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Thermodynamic Behaviour of Complexation Process Between 15-Crown-5 with Li^+, Na^+ and K^+ Cations in Acetonitrile-Water and 1-Propanol-Water Binary Media

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The complexation reactions between Li^+, Na^+ and K^+ metal cations with the macrocyclic ligand,15-crown-5 (15C5) have been studied in acetonitrile-water and 1-propanol(1-PrOH)-water binary systems at different temperatures using conductometric method. In all cases, 15C5 forms 1:1 complexes with these metal cations. The values of stability constants of complexes which were obtained from conductometric data show that the stability of complexes is affected by the nature and composition of the mixed solvents used in these studies. In all cases, a non-linear behaviour was observed for the variation of log K_f of the complexes versus the composition of the mixed solvents. In most cases, the stability sequence of the complexes was found to be : $(15C5\text{-}Na)^+ > (15C5\text{-}Li)^+ > (15C5\text{-}K)^+$. The values of thermodynamic parameters (ΔH°_c , ΔS°_c) for complexation reactions were obtained from temperature dependence of formation constants of complexes using the van't Hoff plots. The results show that in most cases, the complexation reactions are enthalpy stabilized but entropy destabilized and the values of thermodynamic parameters are influenced by the nature and composition of the mixed solvents.

Key Words: 15-Crown-5, Li^+ , Na^+ and K^+ cations, Conductometry, Acetonitrile-water and 1-Propanol-water binary mixtures.

INTRODUCTION

Studies of complexation reactions of crown ethers with metal ions in different solvents show that the thermodynamic and kinetic parameters are affected by the nature and composition of the solvent system[1,2]. Some researches have been carried out using 15-crown-5 and its complexes such as study of thermodynamic behaviour on transfer between polar solvents[3], extraction of some alkali metal picrates into various organic phases[4] and determination of stabilities and transfer activity coefficients from water to some polar non-aqueous solvents[5].

The use of a solvent system as reaction medium makes it possible to control the reaction conditions. Analytical chemists use changes in the medium to adjust the driving force of reactions. In order to achieve appropriate solvent properties, one often use mixture of two solvents. Mixed solvents play important roles in modern electrochemical technologies[6] and can play important role in exploring new chemical possibilities.

Studies of complexation reactions of metal cations with some of the crown ethers in solvent mixtures have been limited so far almost to water-methanol binary mixtures and the data about complexation process for small crown ethers are very sparse. Even though these studies so far have been limited to one temperature only and the thermodynamic quantities for such complexation reactions in binary mixed solvents are not available. Previous studies[7-9] on the thermodynamics of the complexation reactions of some of the crown ethers with several metal cations in mixed solvent systems indicate that the stabilities, the sequences of selectivity, the values of thermodynamic parameters and even the stiochiomity of the crown ether complexes change with the nature and composition of the mixed solvents. Continued investigations of metal ion-crown ether complexes in mixed solvents broaden prespective and deepened understanding of the spectrum of the metal ion-crown ether interactions that occur in solution.

In this paper, the results of thermodynamic study for complexation reactions between 15-crown-5 with Li^+, Na^+ and K^+ cations in AN-H_2O and 1-PrOH-H_2O binary mixtures at different temperatures using conductometric method is reported.

EXPERIMENTAL

15-Crown-5, lithium chloride, sodium nitrate and potassium nitrate purchased from Merck company were used without further purification. Acetonitrile and 1-propanol obtained from Merck company and triplet distilled water were used as solvents.

The experimental procedure to obtain the formation constants of complexes is as follows: a solution of metal salt (5.0×10^{-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 a rapid transfer from crown ether solution prepared in the same solvent (2.5×10^{-2} M) to the titration cell using a microburette and the conductance of the solution in the cell was measured after each transfer at the desired temperature.

The conductance measurements were performed on a digital AMEL conductivity apparatus, model 60, in a water-bath thermostated at a constant temperature maintained within ± 0.03ºC. The conductance of the solution was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 0.79 cm^{-1} was used throughout the studies.

RESULTS AND DISCUSSION

The variation of molar conductance, Λ_m, versus the ligand to the cation molar ratio ($[L]_t/[M]_t$) where $[L]_t$ is the total concentration of the ligand and $[M]_t$ is the total concentration of the metal cations, for complexation of 15C5 with Li^+, Na^+ and K^+ cations in acetonitrile-H_2O and 1-PrOH-H_2O binary systems were studied at different temperatures. Three typical series of molar conductance values as a function of $[L]_t/[M]_t$ for $(15C5\text{-}Li)^+$ in neat acetonitrile, $(15C5\text{-}Na)^+$ in neat acetonitrile and $(15C5\text{-}K)^+$ in acetonitrile-H_2O binary solution (acetonitrile = 25.3 mol %) are shown in Figs. 1-3, respectively.

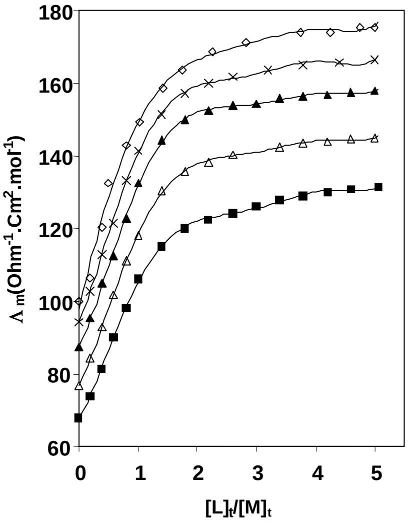

Fig. 1. Molar conductance-mole ratio plots for $(15C5\text{-}Li)^+$ complex in pure acetonitrile at different temperatures (■ = 15ºC, Δ = 25ºC, ▲ = 35ºC, × = 45ºC, ◊ = 55ºC)

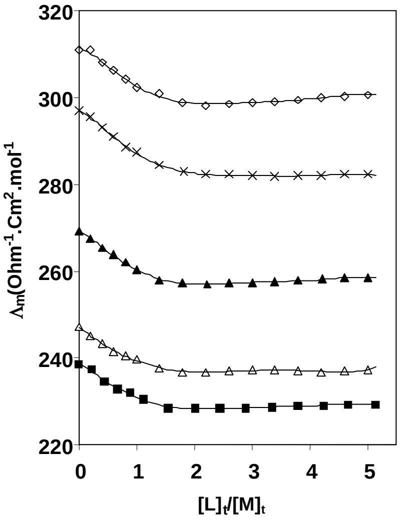

Fig. 2. Molar conductance-mole ratio plots for $(15C5\text{-}Na)^+$ complex in pure acetonitrile at different temperatures (■ = 15ºC, Δ = 25ºC, ▲ = 35ºC, × = 45ºC, ◊ = 55ºC)

The formation constants of the complexes at each temperature were obtained from variation of molar conductance as a function of $[L]_t/[M^+]_t$ molar ratio plots using a GENPLOT computer program[10]. The details of calculation of the stability constants of complexes by conductometric method have been described in reference[11]. The stability constants (log K_f) for 15C5-M^+ ($M^+ = Li^+$, Na^+ and K^+) complexes in various solvent systems are listed in Table-1.

The van't Hoff plots of log K_f *vs.* 1/T for $(15C5\text{-}Li)^+$ complex in acetonitrile-H_2O binary systems (acetonitrile = 25.3, 44.0, 75.3 and 100 mol %) are shown in Fig. 4. The changes in the standard enthalpy (ΔH°_c) for complexation reactions were obtained from the slope of the van't Hoff plots

TABLE-1
log K_f VALUES OF $(15C5\text{-}Li)^+$, $(15C5\text{-}Na)^+$ AND $(15C5\text{-}K)^+$ COMPLEXES IN 1-PrOH-H_2O AND AN-H_2O BINARY MIXTURES AT DIFFERENT TEMPERATURES

Medium	Solvent composition of H_2O (mol %)	Metal ions	log K_f ± SD[a] (ºC)				
			15	25	35	45	55
1-PrOH-H_2O systems	5.00	Li^+	3.49 ± 0.04	3.30 ± 0.09	3.10 ± 0.06	2.90 ± 0.10	2.51 ± 0.04
		Na^+	4.25 ± 0.08	3.69 ± 0.04	3.68 ± 0.02	3.38 ± 0.02	3.19 ± 0.01
		K^+	2.79 ± 0.06	2.68 ± 0.07	2.60 ± 0.03	2.59 ± 0.09	2.55 ± 0.01
	25.00	Li^+	3.20 ± 0.05	2.50 ± 0.05	1.35 ± 0.02	< 1	< 1
		Na^+	3.27 ± 0.03	2.85 ± 0.03	2.01 ± 0.02	< 1	< 1
		K^+	b	b	b	b	b
	45.00	Li^+	2.88 ± 0.02	2.35 ± 0.05	< 1	< 1	< 1
		Na^+	< 1	< 1	< 1	< 1	< 1
		K^+	b	b	b	b	b
	65.00	Li^+	< 1	< 1	< 1	< 1	< 1
		Na^+	< 1	< 1	< 1	< 1	< 1
		K^+	b	b	b	b	b
Aceto-nitrile-H_2O systems	0.00	Li^+	3.74 ± 0.06	3.84 ± 0.07	3.90 ± 0.08	3.92 ± 0.06	3.95 ± 0.08
		Na^+	4.57 ± 0.22	4.38 ± 0.14	4.50 ± 0.21	4.00 ± 0.10	4.38 ± 0.25
		K^+	3.77 ± 0.07	3.52 ± 0.06	3.49 ± 0.05	3.36 ± 0.02	3.29 ± 0.02
	24.70	Li^+	2.41 ± 0.06	2.57 ± 0.05	2.95 ± 0.08	3.0 ± 0.1	3.2 ± 0.1
		Na^+	3.3 ± 0.1	3.7 ± 0.4	3.7 ± 0.5	3.4 ± 0.4	2.8 ± 0.3
		K^+	2.79 ± 0.04	2.66 ± 0.04	2.40 ± 0.04	1.8 ± 0.2	2.73 ± 0.05
	49.60	Na^+	< 1	< 1	< 1	< 1	< 1
		K^+	b	b	b	b	b
	56.00	Li^+	2.38 ± 0.03	2.65 ± 0.07	2.94 ± 0.07	3.10 ± 0.04	3.14 ± 0.02
	74.70	Li^+	2.6 ± 0.1	2.61 ± 0.08	2.72 ± 0.01	2.8 ± 0.1	2.91 ± 0.09
		Na^+	< 1	< 1	< 1	< 1	< 1
		K^+	b	b	b	b	b

[a] SD = standard deviation.

[b] The complexation reaction of K^+ ion with 15C5 in these media is negligible.

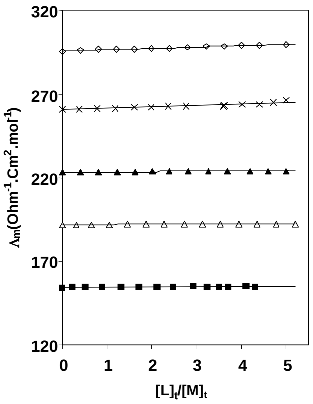

Fig. 3. Molar conductance-mole ratio plots for $(15C5\text{-}K)^+$ complex in acetonitrile-H_2O (acetonitrile = 25.3 (mol %)) at different temperatures (■ = 15ºC, Δ = 25ºC, ▲ = 35ºC, × = 45ºC, ◊ = 55ºC)

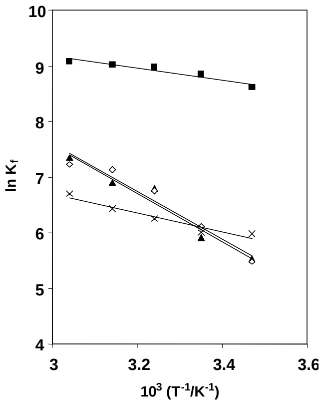

Fig. 4. Van't Hoff plots for $(15C5\text{-}Li)^+$ in acetonitrile-H_2O binary systems (acetonitrile (mol %): × = 25.3, ◊ = 44.0, ■ = 75.3, ▲ =100)

assuming that ΔC_p is equal to zero over the entire temperature range investigated. The changes in the standard entropy ($\Delta S°_c$) were calculated from the relationship $\Delta G°_{c,298.15} = \Delta H°_c - 298.15\ \Delta S°_c$. The results are summarized in Table-2. The variation of log K_f *vs.* the mole fraction of acetonitrile for $(15C5\text{-}Li)^+$ complex in acetonitrile-H_2O binary systems at different temperatures is shown in Fig. 5.

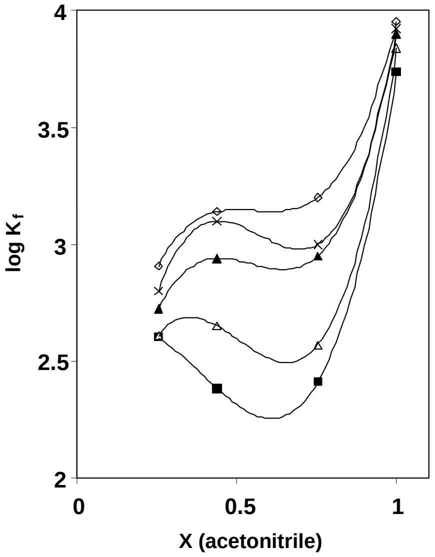

Fig. 5. Variation of stability constant of $(15C5\text{-}Li)^+$ complex with the composition of the AN-H_2O binary systems at different temperatures (■ = 15ºC, Δ = 25ºC, ▲ = 35ºC, × = 45ºC, ◊ = 55ºC)

As is obvious from Fig. 1, addition of 15C5 ligand to a solution of lithium ion in pure acetonitrile at different temperatures shows an increase in molar conductivity with an increase in the ligand concentration. This indicates that the $(15C5\text{-}Li)^+$ complex in pure acetonitrile is more mobile than free solvated Li^+ ion. Similar behaviour was observed for $(15C5\text{-}Li)^+$ and $(15C5\text{-}Na)^+$ complexes in 1-PrOH-H_2O binary solutions (1-PrOH = 95, 75, 55 and 35 mol %) and for $(15C5\text{-}K)^+$ complex in 1-PrOH-H_2O binary solution (1-PrOH = 95 mol %). The slope of the corresponding molar conductivity versus ligand/cation mole ratio plots changes sharply at the point where the ligand to cation mole ratio is 1, which is an evidence for formation of a relatively stable 1:1 complex. As is shown in Fig. 2, addition of the ligand to a solution of sodium ion in pure acetonitrile at various temperatures indicates a decrease in molar conductivity with increasing the ligand concentration. This shows that $(15C5\text{-}Na)^+$ complex in pure acetonitrile is less mobile than free solvated Na^+ ion. Similar behaviour was observed for $(15C5\text{-}K)^+$ complex in pure acetonitrile.

There is no significant changes in molar conductivity upon addition of the ligand to potassium ion solution in acetonitrile-H_2O mixture (acetonitrile = 25.3 mol %) (Fig. 3). Therefore, the complexation reaction between K^+ ion and 15C5 in this solvent system is probably negligible.

As seen from Fig. 1, as the temperature increases, the curvature of the molar conductivity plots of $(15C5\text{-}Li)^+$ complex increases which indicates the formation of a stronger complex at higher temperatures. Therefore, the reaction between Li^+ cation with 15C5 in acetonitrile-H_2O binary mixed solvents is endothermic.

As the concentration of water is increased in 1-PrOH-H_2O and acetonitrile-H_2O binary mixtures, the stability of complexes decreases (Table-1). This behaviour reflects the much stronger cation solvation by water molecules compared with the 1-PrOH and acetonitrile molecules with which the ligand has to challenge. Water with a relatively high Gutmann donor number (DN = 33) solvates the metal cations more strongly than 1-propanol (DN = 18) and acetonitrile (DN = 14.1), therefore, competes with the polyether for the metal ions. As a consequence, the formation of complexes is weakened with increasing the concentration of water in these mixed binary solvents. Thus in most solvent systems, the sequence of stability of the complexes is : $(15C5\text{-}Na)^+ > (15C5\text{-}Li)^+ > (15C5\text{-}K)^+$. Na^+ cation forms the most stable complex with 15C5 since its ionic radius (1.02 Å) is very close to the radius of 15C5 cavity (0.82-0.92 Å)[12].

The variation of stability constants (log K_f) of $(15C5\text{-}Li)^+$ complex with the composition of acetonitrile-H_2O binary system at various temperatures is shown in Fig. 5. As is shown in this figure, a non-linear behaviour is observed between log K_f and the composition of acetonitrile-H_2O binary solvents. It is interesting to note that as the mole fraction of acetonitrile increases, the stability constant of the complex increases (expect in 15ºC) and then decreases until the mole fraction of acetonitrile reaches to about 0.65 and then increases rapidly. The non-linear behaviour which is observed in acetonitrile-H_2O binary solutions may be due to preferential solvation of the ligand and the metal cation in these binary system. Some of the thermodynamic properties and also the distribution of molecular structure may change when these two solvents mix with one another. The effect of properties of acetonitrile-H_2O and other organic-water mixtures on the solvation enthalpy of 15-crown-5 and some of the other crown ethers has been studied by Jozwiak[13] and it has been shown that the crown ethers are preferentially solvated by organic solvents in these binary mixtures and it has been discussed that in these mixed solvents, the energitic effect of the preferential solvation depends quantitatively on the structural and energitic properties of the mixtures.

A non-linear behaviour was also observed for the changes of stability constant (log K_f) of $(15C5\text{-}Li)^+$ complex versus the composition of 1-PrOH-H_2O binary system at various temperatures. This behaviour is probably due to some kinds of solvent-solvent interactions between these two solvent molecules and changing the structure of the solvent system and, therefore, changing the solvation properties of the solvents. The solvation number of the dissolved species are probably strongly influenced by the structure of the solvents. Some of the physico-chemical properties of 1-propanol-water binary mixtures such as viscosity have maxima in certain composition which has been discussed in terms of solvent-solvent interactions between the molecules of these dipolar protic solvents[14].

As is evident from Table-2, the values of thermodynamic parameters for complexation reactions vary with the nature and composition of the mixed solvents. The $\Delta H°_c$ and $\Delta S°_c$ values of $(15C5\text{-}Li)^+$ and $(15C5\text{-}Na)^+$ complexes in 1-PrOH-H_2O binary systems become more positive with increasing the concentration of 1-PrOH in the binary mixture. The experimental values of $\Delta H°_c$ and $\Delta S°_c$ show that in most cases, the complexes are enthalpy stabilized but entropy destabilized, therefore, the enthalpy of complexation reactions is the principal driving force for formation of these complexes in 1-PrOH-H_2O binary solutions.

TABLE-2
THERMODYNAMIC PARAMETERS FOR $(15C5\text{-}Li)^+$, $(15C5\text{-}Na)^+$ AND $(15C5\text{-}K)^+$ COMPLEXES IN 1-PrOH-H_2O AND $(15C5\text{-}Li)^+$ AND $(15C5\text{-}K)^+$ COMPLEXES IN ACETONITRILE-H_2O BINARY MIXTURES

Medium	ΔG^o_c ± SD[a] (25ºC) (Kcal/mol)	ΔH^o_c ± SD[a] (Kcal/mol)	ΔS^o_c ± SD[a] (cal/mol K)
$(15C5\text{-}Li)^+$			
95% 1-PrOH-5% H_2O[b]	-4.47 ± 0.13	-10.30 ± 0.55	-19.57 ± 1.80
75% 1-PrOH-25% H_2O	-3.73 ± 0.07	-12.25 ± 1.08	-28.60 ± 3.53
$(15C5\text{-}Na)^+$			
95% 1-PrOH-5% H_2O[b]	-5.28 ± 0.11	-10.87 ± 0.80	-18.74 ± 2.60
75% 1-PrOH-25% H_2O	-3.81 ± 0.18	-21.69 ± 0.57	-59.95 ± 1.85
$(15C5\text{-}K)^+$			
95% 1-PrOH-5% H_2O[b]	-3.46 ± 0.09	-3.70 ± 0.06	c
$(15C5\text{-}Li)^+$			
Pure acetonitrile	-5.2 ± 0.5	2.2 ± 0.4	24.9 ± 1.2
75.3% Acetonitrile-24.7% H_2O[b]	-4 ± 1	8 ± 1	40 ± 3
44% Acetonitrile-56% H_2O	-3 ± 1	9 ± 1	41 ± 4
25.3% Acetonitrile-74.7% H_2O	-3.5 ± 0.8	3.7 ± 0.5	24 ± 2
$(15C5\text{-}K)^+$			
Pure acetonitrile	-4.9 ± 0.8	-5.0 ± 0.8	-0.3 ± 0.1
75.3% Acetonitrile -24.7% H_2O[b]	-4 ± 1	-5 ± 1	-4 ± 1

[a] SD = standard deviation.
[b] Composition of binary mixtures is expressed in mol% for each solvent system.
[c] With high uncertainty.

Table-2 shows that the values of enthalpy and entropy for complexation reactions between 15C5 and Li^+, Na^+ and K^+ cations in acetonitrile-H_2O and 1-PrOH-H_2O binary mixtures, do not vary monotonically with the solvent composition. Since there are many parameters which contribute to change the complexation enthalpies and entropies, therefore, we should not expect a regularity between these parameters and the solvent composition of these binary mixtures of associated dipolar solvents.

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