

Influence of polar solvents upon the complex formation of 18-crown-6 with cations in chloroform

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Abstract The complex formation of crown ethers with cations in nonpolar medium with small amounts of polar solvents added has been studied. The goal has been to get deeper insight into the influence of solvation (hydration) of the salts for the formation of complexes with the macrocyclic ligand 18-crown-6 (18C6). A linear dependence of the reaction enthalpy for complex formation between 18C6 and alkali metal cations in chloroform in the presence of water or methanol has been observed. The presence of acetonitrile or acetone has had no influence upon the measured reaction enthalpies. The influence of methanol on the complex formation between 18C6 and alkali metal cations in chloroform is weaker than in the case of water. This underpins the selective solvation of alkali cations in chloroform after the addition of small amounts of water or methanol. The experiments have been performed using calorimetric titrations.

Keywords Crown ethers · Cations · Polar solvents · Complex formation · Chloroform

Introduction

Crown ethers are among the most employed host molecules along with cyclodextrins, calixarenes, and cucurbiturils for molecular recognition of appropriate substrates by hydrogen bonds, ionic interactions, and/or hydrophobic

interactions [1, 2]. It is well-known that the recognition is controlled by the conformation of host and the non-covalent interaction between host and guest molecules [3, 4]. The study of interactions involved in complexation of crown ethers and different cations in mixture of solvents is important for a better understanding of the mechanism of biological transport, molecular recognition, and analytical applications.

It is a fact that the stability and selectivity of complex formation between crown ethers and metal ions are strongly influenced by the cavity size of the receptor, the cation diameter, the nature of the heteroatoms in the receptor ring, and the reaction medium [1, 3]. The influence of the environment upon the crown ether complexes with cations depends on the solvation of cations, the solvation of complex formed, and the interactions between the receptors and solvent molecules [5–8].

The processes involved in solvent extraction, biological ion channels, phase transfer catalysis, and the transport through liquid membranes are strongly influenced by the environment. Thus, during the extraction process or transport through liquid membrane, water molecules are co-extracted with the cations onto water-saturated organic solvent used as extractant or membrane solvent [9–13]. The effect of very small amounts of water on the complex formation between 18C6 or [2.2.2] cryptand and K^+ in chloroform has been studied by calorimetric titrations concluding that the water molecules exhibit a pronounced effect upon the complex formation [14]. The water molecules in chloroform are not homogeneously distributed, rather they are located around the cations indicating that a selective solvation of the cations occurs [15].

Molecular dynamics simulations played an important role in the analysis of the recognition properties of such systems [16–19]. Studies of the thermodynamic functions

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in complex formation of benzo-15-crown-5 ether and Na^+ in water–methanol mixtures, revealed that Gibbs energy of the complex formation depends on the base–acid properties of the methanol–water mixture [20].

Our previously reported work was focused on the influence of solvent composition and the selective solvation of cations in dioxane–water mixtures on the complex formation of 18-crown-6 with cations [21]. The interactions between crown ethers and water, methanol, acetone, and acetonitrile molecules in halogenated solvents studied by calorimetric measurements supported the 1:1 stoichiometry of the complex formation between crown ethers and water in chloroform. The hydrogen bonding and ion–dipole interactions are responsible for the complex formation [22]. Moreover, studies on the complex formation of crown ethers and cryptand [2.2.2] with alkali metal cations and ammonium ion as guests in chloroform emphasized the importance of the reaction medium for the complex formation [23].

Following our research on the influence of polar solvents upon the complex formation between crown ethers and cations in nonpolar medium, the present study reveals the influence of polar solvents like water, methanol, acetone, and acetonitrile on the complex formation of 18-crown-6 with Na^+ , K^+ , Rb^+ , and Cs^+ dibenzoyldithiocarbamate salts and ammonium salts in chloroform by means of calorimetric titrations.

Experimental

Materials

The ligand 18-crown-6 (18C6, Merck, >99%) was of the highest purity available. Due to their solubility in chloroform, the dibenzoyldithiocarbamate salts of alkali metal, Na^+ , K^+ , Rb^+ , and Cs^+ ions were synthesized according to the method described in literature [24] and used throughout all the calorimetric titrations. Ammonium 1-pyrrolidinedithiocarbamate (Fluka) was of the highest purity commercial available. The calorimetric titrations were performed using a Tronac Model 450 calorimeter (TRONAC Inc.). The experiments were carried out at 298.15 K.

The following solvents: chloroform (Rathburn), methanol (H_2O content less than 0.003%, Merck), acetonitrile (H_2O content less than 0.005%, Merck), and acetone (H_2O content less than 0.0075%, Merck) were used in the experiments. All solvents were of the highest purity available. Chloroform was dried several weeks using molecular sieves (4 Å). All measurements were performed several times using different samples of chloroform to ensure the reproducibility of the results. Distilled water (Millipore Q-plus 185) was used throughout the experiments.

The reaction enthalpies of complex formation between crown ethers and polar solvents in chloroform were studied by calorimetric titrations. During the calorimetric titration, a solution of the ligand (0.02–0.04 mol/L) was continuously added to the solutions containing the salts (1.8 – 2.5×10^{-3} mol/L) in chloroform. The heat Q produced during the titration is related to the reaction enthalpy ΔH , after correction for all non-chemical heat effects, by the following equation:

$$Q = \Delta n \cdot \Delta H \quad (1)$$

where Δn represents the number of moles of the complex formed. The mathematical treatment of the experimental data has already been described in detail [25–27]. No heats of mixing or dilution has to be taken into account since it was previously shown that these heat values were smaller than 1 kJ/mol [22]. The accuracy of the calorimeter was checked using the reaction of 18C6 with $\text{Ba}(\text{ClO}_4)_2$ in aqueous solution [28]. Each titration was repeated at least five times.

Results and discussion

The solubility of dibenzoyldithiocarbamates in chloroform is sufficient to study the complex formation with macrocyclic ligands. However, the results for these reactions may be influenced by the presence of ion pairs. In pure chloroform, it was found that the effect of ion pairs on the reaction enthalpies for the complex formation is negligible [23]. Thus, the addition of small amount of polar solvents to the chloroform solution should result in strong interactions between the cations and these polar solvent molecules. Consequently, the possible influence of the presence of ion pairs upon the thermodynamic values for the complex formation with macrocyclic ligands is reduced further and the effect of solvation is dominant.

In Table 1, the values of the reaction enthalpies ΔH for the complex formation of alkali metal cations and the ammonium ion with 18C6 in chloroform at different concentrations of water have been summarized. Within the experimental error, the values measured in pure chloroform are identical with the results previously reported [23]. With the exception of the ammonium ion, all values of the reaction enthalpy decrease with increasing water concentration in chloroform.

The addition of small amounts of water to solutions of alkali salts in chloroform results in a hydration of the cations. The water molecules are located at the cations due to strong electrostatic interactions. With the increasing water concentration, the number of water molecules surrounding the cations increases. This process is comparable with the formation of very small water drops with the

Table 1 Reaction enthalpies ΔH (kJ/mol) for the complex formation of 18C6 with alkali and ammonium ions in chloroform at different concentrations of water at 25 °C

Cation	c_{water} (mol/L)	$-\Delta H$	$c_{\text{cation}}:c_{\text{water}}$
Na ⁺	0.000	46.4 ± 0.7	1:0.0
	0.001	43.1 ± 1.1	1:0.5
	0.002	39.6 ± 0.9	1:1.0
	0.003	31.5 ± 1.3	1:1.6
K ⁺	0.000	71.0 ± 1.1	1:0.0
	0.006	67.5 ± 1.3	1:2.3
	0.011	64.2 ± 0.9	1:4.6
	0.017	61.1 ± 1.2	1:6.6
	0.022	58.8 ± 1.1	1:8.9
	0.028	53.5 ± 0.7	1:11.6
	0.033	47.2 ± 1.4	1:13.8
	0.039	41.1 ± 0.8	1:15.4
	0.044	30.9 ± 1.3	1:17.6
Rb ⁺	0.000	67.0 ± 1.2	1:0.0
	0.011	64.4 ± 1.0	1:6.1
	0.022	60.4 ± 1.2	1:12.2
	0.033	56.6 ± 0.9	1:18.5
	0.044	50.0 ± 0.7	1:24.5
Cs ⁺	0.000	58.0 ± 0.9	1:0.0
	0.011	55.8 ± 0.7	1:6.2
	0.022	54.5 ± 0.3	1:12.1
	0.033	53.3 ± 0.5	1:18.0
NH ₄ ⁺	0.000	117.5 ± 3.6	1:0.0
	0.011	118.8 ± 3.2	1:6.0
	0.022	115.6 ± 3.8	1:12.3
	0.033	118.1 ± 2.0	1:18.2
	0.044	116.2 ± 2.6	1:24.1

cations in the middle. During the formation of the crown ether complex, some water molecules are replaced by the macrocyclic ligand. As a result, the values of the reaction enthalpy decrease with the increasing concentration of the water molecules. If the cation is completely surrounded by water molecules, no further dependence of the reaction enthalpies upon the water concentration should be detected. However, due to solubility problems, such water concentration cannot be achieved.

The absence of any influence of the solvation of the ammonium ion upon the reaction with 18C6 is surprising. The value of the reaction enthalpy measured in chloroform is much higher compared with those values observed in other organic solvents [29]. Obviously, the addition of small amounts of water to chloroform does not result in a hydration of the NH₄⁺ ion by these water molecules as observed in the case of the alkali ions. In this case, the

Table 2 Reaction enthalpies ΔH (kJ/mol) for the complex formation of 18C6 with alkali ions in chloroform at different concentrations of methanol at 25 °C

Cation	c_{methanol} (mol/L)	$-\Delta H$	$c_{\text{cation}}:c_{\text{methanol}}$	
Na ⁺	0.000	46.4 ± 0.7	1:0.0	
	0.005	43.3 ± 1.2	1:2.4	
	0.010	41.2 ± 1.0	1:4.8	
	0.015	37.0 ± 1.3	1:7.1	
	0.020	34.8 ± 1.2	1:9.3	
	0.025	32.0 ± 0.9	1:12.0	
	0.030	26.8 ± 1.5	1:14.0	
	0.034	26.5 ± 0.7	1:16.0	
	0.039	23.9 ± 0.8	1:19.4	
	0.044	21.3 ± 1.1	1:22.1	
K ⁺	0.000	71.0 ± 1.1	1:0.0	
	0.005	67.7 ± 2.5	1:2.7	
	0.010	69.0 ± 1.8	1:5.3	
	0.015	67.8 ± 2.2	1:8.1	
	0.025	67.2 ± 1.5	1:13.4	
	0.037	68.1 ± 2.3	1:20.1	
	0.049	67.8 ± 2.0	1:26.3	
	0.074	64.5 ± 1.4	1:40.0	
	0.098	60.9 ± 2.5	1:53.5	
Rb ⁺	0.000	67.0 ± 1.1	1:0.0	
	0.005	63.1 ± 3.5	1:2.7	
	0.017	65.1 ± 2.6	1:8.9	
	0.025	63.2 ± 2.1	1:13.2	
	0.037	65.8 ± 2.8	1:19.9	
	0.049	61.4 ± 2.5	1:26.7	
	0.074	61.7 ± 2.2	1:40.4	
	0.098	61.5 ± 2.0	1:53.4	
	Cs ⁺	0.000	58.0 ± 0.9	1:0.0
		0.012	56.6 ± 1.2	1:6.6
0.025		56.5 ± 0.8	1:13.9	
0.037		54.9 ± 1.1	1:20.2	
0.049		56.2 ± 1.5	1:26.7	
0.074		56.6 ± 0.9	1:39.2	
0.098		55.8 ± 0.7	1:53.5	

water molecules are more or less homogeneously distributed between the chloroform molecules.

For a deeper understanding of the solvation effect, the reactions between the ligand 18C6 and alkali ions in chloroform have been studied in the presence of small amounts of methanol, acetonitrile, and acetone. The corresponding results are given in Tables 2, 3, and 4, respectively. The addition of methanol also influences the measured values of the reaction enthalpies indicating interactions between the cations and this cosolvent. In

Table 3 Reaction enthalpies ΔH (kJ/mol) for complex formation of 18C6 with alkali ions in chloroform at various concentrations of acetonitrile (mol/L) at 25 °C

Cation	$c_{\text{acetonitrile}}$ (mol/L)	$-\Delta H$	$c_{\text{cation}}:c_{\text{acetonitrile}}$
Na ⁺	0.000	46.4 ± 0.7	1:0.0
	0.019	49.3 ± 1.5	1:9.5
	0.038	48.2 ± 1.1	1:18.3
	0.077	47.6 ± 1.2	1:36.4
	0.115	47.2 ± 1.0	1:57.3
K ⁺	0.000	71.0 ± 1.1	1:0.0
	0.004	69.3 ± 1.2	1:1.8
	0.019	69.7 ± 1.8	1:9.3
	0.039	69.4 ± 1.6	1:19.4
	0.057	71.8 ± 2.1	1:28.2
	0.077	71.3 ± 1.9	1:35.8
Rb ⁺	0.000	67.0 ± 1.1	1:0.0
	0.009	65.8 ± 2.1	1:4.5
	0.019	66.1 ± 1.8	1:9.9
	0.029	66.2 ± 2.0	1:13.9
	0.038	65.4 ± 1.6	1:18.9
	0.048	66.0 ± 2.1	1:23.3
	0.057	65.5 ± 1.9	1:30.6
	0.067	64.5 ± 1.6	1:32.2
	0.077	68.4 ± 2.4	1:39.1
	0.086	63.6 ± 2.6	1:42.2
Cs ⁺	0.000	58.0 ± 0.9	1:0.0
	0.021	57.3 ± 1.5	1:9.9
	0.038	58.2 ± 1.3	1:18.9
	0.077	56.6 ± 1.4	1:39.1
	0.115	59.2 ± 1.0	1:58.8

contrast, the addition of acetonitrile or acetone to the chloroform solution does not alter the values of the reaction enthalpies. Obviously, no selective solvation of the alkali ions by acetonitrile and acetone takes place, or the interactions between the alkali ions and these solvent molecules are weak.

Plotting the measured reaction enthalpies for the complex formation of the ligand 18C6 with alkali ions in chloroform as a function of the concentration of the added water or methanol straight lines are obtained, see Fig. 1.

As water or methanol molecules surrounding the cations are partially or completely replaced during the complex formation, the slopes of the lines should correlate with the strength of the interactions between these molecules and cations. However, one has to consider that the solvation of the alkali ions has been studied in chloroform solution and these values differ from the values obtained for the

Table 4 Reaction enthalpies ΔH (kJ/mol) for complex formation of 18C6 with alkali ions in chloroform at various concentrations of acetone (mol/L) at 25 °C

Cation	c_{acetone} (mol/L)	$-\Delta H$	$c_{\text{cation}}:c_{\text{acetone}}$
Na ⁺	0.000	46.4 ± 0.7	1:0.0
	0.014	45.5 ± 0.9	1:6.7
	0.027	44.2 ± 0.8	1:13.5
	0.041	43.8 ± 0.8	1:19.4
	0.054	43.0 ± 0.8	1:27.0
	0.068	44.6 ± 0.7	1:32.4
K ⁺	0.082	43.4 ± 1.0	1:40.0
	0.095	42.5 ± 1.2	1:44.4
	0.000	71.0 ± 1.1	1:0.0
	0.027	67.2 ± 0.6	1:13.3
Rb ⁺	0.054	67.7 ± 1.0	1:26.5
	0.068	71.2 ± 0.9	1:33.5
	0.000	67.0 ± 1.1	1:0.0
	0.027	67.7 ± 0.9	1:13.1
Cs ⁺	0.054	63.0 ± 1.3	1:26.5
	0.068	63.8 ± 1.2	1:34.0

hydration of the alkali metal ions in the gas phase [30]. The slopes are given in Table 5.

The values of the slopes correlate with the expected solvation effects. Under the assumption of ion–dipole interactions, the strength of the interactions should decrease with the increasing of cation size and dielectric constant of the added solvent molecules (water: $\epsilon = 78.39$; methanol: $\epsilon = 32.70$ [31]). This qualitative interpretation is supported by the values presented in Table 5. For a detailed examination, one has to consider the Coulomb law in which the force between two charges is reciprocal dependent on the square of the distance between charges. As a result, a plot of the slopes given in Table 5 as a function of the reciprocal square of the ionic radii should give a straight line, see Fig. 2.

No straight line is observed, which indicates further contributions to the measured values of the reaction enthalpies. However, the electrostatic interactions are predominant. In the case of the caesium ion, the values of the slopes are the lowest and close to zero in comparison with the other ions. Due to the size of this cation, rather weak interactions with solvent molecules are only observed.

The performed measurements have disclosed the influence of cation solvation upon the complex formation with macrocyclic ligands. For the time being, these results cannot be directly compared with the solvation enthalpies obtained in gas phase. The chloroform matrix has some influence on the experimental values. Independent from these considerations, the effect of small amounts of water

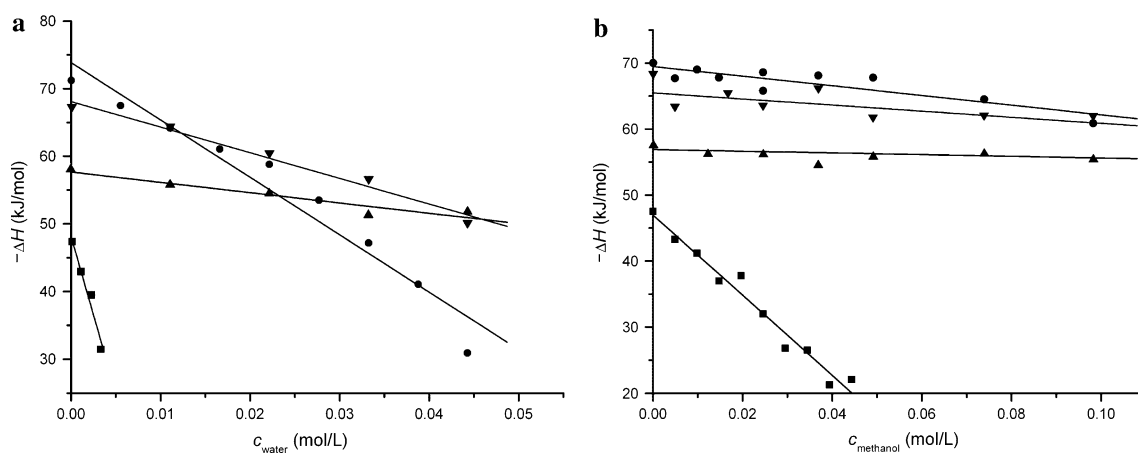


Fig. 1 Reaction enthalpies for the complex formation of 18C6 with alkali ions (Na^+ (filled square), K^+ (filled circle), Rb^+ (filled inverted triangle), Cs^+ (filled triangle)) in chloroform at different concentrations of water (a) and methanol (b) at 25 °C

Table 5 Slopes calculated from the lines shown in Fig. 1

Cation	Radius (\AA) ^a	$-\Delta H/c_{\text{water}}$ (kJ L mol^{-2})	$-\Delta H/c_{\text{methanol}}$ (kJ L mol^{-2})
Na^+	1.02	5150.0 ± 702.5	606.5 ± 37.1
K^+	1.38	848.0 ± 71.9	73.3 ± 14.2
Rb^+	1.52	379.3 ± 35.3	46.2 ± 20.4
Cs^+	1.67	152.6 ± 26.9	12.0 ± 10.3

^a From Ref. [32]

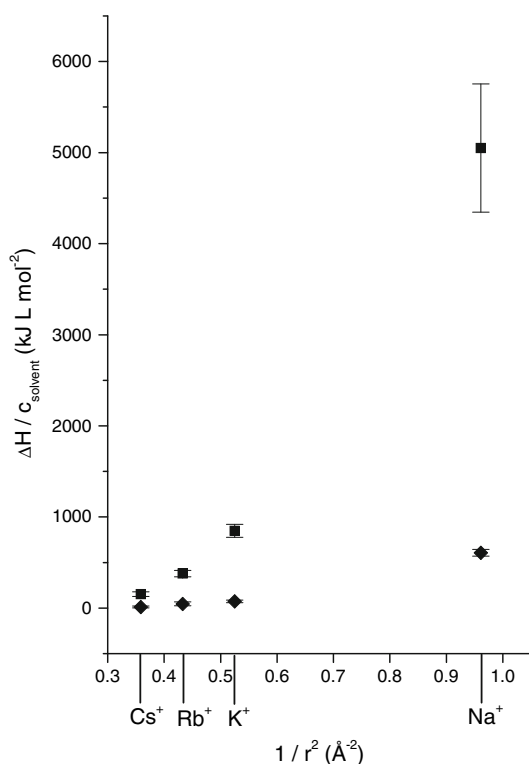


Fig. 2 Slopes ($-\Delta H/c_{\text{solvent}}$) from Table 5 as a function of the reciprocal square of the ionic radii of alkali ions

or methanol on the equilibria in organic solvents during extraction processes is clearly evidenced.

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