

Short Communication

The complex formation of non-cyclic polyethers and crown ethers with Ag^+ in acetone and propylene carbonate studied by potentiometric and calorimetric methods

H.-J. Buschmann *, E. Schollmeyer

Deutsches Textilforschungszentrum Nord-West e.V., Frankenring 2, D-47798 Krefeld, Germany

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Abstract

Potentiometric and calorimetric titrations are performed to study the complexation reactions of non-cyclic polyethers and crown ethers with Ag^+ in acetone and propylene carbonate. With increasing chain length of the non-cyclic ligands the complex stability increases due to favourable enthalpic contributions. The macrocyclic polyethers already possess a preformed cavity for the complexation of the Ag^+ ion. The cavity size and substituents influence the stability constants of the complexes formed. Only the smallest crown ether examined, 12-crown-4, forms 2:1 complexes in acetone and propylene carbonate solutions. The highest values of the stability constants for the reaction of Ag^+ with crown ethers are measured if the dimensions of the silver ion and of the cavities are nearly identical. The results clearly demonstrate the entropic origin of the macrocyclic effect in both solvents. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

After the discovery of the crown ethers [1] their complexation behaviour has been studied in detail. The results have been summarized [2–5]. The most commonly used solvent for these complexation reactions is methanol. The solvent influences the solvation of the cations and also of the ligands. Thus, it is well known that the ligand 18-crown-6 forms nearly insoluble complexes with acetonitrile [6]. Only very few results have been reported for complexation reactions in other solvents.

On the other hand few stability constants for the complex formation of cations with non-cyclic ligands are known [7,8]. These results may help to understand the origin of the macrocyclic effect in case of the crown ethers [9].

Stability constants and thermodynamic data for complexation reactions in propylene carbonate and acetone between polyethers, crown ethers and cryptands have been reported only in the case of alkali and alkaline earth cations [10–13]. It has been shown that the possible formation of ion pairs does not have any influence upon the stability constants with the different types of ligands if their stability constants are higher than the formation constant of the ion pairs [13].

Thus, we decided to study the complexation behaviour of silver ions with polyether and crown ethers in propylene carbonate and acetone. We expect to get further insight in the complexation reactions by the combination of potentiometric and calorimetric methods.

2. Experimental

The non-cyclic polyethers diethyleneglycol (DEG, Merck), diethyleneglycol dimethylether (DG, Merck),

* Corresponding author. Fax: +49-2151-843-143.

E-mail address: dtnw@uni-duisburg.de (H.-J. Buschmann)

triethyleneglycol (TEG, Merck), triethyleneglycol dimethylether (TG, Riedel de Haen), tetraethyleneglycol (TeEG, Merck), tetraethyleneglycol dimethylether (TeG, Riedel de Haen), pentaethyleneglycol (PEG, Columbia), pentaethyleneglycol dimethylether (PG, Riedel de Haen), hexaethyleneglycol (HEG, Columbia), hexaethyleneglycol dimethylether (HG, Riedel de Haen) and 1,11-bis-(8-chinolyloxy)-3,6,9-trioxaundecane (K5, Merck) were of the highest purity commercially available.

The macrocyclic ligands 12-crown-4 (12C4, Merck), 15-crown-5 (15C5, Merck), cyclohexano-15-crown-5 (C15C5, Fluka) benzo-15-crown-5 (B15C5, Merck), 18-crown-6 (18C6, Merck), benzo-18-crown-6 (B18C6, Merck), dibenzo-18-crown-6 (DB18C6, Merck) and dicyclohexano-18-crown-6 (DC18C6, Merck) were used without further purification. The structures of the

macrocyclic ligands are shown in Fig. 1. The silver salts AgNO_3 , AgBF_4 and $\text{CF}_3\text{SO}_3\text{Ag}$ (all Merck) and tetraethylammonium perchlorate (TEAP, Fluka) were used as purchased.

Propylene carbonate (PC, H_2O content < 0.005%, Fluka) and acetone (AC, H_2O content < 0.001%, Merck) were used as solvents.

The experimental setup of the potentiometric titrations has already been described in detail [14]. The activity of the uncomplexed silver ions was measured using a silver electrode (Metrohm EA 282). A ligand solution (1×10^{-2} M) was titrated into a solution containing the silver salt (1×10^{-3} M). The ionic strength was kept constant at $I = 0.05$ M by addition of TEAP as supporting electrolyte. The activity of the uncomplexed silver ions was calculated from the measured emf using the Nernst equation. Using the mass balances, all other concentrations were available. This led directly to the stability constant K . With few exceptions all stability constants reported were determined by potentiometric titrations.

For the calorimetric titrations a Tronac model 458 was used. The ligand solution (0.04–0.08 M) was added continuously to a silver salt solution ($2.5\text{--}5 \times 10^{-3}$ M). Due to the complex formation the temperature in the reaction vessel changed. After corrections for all non-chemical contributions to this change, e.g. the effect of stirring the solution, the heat produced Q was related to the reaction enthalpy ΔH by the following equation

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

where Δn_t is the number of moles of the complexes formed at any time of the titration. Δn_t itself depends upon the value of the stability constant. The stability constant and the reaction enthalpy were calculated from the experimental data by published procedures [15–17]. The temperature change during the calorimetric titration was small so the stability constant was practically unchanged. The reliability of the stability constants determined by the use of different experimental techniques has already been shown [18].

3. Results and discussion

The results for the complex formation between Ag^+ and linear polyethers in acetone and propylene carbonate are given in Table 1.

The behaviour of the non-cyclic ligand K5 does not correspond with that of the other polyethers. The ligand K5 has rigid endgroups which contain additional nitrogen donor atoms. In both solvents it forms the most stable complexes. The stability constants and the values of the reaction enthalpies of the complexes formed with polyethers increase with increasing number of ether donor atoms. Entropic contributions do not

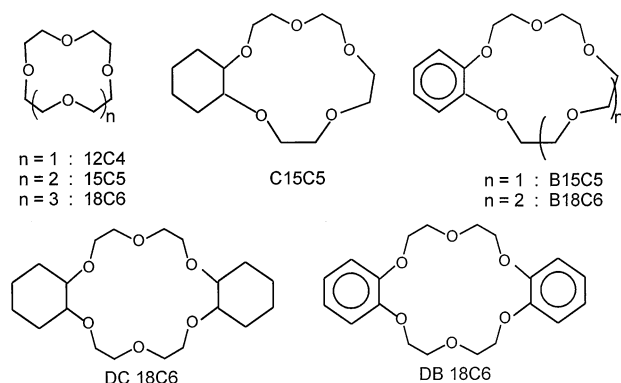


Fig. 1. Structures of macrocyclic polyethers used in this work.

Table 1
Stability constants (K) and thermodynamic values ΔH and $T\Delta S$ for the complexation of Ag^+ by non-cyclic polyethers in acetone at 25°C

Solvent	Ligand	Log K /l mol^{-1}	$-\Delta H/\text{kJ}$ mol^{-1}	$T\Delta S/\text{kJ}$ mol^{-1}
AC	TG	—	4.5 ± 0.9	—
	TeG	—	11.6 ± 1.2	—
	PG	2.81 ± 0.02^a	19.4 ± 1.1	-3.4 ± 1.3
	HG	3.25 ± 0.02^a	23.4 ± 1.5	-4.9 ± 1.6
	K5	9.60 ± 0.01^b	54.6 ± 0.9	-0.1 ± 0.9
PC	DEG	2.06 ± 0.05^a	28.1 ± 1.3	-16.4 ± 1.6
	DG	2.08 ± 0.04^a	19.0 ± 1.5	-7.2 ± 1.7
	TEG	3.32 ± 0.04^a	31.7 ± 1.7	-12.8 ± 2.0
	TG	3.09 ± 0.05^a	25.6 ± 1.5	-8.0 ± 1.7
		2.90 ± 0.03^b		
	TeEG	4.28 ± 0.02^b	38.9 ± 1.2	-14.6 ± 1.3
	TeG	3.97 ± 0.03^b	37.1 ± 0.9	-14.5 ± 1.0
	PEG	4.96 ± 0.01^b	43.3 ± 1.4	-15.1 ± 1.4
	PG	4.55 ± 0.02^b	42.1 ± 1.5	-16.2 ± 1.6
	HEG	5.47 ± 0.02^b	50.7 ± 0.8	-19.6 ± 0.9
	HG	5.03 ± 0.01^b	44.2 ± 1.1	-15.6 ± 1.1
	K5	11.68 ± 0.04^b	75.6 ± 1.3	-9.2 ± 1.5

^a Calorimetric titration.

^b Potentiometric titration.

Table 2

Stability constants (K) and thermodynamic values ΔH and $T\Delta S$ for the complexation of Ag^+ by crown ethers in acetone at 25°C

Ligand	$\text{Log } K^1/\text{l mol}^{-1}$	$-\Delta H^1/\text{kJ mol}^{-1}$	$T\Delta S^1/\text{kJ mol}^{-1}$	$\text{Log } K^2/\text{l mol}^{-1}$	$-\Delta H^2/\text{kJ mol}^{-1}$	$T\Delta S^2/\text{kJ mol}^{-1}$
12C4	2.17 ± 0.05^a	25.3 ± 1.8	$-4.0 \pm$	2.98 ± 0.06^a	34.9 ± 1.5	-18.0 ± 1.9
15C5	4.52 ± 0.02^a	30.6 ± 1.5	-4.9 ± 1.6	— ^c	—	—
C15C5	5.20 ± 0.01^a	29.3 ± 0.9	0.2 ± 1.0	— ^c	—	—
B15C5	3.35 ± 0.03^a , 3.50^b	20.2 ± 1.4	-1.2 ± 1.6	— ^c	—	—
18C6	5.24 ± 0.02^a	37.5 ± 0.8	-7.7 ± 0.9	—	—	—
B18C6	4.66 ± 0.03^a	35.9 ± 1.1	-9.4 ± 1.2	—	—	—
DC18C6	5.63 ± 0.01^a , 5.38^b	26.2 ± 1.4	5.7 ± 1.6	—	—	—

^a Potentiometric titrations.^b Ref. [19].^c No 2:1 complex formation detectable.

Table 3

Stability constants (K) and thermodynamic values ΔH and $T\Delta S$ (kJ/mol) for the complexation of Ag^+ by crown ethers in propylene carbonate at 25°C

Ligand	$\text{Log } K^1/\text{l mol}^{-1}$	$-\Delta H^1/\text{kJ mol}^{-1}$	$T\Delta S^1/\text{kJ mol}^{-1}$	$\text{Log } K^2/\text{l mol}^{-1}$	$-\Delta H^2/\text{kJ mol}^{-1}$	$T\Delta S^2/\text{kJ mol}^{-1}$
12C4	3.72 ± 0.06^a , 3.98^b	34.7 ± 1.6	-13.6 ± 2.0	3.76 ± 0.10^a , 3.31^b	30.2 ± 2.5	-8.8 ± 3.0
15C5	6.30 ± 0.03^a , 6.24^b , 5.78^c	41.2 ± 0.9	-5.4 ± 1.1	— ^e , 1.77^b		
C15C5	7.02 ± 0.01^a	39.8 ± 1.1	0.1 ± 1.1	— ^c		
B15C5	5.12 ± 0.02^a	34.9 ± 1.2	-5.8 ± 1.3	— ^c		
18C6	7.09 ± 0.01^a , 6.86^b , 7.10^d	49.6 ± 0.8	-9.3 ± 0.7			
B18C6	6.50 ± 0.02^a	41.4 ± 0.9	-4.5 ± 1.0			
DB18C6	5.86 ± 0.02^a , 5.82^d	42.2 ± 0.8	-8.9 ± 0.9			
DC18C6	7.98 ± 0.01^a	45.5 ± 0.7	-0.2 ± 0.8			

^a Potentiometric titration.^b Ref. [20].^c Ref. [21].^d Ref. [22].^e No 2:1 complex formation detectable.

favour the complex formation. This is not surprising because with increasing chain length of the polyethers, they wrap around the silver ion. As a result the steric requirements for the complex formation increase.

A linear correlation between the number of ether donor atoms and the values of the reaction enthalpies is observed in both solvents. In propylene carbonate the reaction enthalpies of the ligands PG and HG are nearly identical. Obviously the additional ether donor atom does not take part in the complex formation. In propylene carbonate the glycols and their dimethylethers behave quite differently. The hydroxyl groups of the glycols are involved in the complex formation. From these, correlations values of the reaction enthalpy contribution for one ether donor atom and Ag^+ can be calculated. In propylene carbonate the ligand HG was not considered. One obtains

in acetone: $\Delta H = -6.4 \pm 0.5 \text{ kJ mol}^{-1}$
and
in propylene carbonate: $\Delta H = -8.1 \pm 0.4 \text{ kJ mol}^{-1}$.

In Tables 2 and 3 the results for the complex formation between different crown ethers and Ag^+ in acetone and propylene carbonate are summarized. Results from the literature are included for comparison if available. In both solvents only the ligand 12C4 forms 2:1 complexes.

The stability of the complexes with the ligands 12C4, 15C5 and 18C6 increases with increasing ring size of the ligands. Only enthalpic contributions are responsible. The values of the reaction entropies with the exception of that of 12C4 remain nearly constant in each solvent. The benzene rings in the crown ethers reduce the basicity

Table 4

Experimental (ΔH_{exp}) and calculated (ΔH_{calc}) values of the reaction enthalpies for the complexation of Ag^+ by crown ethers in acetone (AC) and propylene carbonate (PC) at 25°C

Solvent	Value	12C4	15C5	18C6
AC	$\Delta H_{\text{exp}}/\text{kJ mol}^{-1}$	25.3 ± 1.8	30.6 ± 4.5	37.5 ± 0.8
	$\Delta H_{\text{calc}}/\text{kJ mol}^{-1}$	25.6 ± 2.0	32.0 ± 2.5	38.4 ± 3.0
PC	$\Delta H_{\text{exp}}/\text{kJ mol}^{-1}$	34.7 ± 1.6	41.2 ± 0.9	49.6 ± 0.8
	$\Delta H_{\text{calc}}/\text{kJ mol}^{-1}$	32.4 ± 1.6	40.5 ± 2.0	48.6 ± 2.4

of the attached ether donor atoms. As a result the values of the reaction enthalpies for the complex formation decrease.

The values calculated for the interaction between one ether donor atom and Ag^+ can be used to calculate the values of the reaction enthalpies of 12C4, 15C5 and 18C6 in both solvents. The results are given in Table 4. The experimental and calculated values of the reaction enthalpies are identical within experimental error. Thus, the differences of the stability constants of Ag^+ with non-cyclic and macrocyclic ligands is caused by entropic effects.

In the case of the macrocyclic ligands all donor atoms are able to interact with the complexed cation due to their preorganization. In contrast not all donor atoms of the non-cyclic polyethers may take part in the complex formation. Thus, a direct comparison of the results obtained for the complex formation of non-cyclic and macrocyclic polyethers with identical donor numbers may result in misinterpretations. The results show that the main factor responsible for the so-called macrocyclic effect in acetone and propylene carbonate solvents is identical with that obtained in methanol [7]. The macrocyclic effect in these solvents is thus purely entropic.

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