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A test reaction from macrocyclic chemistry for calorimetric titrations

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Dedicated to Prof. R.M. Izatt

Abstract

Titration calorimeters are controlled by standard reactions. One of these reactions is the protonation of trishydroxy methylaminomethane in aqueous solution. However, from this reaction only the reaction enthalpy is measured. Calorimetric titrations are used to study the interactions between macrocyclic (e.g. crown ethers) and macrobicyclic ligands (e.g. cryptands) with neutral or charged guest molecules. From the experimental measurements sometimes the stability constants and the reaction enthalpies are calculated. Thus, a test reaction should not only enable the calculation of the reaction enthalpy but also of the stability constant. A suitable reaction is the complexation of Ba^{2+} by the macrocyclic ligand 18-crown-6. This reaction has been studied in detail. The possible influence of the concentrations of ligand and salt, of the acidity of the solution, of the ionic strength and of the anion upon the stability constant and reaction enthalpy has been measured. The different anions do not influence the reaction enthalpy. However, they are able to change the values of the reaction entropy for the complexation of Ba^{2+} by 18-crown-6 within certain limits. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

To test the accuracy of a calorimeter one or several standard reactions are necessary. Some important requirements are essential for a reaction to be used as standard reaction [1,2]:

1. all chemicals are available in a pure form,
2. no reactions of these chemicals with the atmosphere take place and
3. the chemicals can easily be dried and weighed in the air.

Thus, the protonation reaction of the strong base trishydroxy methylaminomethane (THAM) by hydro-

chloric acid is used for calibration. Some of these results are summarized in Table 1. This neutralization reaction may be influenced by carbon dioxide dissolved in the aqueous solution. Further possible calibration reactions have been discussed in the literature in detail [3].

In the meantime due to the pioneering work of Izatt and coworkers [4] calorimetric titrations have been used to study the interactions between synthetic host and guest molecules. From these titration curves the simultaneous calculation of stability constants and reaction enthalpies is possible if the stability constants are within certain limits [5]. Using appropriate competitive calorimetric titrations even larger stability constants can be obtained experimentally [6]. Under these circumstances the requirements for test reactions increases. These reactions should not only enable the

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Table 1

Reaction enthalpy ΔH (kJ/mol) for the protonation of tris(hydroxymethyl) ammoniummethane (THAM) with hydrochloric acid in aqueous solution at 25°C

$-\Delta H$	Reference
47.50	[22]
47.44	[23]
47.44	[24]
47.32	[25]
47.57	[26]
47.40	[27]
47.44	[28]

calculation of the reaction enthalpy but also of the stability constant to check the accuracy of the calorimeter used.

The main problem is to find a reaction suitable as test reaction for calorimetric titrations in solution.

2. Experimental

The ligand 18-crown-6 (18C6) is used after purification as complex with acetonitrile [7]. The salts $\text{Ba}(\text{ClO}_4)_2$ (Merck), BaF_2 , BaCl_2 , BaBr_2 , BaJ_2 , $\text{Ba}(\text{NO}_3)_2$, $\text{Ba}(\text{CH}_3\text{COO})_2$ and tetraethylammonium perchlorate (TEAP) (all Fluka) and formic acid (Merck) are of the highest purity commercial available. As solvent bidistilled water is used.

The calorimetric titrations are performed using a Tronac Model 450 and Model 458 calorimeter. During the calorimetric titration a solution of the ligand (0.02–0.08 mol/l) is added continuously to the salt solution ($1.25\text{--}510^{-3}$ mol/l). The procedure for the calibration of the calorimeter and for the evaluation of the data has already been described in the literature in detail [8–10]. The reliability of the results obtained compared with the stability constants calculated from other experimental techniques like conductometry and potentiometry has been discussed [5]. Each titration has been repeated at least three times. The calorimetric titrations using $\text{Ba}(\text{ClO}_4)_2$ are performed over a period of several years (see Table 4).

3. Results and discussion

The sensitivity and construction of a titration calorimeter is essential for the upper and lower limits of the

Table 2

Stability constants K (1/mol) and reaction enthalpies ΔH (kJ/mol) for the complexation of alkali and alkaline earth cations by the macrocyclic ligand 18C6 in aqueous solution at 25°C [20]

	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
log K	≥ 1	2.27	1.79	≥ 1	≥ 1	2.81	3.50
$-\Delta H$		15.4	12.3			11.9	30.7

stability constants and reaction enthalpies calculable from thermometric titrations. It is not suitable to look for a calibration reaction at the upper or lower limits of a certain calorimeter. Thus, the stability constant should be in the order of $10^2\text{--}10^4$ (1/mol). The value of the reaction enthalpy should be as high as possible to increase the accuracy. The solvent should be available in high purity without any problems.

A suitable ligand should be easily available for commercial sources. Crown ethers or cryptands are possible candidates. However, the possible protonation of the cryptands may cause some problems for the reproducibility of the measured values. 18C6 seems to be the most promising ligand. Only with the exception for the complexation of Cs^+ no complications may arise for the formation of 2:1-complexes (ratio of ligand to cation) in aqueous solution. Experimental results for the complex formation between the ligand 18C6 and alkali and alkaline earth cations are given in Table 2. These data explicitly show that the reaction between the ligand 18C6 and Ba^{2+} is suitable as possible test reaction.

In Table 3 the results for the complexation of Ba^{2+} by 18C6 taken from the literature are summarized.

Table 3

Stability constants K (1/mol) and reaction enthalpies ΔH (kJ/mol) for the reaction between 18C6 and Ba^{2+} in aqueous solution at 25°C given in the literature

log K	$-\Delta H$	Reference
3.87±0.02	31.68±0.04	[29]
3.80±0.03	29.7±0.5	[30]
3.85±0.04	30.44±0.09	[31]
3.75±0.02	33.1±0.1	[32]
3.77	31.4	[33]
4.15	–	[34]
3.67	–	[35]
3.50	30.7	[36]
3.45	31.8	[37]
3.77±0.02	31.4±0.2	[38]

Table 4

Stability constants K (1/mol) and reaction enthalpies ΔH (kJ/mol) for the reaction between 18C6 and $\text{Ba}(\text{ClO}_4)_2$ in aqueous solution at 25°C determined from single titrations using different calorimeters during a period of several years

log K	$-\Delta H$
3.47	31.9
3.53	31.0
3.51	32.1
3.49	29.4
3.54	29.1
3.57	32.0
3.41	31.8
3.68	31.9
3.43	32.4
3.44	32.5
3.43	32.9
3.50±0.08	31.5±1.2

The reported values of the reaction enthalpy are very close to each other. In contrast the variation of the reported stability constants is relative high. Thus it is surprising that this reaction is already used by some authors as test reaction, see Table 3.

In Table 4 the results for the complexation of $\text{Ba}(\text{ClO}_4)_2$ by 18C6 measured over a period of several years are summarized. The individual results agree very well with each other. Obviously no individual errors are responsible for the different values of the stability constants given in Table 3. The variation of the calculated stability constant for this reaction from experimental data may principally be caused by one or more of the following factors:

1. influence of the concentration of ligand and salt,
2. influence of the ionic strength of the solution,
3. influence of the pH-values of the solution and
4. influence of the anion used.

Table 7

Influence of the concentration of formic acid (vol%) upon the experimental data for the complexation of $\text{Ba}(\text{ClO}_4)_2$ (5×10^{-3} mol/l) by 18C6 (0.08 mol/l) in aqueous solution at 25°C

Formic acid	0	5	10	25	50
log K	3.50±0.08	3.48±0.07	3.56±0.03	3.57±0.01	4.13±0.06a
$-\Delta H$	31.5±1.2	30.5±0.5	27.5±0.2	22.2±0.2 ^a	18.1±0.3 ^a
$T\Delta S$	-11.2±1.2	-10.7±0.9	-7.3±0.4	-2.0±0.1 ^a	5.4±0.7 ^a

^aRef. [39].

Table 5

Stability constants K (1/mol) and reaction enthalpies ΔH (kJ/mol) for the reaction between the ligand 18C6 and $\text{Ba}(\text{ClO}_4)_2$ in aqueous solution at different concentrations of the ligand c_L and salt c_S (both in mol/l)

c_L	0.08	0.06	0.04	0.02
c_S	5×10^{-3}	3.75×10^{-3}	2.5×10^{-3}	1.25×10^{-3}
log K	3.50±0.08	3.47±0.07	3.50±0.02	3.43±0.09
$-\Delta H$	31.5±1.2	32.2±0.5	32.4±0.7	35.3±1.6

Table 6

Influence of the concentration of tetraethyl ammonium perchlorate TEAP (mol/l) upon the experimental data for the complexation of $\text{Ba}(\text{ClO}_4)_2$ (5×10^{-3} mol/l) by 18C6 (0.08 mol/l) in aqueous solution at 25°C

TEAP	0	1×10^{-3}	1×10^{-2}	1×10^{-1}
log K	3.50±0.08	3.41±0.02	3.38±0.07	3.46±0.01
$-\Delta H$	31.5±1.2	33.3±0.1	34.0±0.9	33.2±0.1

In Table 5 the values of the stability constants and reaction enthalpies are summarized measured at different concentrations of the ligand and $\text{Ba}(\text{ClO}_4)_2$. Obviously the concentrations of ligand and salt do not influence the measured values. Thus, under these experimental conditions the salt is completely dissociated. The results obtained at different ionic strengths of the solutions are give in Table 6. The ionic strength does not influence the calculated stability constant. These findings differ with results reported for the complexation of Na^+ by 18C6 in methanol as solvent [11].

In the presence of formic acid also proton complexes may be formed. However, the presence of formic acid has only a minor influence upon the values obtained for the complexation of $\text{Ba}(\text{ClO}_4)_2$ by 18C6, see Table 7. The ligand 18C6 only forms weak complexes with protons in aqueous solution (log $K=1.28$ [12], -0.40 [13] and 1.46 [14]). At high acid con-

Table 8

Stability constants K (l/mol) and thermodynamic values ΔH and $T\Delta S$ (kJ/mol) for the complexation of different barium salts by 18C6 in aqueous solution together with the entropy change $T\Delta S_{Str}$ due to the effects of the anions on the structure of water at 25°C

Salt	BaF ₂	BaCl ₂	BaBr ₂	BaI ₂	Ba(ClO ₄) ₂	Ba(NO ₃) ₂	Ba(CH ₃ COO) ₂
Log K	3.47±0.04 ^a	3.87±0.02 ^b 3.80±0.03 ^c 3.85±0.04 ^d 3.75±0.02 ^e 3.77±0.02 ^f 3.77±0.02 ^g	3.72±0.08 ^a	3.81±0.01 ^a	3.50±0.08 ^a	4.05±0.02 ^a	4.05±0.04 ^a
− ΔH	32.5±0.3 ^a	31.7±0.04 ^b 29.7±0.5 ^c 30.44±0.09 ^d 33.1±0.1 ^e 31.4±0.2 ^f 31.4±0.2 ^g	31.9±0.5 ^a	32.0±0.1 ^a	31.5±1.2 ^a	31.7±0.6 ^a	31.6±0.1 ^a
$T\Delta S$	−12.8±0.4 ^a	−10.0±0.3 ^a	−10.8±1.0 ^a	−10.4±0.2 ^a	−11.2±1.2 ^a	−8.7±0.7 ^a	−8.6±0.3 ^a
$T\Delta S_{Str}^g$	−14.9	3.6	8.6	15.2	11.3	6.3	−18.5

^a This work.

^b Ref. [29].

^c Ref. [30].

^d Ref. [31].

^e cf. [32].

^f Ref. [38].

^g Ref. [21].

centrations the competition between the Ba²⁺ ions and the protons may be responsible for the observed changes. However, also the changes in solvent composition may be responsible. Thus, it is known that formic acid molecules form aggregates in aqueous solution [15,16]. At high formic acid concentrations this solvent mixture may not be compared with pure water [17]. At low concentrations of formic acid the values of the stability constant and of the reaction enthalpy are identical with those obtained in pure water. The reaction is obviously not sensitive to small changes of the pH value of the solution.

In Table 8 the results for the complexation of different barium salts with 18C6 are given. From the literature only one systematic study of the anion influence upon the stability constant and the thermodynamic values is known for the complex formation between 18C6 and K⁺ in aqueous solution [18]. These results are not in accordance with the values reported by others for the complexation of KNO₃ [19] and KClO₄ [20].

Both cations and anions are able to influence the structure of water [21]. The Ba²⁺ ion has water-structure-making properties. The anions examined

posses not only structure-making but also structure-breaking properties. The entropy changes of the anions on the structure of water $T\Delta S_{Str}$ are enclosed in Table 8. Positive values of $T\Delta S_{Str}$ show the structure breaking property of this anion. Values of $T\Delta S_{Str}$ between −9 and +9 (kJ mol^{−1}) may give an unreliable assignment [21]. If the structure-making or -breaking properties of the anions are responsible for the variations of the stability constants given in Table 3 this should have no or only a minor influence upon the values of the reaction enthalpies. The reaction enthalpies are more or less independent of the anions used (Table 8). Thus, mainly changes of the reaction entropies are responsible for the observed differences. As it can be seen in Table 8 the structure-making or -breaking properties of the anions cannot solely be responsible for the observed changes of the reaction entropy.

From the presented results it is obvious that the complexation reactions of 18C6 with all barium salts examined can be used as a test reaction for calorimetric titrations. The most extensively studied complexation reactions with 18C6 are with BaCl₂ and Ba(ClO₄)₂. Unfortunately the influence of the anions

cannot be neglected even at relative low salt concentrations in aqueous solution.

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