

A new calorimetric titration technique for the study of 2:1 crown ether complexes in solution

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Abstract

The formation of 1:1 and 2:1 complexes is treated mathematically. The influence of the values of the stability constant K_2 and reaction enthalpy ΔH_2 upon the heat produced during calorimetric titrations is calculated. From these results the experimental conditions for the simultaneous calculation of stability constants and reaction enthalpies for the formation of 1:1 and 2:1 complexes of crown ethers with cations from calorimetric titrations are discussed. The mathematical treatment of these experiments is rather difficult if four parameters have to be fitted to the experimental data.

Using the information obtained from the calculations an indirect method which is easy to perform is investigated for studying the complexation reactions. Even in this case no four-parameter fit is successful. Using the values for the 1:1 complex formation obtained directly it is possible to calculate the values for the 2:1 complex formation without any problems. This is demonstrated for three different reactions.

INTRODUCTION

Complex formation between cations and macrocyclic (crown ethers) and macrobicyclic ligands (cryptands) has been studied intensively by a large number of scientists [1]. However, only a few data are available on the stability of 2:1 complexes (ratio of ligand to cation) together with their thermodynamic parameters. Most stability constants of 2:1 complexes have been determined using potentiometric [1,2] or NMR techniques [1,3,4]. This can be easily understood because only the two unknown stability constants have to be fitted to the experimental data.

In the case of calorimetric titrations two parameters, the stability constant and the reaction enthalpy, have to be fitted to the experimental data even in the case of the formation of 1:1 complexes. If 2:1 complexes are formed, four parameters have to be optimized. The mathematical treat-

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ment of such data is not straightforward [5] and as a result only a few calorimetric titrations involving crown ethers have been reported [6,7]. A possible way to simplify the calculations is to vary the experimental conditions in such a way that the concentration of one species (1:1 or 2:1 complex) is nearly constant or negligible during titration [8]. If other experimental methods such as potentiometric or conductometric titrations can be used to estimate both stability constants, calorimetric titrations are performed only to measure the reaction enthalpies for the formation of the 1:1 and 2:1 complexes [9,10]. These methods have been questioned by Schwesinger [11] for the reaction of *cis*-benzenetrioxide with Ba^{2+} [12]. Since the technique of calorimetric titration is obviously not well known, it seems worth discussing. We therefore present an alternative procedure for the study of the formation of 2:1 complexes.

EXPERIMENTAL

Materials

The salts used, $\text{Ba}(\text{ClO}_4)_2$ and AgNO_3 (both Merck), were anhydrous and of the highest purity available.

The ligands *cis*-benzenetrioxide (*c*-BTO), 12-crown-4 (12C4, Merck), 1,7-diaza-12-crown-4 (11), and the cryptand (222) (Merck) were used without further purification. Anhydrous methanol (Merck, max. 0.01% H_2O) was used as solvent.

All calorimetric titrations were performed using a Tronac Model 450 calorimeter.

Procedure

A FORTRAN routine for the calculation of stability constants and reaction enthalpies in the case of 1:1 complex formation has been published [13]. A BASIC version of this routine was used.

Two different types of calorimetric titration were performed.

(a) During the titration, a maximum of 2 ml of a solution of the ligand (0.04–0.08 N) are titrated into 40 ml of the salt solution ((1×10^{-4}) – (6×10^{-3}) N). From the measured heat changes, the stability constant and the reaction enthalpy can be calculated using the program mentioned above. In cases where the value of the stability constant is higher than $10^{5.5} \text{ M}^{-1}$, only the reaction enthalpy can be calculated from the thermogram.

(b) A solution of the cryptand (222) (0.02–0.04 N) is titrated into 40 ml of a solution containing the salt ($(5$ – $6) \times 10^{-4}$ N) and variable concentrations of the ligand ($(0$ – $4) \times 10^{-2}$ N). Since the stability constants of the cryptand (222) with Ag^+ ($\log K = 12.22$ [14]) and with Ba^{2+} ($\log K = 12.9$ [15]) are very high, the measured heat changes during the titration are

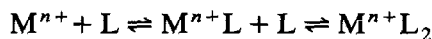
linear with respect to the concentration of the added cryptand. Therefore complex formation with the cryptand is complete during the titration. The number of moles of the cryptand complex formed is identical with the number of moles of the ligand Δn added. The measured heat Q is related to the reaction enthalpy ΔH_{obs} by

$$Q = \Delta n \Delta H_{\text{obs}}$$

The values of the measured heat Q are, however, influenced by the ratio of the concentrations of the monocyclic ligand and the salt. With increasing concentration of this ligand more and more cations will be complexed. Thus not only 1:1 but also 2:1 and even $x:1$ complexes may exist in the titrated solution.

RESULTS AND DISCUSSION

Between a ligand L and a cation M^{n+} the following reactions take place in solution:



The stability constants K_1 and K_2 for the formation of 1:1 and 2:1 complexes are defined by

$$K_1 = \frac{[M^{n+}L]}{[M^{n+}][L]} \quad (1)$$

and

$$K_2 = \frac{[M^{n+}L_2]}{[M^{n+}L][L]} \quad (2)$$

The material balances for ligand and cation are given by

$$c_L = [L] + [M^{n+}L] + 2[M^{n+}L_2] \quad (3)$$

$$c_M = [M^{n+}] + [M^{n+}L] + [M^{n+}L_2] \quad (4)$$

with the total concentrations of the monocyclic ligand c_L and the cation c_M . The experimentally measured heat Q during titration in the case of the formation of 1:1 and 2:1 complexes is given by

$$Q = \Delta H_1[M^{n+}L] + (\Delta H_1 + \Delta H_2)[M^{n+}L_2] \quad (5)$$

Using eqns. (1)–(5) it is possible to calculate values of Q . In Fig. 1 the results for such calculations are shown. For given values of K_1 , ΔH_1 and ΔH_2 the influence of the value of K_2 on the measurable heat is demonstrated. The differences between the curve in the case of only 1:1 complex formation ($K_2 = 0$) and the other curves, taking into account the formation of 2:1 complexes, are small at ratios of the ligand to cation smaller than

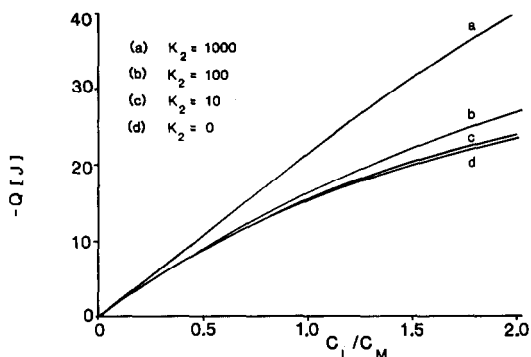


Fig. 1. Calculated heats, Q , for the simultaneous formation of 1:1 and 2:1 complexes during a titration for given values of K_1 (1000 M^{-1}), ΔH_1 (40 kJ mol^{-1}) and ΔH_2 (40 kJ mol^{-1}) and different values of K_2 as a function of the ratio of the concentrations of ligand c_L to cation c_M .

0.5. The same result is obtained if the value of ΔH_2 is varied and the values of K_1 , K_2 and ΔH_1 are kept constant, as shown in Fig. 2.

This behaviour can be understood if the concentration of the 1:1 complex $[M^{n+}L]$ is calculated, as shown in Fig. 3, for different values of the stability constant K_2 at varying ratios of ligand to cation concentration. At low values of c_L/c_M the concentration of the 1:1 complexes in solution is not significantly affected by the formation of 2:1 complexes.

To obtain experimental titration curves which allow the calculation of K_1 , K_2 , ΔH_1 and ΔH_2 the concentration of the ligand should be at least two times higher than the concentration of the cation at the end of the titration. The mathematical treatment of the resulting titration curves, however is difficult [5]. Therefore we looked for another possible way to study the formation of 2:1 complexes.

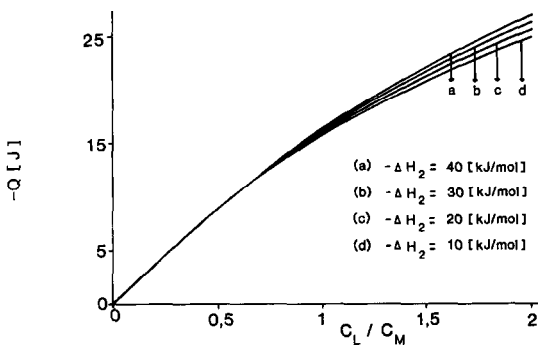


Fig. 2. Calculated heats, Q , for the simultaneous formation of 1:1 and 2:1 complexes during a titration for given values of K_1 (1000 M^{-1}), K_2 (100 M^{-1}) and ΔH_1 (40 kJ mol^{-1}) and different values of ΔH_2 as a function of the ratio of the concentrations of ligand c_L to cation c_M .

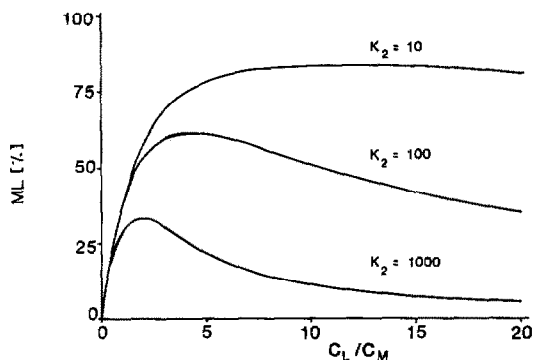


Fig. 3. Concentration of the 1:1 complex in solution for a given value of the stability constant K_1 (1000 M^{-1}) and different values of K_2 as a function of the ratio of ligand c_L to cation c_M concentration.

If the experimental conditions are arranged such that the ratio of ligand to cation is smaller than 0.5 during the calorimetric titrations it is possible to calculate from the thermogram the values of the stability constant and reaction enthalpy for the formation of 1:1 complexes. The error in the values due to the simultaneous formation of 2:1 complexes is very small.

As already mentioned in the Experimental section, it is possible to titrate a solution containing a cryptand into a solution of a cation and another ligand. According to the general reaction scheme given above the solution consists of the uncomplexed cation, the 1:1 complex and the 2:1 complex. The concentrations of each species depend on the ratio of the concentrations of the ligand to the cation. The experimentally obtained heat of reaction ΔH_{exp} of all species with the cryptand is given by

$$\Delta H_{\text{exp}} = x \Delta H(\text{M}^{n+}) - y \Delta H_1 - z \Delta H_2 \quad (6)$$

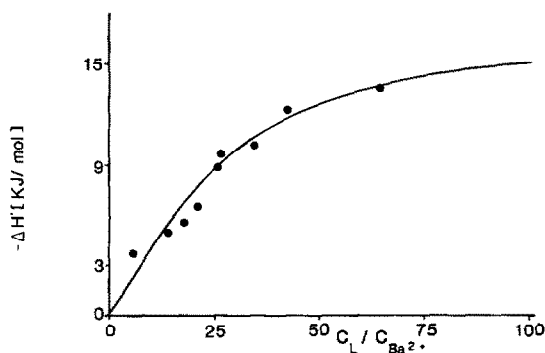


Fig. 4. Reaction enthalpies, $\Delta H'$, for the calorimetric titration of solutions containing the ligand *c*-BTO and Ba^{2+} at different concentration ratios with the cryptand (222).

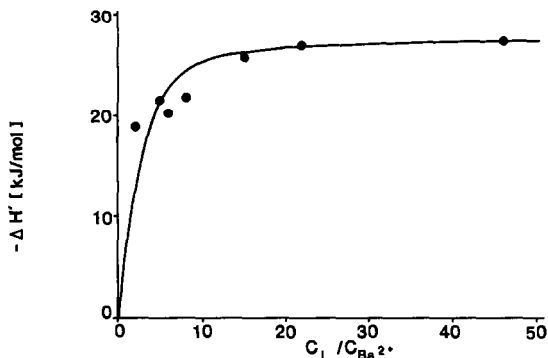


Fig. 5. Reaction enthalpies, $\Delta H'$, for the calorimetric titration of solutions containing the ligand 12C4 and Ba^{2+} at different concentration ratios with the cryptand (222).

These titrations are performed at different ratios of the ligand and cation concentration (see Figs. 4–6). If the concentration of the ligand L is zero, the reaction enthalpy $\Delta H(\text{M}^{n+})$ for complex formation of the cryptand with the cation M^{n+} is measured. To simplify eqn. (6) one can write

$$\begin{aligned} \Delta H' &= \Delta H_{\text{exp}} - \Delta H(\text{M}^{n+}) \\ &= -[\text{M}^{n+}\text{L}]/c_{\text{M}} \Delta H_1 - [\text{M}^{n+}\text{L}_2]/c_{\text{M}}(\Delta H_1 + \Delta H_2) \end{aligned} \quad (7)$$

Using eqns. (1)–(4) and (7) one obtains

$$\Delta H' = \frac{K_1 \Delta H_1 [\text{L}] + K_1 K_2 (\Delta H_1 + \Delta H_2) [\text{L}]^2}{1 + K_1 [\text{L}] + K_1 K_2 [\text{L}]^2} \quad (8)$$

with

$$c_{\text{L}} = [\text{L}] + c_{\text{M}} \frac{K_1 [\text{L}] + 2K_1 K_2 [\text{L}]^2}{1 + K_1 [\text{L}] + K_1 K_2 [\text{L}]^2} \quad (9)$$

All attempts to fit the four unknown parameters K_1 , K_2 , ΔH_1 and ΔH_2 according to eqns. (8) and (9) to the experimental data failed. Owing to

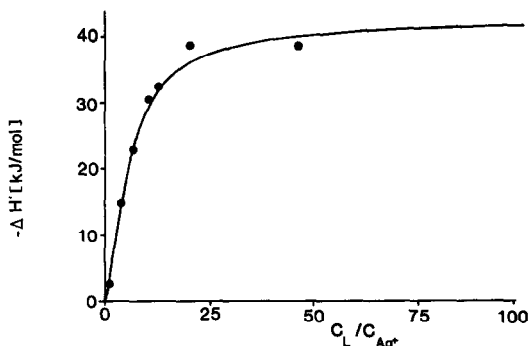


Fig. 6. Reaction enthalpies, $\Delta H'$, for the calorimetric titration of solutions containing the ligand 12C4 and Ag^+ at different concentration ratios with the cryptand (222).

TABLE 1

Stability constants ($\log K$; K in M^{-1}) and thermodynamic values (kJ mol^{-1}) for the formation of 1:1 and 2:1 complexes in methanol at 25°C

Reaction	$\log K_1$	$-\Delta H_1$	$T\Delta S_1$	$\log K_2$	$-\Delta H_2$	$T\Delta S_2$
$c\text{-BTO} + \text{Ba}^{2+}$	1.88 ^a	7.9 ^a	2.7 ^a	1.90 2.45 ^a	9.6 5.9 ^a	1.2
$12\text{C4} + \text{Ba}^{2+}$	2.56 ^b	21.4 ^b	-6.9 ^b	2.39	6.3 5.9 ^b	7.3
$12\text{C4} + \text{Ag}^+$	1.61 ^b	10.7 ^b	-1.6 ^b	1.72	31.7 27.9 ^b	-21.9

^a From ref. 12.

^b From ref. 10.

experimental error, no absolute minimum in the error square sum could be found.

As already discussed in detail, calorimetric titrations can be performed even in the case of 2:1 complex formation to obtain reliable values of the stability constant K_1 and the reaction enthalpy ΔH_1 . Using these values, only the stability constant K_2 and the reaction enthalpy ΔH_2 have to be fitted using eqns. (8) and (9) to the experimental data for the formation of 1:1 and 2:1 complexes. These data together with the fitted curves for different complexation reactions are shown in Figs. 4–6. Obviously the experimental data are described extremely well by the equations used for the formation of 1:1 and 2:1 complexes. No systematic deviations of the experimental curves from the calculated ones are observable. Schwesinger [16] found such deviations by fitting the experimental data for the complex formation of *c*-BTO with Ba^{2+} to a model for the formation of 1:1 and 2:1 complexes.

The calculated values for the stability constants and reaction enthalpies are given in Table 1. With the exception of the reaction between *c*-BTO and Ba^{2+} no stability constants for the formation of 2:1 complexes have been published. However, the agreement between the values of $\log K_2$ obtained from a direct calorimetric titration of the ligand *c*-BTO with a solution containing Ba^{2+} [12] and the value of $\log K_2$ obtained from the indirect titration described in this paper is good.

For all three reactions given in Table 1 the reaction enthalpies calculated by this indirect method are in good agreement with the values obtained from direct titrations of the ligands with the corresponding cations.

CONCLUSIONS

Schwesinger [11] states, "The only reliable method of solving thermograms with $\log K_1$ and $\log K_2$ values smaller than $[2 - \log c]$ is certainly

an error minimisation including all four parameters K_1 , K_2 , ΔH_1 and ΔH_2 ...". Our results and those of Izatt et al. [5] demonstrate why such a four-parameter fit is not easy to do and which experimental conditions have to be fulfilled. In any case the mathematical treatment of such experimental data is difficult.

A more convenient way is to reduce the parameters which have to be fitted to the experimental data. Using the experimental methods described for the study of the simultaneous formation of 1:1 and 2:1 complexes it is possible to calculate all stability constants and reaction enthalpies from easily performable experiments without any problems.

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REFERENCES

- 1 R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen and D. Sen, *Chem. Rev.*, 85 (1985) 271.
- 2 H.K. Frensdorff, *J. Am. Chem. Soc.*, 93 (1971) 600.
- 3 E. Mei, J.L. Dye and A.I. Popov, *J. Am. Chem. Soc.*, 99 (1977) 5308.
- 4 E. Mei, A.I. Popov and J.L. Dye, *J. Phys. Chem.*, 81 (1977) 1677.
- 5 R.M. Izatt, D. Eatough, R.L. Snow and J.J. Christensen, *J. Phys. Chem.*, 72 (1968) 1208.
- 6 R.M. Izatt, R.E. Terry, D.P. Nelson, Y. Chan, D.J. Eatough, J.S. Bradshaw, L.D. Hansen and J.J. Christensen, *J. Am. Chem. Soc.*, 98 (1976) 7626.
- 7 R.B. Davidson, R.M. Izatt, J.J. Christensen, R.A. Schultz, D.M. Dishong and G.W. Gokel, *J. Org. Chem.*, 49 (1984) 5080.
- 8 H.-J. Buschmann, *Chem. Ber.*, 118 (1985) 2746.
- 9 H.-J. Buschmann, *Thermochim. Acta*, 107 (1986) 219.
- 10 H.-J. Buschmann, *J. Solut. Chem.*, 16 (1987) 181.
- 11 R. Schwesinger, *Inorg. Chim. Acta*, 155 (1989) 145.
- 12 R. Benken and H.-J. Buschmann, *Inorg. Chim. Acta*, 134 (1987) 49.
- 13 D.J. Eatough, J.J. Christensen and R.M. Izatt, *Experiments in Thermometric Titrimetry and Titration Calorimetry*, Brigham Young University Press, Provo, 1974.
- 14 H.-J. Buschmann, *Chem. Ber.*, 118 (1985) 4297.
- 15 M.K. Chantooni and J.M. Kolthoff, *Proc. Natl. Acad. Sci. U.S.A.*, 78 (1981) 7245.
- 16 R. Schwesinger, private communication, 1986.