

Complex formation of crown ethers and cryptands with Ba²⁺ in the biphasic system chloroform/water studied by titration calorimetry

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Abstract

Calorimetric titrations have been performed in the liquid biphasic system chloroform/water. The reactions between salts in aqueous in different crown ethers and a cryptand in chloroform solution have been studied. After saturation of each solvent with the other no heats of mixing are detected. The values of the stability constants are related to different individual reaction steps during the complex formation. The experimental values show that the complex formation itself is not measured. Other steps e.g. transfer of the salt from one solvent to the other are responsible for the calculated values. On the other hand the overall reaction enthalpies show a significant contribution resulting from the interactions between the ligands and the cation or salt. A more detailed discussion is not possible at the moment.

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1. Introduction

The interface between two immiscible liquids play an important role in chemical process like e.g. liquid–liquid extraction [1,2]. Although extraction processes are widely used in the laboratory and in industrial processes the knowledge about the detailed reactions taking place at the interface between both liquids is rather small. The transfer of ions across such interfaces also plays an important role in electrochemistry, heterogeneous catalysis and the action of drugs. Mainly electrochemical studies have been performed to study the ion transfer from one solvent to the other [3]. The properties of interfaces are quite different from the pure solvents [4]. Thus, the solvation of ions in the interface differs from the one in the pure solvents. On the other hand, the complex formation with organic extractants at the interface is influenced by the solvation of the cations and extractants. Numerous papers have been published about the use of macrocyclic ligands as e.g. crown ethers, cryptands or calixarenes as extractants [5,6]. The knowledge of the

microscopic structure of the interface between two immiscible liquids has recently increased from computer simulations [7–9]. At this interface exists a small area where both solvents are mixed. During the complex formation between a cation in the aqueous phase and a macrocyclic ligand in the organic phase the cations remain in contact with water molecules. As a result a complex is formed which is surrounded by water molecules. These water molecules are at least transferred into the organic phase together with the complex. The different reaction steps have not been well understood up to now due to the lack of experimental results.

In homogeneous solutions the complex formation between macrocyclic ligands and cations has been studied using different experimental techniques. Most commonly potentiometric, conductometric, spectrometric and calorimetric methods have been used [10]. Up to now mostly electrochemical methods have been used to study the transfer of ions from one solvent to the other [3–11]. To our knowledge no results from calorimetric titrations in liquid biphasic systems have been published.

In this paper, we report the first data for the complexation of cations by different crown ethers and the cryptand 222BB in the system chloroform/water as solvents obtained from calorimetric titrations.

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2. Experimental

The crown ethers dibenzo-15-crown-5 (DB15C5, Fluka), 18-crown-6 (18C6, Merck), benzo-18-crown-6 (B18C6, Merck), dibenzo-18-crown-6 (DB18C6, Merck), dicyclohexano-18-crown-6 (DC18C6, Fluka), dibenzo-21-crown-7 (DB21C7, Fluka), dibenzo-24-crown-8 (DB24C8, Fluka), diazacrown ether 22DD (Merck) and cryptand 222BB (Merck) are used without further purification. The synthesis, purification and characterization of the ligand 22(Mbp)₂ has already been described [12]. The molecular structures of the ligands used are given in Fig. 1.

The salts Ba(ClO₄)₂ (Merck), BaF₂ (Aldrich), BaI₂ (Aldrich), Ba(SCN)₂ (Faltz and Bauer), Ba(CH₃COO)₂ (Aldrich) are of the highest purity commercially available. Barium heptafluorobutyrate (Ba(C₃F₇COO)₂) is prepared

from the reaction of Ba(OH)₂ (Merck) with heptafluorobutyric acid (Fluka). The salt is washed with water, recrystallized from acetone–water mixtures and dried carefully under reduced pressure.

As solvent chloroform (Rathburn Chemicals Ltd.) and bidistilled water are used. The solvents are saturated with each other to prevent any heat effect from mixing. During a calorimetric titration a solution of the ligand (0.07–0.09 mol/l) in chloroform is added continuously to an aqueous salt solution (0.004–0.006 mol/l). During the titration a maximum of 2 ml of a solution of the ligand are titrated into a reaction vessel with 40 ml of the salt solution. Some ligands examined are able to form not only 1:1 but also 2:1-complexes (ratio of ligand to cation). In this case the concentrations of the ligand and salt solutions are varied to favorise the formation of 1:1-complexes.

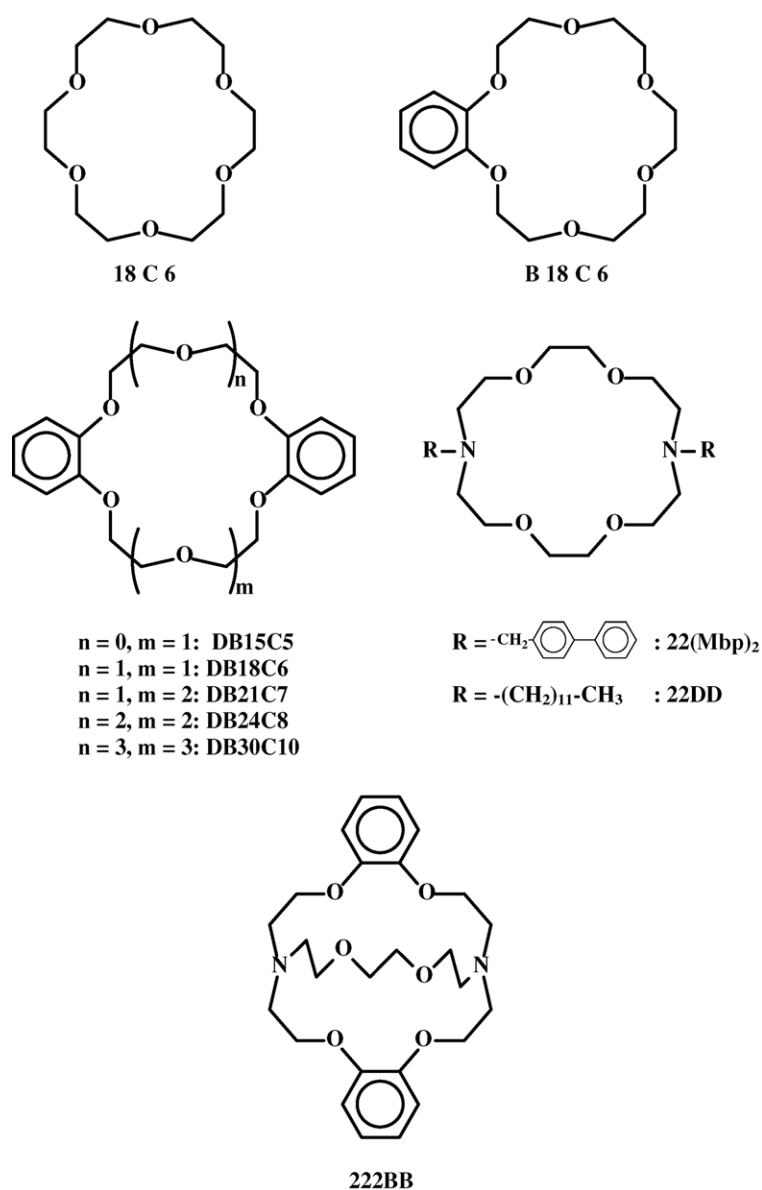


Fig. 1. Chemical structures of the ligands used.

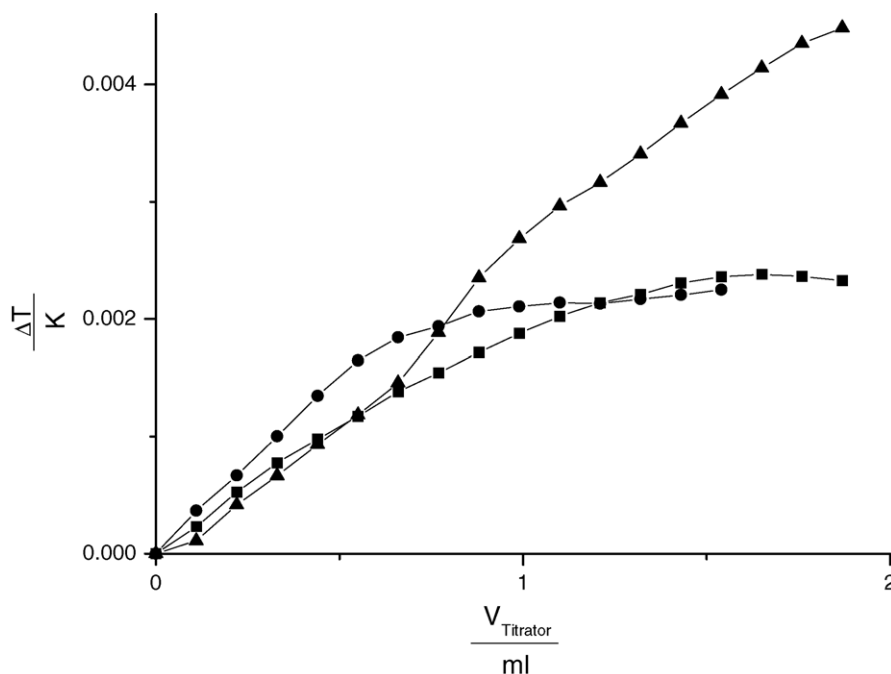


Fig. 2. Calorimetric titration curves for the reaction of the ligand DB18C6 (chloroform phase) with $\text{Ba}(\text{CH}_3\text{COO})_2$ (▲); BaCl_2 (■) and $\text{Ba}(\text{ClO}_4)_2$ (●) (aqueous phase) in the biphasic system chloroform/water at 25°C .

All reactions enthalpies are determined by titration calorimetry using a Tronac Model 450 calorimeter. From the measured heat changes, the stability constant and the reaction enthalpy can be calculated. This procedure has been described in the literature in detail [13–15]. For the evaluation of the titration curves it is essential that at any time during the titration all reactions are in equilibrium. All the experiments are repeated several times. Some typical calorimetric titration curves are shown in Fig. 2. From these curves values of stability constants and reaction enthalpies can be calculated.

To ensure that the experimentally observed heat effects are only caused by reactions of the macrocyclic ligands with cations the following titrations have been performed:

- a solution of chloroform (saturated with water) is titrated into water (saturated with chloroform);
- a solution of 18C6 (in chloroform) is titrated into water;
- a solution of DB18C6 (in chloroform) is titrated into water ;
- chloroform is titrated into a solution of $\text{Ba}(\text{ClO}_4)_2$.

During all of these titrations no measureable heat effects are observed.

3. Results and discussion

In homogeneous solution the following reaction between a ligand L and a metal ion M^{n+} takes place:



The stability constant K of the 1:1-complex is given by:

$$K = \frac{[\text{LM}^{n+}]}{[\text{L}][\text{M}^{n+}]} \quad (2)$$

However, in biphasic liquid systems different reaction steps have to be assumed during the extraction and complexation of the salt:

- partially desolvation of the cation and anion;
- formation of an ion pair;
- complex formation of the salt with the macrocyclic ligand;
- transfer of the complex from one solvent to the other.

The overall stability constant β for all possible processes is given by:

$$\beta = \prod_n^{i=1} K_i \quad (3)$$

and the overall reaction enthalpy ΔH_{ov} :

$$\Delta H_{\text{ov}} = \sum_n^{i=1} \Delta H_i \quad (4)$$

During a calorimetric titration the observed heat effect Q_{ov} is directly related to:

$$Q_{\text{ov}} = \sum_n^{i=1} \Delta n_i \Delta H_i \quad (5)$$

where Δn_i is the number of moles of the product i formed at any time of the titration and is a function of the equilibrium

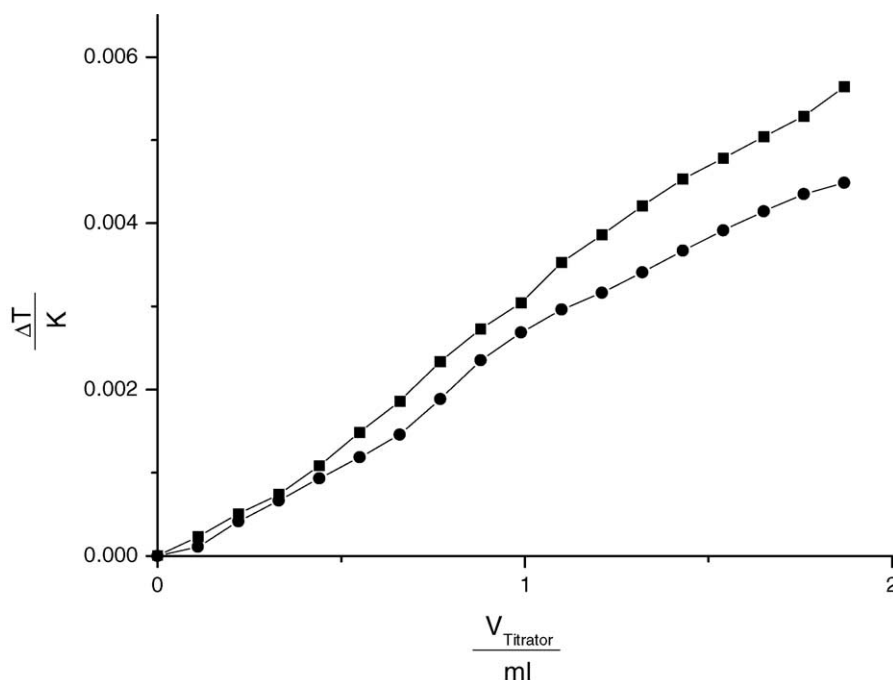


Fig. 3. Calorimetric titration curves for the reaction of the ligand DB186 (chloroform phase) with BaI_2 (■) and $\text{Ba}(\text{SCN})_2$ (●) (aqueous phase) in the biphasic system chloroform/water at 25°C .

constant K_i . If Δn_i or ΔH_i for a reaction are small they do not contribute noticeably to the overall heat effect Q_{ov} . In case of stability constants higher than 10^5 l/mol Δn is constant during the titration. Under this condition the temperature change is linear. A curvature of the thermogram is only observable if $\log K_i$ is smaller than five and higher than one [15,16].

Since no experience about calorimetric titrations in liquid biphasic systems with macrocyclic ligands and salts exists several barium salts have been tested for evaluating the anion effect on the observed heat effects. Anions such I^- , F^- , Br^- , SCN^- , gives thermograms not mathematically interpretable at the moment, see Fig. 3. With these anions S-shaped titration curves are observed indicating a slow reaction at the beginning of the titration. It takes a little time before all reactions taking part have reached an equilibrium during the titration. For the calculation of stability constants and reaction enthalpies from the titration curves it is essential that the reaction has reached equilibrium at any time during the titration. No corrections for this kinetic aspects are possible at the moment. Since this reaction is depending on the anions their desolvation or their transfer to the organic solvent may be responsible. Only thermograms obtained using ClO_4^- , Cl^- and acetate anions are calculable due to the absence of any kinetic effects.

In Table 1 the values of the stability constants $\log \beta$ and the reaction enthalpies ΔH_{ov} for the reaction of DB18C6 with different barium salts in the biphasic system chloroform/water at 25°C are given. The values of $\log \beta$ are nearly identical and the reaction enthalpies are of the same order of magnitude. Obviously the influence of the anion upon the

reaction enthalpy is neglectable in the case of the perchlorate and acetate anion. Thus, $\text{Ba}(\text{ClO}_4)_2$ is used for further studies.

Different macrocyclic and macrobicyclic ligands have been used to study the ligand influence upon the reaction with $\text{Ba}(\text{ClO}_4)_2$ in the chloroform/water biphasic system. In Table 2 the corresponding results are summarised. All calculated values of $\log \beta$ are nearly identical. From studies in homogenous solutions it is known that the values of the stability constants for the complexation of Ba^{2+} vary several orders of magnitude [17,18]. The only possible explanation is that $\log \beta$ is not related with the reaction between the ligand and the salt. Other reaction steps during the liquid biphasic titration as e.g. the transfer of the salt from one solvent to the other are responsible for the curvature of the titration curves. However, the values of the reaction enthalpy ΔH_{ov} show a distinct variation with

Table 1

Stability constants $\log \beta$ and thermodynamic values ΔH_{ov} (kJ/mol) for the complexation of DB18C6 with $\text{Ba}(\text{ClO}_4)_2$, BaCl_2 and $\text{Ba}(\text{CH}_3\text{COO})_2$ in the biphasic system chloroform/water at 25°C

Salt	$\log \beta$	$-\Delta H_{\text{ov}}$
BaF_2	— ^a	
BaCl_2	2.54 ± 0.01	14.0 ± 1.2
BaBr_2	— ^a	
BaI_2	— ^a	
$\text{Ba}(\text{ClO}_4)_2$	2.53 ± 0.02	8.8 ± 1.2
$\text{Ba}(\text{CH}_3\text{COO})_2$	2.59 ± 0.02	8.8 ± 1.2
$\text{Ba}(\text{SCN})_2$	— ^a	

^a Mathematical treatment of the titration curves not possible.

Table 2

Stability constants $\log \beta$ and the reaction enthalpy ΔH_{ov} (kJ/mol) for the reaction of different ligands with $\text{Ba}(\text{ClO}_4)_2$ in the biphasic system chloroform/water at 25 °C

Ligand	$\log \beta$	$-\Delta H_{ov}$
DB15C5	2.54 ± 0.01	16.6 ± 0.8
18C6	2.54 ± 0.01	40.7 ± 1.2
B18C6	2.55 ± 0.01	43.0 ± 2.9
DB18C6	2.53 ± 0.02	8.8 ± 1.2
DC18C6	2.52 ± 0.01	10.9 ± 1.0
DB21C7	2.55 ± 0.02	16.4 ± 0.1
DB24C8	2.54 ± 0.01	22.6 ± 3.6
DB30C10	2.53 ± 0.01	27.1 ± 2.8
22DD	2.52 ± 0.01	12.1 ± 1.9
22(Mbp) ₂	2.53 ± 0.02	22.6 ± 1.7
222BB	2.52 ± 0.02	28.4 ± 4.3

the ligand size and structure. The number of oxygen donor atoms and their basicity influence the reaction enthalpies ΔH_{ov} . This is in accordance with results obtained in homogenous solution. The presence of benzene substituents near ether donor atoms reduces the basicity of these donor atoms. With increasing number of ether donor atoms the values of ΔH_{ov} increase. The only exception is with the ligand DB15C5. Other factors should be responsible for the high value of the overall reaction enthalpy. The substitution of two ether donor atoms by nitrogen atoms also causes a reduction of the values of ΔH_{ov} . This is partly compensated by the macrobicyclic structure of the cryptand 222BB. A more detailed discussion is not possible at the moment. Due to the limited experimental results no separation of the overall reaction enthalpies into individual values for the different reaction steps is meaningful at the moment.

The calculation of reaction entropies is not meaningful because the values of $\log \beta$ and ΔH_{ov} can not be attributed to defined reaction steps. Even with the discussed limitations the presented experimental results demonstrate the possibility of calorimetric titrations in liquid biphasic systems. With an increasing number of experimental results this technique enables a better understanding of the individual processes taking place during the extraction of salts from an aqueous to an organic solution.

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