3–0.4 M) and of the amines (0.02–0.03 M) were used.

The heat Q_t measured during the titration is related to the reaction enthalpy ΔH of the corresponding reaction after correction for all non-chemical heat effects, e.g. heat of dilution and the heat produced by the stirring of the solution, by the following equation:

$$Q_t = \Delta n_t \times \Delta H$$

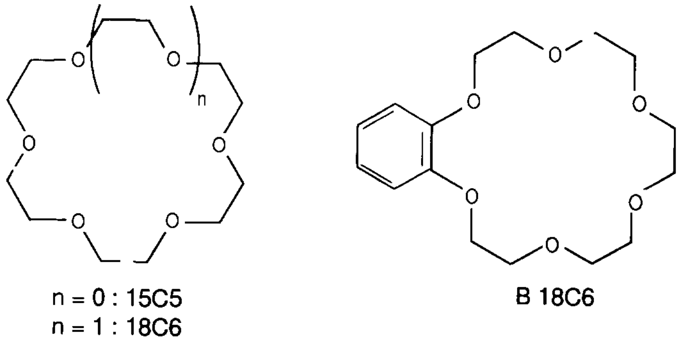

Fig. 1. Chemical structures of the crown ethers used in this work.

with the number of moles Δn_t of the complex formed at any time of the titration. The value of Δn_t depends on the stability of the complex formed. The reaction of a ligand L with an amine A to form a complex LA can be written as:

$$\mathrm{L} + \mathrm{A} \rightleftharpoons \mathrm{LA}$$

The stability constant K for this reaction is defined in the following way:

$$\mathrm{K} = \frac{[\mathrm{LA}]}{[\mathrm{L}][\mathrm{A}]}$$

The mathematical treatment of the experimental data to calculate simultaneously the stability constant and the reaction enthalpy from the measured curve has already been described in detail in the literature [13–16].

3. Results and discussion

Values of the stability constants, reaction enthalpies, and entropies for the complexation of some amines by crown ethers in methanol as solvent are summarized in Table 1.

The values of all stability constants given are nearly identical. In the case of the smallest crown ether 15C5 the values of the reaction enthalpies are small and close to zero. Therefore, complex formation with the amines is only favoured by entropic contributions. In contrast high values of the reaction enthalpies are observed for the reaction of primary amines with the ligand 18C6. They decrease drastically for the reactions of secondary amines with this ligand to identical values as for the reaction of amines with the crown ether 15C5. Complex formation of primary amines with the crown ether 18C6 is favoured by enthalpic and disfavoured by entropic contributions. For secondary amines exactly the opposite behaviour is observed.

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

Ligand	Value	n-BA[a]	n-DbA[a]	BeA[a]	N-MBeA[a]
15C5	$\log K$	2.56 ± 0.04	2.57 ± 0.05	2.57 ± 0.02	2.43 ± 0.04
	$-\Delta H$	2.2 ± 0.5	1.9 ± 0.6	3.1 ± 0.3	2.4 ± 0.5
	$T\Delta S$	12.4 ± 0.8	12.7 ± 0.9	11.5 ± 0.4	11.4 ± 0.7
18C6	$\log K$	2.60 ± 0.05	2.51 ± 0.06	2.46 ± 0.02	2.47 ± 0.04
	$-\Delta H$	31.5 ± 0.3	2.0 ± 0.3	22.5 ± 0.3	1.2 ± 0.3
	$T\Delta S$	-16.7 ± 0.6	12.3 ± 0.6	-8.5 ± 0.4	12.8 ± 0.6
B18C6	$\log K$	2.37 ± 0.04	2.51 ± 0.07	2.53 ± 0.4	2.35 ± 0.07
	$-\Delta H$	7.7 ± 0.4	0.4 ± 0.3	5.7 ± 0.7	0.4 ± 0.3
	$T\Delta S$	5.6 ± 0.7	13.9 ± 0.7	8.7 ± 0.9	13.0 ± 0.7

[a] abbreviations: n-BA = *n*-butylamine, n-DbA = *n*-dibutylamine, BeA = benzylamine, N-MBeA = *N*-methylbenzylamine.

The basicity of the two oxgen donor atoms attached to the benzo group of the crown ether B18C6 is reduced [17, 18]. As a result the values of the reaction enthalpy decrease compared with 18C6. However, the values for the complexation of primary amines are higher when compared with those for secondary amines.

The ligands 15C5 and B18C6 behave in a nearly identical manner. This is only possible if both ligands have similar strength of interactions and also possess comparable steric requirements during complex formation. The crown ether 15C5 is too small and the basicity of the two oxygen donor atoms of the crown ether B18C6 is too low to form all possible hydrogen bonds with the amines examined. Therefore, only the ligand 18C6 shows optimal interactions with primary amines. They are compensated by high steric requirements on the complexes formed and as a result complex formation is disfavoured by entropic contributions. However, if the number of possible hydrogen bonds is reduced, as in the case of secondary amines, nearly identical results are obtained when compared with the other ligands examined.

The results of complex formation of the ligand 18C6 with amines in different solvents are given in Table 2. The values of the stability constants are nearly identical in all solvents. The values for the reaction enthalpies for the complexation of the amines

Table 2

Stability constants ($\log K$, K in M^{-1}) and thermodynamic parametersΔH and $T\Delta S$ (in kJ mol^{-1}) for the complexation of amines by the ligand 18C6 in different solvents at 25°C

Solvent[a]	Value	n-BA[b]	n-DbA[b]	BeA[b]	N-MBeA[b]
MeOH	$\log K$	2.60 ± 0.05	2.51 ± 0.06	2.46 ± 0.02	2.47 ± 0.04
	$-\Delta H$	31.5 ± 0.3	2.0 ± 0.3	22.5 ± 0.3	1.2 ± 0.3
	$T\Delta S$	−16.7 ± 0.6	12.3 ± 0.6	−8.5 ± 0.4	12.8 ± 0.6
PC	$\log K$	2.53 ± 0.01	2.52 ± 0.03	2.24 ± 0.4	2.51 ± 0.07
	$-\Delta H$	7.1 ± 0.2	1.0 ± 0.4	9.2 ± 1.7	3.7 ± 0.6
	$T\Delta S$	7.3 ± 0.4	13.3 ± 0.6	3.5 ± 2.0	10.6 ± 1.0
AN	$\log K$	1.70 ± 0.05	2.58 ± 0.07	2.51 ± 0.1	2.41 ± 0.08
	$-\Delta H$	4.5 ± 0.3	1.8 ± 0.7	1.5 ± 0.4	0.8 ± 0.5
	$T\Delta S$	5.2 ± 0.5	12.9 ± 1.1	12.3 ± 1.4	12.9 ± 1.0
Tl	$\log K$	3.73 ± 0.1	–[c]	–[c]	–[c]
	$-\Delta H$	2.9 ± 0.4	2.2 ± 0.5	0.5 ± 0.5	1.1 ± 0.6
	$T\Delta S$	18.3 ± 1.0			
Ch	$\log K$	–[c]	–[c]	–[c]	–[c]
	$-\Delta H$	4.8 ± 0.3	1.3 ± 0.4	1.8 ± 0.6	1.4 ± 0.5
	$T\Delta S$				
CCl_4	$\log K$	3.67 ± 0.09	2.80 ± 0.08	–[c]	2.95 ± 0.08
	$-\Delta H$	2.3 ± 0.4	1.7 ± 0.5	1.5 ± 0.2	1.5 ± 0.3
	$T\Delta S$	18.6 ± 0.9	14.2 ± 1.0		15.3 ± 0.7

[a] abbreviations: MeOH = methanol, PC = propylene carbonate, AN = acetonitrile, Tl = toluene, Ch = cyclohexane. [b] abbreviations: n-BA = *n*-butylamine, n-DbA = *n*-dibutylamine, BeA = benzylamine, N-MBeA = *N*-methylbenzylamine. [c] not possible to calculate stability constants from the experimental data.

examined are of the same order of magnitude in all solvents with the exception of methanol. Also the difference of reaction enthalpies between primary and secondary amines is much smaller in all solvents when compared with methanol.

All results can be explained by the solvation of the amines. In protic solvents such as methanol strong hydrogen bonds between primary amines and the solvent molecules are formed. As a result of these interactions a partially positive charge is induced at the nitrogen atom. Therefore, the interactions between the hydrogen bonded amines and the crown ether 18C6 are relatively strong compared with the interactions of *n*-butylamine hydrochloride ($-\Delta H = 41.5$ kJ mol^{-1}) [7] in the same solvent. In methanol the solvent molecules are directly involved in the complex formation of primary amines with 18C6 and as a result these reactions are disfavoured by entropic contributions.

In all other polar and non-polar solvents nearly identical results are found. Obviously the interactions between the amines and all other solvents examined do not induce a positive charge at the nitrogen atoms of the amines. Thus secondary amines in methanol and all amines in the other solvents behave nearly identical if they are complexed by the ligand 18C6.

Acknowledgements

Financial support of this research project by the NATO under research grant No. 941403 is greatfully acknowledged.

References

[1] G.A. Jeffrey and W. Saenger, Hydrogen Bonding in Biological Structures, Springer, Heidelberg, 1994.
[2] R.B. Davidson, N.K. Dalley, R.M. Izatt, J.J. Christensen, J.S. Bradshaw and C.F. Campana, Isr. J. Chem., 25 (1985) 27.
[3] J.S. Bradshaw, P. Huszthy, C.W. McDaniel, C.Y. Zhu, N.K. Dalley, R.M. Izatt and S. Lifson, J. Org. Chem., 55 (1990) 3129.
[4] A.F. Danil de Namor, M.C. Ritt, D.F.V. Lewis, M.J. Schwing-Weill and F. Arnaud Neu, Pure Appl. Chem., 63 (1991) 1435.
[5] A.F. Danil de Namor, Pure Appl. Chem., 62 (1990) 2121.
[6] A.F. Danil de Namor, M.C. Ritt, M.-J. Schwing-Weill, F. Arnaud-Neu and D.F.V. Lewis, J. Chem. Soc., Chem. Commun., (1990) 116.
[7] H.-J. Buschmann and L. Mutihac, Rev. Roum. Chim., 39 (1994) 563.
[8] H.-J. Buschmann and L. Mutihac, Thermochim. Acta, 237 (1994) 203.
[9] D.H. Aue and M.T. Bowers, in M.T. Bowers (Ed.), Gas Phase Ion Chemistry, Vol 2, Academic Press, New York, 1979, p. 1.
[10] D.H. Aue, H.M. Webb and M.T. Bowers, J. Am. Chem. Soc., 98 (1976) 318.
[11] A. Mucci, R. Domain and R.L. Benoit, Can. J. Chem., 58 (1980) 953.
[12] J.A.A. de Boer and D.N. Reinhoudt, J. Am. Chem. Soc., 107 (1985) 5347.
[13] J.J. Christensen, J. Ruckman, D.J. Eatough and R.M. Izatt, Thermochim. Acta, 3 (1972) 203.
[14] D.J. Eatough, J.J. Christensen and R.M. Izatt, Thermochim. Acta, 3 (1972) 219.
[15] D.J. Eatough, R.M. Izatt and J.J. Christensen, Thermochim. Acta, 3 (1972) 233.
[16] H.-J. Buschmann, Inorg. Chim. Acta, 195 (1992) 51.
[17] R.M. Izatt, G.A. Clark, J.D. Lamb, J.E. King and J.J. Christensen, Thermochim. Acta, 97 (1986) 115.
[18] H.-J. Buschmann, Polyhedron, 11 (1992) 559.