Thermochimica Acta 472 (2008) 17–19

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Complex formation of 18-crown-6 with metal cations and ammonium ions in dioxane–water mixtures

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ARTICLE INFO

Article history:
Received 10 December 2007
Received in revised form 11 March 2008
Accepted 17 March 2008
Available online 25 March 2008

Keywords:
Complex formation
18-Crown-6
Alkali and alkaline earth ions
Ammonium ions
Dioxane–water mixtures
Calorimetric titrations

ABSTRACT

The complex formation of 18-crown-6 with some alkali, alkaline earth, and ammonium ions in dioxane–water mixture has been studied by means of calorimetric titrations. The stability constants, reaction enthalpies and entropies for the complex formation in mixtures of water and dioxane at various proportions have been measured. The results clearly indicate the preferential solvation of the alkali and alkaline earth cations by water molecules. Thus, the values of the reaction entropies for a given cation are independent of the solvent composition. In the case of ammonium ions, the formation of hydrogen bonds between the NH-groups of the ammonium and mono and di-substituted ammonium cations and the water molecules has a pronounced influence upon the thermodynamic values measured. The results strongly demonstrate the influence of solvent composition and of selective solvation of cations in dioxane–water mixtures on the complex formation of 18-crown-6 with cations.

1. Introduction

The complex formation of macrocyclic ligands with various cations and anions is strongly influenced by the solvent nature. The influence of the solvent on a variety of chemical phenomena, including solubility, phase transfer, and chemical equilibria and kinetics are among the most important issues in molecular recognition processes [1–3]. Thus, the solvent characteristics, which include properties such as the level of structure, polarity, hydrogen bond donor/acceptor ability, polarizability, acidity/basicity, and hydrophobicity/hydrophilicity or other empirical parameters, mainly affect the interaction strength between the compounds [4–8]. Recently, significant progress has been made in theoretical calculations of free energies of solvation [9].

Crown ethers are macrocyclic ligands which form complexes with cations. The chemical structure is given in Fig. 1. Due to their structure interactions between the complexed cations and solvent molecules are possible. As a result the stability and selectivity of crown ether complex formation with cations is influenced by the interaction of the cation with the solvent and the crown ether, as well. Thus, if the solvent medium is changed, the significant effect on the binding constant is observed especially where cations are strongly solvated in one solvent and not in another [10]. In view of a deeper insight into the effects of solvent on the stabilities of complexes formed, the calorimetric titration study of the interaction of some mono- and divalent cations with crown ethers in methanol–water solvents has been performed [11]. These experiments indicate that the selectivity of crown ethers towards alkali and alkaline earth metal ions is dependent on the solvent nature. The complex formation may be strongly affected by solvation of the reactants. The effect of solvent on the complexation of crown ethers with alkali metal cations by means of different techniques has been a subject of interest during years [12–15].

In aqueous solution, most of the crown ethers are less selective and their complexes are less stable than in less polar solvents. For instance, the stability of the complex between K^+ and 15C5 increases when the solvent is changed from water to methanol or acetonitrile [14,16]. Moreover, the studies on the interactions of Na^+ with 15C5 and 18C6 in mixed methanol–water solvents as function of methanol:water composition revealed that replacement of water by methanol led to an increase in complex stability [13]. By studying the complexation of cryptand [2.2.2] with Na^+ and K^+ and 18-crown-6 with Na^+ in dioxane–water solvent mixtures Izatt and Wu [17] pointed out the influence of ligand structural features and preferential solvation properties. The complexes of Na^+ and K^+ with 12-crown-6, 15-crown-5, and 18-crown-6 in dioxane–water mixture studied by potentiometric [18] or conductometric [19] measurements emphasized the complex dependence on the chemical characteristics of all ligands and solvents. These measurements have been performed only in few mixtures of 1,

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doi:10.1016/j.tca.2008.03.010

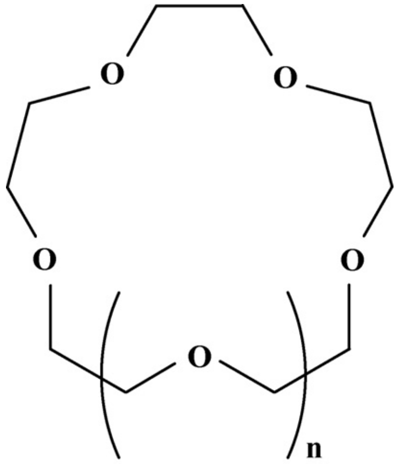

Fig. 1. Chemical structures of crown ethers ($n = 1$: 15-crown-5 (15C5); $n = 2$: 18-crown-6 (18C6).

4-dioxane–water (50/50, v/v; 80/20, v/v). In such systems, the electrostatic ion–dipole interactions depend on the macroscopic dielectric constant of the solvent mixtures and on the dipole moment of the ligands [19].

In this study the complexation of 18-crown-6 with alkali-metal and ammonium ions in mixtures of dioxane–water (20/80, v/v up to 80/20, v/v) are investigated by means of calorimetric titration to obtain more experimental results for the discussion of the influence of solvent composition on the complex formation.

2. Experimental

2.1. Chemicals

The ligand 18-crown-6 (18C6, Merck) was of the highest purity available. All salts $NaClO_4$, $KClO_4$, $Sr(NO_3)_2$, $Ba(ClO_4)_2$, NH_4ClO_4, CH_3NH_3Cl and $(CH_3)_2NH_2Cl$ (reagent grade, Fluka) were used as purchased. Distilled and deionised water was used throughout the experiments. As organic solvent 1,4-dioxane (≥99.9%, Fluka) was used without further purification.

2.2. Measurements and calculations

The calorimetric titrations were performed using a Tronac Model 450 calorimeter (TRONAC Inc.). During the calorimetric titration a solutions of the ligand (0.06–0.08 M) was added continuously to solutions containing the cations ($4.0–5.0 \times 10^{-3}$ M) in different mixture of dioxane with water (%v/v). The heat Q produced during the titrations is related to the reaction enthalpy ΔH after correction for all non-chemical heat effects, e.g. heat exchange with the surrounding and stirring of the solution, by the following equation:

$$Q = \Delta n \, \Delta H \tag{1}$$

with Δn indicating the number of moles of the complex formed. The mathematical treatment of the experimental data has been described in detail in the literature [20–22]. The accuracy of the calorimeter was controlled using as standard reaction the reaction between the crown ether 18C6 and $Ba(ClO_4)_2$ in aqueous solution [23].

3. Results and discussion

Table 1
Stability constants $\log K$ (K in $\mathrm{l\,mol^{-1}}$) and thermodynamic values ΔH and $T\Delta S$ (both in $\mathrm{kJ\,mol^{-1}}$) for the complex formation of 18C6 with alkali and alkaline earth cations in mixtures of water with different amounts of dioxane (% v/v) at $T = 298.15$ K

Cation	Dioxane	$\log K$	$-\Delta H$	$T\Delta S$
Na^+	0	0.8[a]	9.4[a]	−4.8[a]
	20	1.19[b]	10.4[b]	−3.6[b]
	35	1.48[b]	11.2[b]	−2.7[b]
	50	1.78[b]	11.9[b]	−1.7[b]
	70	2.16[b]	17.2[b]	−4.8[b]
	80	2.47 ± 0.01	22.6 ± 1.4	−8.6 ± 1.5
	100	4.54[c]		–
K^+	0	2.10 ± 0.08	25.0 ± 1.3	−13.1 ± 1.8
	20	2.46 ± 0.03	24.2 ± 0.3	−10.2 ± 0.5
	50	3.08 ± 0.09	31.8 ± 0.7	−14.3 ± 1.2
	60	4.24 ± 0.12	33.8 ± 0.5	−9.7 ± 1.2
	70	4.30 ± 0.15	34.8 ± 0.4	−10.4 ± 1.3
	80	4.72 ± 0.08	37.3 ± 0.5	−10.5 ± 1.0
Sr^{2+}	0	2.31 ± 0.06	17.4 ± 1.2	−4.3 ± 1.4
	20	2.46 ± 0.01	21.8 ± 0.9	−7.8 ± 1.0
	50	2.79 ± 0.02	28.9 ± 0.2	−13.1 ± 0.4
	60	3.99 ± 0.02	30.7 ± 0.4	−8.0 ± 0.5
	70	4.37 ± 0.03	33.9 ± 0.1	−9.1 ± 0.3
	80	4.82 ± 0.02	39.2 ± 0.2	−11.8 ± 0.3
Ba^{2+}	0	3.51[d]	31.5[d]	−11.6[d]
	20	3.94 ± 0.03	32.1 ± 0.8	−9.7 ± 1.0
	50	4.56 ± 0.01	37.8 ± 0.5	−11.9 ± 0.6
	60	4.71 ± 0.02	39.6 ± 0.6	−12.8 ± 0.7
	70	4.99 ± 0.05	41.6 ± 1.1	−13.2 ± 1.4
	80	>5	46.6 ± 0.9	–

[a] Ref. [11].
[b] Ref. [17].
[c] Ref. [24].
[d] Ref. [23].

The values of the stability constants ($\log K$) and the reaction enthalpies and entropies for the complexation of the crown ether 18C6 with alkali and alkaline earth cations in mixtures of dioxane–water together with published results are summarized in Table 1. Due to the complete mixing of 1,4-dioxane and water a large range of relative permittivity is adjustable between the value of pure water (78.39) and pure dioxane (2.209) [1]. Values of the relative permittivity of mixtures of 1,4-dioxane with water have also been published [1].

In water as solvent, the values of the stability constants for the complex formation between 18C6 and alkali and alkaline earth cations have the lowest values compared with all obtained in the dioxane–water mixture. The stability of the complexes increases with the increasing content of dioxane. The values of stability constants for the complex formation between 18C6 and Na^+, K^+, Ba^{2+}, and Sr^{2+} increase by two orders of magnitude going from pure water to mixture of dioxane–water (80/20, v/v). Due to solubility problems no measurements have been performed in pure dioxane. Also the values of the reaction enthalpies increase for all cations. Surprisingly, the increase for various cations with the exception of Sr^{2+} is constant going from pure water to (80/20, v/v) mixture of dioxane–water. The difference between the values of the reaction enthalpies in pure water and the mixture of dioxane–water (80/20, v/v) is $13.1 \pm 1.1\ \mathrm{kJ\,mol^{-1}}$. Mainly ion–dipole interactions between the metal cations and solvent molecules are responsible for the strength of solvation. Due to the presence of dioxane in aqueous solution the interactions between the metal cations and the surrounding water molecules are reduced. However, for all metal cations the composition of the solvation shell is more or less identical. This interpretation is supported by the values of the reaction enthalpies. These values are a nearly constant for each metal cation. As the dipole moment of water (1.83 D [1]) is much higher compared with 1,4-dioxane (0.45 D [1]) the number of water

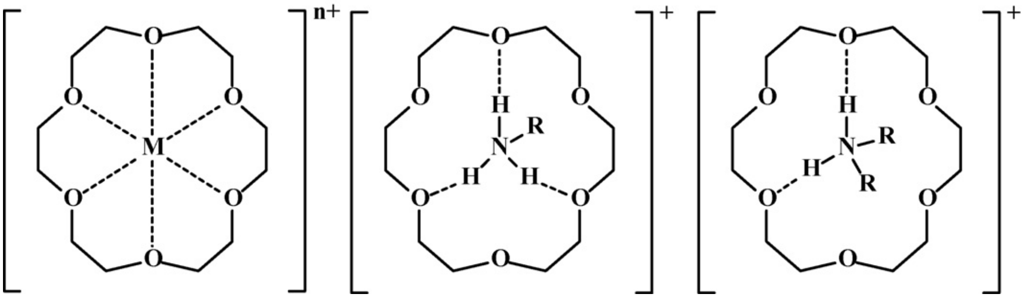

Fig. 2. Crown ether complexes with cations formed by ion–dipole interactions and with primary and secondary ammonium ions by hydrogen bonds between the ions and the oxygen donor atoms of the crown ether.

Table 2
Stability constants log K (K in l mol^{-1}) and ΔH and $T\Delta S$ (both in kJ mol^{-1}) for the complex formation of 18C6 with different ammonium ions in mixtures of water with different amounts of dioxane (% v/v) at T = 298.15 K

Cation	Dioxane	log K	$-\Delta H$	$T\Delta S$
NH_4^+	0	2.0[a]	3.0[a]	8.4[a]
	20	1.87 ± 0.01	11.5 ± 0.1	−0.9 ± 0.2
	40	2.22 ± 0.02	13.9 ± 0.2	−1.3 ± 0.3
	60	2.55 ± 0.03	24.5 ± 1.1	−10.0 ± 1.3
	80	3.00 ± 0.09	33.5 ± 1.3	−16.5 ± 1.9
$CH_3NH_3^+$	0	2.13 ± 0.03	1.0 ± 0.1	11.1 ± 0.3
	20	2.19 ± 0.04	1.1 ± 0.2	11.3 ± 0.4
	50	2.15 ± 0.01	15.2 ± 0.1	−3.0 ± 0.2
	60	2.29 ± 0.02	16.0 ± 0.9	−3.0 ± 1.0
	70	2.43 ± 0.03	25.3 ± 1.3	−11.5 ± 1.5
	80	2.45 ± 0.04	37.4 ± 1.2	−23.5 ± 1.4
$(CH_3)_2NH_2^+$	0	2.30 ± 0.05	0.8 ± 0.1	12.3 ± 0.4
	20	2.54 ± 0.09	0.5 ± 0.4	13.9 ± 0.9
	50	1.84 ± 0.01	0.5 ± 0.1	10.0 ± 0.2
	60	2.25 ± 0.01	0.7 ± 0.2	12.1 ± 0.3
	70	2.53 ± 0.01	0.8 ± 0.1	13.6 ± 0.2
	80	2.29 ± 0.07	0.8 ± 0.2	12.2 ± 0.6

[a] Ref. [30].

molecules surrounding the cations are higher in the solvation shell of the cations compared with the bulk phase. This observation is well known for the solvation of cations in different solvent mixtures [25] As a result, the number of solvent molecules released for a given cation due to the complex formation is independent from the solvent composition.

It is well known that crown ethers interact strongly with alkali metal cations by ion–dipole interactions [26] while the NH_4^+ ion forms hydrogen bonds to the oxygen donor atoms of the ligand 18C6 [27,28], see Fig. 2. The crystal structures of the ammonium ion complexes suggest that the complimentarity of the radius of the NH_4^+ (r = 1.48 Å) cation and the radius of the cavity of 18C6 (r = 1.4 Å) is nearly perfect [29]. The values of the stability constants (log K) and the thermodynamic parameters for the complex formation of 18C6 with ammonium ions in dioxane–water mixtures are given in Table 2.

In contrast with the results obtained for alkali and alkaline earth cations, the values of stability constants for the complex formation of 18C6 with NH_4^+ and $CH_3NH_3^+$ ions increase only slightly with increasing amounts of dioxane. A strong increase is again found for the magnitude of the reaction enthalpies which are nearly compensated by the reaction entropies. The reaction entropies change from positive to negative values with increasing dioxane content of the mixture with water. Obviously, the composition of the solvation shell is strongly influenced by the dioxane content of the bulk solvent mixture. Thus, the number of solvent molecules liberated during the complex formation of these ammonium ions with 18C6 is strongly dependent upon the solvent composition.

Sterical effects are responsible for the weak interactions between 18C6 and $(CH_3)_2NH_2^+$. Thus, the values of the reaction enthalpies are small and constant for all mixtures of water and dioxane. The number of hydrogen bonds between $(CH_3)_2NH_2^+$ and water molecules in the solvation shell is small and independent of the solvent composition. As a result, the reaction entropies are independent of the solvent composition too.

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