



The Interpretation of Thermodynamic Data for the Complex Formation of Cations with Crown Ethers and Cryptands. Part I: The Reaction Entropy

Dedicated to Professor H. Strehlow on the occasion of his 80th birthday

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Abstract. The complex formation between cations and crown ethers or cryptands is influenced by enthalpic and entropic contributions. The solvation of cations and ligands plays an important role and influences both thermodynamic parameters. Changes in solvation and their influence upon the reaction entropy is discussed in detail for some selected reactions in different solvents. Other contributions e.g., from the deformation of the ligands are eliminated. Thus, the results obtained are valid for all complexation reactions between cations and macrocyclic and macrobicyclic ligands.

Key words: crown ethers, cryptands, complex formation, reaction entropy

1. Introduction

Numerous articles about the complex formation between cations and crown ethers and cryptands have been published since 1967 [1–4]. In this year Pedersen discovered the ability of crown ethers to form complexes with alkali and alkaline earth cations [5]. Two years earlier Pressman published his first results about the ability of natural occurring substances to transport cations selectively through biological membranes [6]. In 1969 Izatt suggested that crown ethers may act as model substances of the natural occurring ionophores [7]. Thus, the study of the complex formation of crown ethers with cations should give some insight into the factors influencing the selective complex formation of alkali and alkaline earth cations.

In the meantime the articles published on crown ether and cryptand complexes, complex stabilities and values of the reaction enthalpies and entropies cannot be counted. Surprisingly, the reported number of thermodynamic values of the complex formation is much smaller compared with the number of stability constants reported [1–4].

The interpretation of the reaction enthalpies and entropies is not trivial because many factors influence them. A discussion mainly about the enthalpic effects during the complex formation has been published [8]. Some factors influencing the experimental values of the reaction entropies have been discussed [9–13]. However, a more general discussion is missing up to now. In this review we try to

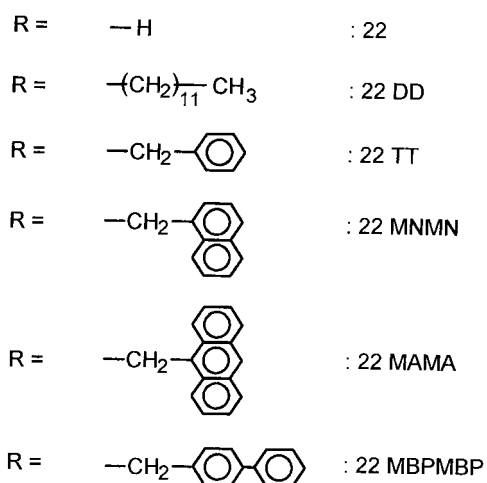
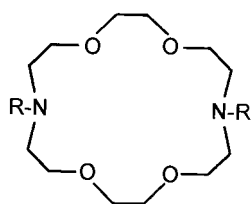


Figure 1. Chemical structures of substituted diaza-18-crown-6 ethers used in this study.

summarize some results already published and combine them with new results to get more insight into the factors influencing the reaction entropy.

2. Experimental

All ligands used were commercially available e.g. 18-crown-6 (18C6) or they were synthesized as described in the articles cited. The chemical structures of the different diazacrown ethers and of the cryptands are given in Figures 1 and 2.

As solvents propylene carbonate (PC), acetonitrile (AN), dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and acetone (AC) (all Merck) were used. They were of the highest purity available. The solvents were dried over molecular sieves prior to use.

The experimental conditions for the potentiometric and calorimetric titrations have already been discussed in detail [14].

3. Results and Discussion

The reaction entropy for the complex formation between cations and macrocyclic and macrobicyclic ligands is the sum of different contributions:

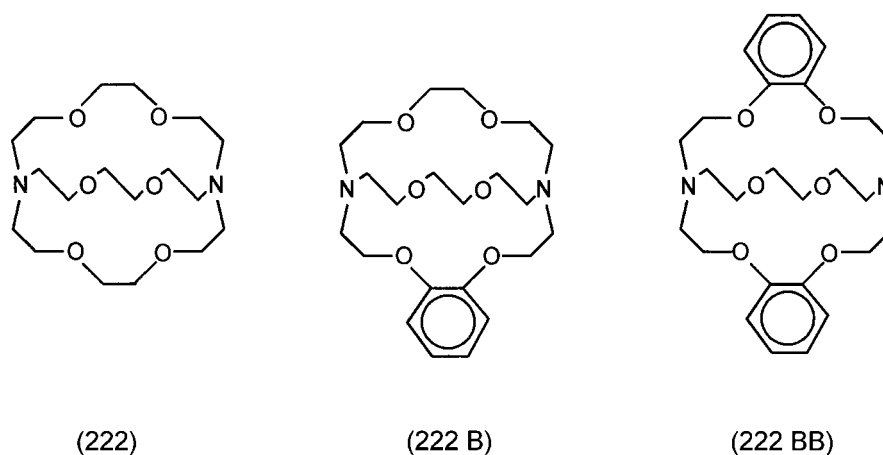


Figure 2. Chemical structures of different cryptands used.

- changes in the solvation of the cation (ΔS_{cation}),
- changes in the solvation of the ligand (ΔS_{ligand}),
- changes in the ligand's internal entropy due to orientation, rigidification and conformational changes ($\Delta S_{\text{internal}}$) and
- changes of the number of particles ($\Delta S_{\text{particles}}$).

The influence of the translational, rotational and conformational entropy contributions has already been described in the literature [15]. However, it is not possible to quantify all individual contributions to the reaction entropy. Therefore one should keep all contributions constant with the exception of one. Now the changes of the experimental reaction entropy can be discussed with respect to this contribution. From this point of view the solvation effects upon cations, ligands and complexes respectively are accessible.

3.1. SOLVATION OF THE CATIONS

The interactions between cations and different solvent molecules are well known [16–20]. In solvent mixtures a selective solvation of a cation by only one solvent component has been reported [17, 20]. Thus, it is not surprising that the solvation of cations plays an important role during complex formation [1–4]. However, this has already been discussed in great detail in numerous articles and books.

3.2. SOLVATION OF THE LIGANDS

Only a few results have been reported about the interactions between solvent molecules and crown ethers [21–25] and the cryptand (222) [26]. For the ligand 18C6 thermodynamic values of transfer from water to methanol [25] and for the diaza crown ether (22) and the cryptand (222) also to other solvents or solvent mixtures

Table I. Thermodynamic values (in kJ/mol) of transfer from water to methanol at 25 °C

Ligand	ΔG_{tr}	ΔH_{tr}	$T \Delta S_{tr}$
18C6 ^a	6.0	56.8	50.8
(22) ^b	3.6		
(222) ^c	3.8	58.2	54.4

^a Ref. 25.

^b Ref. 27.

^c Ref. 26.

have been determined [26–28]. Some results from the literature for the transfer of these ligands from water to methanol are given in Table I.

The large positive values of the entropies of transfer from water to methanol of both ligands are discussed in the literature to be caused by the loss of hydrogen bonds [25, 26]. However, also the gain of conformational entropy may contribute to the entropies of transfer. Comparable results are obtained for the transfer from water to other solvents.

The formation of an insoluble complex between 18C6 and AN has been used to purify this crown ether [21]. In AN the ligand 18C6 forms a 1 : 2 complex (ratio of ligand to guest molecule) with the solvent [23]. Comparing the reaction entropies for the complexation of e.g., sodium, potassium and barium ions with 18C6 in the solvents MeOH and AN one gets the values in Table II. In MeOH the complex formation is disfavoured and in AN it is favoured by entropic factors. The reaction entropies in AN are even positive. During the complex formation in AN the solvent molecules strongly bound by the ligand 18C6 are set free and as a result the number of particles increases. Identical observations are made in the case of other ions. During the complex formation in MeOH solvent molecules are also liberated from the ligand 18C6. Due to weaker interactions between the ligand and the solvent molecules this contribution to the overall reaction entropies is smaller than in AN. Comparing the reaction entropies in both solvents it is not possible to calculate the number of solvent molecules bound by the ligand 18C6 in MeOH and AN.

3.3. CHANGES OF SOLVATION DURING COMPLEX FORMATION

During the complex formation the solvation of the cations and of the ligands changes. For a better understanding of the factors influencing the reaction entropy it is important to keep as many factors as possible constant. Under these conditions the number of solvent molecules set free during complex formation either from the ligands or from the cations may be calculated. Due to the liberation of bound solvent molecules the reaction entropy increases. In Table III some entropies of

Table II. Stability constants ($\log K$, K in l/mol) and thermodynamic parameters ΔH and $T \Delta S$ (kJ mol⁻¹) for the complexation of some cations with the ligand 18C6 in MeOH and AN at 25 °C

Solvent	Cation	$\log K$	$-\Delta H$	$T \Delta S$
MeOH	Na ⁺ ^a	4.32	34.0	-9.5
	K ⁺ ^a	6.29	54.9	-19.2
	Ba ²⁺ ^b	7.38	48.5	-6.5
AN	Na ⁺ ^c	4.71	-2.3	29.1
	K ⁺ ^c	5.72	9.9	22.6
	Ba ²⁺ ^c	8.88	19.8	30.7

^a Ref. 31.

^b Ref. 32.

^c Ref. 33.

Table III. Entropies of fusion $T \Delta S_{\text{fusion}}$ (kJ mol⁻¹) of some solvents at 25 °C

Solvent	$T \Delta S_{\text{fusion}}$
H ₂ O	6.6 ^a
MeOH	4.1 ^b
AN	10.7 ^b
PC	9.0 ^b
DMF	24.4 ^b
DMSO	14.9 ^b

^a Ref. 34.

^b Ref. 30.

fusion of some solvents are summarized. They will be used to calculate the number of solvent molecules liberated during the complex formation.

In the following text some examples will be discussed in detail.

3.3.1. Changes of the ligand solvation during complex formation

Stability constants and thermodynamic data obtained for the reaction of Ag⁺ with some substituted diaza-18-crown-6 ligands, see Figure 1, are summarized in Table IV.

The observed reaction entropy ΔS for the complex formation with one ligand (L_1) is the sum of different contributions:

$$\Delta S(L_1) = \Delta S_{\text{cation}}(L_1) + \Delta S_{\text{ligand}}(L_1) + \Delta S_{\text{internal}}(L_1) + \Delta S_{\text{particles}} \quad (1)$$

Table IV. Stability constants ($\log K$, K in l/mol) and thermodynamic parameters ΔH and $T\Delta S$ (kJ mol⁻¹) for the complexation of Ag⁺ and Ba²⁺ by different diaza-18-crown-6 ligands in MeOH at 25 °C

Cation	Ligand	$\log K$	$-\Delta H$	$T\Delta S$
Ag ⁺	(22) ^a	10.02	44.9	12.0
	(22BuBu) ^b	10.01	60.5	-3.6
	(22OcOc) ^b	10.20	62.3	-4.3
	(22DD) ^b	10.28	61.1	-2.7
	(22TT) ^b	9.70	68.5	-13.4
	(22MnMn)	8.65	51.3	-2.2
Ba ²⁺	(22) ^c	6.12	10.0	24.8
	(22DD) ^c	5.84	32.9	0.3
	(22TT)	4.76	29.9	-2.9
	(22MnMn)	2.45	21.8	-7.9

^a Ref. 35.

^b Ref. 11.

^c Ref. 36.

An identical expression is valid for the complex formation with another ligand (L_2).

The silver(I) ion strongly interacts with both nitrogen donor atoms of these ligands. Thus, a deformation of the ligands during complex formation is possible. Under the assumptions that the different substituents have no influence upon this deformation process and upon the partial desolvation of Ag⁺ both contributions to the reaction entropy are nearly identical:

$$\Delta S_{\text{internal}}(L_1) \approx \Delta S_{\text{internal}}(L_2),$$

$$\Delta S_{\text{cation}}(L_1) \approx \Delta S_{\text{cation}}(L_2).$$

Thus, the differences in the reaction entropies of both ligands are mainly caused by the desolvation of the ligands during the reaction:

$$\Delta S(L_1) - \Delta S(L_2) \approx \Delta S_{\text{ligand}}(L_1) - \Delta S_{\text{ligand}}(L_2).$$

With this assumption it becomes possible to calculate the difference between the number of moles of solvent liberated during the complexation by two ligands taking into account the entropy of fusion (ΔS_{fusion}) of methanol. This is demonstrated for example for the ligands (22) and (22BuBu), with n as the number of moles of solvent molecules additionally liberated:

$$n = \frac{T\Delta S_{(22)} - T\Delta S_{(22\text{BuBu})}}{T\Delta S_{\text{fusion}}} = 3.8. \quad (2)$$

Table V. Differences between the reaction entropy for the complexation of Ag^+ and Ba^{2+} by the ligand (22) and different substituted diaza-18-crown-6-ethers and the change in the number of solvent molecules n liberated during complex formation with both ligands in MeOH at 25 °C

Cation	Ligands	$T \Delta S_{(22)} - T \Delta S_{(l)}$	n
Ag^+	(22)–(22BuBu) ^a	15.6	3.8
	(22)–(22OcOc) ^a	16.3	4.0
	(22)–(22DD) ^a	14.7	3.6
	(22)–(22TT) ^a	25.4	6.2
	(22)–(22MnMn)	14.2	3.5
Ba^{2+}	(22)–(22DD)	24.5	6.0
	(22)–(22TT)	27.7	6.8
	(22)–(22MnMn)	32.7	8.0

^a Ref. 11.

During the complex formation of the silver(I) ion with the ligand (22) four additional solvent molecules are set free as compared to ligand (22BuBu). In Table V corresponding results for other substituted diaza 18-crown-6 ligands are given. Obviously the effect of the different substituents upon the entropies of deformation of these ligands is small. As a result the values of n are nearly identical.

In all cases the number of solvent molecules n set free during the complex formation is higher for the unsubstituted ligand compared to the substituted ones. The substitution of the proton at the nitrogen donor atoms of the ligand (22) reduces the interactions between the ligands and the solvent molecules.

Comparable results are obtained for the complex formation between these ligands and Ba^{2+} . The Ba^{2+} -ion fits optimally into the cavity of the ligand (22). As a result no deformation of this ligand is expected during complex formation. Some results for the complexation of Ba^{2+} by different substituted diaza crown ethers are given in Table IV. As already described the differences in solvation of the diaza crown ethers can be calculated from these reaction entropies. The results are summarized in Table V. The number of solvent molecules liberated during complex formation with Ba^{2+} are with one exception greater than for Ag^+ .

With other cations similar results are obtained. However, some additional effects have to be taken into account. If these cations are too small or too big to fit optimally into the cavity of these ligands and if they show only weak interactions with nitrogen donor atoms serious problems may arise. These cations may not interact with all oxygen donor atoms. Thus, the conformational changes of the ligands may depend upon the kind of substituents on the nitrogen atoms. The effect of ligand desolvation of the diaza crown ethers obtained for Ag^+ and Ba^{2+} contributes to all other complex formation processes with other cations.

Table VI. Solvation numbers of some cations in different solvents obtained from their entropies of solvation [30]

Solvent Cation	H ₂ O ^a	MeOH	AN	PC	DMF	DMSO
Na ⁺	3.5	11.2	4.8	5.1	1.7	2.7
K ⁺	2.6	8.6	3.8	4.3	1.5	2.5
Rb ⁺	2.4	7.3	3.5	3.6	1.3	2.4
Cs ⁺	2.1	6.2	3.3	3.1	1.2	2.0
Ba ²⁺	5.3	25	9.6		4.1	6.7

^a Ref. 37.

3.4. CHANGES OF THE CATION SOLVATION DURING THE COMPLEX FORMATION

In polar solvents cations and anions are solvated. The solvent molecules arranged around the ions normally form a first solvation shell and further ones [20, 29]. For a given ion, the solvation number is operationally defined by the method of measurement [20]. Using entropies of solvation of salts the number of solvent molecules translationally immobilized during the solvation process can be calculated [30]. During the complex formation between the solvated cations and ligands these solvent molecules will mainly contribute to the entropic changes. Some solvation numbers for cations are given in Table VI.

Due to the fact that the solvation of the ligand and of the cation are influenced during the complexation reaction it is not possible to discuss changes of the solvation for one cation only during the reaction. Comparing the results obtained for two cations with nearly identical ionic radii eliminates all other effects like e.g., ligand desolvation and ligand deformation during the complexation.

Using the results given in Table II and Table VII it is possible to calculate the effect of cation solvation for K⁺ and Ba²⁺, e.g., in MeOH and AN. In analogy starting with Equation (1) one obtains for the change in solvation between Ba²⁺ and K⁺ during the complex formation with 18C6 in MeOH:

$$n = \frac{T \Delta S_{(\text{Ba}^{2+})} - T \Delta S_{(\text{K}^{+})}}{T \Delta S_{\text{fusion}}} = 4.1. \quad (3)$$

During to the complex formation of 18C6 with Ba²⁺ four additional solvent molecules are set free compared with the reaction with K⁺. The results for the ligands 18C6 and (222) are summarized in Table VIII. Treating the experimental results in this way one completely eliminates the solvation changes of the ligands.

From the solvation numbers for K⁺ and Ba²⁺ in Table VI one would expect that during the complex formation in MeOH more solvent molecules are set free than in AN. This is confirmed by the results given in Table VIII. However, in the case of

Table VII. Stability constants ($\log K$, K in l/mol) and thermodynamic parameters ΔH and $T\Delta S$ (kJ mol^{-1}) for the complex formation of the cryptands (222), (222B) and (222BB) with K^+ and Ba^{2+} in different solvents at 25 °C

Solvent	Ligand	Cation	$\log K$	$-\Delta H$	$T\Delta S$
H ₂ O	(222)	K^+	6.0 ^a	52.3 ^a	-18.2 ^a
		Ba^{2+}	9.5 ^a	62.8 ^a	-8.8 ^a
	(222B)	K^+	5.1 ^b	38.3 ^b	-9.2 ^b
		Ba^{2+}	7.6 ^b	50.5 ^b	-0.9 ^b
	(222BB)	K^+	5.01 ^b	36.7 ^b	-8.1 ^b
		Ba^{2+}	5.65 ^b	30.6 ^b	1.6 ^b
MeOH	(222)	K^+	10.49 ^c	75.0 ^c	-15.4 ^c
		Ba^{2+}	12.9 ^d	68.9 ^e	4.4 ^e
	(222B)	K^+	9.21 ^f	65.3 ^f	-13.0 ^f
		Ba^{2+}	10.99 ^g	53.9 ^g	8.5 ^g
	(222BB)	K^+	8.74 ^h	66.2 ^h	-16.5 ^h
		Ba^{2+}	8.85 ⁱ	33.5 ^g	16.8 ^g
AN	(222)	K^+	9.56 ^k	74.0 ^k	-19.7 ^k
		Ba^{2+}	17.90 ^l	108.8 ^l	-7.1 ^l
	(222BB)	K^+	8.66 ^m	71.1 ⁿ	-21.9
		Ba^{2+}		76.6	
PC	(222)	K^+	11.00 ^o	72.8 ^o	-10.3 ^o
		Ba^{2+}	17.1 ^p	105.1 ^q	-7.9 ^q
	(222BB)	K^+	9.00 ^p	75.8	-24.7
		Ba^{2+}	13.5 ^p	66.4	10.3
DMF	(222)	K^+	8.03 ^p	57.8	-12.2
		Ba^{2+}	8.04 ^l	50.6 ^l	-4.9 ^l
	(222BB)	K^+	6.10 ^m	62.1	-27.4
		Ba^{2+}	4.32 ^p	33.4	-8.9
DMSO	(222)	K^+	7.18 ^p	57.2	-16.4
		Ba^{2+}	6.36 ^l	47.8 ^l	-11.7 ^l
	(222BB)	K^+	5.8 ^p	64.5	-31.6
		Ba^{2+}	3.48 ^p	22.1	-2.3

^a Ref. 40. ^b Ref. 12. ^c Ref. 41. ^d Ref. 42. ^e Ref. 36. ^f Ref. 43. ^g Ref. 9. ^h Ref. 44. ⁱ Ref. 45. ^k Ref. 46. ^l Ref. 47. ^m Ref. 48. ⁿ Ref. 49. ^o Ref. 50. ^p Ref. 51. ^q Ref. 52.

Table VIII. Differences between the reaction entropies for the complexation of Ba^{2+} and K^+ by the ligands 18C6 and (222) and the number of solvent molecules n liberated during complex formation in different solvents at 25 °C

Solvent	Ligand	$T \Delta S_{(\text{Ba}^{2+})} - T \Delta S_{(\text{K}^+)}$	n
$\text{H}_2\text{O}^{\text{a}}$	18C6	4.7	0.7
MeOH^{b}	18C6	12.7	4.1
AN^{b}	18C6	8.1	0.8
$\text{H}_2\text{O}^{\text{c}}$	222	9.4	1.4
MeOH^{c}	222	19.9	4.9
AN^{c}	222	13.1	1.2

^a Ref. 38.

^b See Table II for references.

^c See Table VII for references.

the macrocyclic ligand 18C6 some solvent molecules are expected to remain in the first solvation shell. The macrobicyclic cryptand (222) encapsulates the ions and as a result more solvent molecules are liberated compared with 18C6.

In the case of the macrobicyclic cryptands these ligands are able to encapsulate the cations more or less completely. Thus, they form the first "solvation shell" of the complexed cations. The data in Table IX give no information about the interactions between the complexes and further solvent molecules. To disturb a possible second solvation shell of the cations it is necessary to increase the distance between the complexed cations and the surrounding solvent molecules. With increasing thickness of the macrobicyclic cryptands the interactions between the cations complexed and the solvent molecules should decrease. The incorporation of one or two benzene groups into the cryptand (222), see Figure 2, changes the thickness of these ligands. The thickness of the cryptands increases from (222) with 4.1 Å, over (222B) with 4.25 Å to (222BB) with 4.4 Å [39]. In Table VII stability constants and thermodynamic data for the complex formation of these cryptands with K^+ and Ba^{2+} in different organic solvents are given.

From the values of the reaction entropies for the complexation of K^+ and Ba^{2+} by different cryptands, see Table VII, it becomes possible to estimate the influence of the thickness of these macrobicyclic ligands. Using Equation (3) the changes of the solvation can be calculated. The results are given in Table IX.

In aqueous solution the thickness of the cryptands obviously has no influence on the reaction entropies. The results obtained in methanol as solvent indicate that one benzene group of the cryptands does not disturb the second solvation shell of the Ba^{2+} ion. However, the second benzene group reduces the interactions between the cation complexed and the solvent molecules. Comparable results are obtained in all other organic solvents examined.

Table IX. Differences between the reaction entropies for the complexation of Ba^{2+} and K^+ by the cryptands (222), (222B) and (222BB) and the number of solvent molecules n liberated during complex formation in different solvents at 25 °C

Solvent	Ligand	$T \Delta S_{(\text{Ba}^{2+})} - T \Delta S_{(\text{K}^+)}$	n
H ₂ O	(222)	9.4	1.4
	(222B)	8.3	1.3
	(222BB)	9.7	1.5
MeOH	(222)	19.8	4.8
	(222B)	21.5	5.2
	(222BB)	33.3	8.1
AN	(222)	12.6	1.2
	(222BB)	–	–
PC	(222)	2.4	0.3
	(222BB)	35.0	3.9
DMF	(222)	7.3	0.3
	(222BB)	18.5	0.8
DMSO	(222)	4.7	0.3
	(222BB)	29.3	2.0

By comparison of the results given in Table VI and Table IX it is obvious that the difference of the solvent molecules released from the K^+ and from the Ba^{2+} complexes depends on the solvation of these cations in the organic solvents. Thus, during the complex formation of both cations with (222BB) in MeOH and PC more solvent molecules are set free from the Ba^{2+} complex than in DMF and DMSO.

4. Conclusions

The presented results demonstrate the influence of the solvents upon the complexation reactions of crown ethers and cryptands. Changes in the solvation of ligands and cations play an important role during the complex formation. During the reaction the flexibility of the ligands is reduced which also influences the observed reaction entropies. Unfortunately, this effect could not be discussed using the presented experimental data. However, this discussion of the solvation effects should be understood as the beginning of a detailed interpretation of thermodynamic data for the reactions of crown ethers and cryptands.

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