

## COMPLEX FORMATION OF CROWN ETHERS AND CRYPTANDS WITH MONO- AND BIVALENT CATIONS STUDIED BY CALORIMETRIC COMPETITION REACTIONS

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### ABSTRACT

Direct titrations proved to be a very useful method to study the complexation reactions of noncyclic ligands and monocyclic crown ethers with different cations. However, this method cannot be applied in cases where (a) the values of the stability constants are higher than  $10^5$ , or (b) the values of the reaction enthalpies are close to zero. In these cases a calorimetric competition reaction was used successfully. The experimental data obtained from these reactions allow one to calculate the unmeasurable stability constants and reaction enthalpies. By reducing the burette delivery rate it becomes possible to study competition reactions with the slowly decomposing bicyclic cryptand complexes.

### INTRODUCTION

There are many experimental techniques available for the study of the complex formation of cations with inorganic and organic ligands [1–3]. Each method has its specific advantages and disadvantages. Thus, most commercially available ion-selective electrodes are damaged in solvents other than water. Photometric titrations are possible if at least one species present in the solution absorbs light. In order to make conductivity measurements applicable this physical property has to change to an observable extent during the reaction. The reaction enthalpy for a given reaction has to differ from a value near zero to get information about the complex stability and reaction enthalpy from calorimetric titrations. Such disadvantages are also known for the methods which are not mentioned here. Further problems arise in cases where the stability constant reaches a specific limiting value, which may vary for every method. As a consequence no stability constant can be calculated from the experimental values.

Izatt and co-workers [4] and Izatt et al. [5] did pioneering work by using calorimetric titrations in order to study the interactions of crown ethers and cations in solution. In most cases this technique allows one to estimate the

stability and reaction enthalpy of the complexes formed [6–9]. To overcome the known disadvantages a competitive technique may be used [10,11]. Surprisingly, only a few experiments with crown ethers have been reported using this calorimetric method [12,13]. The aim of the present work was to obtain more information about this experimental method and the complex formation of crown ethers and cryptands with cations.

## EXPERIMENTAL

### *Materials*

All crown ethers and cryptands, see Fig. 1, (Merck) were used without further purifications. The salts were of the highest purity commercially available. As solvent, anhydrous methanol ( $H_2O$  content less than 0.01%; Merck) was used.

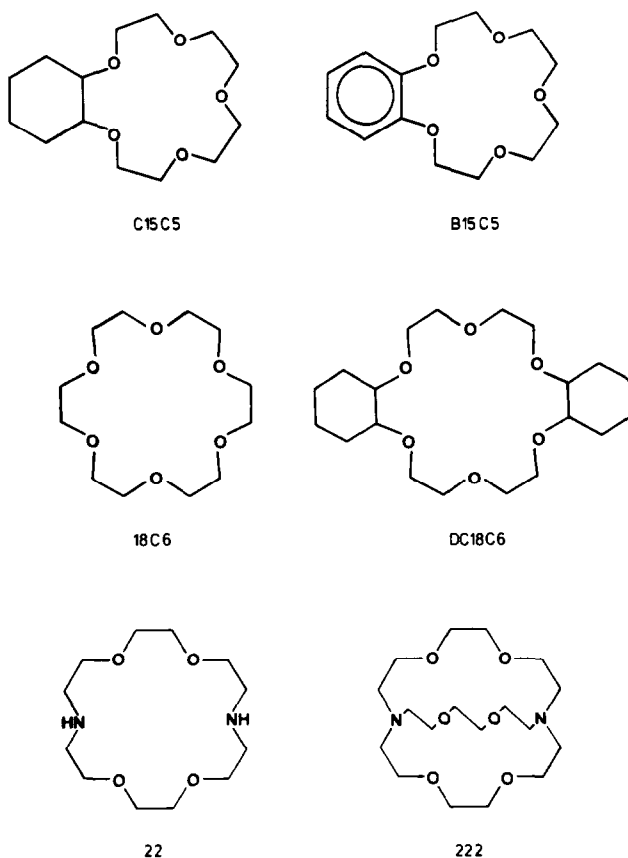


Fig. 1. Ligands used in this work.

### Procedure

Stability constants and reaction enthalpies were determined using a Tronac Model 450 calorimeter [14–16]. Two different types of calorimetric competitive titrations were performed:

(a) a solution of a ligand (0.02–0.04 N) and a metal ion ( $5 \times 10^{-3}$  N) is titrated using another ligand solution (0.08 N). The following reaction takes place



$$\text{with } K_1 = \frac{[ML_1^{n+}] \cdot [L_2]}{[ML_2^{n+}] \cdot [L_1]}$$

(b) a solution of a cation (0.02–0.05 N) and a ligand ( $5 \times 10^{-3}$  N) is titrated using another salt solution (0.08 N). In this case the following reaction is observed



$$\text{with } K_2 = \frac{[M_1L^{m+}] \cdot [M_2^{n+}]}{[M_2L^{n+}] \cdot [M_1^{m+}]}$$

The evaluation of the measured thermograms is only possible if the observed reaction is—at any time—in an equilibrium state during the titration. To fulfil this condition, the burette delivery rate has to be reduced in some cases using a Perfusor V (B. Braun Melsungen AG) equipped with a precision syringe (2.5 ml; Hamilton). The delivery rate could be changed in steps from  $6.87 \times 10^{-7} \text{ dm}^3 \text{ min}^{-1}$  to  $6.87 \times 10^{-4} \text{ dm}^3 \text{ min}^{-1}$ . The value of the normal rate is  $3.26 \times 10^{-4} \text{ dm}^3 \text{ min}^{-1}$ . The stability constants for the formation of the  $ML_1^{n+}$ —or  $M_1L^{m+}$ —complex which is not directly measurable can be calculated from the values of  $K_1$  or  $K_2$  using the separately estimated stability constants for the formation of the  $ML_2^{n+}$ —or  $M_2L^{n+}$ —complexes.

### RESULTS AND DISCUSSION

To test the accuracy of calorimetric competition titrations measurements were performed where the stability constants and reaction enthalpies for the direct complex formation are known



$$K = \frac{[ML^{n+}]}{[M^{n+}][L]}$$

The combination of these values should give  $K_1$  or  $K_2$  and the corresponding reaction enthalpies. The measured and calculated values are summarized in Table 1. Obviously they agree very well. Using this experimental

TABLE 1

Stability constants  $K_n$  and reaction enthalpies  $\Delta H_n$  [kJ M<sup>-1</sup>] measured by means of calorimetric competition reactions and the corresponding values  $K_c$  and  $\Delta H_c$  for comparison in methanol at 25°C

Titrant	Titrate	$\log K_n$ <sup>a</sup>	$-\Delta H_n$ <sup>a</sup>	$\log K_c$ <sup>b</sup>	$-\Delta H_c$ <sup>b</sup>
18C6	DC18C6 Ca <sup>2+</sup>	0.25	13.8	0.33	13.0
18C6	C15C5 Ca <sup>2+</sup>	1.92	11.4	1.99	6.5
18C6	B15C5 Na <sup>+</sup>	1.32	14.9	1.29	12.9
222	18C6 Ca <sup>2+</sup>	$\geq 5$	11.1	4.27	10.8
K <sup>+</sup>	222 Na <sup>+</sup>	2.51	34.3	2.42	34.3
K <sup>+</sup>	222 Ca <sup>2+</sup>	1.66	52.3	1.68	46.7

<sup>a</sup>  $n = 1$  or  $2$ .

<sup>b</sup> Values were calculated using data given in refs. 17–19.

technique it is possible to determine stability constants higher than  $10^5$ . Under these circumstances the directly measured and indirectly calculated reaction enthalpies may be used to test the applicability of the titrations performed. A second advantage is to study reactions where no heat is produced during the direct titration.

In the literature there are examples of reactions with crown ethers in methanol where no possibility exists for calculating the stability constants of the formed complexes from direct titrations due to the high complex stability [12,13,17]. The results for these crown ether complexes are given in

TABLE 2

Stability constants ( $\log K_c$ ;  $K_c$  in M<sup>-1</sup>) and reaction enthalpies  $\Delta H_c$  [kJ M<sup>-1</sup>] calculated from values ( $\log K_n$  and  $\Delta H_n$ ) obtained using calorimetric competition reaction in methanol at 25°C

Studied reaction	$\log K_n$ <sup>a</sup>	$-\Delta H_n$ <sup>a</sup>	Calculated reaction	$\log K_c$	$-\Delta H_c$	$-\Delta H_d$ <sup>b</sup>
K <sup>+</sup> + 18C6 Na <sup>+</sup>	1.97	22.5	18C6 + K <sup>+</sup>	6.29	56.5	56.1
K <sup>+</sup> + 18C6 Cs <sup>+</sup>	1.63	6.9	18C6 + K <sup>+</sup>	6.07	56.8	56.1
Rb <sup>+</sup> + 18C6 Na <sup>+</sup>	1.50	13.1	18C6 + Rb <sup>+</sup>	5.82	47.1	49.6
Sr <sup>2+</sup> + 18C6 Ca <sup>2+</sup>	2.97	20.2	18C6 + Sr <sup>2+</sup>	6.84	31.4	37.2
Ba <sup>2+</sup> + 18C6 Na <sup>+</sup>	2.99	13.4	18C6 + Ba <sup>2+</sup>	7.31	47.4	48.5
Ba <sup>2+</sup> + 18C6 Ag <sup>+</sup>	2.80	9.3	18C6 + Ba <sup>2+</sup>	7.38	48.4	48.5
K <sup>+</sup> + DC18C6 Na <sup>+</sup>	1.35	26.1	DC18C6 + K <sup>+</sup>	5.63 <sup>c</sup>	45.2	44.4
Sr <sup>2+</sup> + DC18C6 Ca <sup>2+</sup>	1.96	13.0	DC18C6 + Sr <sup>2+</sup>	5.50	18.5	16.4
Ba <sup>2+</sup> + DC18C6 Na <sup>+</sup>	1.57	14.4	DC18C6 + Ba <sup>2+</sup>	5.84	34.3	34.4
Ba <sup>2+</sup> + DC18C6 Ag <sup>+</sup>	1.27	11.6	DC18C6 + Ba <sup>2+</sup>	5.91	34.4	34.4
18C6 + B15C5 Ca <sup>2+</sup>	2.31	13.0	B15C5 + Ca <sup>2+</sup>	1.56	-1.8	-
22 + B15C5 Sr <sup>2+</sup>	2.95	7.4	B15C5 + Sr <sup>2+</sup>	2.94	2.6	2.3

<sup>a</sup>  $n = 1$  or  $2$ .

<sup>b</sup> From ref. 17.

<sup>c</sup> Potentiometric titrations using a K<sup>+</sup>-ion selective electrode gave  $\log K = 5.65$ .

Table 2. Polarographic methods have been used to determine the stability of the complexes of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  with 18C6 [18]. These values agree very well with the ones estimated in the present study.

Compared with 18C6, the ligand DC18C6 forms less stable complexes. Due to the more rigid structure, DC18C6 is not able to achieve optimal interactions with the complexed cations. This explains the measured reaction enthalpies. The same behaviour was found for the reactions of other substituted crown ethers [17].

During the direct calorimetric titration of  $\text{Ca}^{2+}$ -solutions with the ligand B15C5 no temperature change was observed [17]. Thus, the values of the stability constant or of the reaction enthalpy may be very small or even zero. A potentiometric competition reaction with silver ions also gave no evidence for the formation of a  $\text{Ca}^{2+}$ -complex. This can be attributed to the low stability of the silver complex. The calorimetric titration of a solution of  $\text{Ca}^{2+}$  and B15C5 with the crown ether 18C6 produced a measurable temperature change. This thermogram could be interpreted without any difficulty. From the data obtained the stability and reaction enthalpy for the formation of the  $\text{Ca}^{2+}$ -complex with B15C5 were calculated, see Table 2. The value of the reaction enthalpy is slightly positive. Thus, it is not surprising that the direct calorimetric titration failed.

A similar situation was found for the reaction of B15C5 with  $\text{Sr}^{2+}$ . The measured heat during the direct titration was rather small. The evaluation of the thermogram could, therefore, give incorrect values. There was no possibility of checking the results by means of potentiometric competition reactions because the stability constants of all B15C5-complexes are almost identical. A calorimetric competition reaction with the azacrown ether (22) definitely confirms the primary results [17], see Table 2. The values of the stability constant and reaction enthalpy for the reaction of the ligand (22) with  $\text{Sr}^{2+}$  were taken from the literature [18]. The examples given clearly demonstrate the usefulness of calorimetric competition reactions. This method gives reliable results in all cases where the normal calorimetric titrations do not work. It is, therefore, a very useful complementary method to other well known techniques.

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