Solvent Effect on Stability and Thermodynamic Behavior of Complex of 18-Crown-6 with Hydroxyl Ammonium Cation

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ABSTRACT: *The complexation reaction between hydroxyl ammonium ($HONH_3^+$) cation with 18-crown-6 (18C6) ligand was studied in dimethylsulfoxide – water (DMSO-H_2O), methanol – water (MeOH-H_2O) and dimethylformamid – methanol (DMF-MeOH), binary solutions at different temperatures using conductometric method. The obtained results show that the stoichiometry of the complex formed between $HONH_3^+$ cation with (18C6) in all of the binary mixed solvents is 1:1[ML], as well as, these results show that the nature and the composition of the solvent systems are important factors that are effective on the stability of the complex formed between the macrocyclic ligand and metal cation in solutions. A non-linear behavior was observed for changes of stability constants of the complex versus the composition of the binary mixed solvents. The values of thermodynamic parameters show that the thermodynamics of complexation reaction is affected by the nature and composition of the mixed solvents and the complex is entropy stabilized, but enthalpy destabilized in most compositions of binary solutions.*

KEY WORDS: *18-crown-6; $HONH_3^+$, Binary mixed solvent, Thermodynamic behavior, Conductometry.*

INTRODUCTION

Thermodynamic studies on the complexation of 18C6 with the $HONH_3^+$ cation have been performed in order to elucidate the nature of the cation-binding behavior from the thermodynamic point of view and also to gain insights into the factors governing cation–ligand complexation phenomena[1-3]. The ability of the solvent molecules to compete with the donor atoms of the ligand toward the cation, is one of the critical factors that can thermodynamically influence the complexation process. The influence of the solvent on the complexation of cations by macrocyclic ligands is not restricted to the solvation of the cation, but the interaction between the ligand and solvent molecules and the solvation of the resulting complex may also play an important role in complexation reactions [4, 5]. As a result, the stability of complexes and the thermodynamics of complexation processes can be greatly altered by changing the solvent properties [6]. In order to achieve appropriate solvent properties, we often use mixtures of two solvents. The physiochemical properties of mixed solvents are interesting both from a theoretical and practical point of view, because many chemical and electrochemical reactions might be carried out advantageously in these media. Usually mixed solvents do not behave as expected

from statistical considerations, the solvating ability of solvents in mixtures can be different from those of neat media [7]. The deviations from ideal behavior are indicative of the extent of preferential solvation and the existence of specific solvent–solute and solvent–solvent interactions [8, 9]. Although the complexation reaction of macrocyclic polyethers with metal cations has been extensively studied during the past three decades, little attention has been paid to the study of non-metal cations complexations in mixed solvents [2, 3, 10–20].

In this paper, the results of thermodynamic study for complexation reactions between hydroxyl ammonium cation with 18C6 ligand was studied in DMSO-H_2O, MeOH-H_2O and DMF-MeOH binary mixtures at different temperatures using conductometric method are reported.

EXPERIMENTAL SECTION
Reagent and Apparatus

18-crown-6, hydroxyl ammonium chloride, dimethylsulfoxide, dimethylformamide and methanol, all from (Merck), were used with the highest purity.

The conductance measurements were performed using a digital, Jenway conductivity apparatus model 4510 in a water bath thermostated with a constant temperature within ±0.03ºC. A conductometric cell with a cell constant of 0.97 cm⁻¹ was used throughout the studies.

Methods

The experimental procedure to obtain the stability constants of $(18C6.HONH_3)^+$ complex was as follows: a solution of hydroxyl ammonium chloride salt (5×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, then a step-by-step increase in the crown ether concentration was performed by rapid transfer from crown ether solutions prepared in the same solvent (2×10^{-2} M) to the titration cell using a micropipette. The conductance of the solution in the cell was measured after each addition at different temperatures.

RESULTS AND DISCUSSION

The changes of molar conductance (Λ_m) versus the ligand to metal cation, $[L]_t / [M]_t$, for complexation of 18C6 with $HONH_3^+$ cation in various binary mixed solvents were studied at different temperatures. $[L]_t$ is the total concentration of the ligand and $[M]_t$ is the total
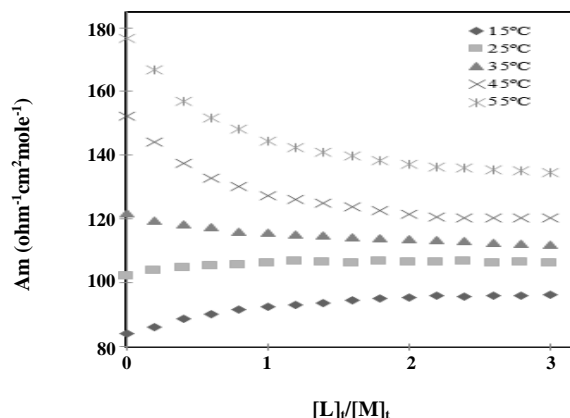

Fig. 1: Molar conductance-mole ratio plots for $(18C6.HONH_3)^+$ complex inMeOH-H_2O binary system (mole% MeOH=20) at different temperatures

concentration of $HONH_3^+$ cation. A typical series of molar conductance values as a function of ligand–metal cation mole ratios in methanol -water binary mixtures is shown in Fig.1. The stability constants of $(18C6.HONH_3)^+$ complex in various solvent systems at different temperatures was calculated from variation of molar conductance as a function of ligand/cation mole ratios using a GENPLOT computer program. The details of the calculation of the stability constants of complex by conductometric method has been described in [21]. The values of stability constants of $(18C6.HONH_3)^+$ complex in various solvent systems are listed in Table 1. Plots of Ln K_f versus 1/T in all cases were linear and the changes in the standard enthalpy (ΔH_c°) for complexation reaction were determined in the usual manner from the slope of the van't Hoff plots assuming that (ΔC_p) is equal to zero over the entire temperature range investigated. The changes in standard entropy (ΔS_c°) were calculated from the relationship $\Delta G_{c-298.15}^{\circ} = \Delta H_c^{\circ} - 298.15 \, \Delta S_c^{\circ}$. The results are summarized in Table 2. The changes of stability constant (log K_f) of $(18C6.HONH_3)^+$ complex with the composition of DMSO-H_2O, MeOH-H_2O and DMF-MeOH binary systems at different temperatures are shown in Figs. 2, 3 and 4 respectively.

As is seen from Fig. 1 addition of 18C6 to $HONH_3^+$ cation in MeOH -H_2O binary solution at 35ºC, 45ºC, 55ºC shows a decrease in molar conductivity with an increase in the ligand concentration, which indicates that the $(18C6.HONH_3)^+$ complex in this solution is less

Table 1: Formation constants of 18C6- HONH$_3^+$complex in DMSO-H$_2$O , MeOH –H$_2$O and DMF-MeOH binary mixtures at different temperatures.

Medium[b]	Log K$_f$ ± SD[a]				
	15˚C	25˚C	35˚C	45˚C	55˚C
DMSO-H$_2$O					
Pure DMSO	3.05 ± 0.20	3.15 ± 0.12	4.07 ± 0.30	4.27 ± 0.18	4.22 ± 0.20
80%DMSO-20% H$_2$O	2.97 ± 0.11	c	3.33 ± 0.26	3.47 ± 0.20	3.51 ± 0.19
60%DMSO- 40% H$_2$O	3.51 ± 0.04	c	3.39 ± 0.27	3.57 ± 0.13	3.69± 0.06
40%DMSO- 60% H$_2$O	3.31± 0.25	c	3.70± 0.19	3.88± 0.04	3.67 ± 0.06
20%DMSO- 80% H$_2$O	c	4.19 ± 0.31	3.58 ± 0.08	3.46 ± 0.07	3.36 ± 0.24
Pure H$_2$O	3.32 ± 0.21	c	3.40± 0.19	4.17± 0.18	4.12 ± 0.08
MeOH –H$_2$O					
Pure MeOH	3.06 ± 0.35	c	3.46 ± 0.19	3.45 ± 0.19	3.68 ± 0.21
80%MeOH-20% H$_2$O	3.02 ± 0.29	c	3.53 ± 0.19	3.87 ± 0.06	4.38 ± 0.18
60%MeOH- 40% H$_2$O	4.04 ± 0.16	c	3.54 ± 0.09	3.27 ± 0.17	3.25± 0.33
40%MeOH- 60% H$_2$O	3.49± 0.16	c	3.84± 0.08	4.04± 0.08	4.24 ± 0.10
20%MeOH- 80% H$_2$O	3.25± 0.21	c	3.51 ± 0.12	4.24 ± 0.13	4.25 ± 0.12
Pure H$_2$O	3.32 ± 0.21	c	3.40± 0.19	4.17± 0.18	4.12 ± 0.08
DMF-MeOH					
Pure DMF	2.91 ± 0.10	c	3.92 ± 0.28	3.70 ± 0.37	4.47± 0.37
80%DMF-20% MeOH	3.94 ± 0.15	2.76 ± 0.10	3.14 ± 0.24	3.69 ± 0.23	3.74 ± 0.17
60%DMF- 40% MeOH	3.92 ± 0.12	3.79 ± 0.25	2.18 ± 0.20	3.40 ± 0.17	3.33± 0.17
40%DMF- 60% MeOH	3.19± 0.25	c	3.57± 0.06	3.66± 0.05	4.22 ± 0.23
20%DMF- 80% MeOH	3.94 ± 0.14	3.01 ± 0.29	3.46 ± 0.06	3.88 ± 0.04	4.05 ± 0.09
Pure MeOH	3.06 ± 0.35	c	3.46± 0.19	3.45 ± 0.19	3.68 ± 0.21

[a] *SD=standard deviation*
[b] *The composition of binary solvents is expressed in mole% of each solvent*
[c] *The data cannot be fitted in equations*

mobile than free solvated HONH$_3^+$ cation, but a different behavior was observed at 15ºC and 25ºC which the mobility of the cation is less than that of (18C6.HONH$_3$)$^+$ complex. The slope of corresponding molar conductivity versus [L]$_t$/[M]$_t$ plots changes sharply at the point where the ligand to cation mole ratio is about 1, which is an evidence for formation of a relatively stable 1:1 complex between HONH$_3^+$ cation and 18C6 in these solutions.

As is seen from Figs. 2, 3, and 4, the changes of the stability constant (log K$_f$) of (18C6.HONH$_3$)$^+$ complex with the composition of DMSO-H$_2$O, MeOH-H$_2$O and DMF-MeOH binary systems is not monotonic. This behavior may be related to changes occurring in the structure of the solvent mixtures and, therefore, changing in the solvation properties of the cyclic polyether, cation and even the resulting complex in these solvent mixtures. These structural changes may result in changing the interactions of those solvents with the solutes [22]. Moreover, the Preferential solvation of the cation and ligand by one of the components of a mixed solvent system depends on two factors: the relative donor–acceptor abilities of the component molecules of solvents
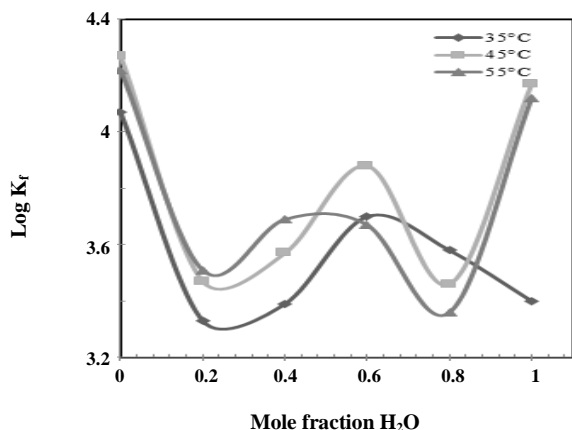
Fig. 2: Changes of the stability constant (log K_f) of (18C6.HONH_3)^+ complex with the composition of DMSO–H_2O binary systems at different temperatures.

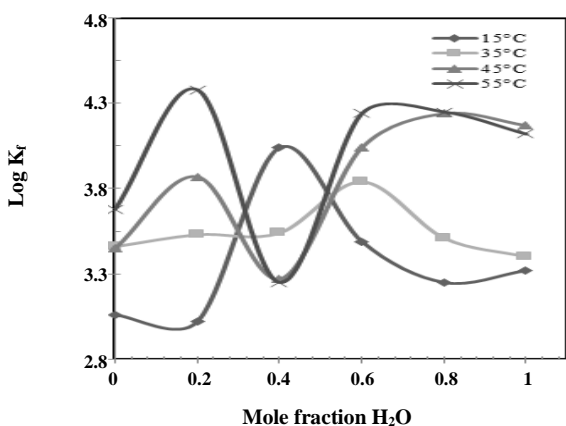***Fig. 3: Changes of the stability constant (log K_f) of (18C6.HONH_3)^+ complex with the composition of MeOH–H_2O binary systems at different temperatures.***
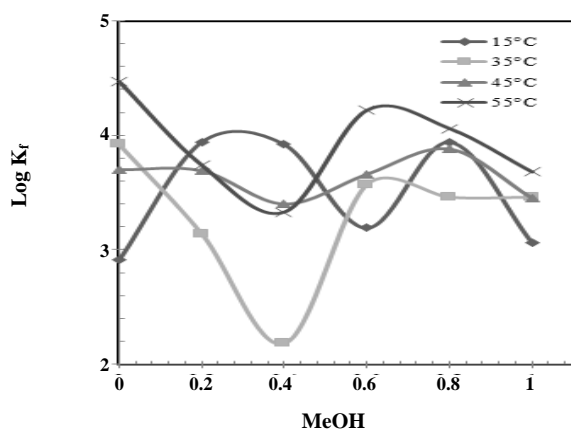

Fig. 4: Changes of the stability constant (log K_f) of (18C6.HONH_3)^+ complex with the composition of DMF–MeOH binary systems at different temperatures.

and the interactions between solvent molecules themselves. SzymanS.C. reported that the solvating properties of the components in mixed solvents can be significantly modified by solvent– solvent interactions when the energy of the latter is comparable with the energy of solvent–ion interactions for both components[23]. The experimental values of standard enthalpy (ΔH_c°) and standard entropy (ΔS_c°) which are given in Table 2, would show that in most cases, the (18C6.HONH_3)^+ complex is enthalpy destabilized but entropy stabilized, therefore, the entropy of the complexation reaction is the principal driving force for formation of this complex in all solvent systems. During the complexation of the cation by a macrocyclic ligand, most of the coordinated solvent molecules are replaced by the donor atoms of the ligand, therefore, desolvation of cation, may result in some positive entropic gain. In the cases where the macrocycle has also some interaction with solvent molecules, the release of some solvent molecules involved in interaction with the ligand, may also contribute to the positive entropy values [24, 25]. It should be mentioned, however, that the complexation process involves not only a change in solvation phenomena but also change in the flexibility of the ligand upon complexation [26].

The results in Table 2 show that, the thermodynamic data (ΔH_c°, ΔS_c°) vary nonmonotonically with the composition of the mixed solvents. This is due to variations in the extent of the contribution of such important parameters as solvation–desolvation of the species involved in the complexation reaction (i.e., HONH_3^+ cation, macrocycle and the resulting complex), and also the conformational changes of the macrocyclic ligand upon complexation in the binary solutions[27-29]. These variation may be due to solvent-solvent interactions which result in changing in some of the chemical and physical properties of the solvent system, and therefore, changing its interactions towards the dissolved species.A nonmonotonic behavior has also been observed for thermodynamic functions of several crown ether-metal ion complex formation in some binary mixed solvents [30,31].The relative enthalpy and entropy changes can be better understood if the ligand solvation is taken into consideration but Information on the interaction of macrocyclic ligands with the solvent molecule is sparse. The analysis of solvation enthalpy of some crown ethers in several mixed solvents

Table 2: Thermodynamic parameters for 18C6– HONH$_3^+$ complex in DMSO-H$_2$O , MeOH –H$_2$O and DMF-MeOH binary mixtures.

Medium[b]	$-\Delta G_c^\circ \pm SD$[a] kJ/mol	$\Delta H_c^\circ \pm SD$[a] kJ/mol	$\Delta S_c^\circ \pm SD$[a] J/mol
DMSO-H$_2$O			
Pure DMSO	17. 4 ± 0.7	63.2±15.6	270.4±52.5
80%DMSO-20% H$_2$O	16.4± 0.7	25.4±3.4	145.0±12.1
60%DMSO- 40% H$_2$O	17.7± 0.2	22.1±2.8	138.0±9.9
40%DMSO- 60% H$_2$O	18.3± 1.4	20.2±10.4	133.5±36.6
20%DMSO- 80% H$_2$O	24.0± 1.8	-40.8± 15.3	-86.9±51.6
Pure H$_2$O	18.3±1.1	41.3±17.4	193.3±60.6
MeOH –H$_2$O			
Pure MeOH	19.1± 1.9	26.4±4.6	157.9±17.4
80%MeOH-20% H$_2$O	16.7± 1.6	59.0±8.7	262.6±30.7
60%MeOH- 40% H$_2$O	22.3± 0.9	-38.1±5.4	-54.7±19.0
40%MeOH- 60% H$_2$O	19.3± 0.9	33.5±1.8	183.1±7.1
20%MeOH- 80% H$_2$O	17.9± 1.2	49.7± 14.8	234.9±51.6
Pure H$_2$O	18.3±1.1	41.3±17.4	193.3±60.6
DMF-MeOH			
Pure DMF	16. 0± 0.6	63.3±18.2	257.3±63.1
80%DMF-20% MeOH	15.8± 0.6	65.7±12.2	273.3±40.9
60%DMF- 40% MeOH	21.6± 1.4	-28.4±2.6	-22.8±9.5
40%DMF- 60% MeOH	17.6± 1.4	41.9±11.0	206.5±38.6
20%DMF- 80% MeOH	17.2± 1.6	66.8± 7.2	281.7±24.8
Pure MeOH	19.1±1.9	26.4±4.6	157.9±17.4

[a] SD=standard deviation

[b] The composition of binary solvents is expressed in mole% of each solvent

has been studied by Jazwiak [32] and a non-linear behavior has been observed between the solvation enthalpy of some crown ethers and the composition of binary solutions. The observed behavior has been discussed in terms of preferential solvation of the crown ether molecules which in turn depends quantitatively on the structural and energetic properties of the mixed solvent system.

CONCLUSIONS

Since there are many factors which affect the complexation reaction and it seems that a delicate balance among these factors determine the stability and thermodynamic behavior of the complex, therefore, we should not expect a monotonic relationship between these parameters and the solvent composition of these mixed solvents. The comparison of results in this study with results that are obtained in the study of complexation of ammonium cation with 18C6 ligand, indicate that the stability of hydroxylammonium complex are greater than that of ammonium complex in the same media[33]. The substitution of one hydrogen atom by hydroxyl group in the ammonium cation, increases the stability of related complex.

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