

ANALYTICAL STUDY OF NON-AQUEOUS SOLUTIONS OF CROWN ETHERS COMPLEXES BY CONDUCTIVITY

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Abstract: The conductivity of NaCl, KCl and RbCl in ethanol has been studied in absence and presence of crown ethers 12C4, 15C5, 18C6 and DC18C6. The stability constant "logK" of the resulting 1:1 complexes between cations (Na^+ , K^+ and Rb^+) with crown ethers were determined by molar conductivity–mole ratio data. The order of logK values for Na^+ DC18C6 > 18C6 > 15C5, K^+ DC18C6 > 18C6 > 15C5 > 12C4 and Rb^+ 18C6 > DC18C6 > 15C5 > 12C4. The thermodynamic formation of complexation were determined, it reflects the tight association between cation and donor atoms of crown ethers. The solvent effect was also studied and results revealed that this effect follow the dielectric constant of solvent.

1. Introduction

The synthesis of crown ethers and observation of their ability to form complexes with a variety of metal ions and neutral molecules has led to an extensive study of these ligands and their complexes^[1-3]. The importance of fundamental thermodynamics to explain the conductivity observed by the addition of crown ethers to salt electrolytic solution in non-aqueous solvent such as methanol, acetonitrile, propylene carbonate and mixture solvents^[4-7]. The stability of crown ethers complexes depends on several factors including the relative size of the cation and the macrocyclic cavity, the acid–base character of metal ions, the number and nature of binding sites and the nature of the solvent^[8-11].

As far as the effect of adding different crown ethers is concerned, it appears that the addition of 12-crown-4 and 15-crown-5 to solution of Sodium and Potassium salts gives rise to a conductivity decrease which is small, while the addition of dicyclohexyle-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) to the same solution gives rise to a dramatic decrease in conductivity^[12,13].

The importance of fundamental thermodynamic to explain the conductivity enhancement observed by addition of crown ethers, this behavior due to interaction forces correlated with the ions, solvent and

crowns which effect the ion-dipole forces acting between cations and crown ethers ^[14].

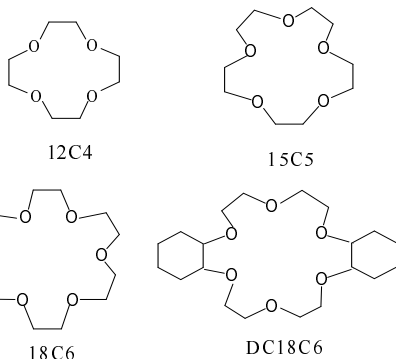
There are a few reports of thermodynamic data in solutions other than water and methanol. In this work the effect of adding 12C4,15C5,18C6 and DC18C6 in ethanol has been studied by conductivity, the conductivity data were analyzed according to nonlinear least square curve fitting procedure based on a 1:1 metal to ligand complex formation model. Least square analysis of logK vs 1/T data was carried out and the enthalpy and entropy of crown complexation reacton determined from the temperature dependence of complexation constant.

2. Experimental

2.1 Material

Reagent grade Sodium chloride, Potassium chloride (Riedel-Dehean) and Rubidium chloride (BDH) commercial purity (99.8%) and were recrystallized three times from a water-ethanol mixture and dried below their decomposition temperature, ethanol (Merck) was used as a solvent.

The crown ethers 12-crown-2 (12C4), 18-crown-6 (18C6), DC18-crown-6 (DC18C6) (Merck) and 15crown5 (15C5) (Fluka) of high purity were used as received.



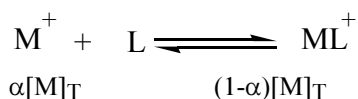
2.2 Conductivity Measurements

Conductivity measurements were obtained using Philips conductivity meter (PW526). The conductivity cell was used with cell constant of 1.072 cm^{-1} , calibrated with standard aqueous KCl solutions ^[15].

The molar conductivity was determined by dilution of an initially concentrated solution^[12], the concentration range studied was varied in general from 1×10^{-4} – 2×10^{-3} mol L⁻¹ in water – jacketed glass vessel thermostated at the desired temperature ± 0.01 °C using thermostat control from OLLMAN & CO KG Co.

3. Results and Discussion

Where the ligand (L) form (1:1) complexes with cations under these conditions the following equilibrium can be described by the equation



Where M⁺, L, ML and K represent the free cation, the free ligand, the complex and the equilibrium constant respectively. The stability constant (K) is defined by

$$K = \frac{[ML^+]}{[M^+][L]} \quad (1)$$

Where [M⁺], [L] and [ML⁺] represent the molar concentration of free cation, free ligand and the complex, if α is the fraction of free cation then $\alpha[M]_t$ ($1-\alpha$)[M]_t represent the fraction of total free cation and the complex concentration (mol L⁻¹) then

$$K = \frac{[ML^+]}{[M^+][L]} = \frac{(1-\alpha)}{\alpha[L]} \quad (2)$$

The molar conductivities (Λ) can be calculated using equation

$$\Lambda(\text{S cm}^2 \text{ mol}^{-1}) = \frac{10^3 \kappa}{[M]_T} \quad (3)$$

Where κ is the specific conductivity of test solution in S cm⁻¹. On other hand Λ can be related to α by the following equation

$$\Lambda = \alpha \Lambda_{MX} + (1-\alpha)\Lambda_{MLX} \quad (4)$$

where Λ_{MX} and Λ_{MLX} represent the molar conductivities of the metal salt solution and complexed cation solution at the same concentration .

From Eq.(4)

$$\alpha = \frac{(\Lambda - \Lambda_{MLX})}{(\Lambda_{MX} - \Lambda_{MLX})} \quad (5)$$

Substitution of Eq. (5) in to Eq. (2) then

$$K = \frac{(\Lambda_{MX} - \Lambda)}{[L] (\Lambda - \Lambda_{MLX})} \quad (6)$$

Where

$$[L] = [L]_T - [M]_T \frac{(\Lambda_{MX} - \Lambda)}{(\Lambda - \Lambda_{MLX})}$$

where Λ_{MLX} value was estimated from the Λ values at the points large $[L]_t/[M]_t$ by non-linear least square curve fitting. The $\log K$ values were calculated at (1:1) metal to ligand, using computerize program^[16,17].

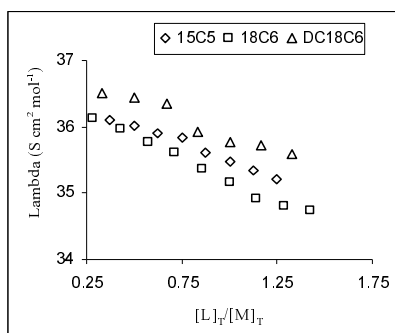


Figure 1. Molar conductance vs $[L]_T/[NaCl]_T$ in ethanol at 25 °C

The molar conductance of the chloride salts of Na^+ , K^+ and Rb^+ in ethanol was monitored as a function of 12C4, 15C5, 18C6 and DC18C6 to metal ion mole ratio at 25 °C.

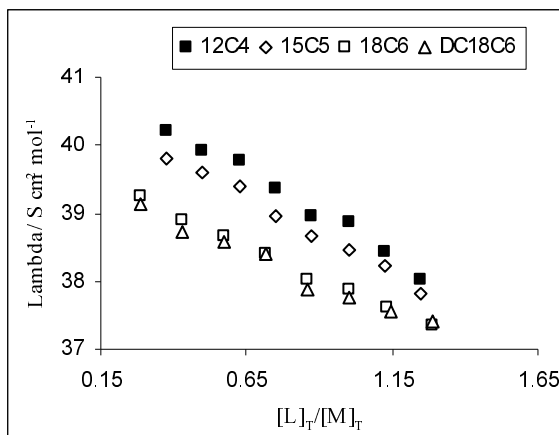


Figure 3. Molar conductance vs $[\text{L}]_{\text{T}}/[\text{RbCl}]_{\text{T}}$ in ethanol at 25 °C

The molar conductance by the addition of neutral species to constant concentration of electrolyte solutions can be explained by the results of the viscosity changes, ion-pairing or complexation. In this study the concentration of cation chloride or added crown ethers were kept very low, the influences of viscosity and ion-pairing on the change of Λ could be negligible^[18,19]. The Figures(1,2) show the decrease of the molar conductance of chloride salts with addition of crown ethers can be explained by assuming that the cations are less strongly bonded to the solvent dipoles than to the negatively charged oxygen of crown ethers, then the crown ethers interact with the cations to form complexes through the relationship



These behavior observed in the literature^[14,20] give assurance that all the cations can be considered complexed and therefore the measured conductivity is only due to Cl^-M^+ and ML^+ .

Table 1. logK complexation for cations with crown ethers in ethanol at 25 °C

Ligand	LogK		
	Na ⁺ (r =1.02 Å) ^a	K ⁺ (r =1.38 Å) ^a	Rb ⁺ (r =1.49 Å) ^a
12C4 (r =0.65 Å) ^b	N.C	2.96	3.10
15C5 (r =0.9 Å) ^b	2.71	3.93	3.16
16C6(r =1.4 Å) ^b	3.67	6.23	4.83
DC18C6(r =1.4 Å) ^b	4.34	5.70	4.10

N.C: no conductivity change r: cavity and cation diameters

^a Ref.[21] ^b Ref.[22]

According to Table.1 the stability constant "logK" concerning (1:1) complexation of crown ethers for each cations depends specifically on the interaction forces which act in solution between the components and characteristic properties the (cavity size to ionic ratio, number of donor atoms, dipole moment, polarizability of donor atoms, steric hindrance of polyether ring and solvation of the cation).

The "logK" values for the complexation of K⁺ with each crown ethers are much higher than those for the other cations, the logK sequences of M⁺ with ligands are 18C6>DC18C6>15C5>12C4, these reflect the effect the number of donor atoms of the ligands in the complexes. The stability constant of cations is influenced by cavity size to ionic size ratio, this can be seen for K⁺ which forms the most stable complex by 18C6, the ion fits into the cavity the stronger generally are the interaction between K⁺ ion and all donor atoms of the ligand. On the other hand Dicyclohexyl groups substituted crown ether may increase the steric hindrance of polyether ring. Thus in comparison to the corresponding unsubstituted crown ether complex the stability constant of DC18C6 by K⁺ decrease.

The Na⁺ ion is smaller than the cavities of 18C6 and DC18C6, this ion is allowed to form interaction with some donor atoms of both ligand. On the other hand the stability constant values of Na⁺ with ligands lower than the corresponding K⁺ and Rb⁺ ions suggesting that

Na⁺ owing to their high charge density involve a greater number of solvent molecule than K⁺ and Rb⁺ ions in the formation of the primary solvating layer. Thus no observed change in conductivity of NaCl solution with 12C4. Bigger ion Rb⁺ which do not fit well into the cavity is due to the weakening of the interaction with donor atoms.

In order to achieve better understanding of the complexation process, a thermodynamic study was conducted, where the molar conductance – mol ratio was measured at various temperatures, typical Vant Hoff plots of logK vs 1/T were obtained, ΔH and ΔS were calculated for 1:1 complexes and are recorded in Table (2).

Table 2. Stability constant, enthalpies and entropies for different crown ethers complexes in ethanol

System	logK				- ΔH (KJ/mol)	ΔS (KJ/mol)
	5 °C	15 °C	25 °C	35 °C		
NaCl-15C5	2.75	2.74	2.71	2.69	3.38	40.51
NaCl-18C6	3.75	3.71	3.67	3.63	6.25	49.19
NaCl-DC18C6	4.46	4.39	4.34	4.30	8.16	55.67
KCl-12C4	3.10	2.98	2.96	2.92	8.22	29.02
KCl-15C5	4.10	3.98	3.93	3.87	11.19	37.52
KCl-18C6	6.49	6.29	6.23	6.08	19.76	53.20
KCl-DC18C6	5.86	5.79	5.70	5.61	13.24	64.45
RbCl-12C4	3.17	3.13	3.10	2.96	9.38	26.89
RbCl-15C5	3.27	3.19	3.16	3.05	10.53	24.28
RbCl-18C6	5.95	5.87	5.83	5.72	11.40	54.05
RbCl-DC18C6	4.26	4.18	4.10	3.94	14.24	22.79

As can be seen from Table. 2., in all the systems that the values ΔH and ΔS indicate the formation of the complex is favored, the thermodynamic data reflect the tight association between cations and donor atoms of crown compound over the entire temperature range. This tightness was confirmed by the negative value of enthalpy. The enthalpy changes shift to more negative values as the cavity of the crown increases. This behavior is due to the increases of oxygen donor atoms.

The enthalpy formation of 18C8 with K^+ is higher than the other complexes, this due to the matching principle. On the other hand, the decrease of enthalpy of complexation of Rb^+ with ligand compared K^+ complexes may be due to form complex (2:1) ligand: salt which have Rb^+ outside the plane of the cycle as has been shown in literature [22].

The entropy for the complex formation is the sum of different contribution due to solvation of the cation and ligand, changes of internal entropy (orientation, conformation and translation)^[23]. Only a few results have been reported about the interaction between solvent molecules and crown ethers. Thus, the changes of experimental reaction entropy can be discussed with respect to with contribution.

Table 3. Stability constant for cations in different solvents

System	Solvent	logK						
		Na ⁺	K ⁺	Rb ⁺	Solvent	Na ⁺	K ⁺	Rb ⁺
12C4 – KCl		N.C	2.96	3.10		-	2.34	2.23
15C5 – KCl	EtOH	2.71	3.93	3.16	MeOH ^a	2.94	3.23	2.79
18C6 – KCl	($\epsilon=24.55$) ^b	3.67	6.23	5.83	($\epsilon=32.70$) ^b	4.05	6.11	5.54
DC18C6 – KCl		4.34	5.70	4.10		4.06	5.66	4.48

^a values of logK taken directly from Ref. [16] ^b Ref. [24]

The data in Table (3) illustrate the influence of the solvent properties on the stability constant, these results are interpreted in term of the competition between ion and solvent molecule due to interaction with cavity of crown ethers. On other hand the interaction between ion-solvent (solvated ions) and solvent-solvent are well known^[24]

The presented results demonstrate the influence of the solvents upon the logK, since the stability constant for K^+ and Rb^+ with crown ethers in EtOH are higher than compared in MeOH, which can be interpreted the dielectric constant(ϵ)of solvents. MeOH as a solvent of high dielectric constant ($\epsilon=32.70$) strongly competes with the crown ethers. The logK values for Na^+ in different solvents with crown ethers may be regarded as a result of the solvation energy principle for ion in non-aqueous solvents which is related to the size of ion and ion – solvent interaction^[25].

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