

# Proton NMR study of the stoichiometry, stability and thermodynamics of complexation of Rb<sup>+</sup> ion with 18-crown-6 in binary dimethylsulfoxide–nitrobenzene mixtures

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Received: 10 May 2009 / Accepted: 20 July 2009 / Published online: 4 August 2009  
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**Abstract** Proton NMR was used to study the complexation reaction of Rb<sup>+</sup> ion with 18-crown-6 (18C6) in a number of binary dimethylsulfoxide (DMSO)–nitrobenzene (NB) mixtures at different temperatures. In all cases, the exchange between free and complexed 18C6 was fast on the NMR time scale and only a single population average <sup>1</sup>H signal was observed. The formation constants of the resulting 1:1 complexes in different solvent mixtures were determined by computer fitting of the chemical shift mole ratio data. There is an inverse relationship between the complex stability and the amount of DMSO in the solvent mixtures. The enthalpy and entropy values for the complexation reaction were evaluated from the temperature dependence of formation constants. In all solvent mixtures studied, the resulting complex is enthalpy stabilized but entropy destabilized. The  $\Delta H^\circ$  versus  $T\Delta S^\circ$  plot of all thermodynamic data obtained shows a fairly good linear correlation indicating the existence of enthalpy–entropy compensation in the complexation reaction.

**Keywords** 18-crown-6 · Rubidium · Dimethylsulfoxide · Nitrobenzene · Proton NMR spectroscopy · Thermodynamic study

## Introduction

Crown ethers are compounds with multiple oxygen heteroatoms (three or more) incorporated in a monocyclic carbon backbone. They were first synthesized by Pedersen

[1, 2]. Their generic name originates from their molecular shape, reminiscent of a royal crown. According to the “hard–soft” acid–base theory and owing to the nature of their binding sites and to the presence of a hydrophilic cavity delineated by a lipophilic envelope, crown ethers exhibit a strong affinity and high selectivity for ammonium, alkali and alkaline earth metal ions [3–9]. Crown ethers were the first synthetic ligands for which this pronounced selectivity was identified [10]. Furthermore, because of their selective complex formation with hard metal ions as well as their negligible water solubility, crown ethers have been extensively used as suitable ion-carriers in solvent–solvent and solid phase extractions [11–14], ion-transport [15–17], ion-selective and PVC membrane ion-selective electrode studies [18–20], and the crown ether complexes used as a nano-switch recently [21–23]. Crown ethers were also extensively studied in parallel with natural ion-selective cyclic antibiotics such as valinomycin or enniatin for which they serve as simple models, helping to explain the transport of these biologically relevant cations and the mechanism of neurotransmission [24–27]. Furthermore, studies of the toxicity of crown ethers indicated that the compounds are not genotoxic in mammalian cells despite their cytotoxicity, but they have been shown to be highly toxic in prokaryotes and eukaryotes [28].

Different physicochemical methods such as mass spectroscopy [29, 30], UV–Vis spectroscopy [31], electrochemistry [32] and calorimetry [33] and proton NMR [6, 7, 34–42] have been frequently used to study the thermodynamics and kinetics of complexation of several crown ethers in a large number of nonaqueous solvents and solvent mixtures. In this work, we studied the stoichiometry and thermodynamics of complexation of Rb<sup>+</sup> with 18C6 in a number of binary dimethylsulfoxide (DMSO) nitrobenzene (NB) mixtures, using the <sup>1</sup>H NMR technique and

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found similar results with theoretical investigation on the same reaction published recently [43].

## Experimental

Reagent grade 18C6 (Aldrich) and rubidium nitrate (Fluka) were of the highest purity available and used without further purification except for vacuum drying. Reagent grade deuterated dimethylsulfoxide (DMSO, Merck) and extra pure nitrobenzene (NB, Merck) were used to prepare the solvent mixtures by weight.  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance (DPX) 200FT Spectrometer with field strength of 4.7 Tesla (a frequency of 200.13 MHz) equipped with a temperature controller. In all experiments, TMS was used as an internal standard. The temperature of the probe was adjusted to an accuracy of  $\pm 0.1$  °C using a heating element. Throughout the entire temperature range studied, it was found that 10-min thermostating prior to data collection was adequate for each sample to reach the equilibrium temperature.

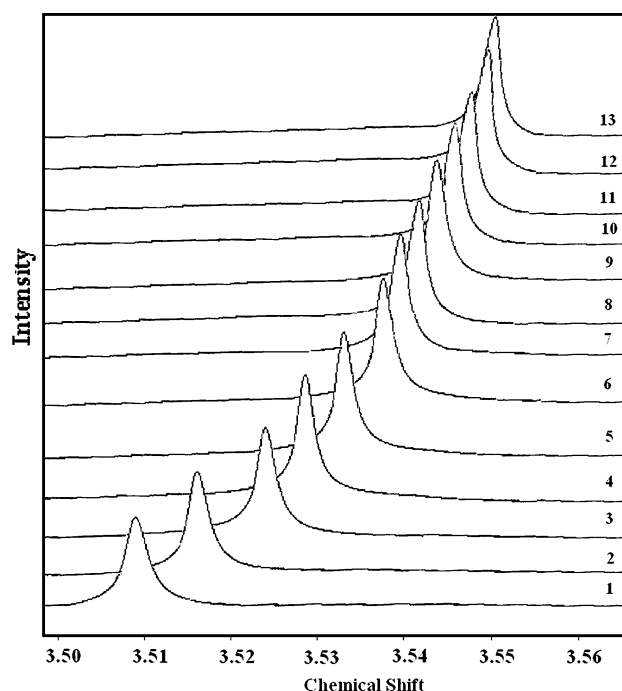
## Results and discussion

A series of binary DMSO–NB mixtures containing 18C6 ( $1.0 \times 10^{-2}$  M) in the presence of different amounts of  $\text{Rb}^+$  were prepared and allowed to reach equilibrium and then  $^1\text{H}$  NMR spectra of the resulting solutions were recorded at 30.0, 40.0, 50.0 and 60.0 ( $\pm 0.1$ ) °C. Because of the large difference physico-chemical properties of NB and DMSO such as Guttmann donor number (DN) and dielectric constant, NB was applied as a second solvent in order to reduce the solvent polarity and donor number. In addition, nitrobenzene is an ideal cosolvent in NMR studies with no interference in signal reading (its signal appears far from the studied region).

At all mole ratios studied, only one population average  $^1\text{H}$  signal was observed for 18C6, indicating a fast exchange of the crown ether between the free and the rubidium ion-complexed situation. Sample  $^1\text{H}$  NMR spectra at various  $[\text{Rb}^+]/[18\text{C}6]$  mole ratios in pure DMSO at 30.0 °C show a unique signal, due to the  $-\text{CH}_2-\text{CH}_2-$  groups of the ligand, are shown in Fig. 1.

The resulting chemical shift-mole ratio plots in pure DMSO and three different solvent mixtures of 90% DMSO + 10% NB, 80% DMSO + 20% NB and 60% DMSO + 40% NB at various temperatures are shown in Fig. 2.

As is obvious, upon an increase in the rubidium ion concentration, the proton resonance of 18C6 gradually shifts up-field until a  $[\text{Rb}^+]/[18\text{C}6]$  mole ratio of about 1 is reached, and tends to level off at higher mole ratios. This



**Fig. 1** Proton NMR spectra of 18C6 at various  $[\text{Rb}^+]/[18\text{C}6]$  mole ratios in pure DMSO at 30 °C.  $[\text{Rb}^+]/[18\text{C}6]$  mole ratios are: (1) 0.00, (2) 0.21, (3) 0.40, (4) 0.58, (5) 0.75, (6) 0.91, (7) 1.04, (8) 1.18, (9) 1.30, (10) 1.51, (11) 2.00, (12) 2.57, (13) 3.49

behavior is clearly indicative of the formation of a 1:1 complex in all solvent mixtures studied. Formation constants of the resulting 1:1 complexes were calculated by a fitting program KINFIT. It should be noted that changes in the chemical shift is implying on the interaction between ligand and metal, showing that its quantity is not important while the trend of its variation is used to evaluate the complex stability [44, 45]. An example of Computer fit is shown in Fig. 3 and all the calculated  $K_f$  values are summarized in Table 1. The great confidence interval of  $K_f$  has reported by KINFIT program result from the high degree of confidence in KINFIT program.

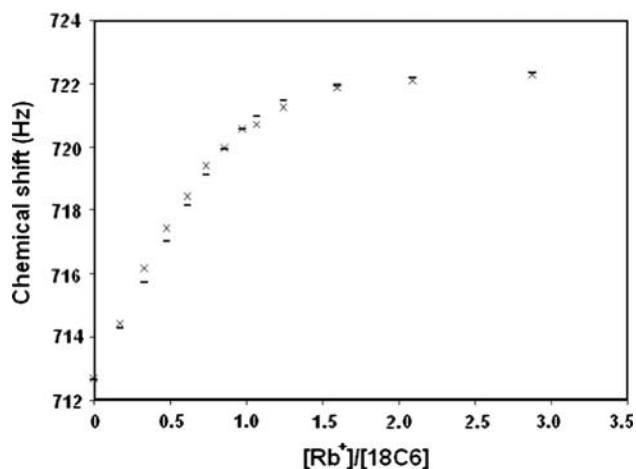
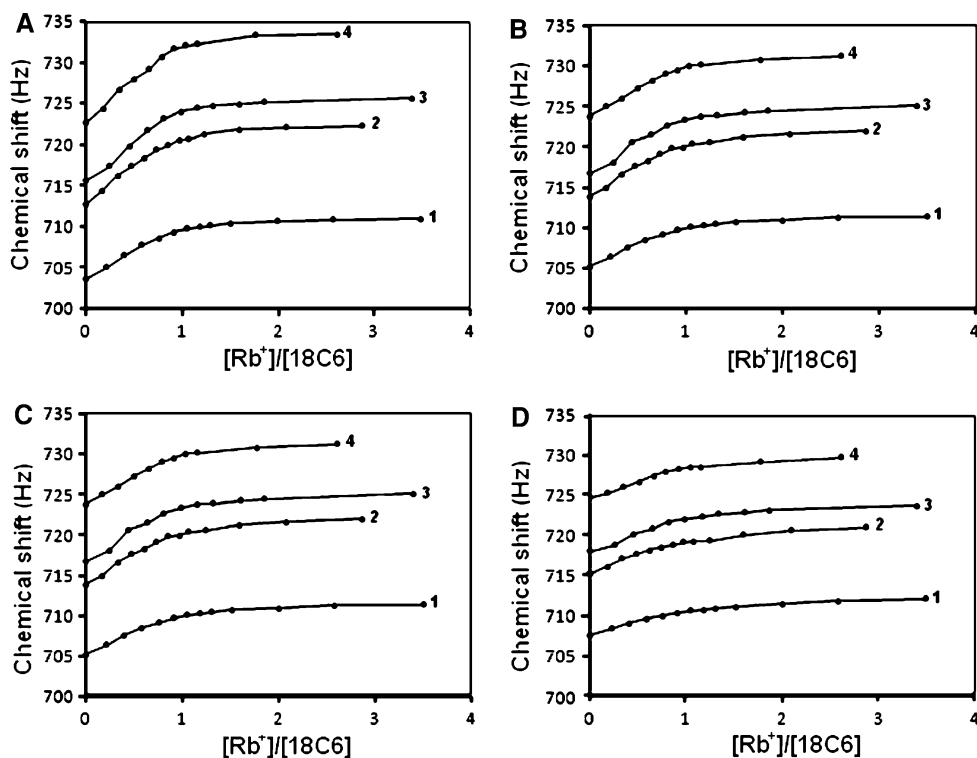
As it is seen from Fig. 3, there is a satisfactory agreement between the calculated and observed chemical shifts, supporting the formation of a 1:1 complex in solution.

To have a better understanding of the thermodynamics of the complexation reaction, it is useful to consider the enthalpic and entropic contributions of the reaction. The  $\Delta H^\circ$  and  $\Delta S^\circ$  values for the complexation reaction were evaluated from the temperature dependence of  $K_f$  by applying a linear least-squares analysis according the van't Hoff equation (Eq. 1):

$$2.203 \log K_f = (\Delta S^\circ/R) - (\Delta H^\circ/RT). \quad (1)$$

The van't Hoff plots of  $\log K_f$  of the resulting 1:1 complex in different solvent mixtures versus  $1/T$  are shown in Fig. 4 and all  $\Delta H^\circ$  and  $\Delta S^\circ$  values, evaluated in the usual

**Fig. 2** Chemical shift mole ratio plots for complexation of  $\text{Rb}^+$  with 18C6 at different temperatures in: (1) DMSO, (2) 90% DMSO, (3) 80% DMSO, and (4) 60% DMSO. Temperatures are: a 30 °C, b 40 °C, c 50 °C, d 60 °C



**Fig. 3** Computer fit of the chemical shift mole ratio data for complexation  $\text{Rb}^+$  with 18C6 at 30 °C in 90% DMSO and 10% NB (x) Experimental point, (—) theoretical point

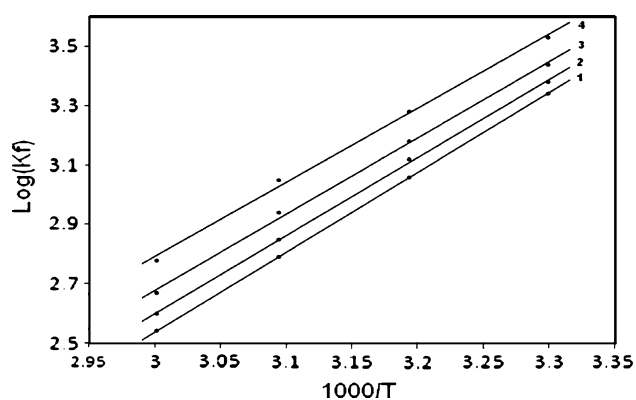
manner from the slope and intercept of the resulting linear plots, respectively, are also included in Table 1.

The stability constants of  $[\text{Rb}(18\text{C}6)]^+$  complexes in solution could be interpreted as representing the overall equilibrium constants of a series of reactions including [47] (i) partial or complete desolvation of  $\text{M}^+$  ion, (ii) partial or complete desolvation of the crown ether, (iii) configurational change of the crown ether, (iv) formation of the  $\text{M}^+$ –crown complex, and (v) solvation of the resulting charged complex. As is evident, the solvent molecules are directly involved in three of the five possible equilibria. Thus, it is expected that solvent properties such as dielectric constant, solvating ability and potentiality for hydrogen bonding will affect the process of complexation considerably.

Table 1 shows that the thermodynamic data of the  $[\text{Rb}(18\text{C}6)]^+$  complex vary significantly with the solvent properties. It is well known that the solvating ability of the solvent, as expressed by the Guttmann donor number (DN)

**Table 1** Formation constants and thermodynamic parameters for complexation  $\text{Rb}^+$  with 18C6 in binary DMSO–NB mixtures

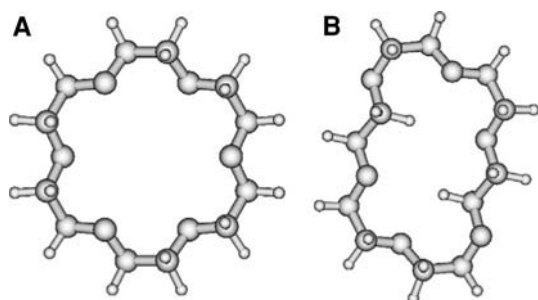
Solvents	Log $K_f$				$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> k <sup>-1</sup> )	$\Delta G_{318}$ (kJ mol <sup>-1</sup> )
	30 °C	40 °C	50 °C	60 °C			
100% DMSO	3.34 ± 0.05 [46]	3.06 ± 0.04	2.79 ± 0.03	2.54 ± 0.03	-51.6 ± 0.6	-106 ± 1	-17.8 ± 0.8
90% DMSO	3.38 ± 0.07	3.12 ± 0.06	2.85 ± 0.05	2.60 ± 0.04	-50.4 ± 0.7	-101 ± 2	-18.1 ± 0.9
80% DMSO	3.44 ± 0.07	3.18 ± 0.07	2.94 ± 0.04	2.67 ± 0.04	-49.2 ± 1.4	-96 ± 4	-18.6 ± 2.1
60% DMSO	3.53 ± 0.07	3.28 ± 0.05	3.05 ± 0.05	2.78 ± 0.06	-47.8 ± 1.7	-90 ± 5	-19.4 ± 2.5



**Fig. 4** van't Hoff plots for  $\text{Rb}^+$ –18C6 system in (1) DMSO, (2) 90% DMSO, (3) 80% DMSO, and (4) 60% DMSO

[48] plays an important role in different complexation reactions DMSO as a solvent of high solvating ability ( $\text{DN} = 29.8$ ) can compete with the crown ether for the metal ions much more than nitrobenzene, as a low donicity solvent ( $\text{DN} = 4.4$ ). Thus, it is not surprising that addition of nitrobenzene to dimethylsulfoxide will increase the stability of the  $\text{Rb}^+$ –crown ether complexes. In addition, the lower dielectric constant of NB (34.8) in comparison with that of DMSO (46.7) would also cause the electrostatic contribution to the bond formation to increase with increasing fraction of NB in the solvent mixture [6]. These phenomena illustrate the stability trend of the  $[\text{Rb}(\text{18C6})]^+$  complex, as expressed by  $\log K_f$  in Table 1.

Recently, the molecular structures of the uncomplexed 18C6 and the resulting 1:1 complex with  $\text{Rb}^+$  ion were investigated with theoretical method [43]. It is shown that 18C6 has different symmetries in different solvents [49–53]. Monte Carlo and molecular dynamics simulations demonstrated that 18C6 prefers the prolate  $C_i$  configuration in non-polar solvents; this is the configuration that was also observed in crystals [54, 55]. However, in a polar solvent, 18C6 prefers to have the  $D_{3d}$  symmetry [49–53]. The structural differences between these two conformers are shown in Fig. 5.



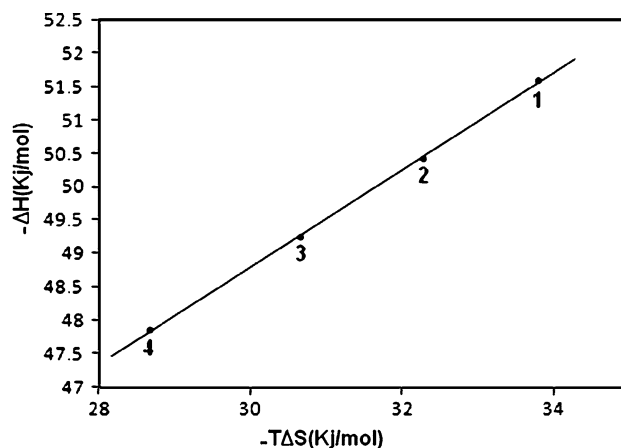
**Fig. 5** The  $D_{3d}$  (a) and  $C_i$  (b) configurations of 18-crown-6

In the alkali metal series however, the complexes have different symmetries. All alkali metals prefer  $C_{3v}$  configuration because the guest cations do not remain at the centre and are displaced from the plane of the ring. While the  $\text{Rb}^+$  ion is efficiently large to bind in the centre of the 18C6 host ring and produces  $D_{3d}$  symmetry. It's obvious that this configuration preference is independent from solvent polarity [43].

In this study, both free 18C6 and  $\text{Rb}[\text{18C6}]^+$  have the  $D_{3d}$  symmetry in polar solvents [43, 49–53]. In non polar solvents 18C6 configuration with  $C_i$  symmetry must have an significant ligand shape variation to convert complexed 18C6 configuration with  $D_{3d}$  symmetry. These phenomena can illustrate  $\Delta H^\circ$  variation with change in polarity of solvents in this study successfully.

It is interesting to note that in all solvent mixtures, the resulting  $[\text{Rb}(\text{18C6})]^+$  complex is enthalpy stabilized but entropy destabilized. The observed decrease in entropy of the system in the course of complexation reaction is mainly due to the configurational change of the macrocyclic ligand from a rather flexible configuration in the free state to a rigid one in the complexed form [56, 57].

A fairly good linear correlation between  $\Delta H^\circ$  and  $\Delta S^\circ$  values was seen in Fig. 6 that indicates the existence of an enthalpy–entropy compensation in the complexation reaction between  $\text{Rb}^+$  ion and 18C6 in the solvent systems studied. The existence of such a compensating effect between  $\Delta H^\circ$  and  $\Delta S^\circ$  values, which has been frequently reported for a variety of metal–ligand systems [7, 56, 58–61], would cause the overall change in Gibbs energy of the complex to be smaller than might be expected from the change in both  $\Delta H^\circ$  and  $\Delta S^\circ$  independently.



**Fig. 6** Enthalpy–entropy compensation in complexation reaction of  $\text{Rb}^+$  with 18C6 in different DMSO–NB mixtures: (1) 100% DMSO, (2) 90% DMSO, (3) 80% DMSO, (4) 60% DMSO

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