

# The Complexation Behaviour of Crown Ethers with Some Divalent Transition Metal and Silver Ions in a 40%(v/v) Ethanol + Water Medium

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The stability constants in 40%(v/v) ethanol + water mixture were evaluated for complexes of Ni<sup>II</sup>, Co<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Mn<sup>II</sup> and Ag<sup>I</sup> with the macrocyclic polyethers 15-crown-5, benzo-15-crown-5, 18-crown-6 and dicyclohexano-18-crown-6 by conductometric titrations. In addition, a potentiometric study of the Cu<sup>II</sup> and Ag<sup>I</sup> complexes was undertaken to compare

the results with those obtained by conductivity measurements. The complexation studies indicate 1:1 complex formation between the metal ion and crown ether and the log  $K_{ML^{n+}}$  values are in the range 1.0–3.0. The limiting molar conductivities of the metal ions and their crown ether complexes were also determined.

## Introduction

The complexation of alkali cations by neutral molecules was quite uncommon till the discovery of crown ethers by Pedersen,<sup>[1]</sup> who prepared and studied several crown ether complexes of alkali and alkaline earth metal ions.<sup>[2,3]</sup> Until now the complexation behaviour of alkali and alkaline earth metal ions with crown ethers has been extensively studied<sup>[4–8]</sup> in various solvents. The complexation of transition metal ions has been studied mainly with respect to aza and thia crown ethers,<sup>[4,8–12]</sup> as they are softer ligands. Little attention, however, has been given to the complexation behaviour of transition metal ions with oxygen-containing crown ethers.<sup>[7,13–16]</sup>

The object of the present work was to study the complexation behaviour of Ni<sup>II</sup>, Co<sup>II</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, Mn<sup>II</sup> and Ag<sup>I</sup> perchlorates with 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6) and dicyclohexano-18-crown-6 (DCH18C6) in a 40%(v/v) ethanol + water medium by conductometry. The complexation of Cu<sup>II</sup> and Ag<sup>I</sup> has been studied by potentiometry as well in order to compare these results with those obtained by conductometric measurements. Aqueous alcohol is widely used as a physiological substrate. Also, as this particular composition ensured the solubility of B15C5 and DCH18C6, and, interestingly, lies on the maxima of the viscosity curve of ethanol + water mixtures, it was chosen for the present study.

## Theory

The conductance data of the divalent metal perchlorates were treated by the Fuoss and Edelson method as used in previous studies.<sup>[6]</sup> The method consists of evaluating the limiting equivalent conductance ( $\Lambda_0$ ) and the first step asso-

ciation constant ( $K_A$ ) of an electrolyte  $MX_2$  in 40% ethanol + water based on the following equilibrium:

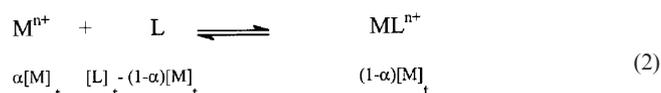


where  $M = Ni, Co, Cu, Zn, Mn$ . The equilibrium leading to the neutral species  $M(ClO_4)_2$  is neglected in this method.

The treatment of conductance data for silver perchlorate was done by using the Shedlovsky function.<sup>[17]</sup> The equations<sup>[6,7,18]</sup> used for the calculation of the stability constants are described briefly in the following sections.

## Conductometric Study of Crown Ether Complexation with Metal Perchlorates

The complexation of a metal ion ( $M$ ) with a crown ether ( $L$ ) may be represented as:



where  $[M]_t$ ,  $[L]_t$  and  $\alpha$  are the total concentration of cation, the total concentration of crown ether and the fraction of uncomplexed cation, respectively. Accordingly the thermodynamic stability constant  $K'_{ML^{n+}}$  is given by:

$$K'_{ML^{n+}} = [ML] \cdot f_{ML^{n+}} / [M] \cdot f_{M^{n+}} \cdot [L] \cdot f_L \quad (3)$$

Where  $[ML]$ ,  $[M]$  and  $[L]$  are the concentrations of complexed cation, uncomplexed cation and uncomplexed crown ether, respectively, and  $f_{ML^{n+}}$ ,  $f_{M^{n+}}$  and  $f_L$  are the corresponding activity coefficients. The concentration stability constant  $K_{ML^{n+}}$ , which is reported, since  $f_{ML^{n+}}$  and  $f_{M^{n+}}$  are unknown, is given by:

$$K_{ML^{n+}} = K'_{ML^{n+}} \cdot f_{M^{n+}} / f_{ML^{n+}} = [ML] / [M][L] = (1-\alpha) / \alpha [L] \quad (4)$$

The conductivity ( $\kappa$ ) of a solution containing metal perchlorate and crown ether is written as:

$$\kappa = \kappa_{MClO_4} + \kappa_{MClO_4} \quad (5)$$

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where  $\kappa_{\text{MClO}_4}$  and  $\kappa_{\text{MClO}_4}$  are the conductivities of metal perchlorate and metal crown ether perchlorate, respectively. The respective molar conductivities are given by:

$$\Lambda_{\text{MClO}_4} = \kappa_{\text{MClO}_4}/[M] = \kappa_{\text{MLClO}_4}/\alpha[M]_t \quad (6)$$

and

$$\Lambda_{\text{MLClO}_4} = \kappa_{\text{MLClO}_4}/[ML] = \kappa_{\text{MLClO}_4}/(1 - \alpha)[M]_t \quad (7)$$

Equation (5) may be written in terms of molar conductance ( $\Lambda$ ) by considering the total concentration  $[M]_t$  from Equation (6) and (7), to give:

$$\Lambda = \kappa/[M]_t = \alpha\Lambda_{\text{MClO}_4} + (1 - \alpha)\Lambda_{\text{MLClO}_4} \quad (8)$$

The correction for the viscosity changes is neglected, as the crown ether concentration was kept low. From Equation (4) and (8) one obtains:

$$K_{\text{ML}^{n+}} = (\Lambda_{\text{MClO}_4} - \Lambda)/(\{\Lambda - \Lambda_{\text{MLClO}_4}\}[L]) \quad (9)$$

where  $[L] = [L]_t - \{[M]_t \cdot (\Lambda_{\text{MClO}_4} - \Lambda)/(\Lambda_{\text{MClO}_4} - \Lambda_{\text{MLClO}_4})\}$ . The  $\Lambda_{\text{MLClO}_4}$  value is estimated from the  $\Lambda$  values at the point of a large  $[L]_t$ -to- $[M]_t$  ratio. With this value of  $\Lambda_{\text{MLClO}_4}$ , the  $K_{\text{ML}^{n+}}$  value in Equation (9) can be calculated.

The procedure for obtaining the limiting ionic conductivity is as follows. From the principle of mass balance, the total concentration can be written as:

$$[M]_t = [M] + [ML] \quad (10)$$

$$[L]_t = [L] + [ML] \quad (11)$$

Combining Equation (4) with Equation (10) and (11), the following quadratic equation is obtained:

$$K_{\text{ML}^{n+}} \cdot [ML]^2 - \{1 - K_{\text{ML}^{n+}}([M]_t + [L]_t)\}[ML] + K_{\text{ML}^{n+}}[M]_t[L]_t = 0 \quad (12)$$

The  $[M]$  value is obtained from Equation (10) using the  $[ML]$  value calculated from Equation (12) at a particular concentration of metal perchlorate  $[M]_t$  and crown ether  $[L]_t$ . The  $\kappa_{\text{MClO}_4}$  value in Equation (5) at this  $[M]$  point can be obtained from the  $\Lambda_{\text{MClO}_4}$  vs.  $[\text{MClO}_4]^{1/2}$  plot. Then, the  $\Lambda_{\text{MLClO}_4}$  value at the corresponding  $[ML]$  point can be calculated from Equation (5) and (7) using this  $\kappa_{\text{MClO}_4}$  value and organised in the form of a  $\Lambda_{\text{MLClO}_4}$  vs.  $[\text{MClO}_4]^{1/2}$  plot. The limiting molar conductance ( $\Lambda_0$ ) of the metal-crown ether perchlorate is determined by extrapolation of the plot generated in the above manner. The limiting ionic conductance ( $\lambda_{\text{ML}^{n+}}^0$ ) value of the metal-crown ether complex is obtained by using the value  $\lambda_{\text{ClO}_4^-}^0 = 26.8 \text{ S cm}^2 \text{ mol}^{-1}$ . This value was obtained indirectly from the limiting molar conductivities of  $\text{AgClO}_4$ ,  $\text{AgNO}_3$ ,  $\text{KCl}$  and  $\text{KNO}_3$ .

### Potentiometric Study of Crown Ether Complexation with Silver and Copper Perchlorates

The stability constant ( $K_{\text{ML}^{n+}}$ ) for  $\text{Ag}^I$  with crown ether, from Equation (2) and (4), is given by:

$$K_{\text{ML}^{n+}} = (1 - \alpha)/(\alpha\{[L]_t - [M]_t(1 - \alpha)\}) \quad (13)$$

The determination of  $\alpha$  is based on the measurement of the emf of the cell:

$\text{Ag}/\text{AgCl}$  reference electrode //  $\text{AgClO}_4 + \text{L} / \text{Ag}$  in 40% ethanol + water

The conductance and potentiometric studies on  $\text{AgClO}_4$  in 40% ethanol + water show that it is completely dissociated and the silver electrode behaves linearly over the range  $1 \times 10^{-1} \text{ M} - 1 \times 10^{-5} \text{ M}$ . Therefore, the difference ( $\Delta V$ ) between the emf of the salt solution and that of the salt + crown ether solution can be taken to reflect the concentration ratios. The Nernst equation is used to give the following relation:

$$\alpha = 10^{-\Delta V/59.16 \text{ mV}} \quad (14)$$

Putting this value of  $\alpha$  in Equation (13),  $K_{\text{ML}^{n+}}$  is obtained.

Equation (15) was used to determine  $\alpha$  for  $\text{Cu}^{II}$ :

$$\alpha = 10^{-\Delta V/29.58 \text{ mV}} \quad (15)$$

## Results and Discussion

On treatment of the conductance data of the divalent metal perchlorates and silver perchlorate with the Fuoss-Edelson and Shedlovsky equations, respectively, it was found that none of them showed any association in this solvent mixture. Similar observations were made by earlier workers<sup>[17,19]</sup> i.e. measurable association was found in cases where the ethanol percentage was greater than about 45% (v/v) for salts like potassium picrate, potassium chloride, cesium chloride, lithium chloride, etc. The values of the limiting molar conductivities,  $\lambda_{\text{M}^{n+}}^0$  of the metal ions derived from the Fuoss-Edelson and Shedlovsky plots are given in Table 1 along with the limiting molar conductivities of the complexes.

Table 1. Limiting molar conductivities of  $\text{M}^{n+}$  and  $\text{ML}^{n+}$

Metal ion	Solvated metal ion	$\lambda_{\text{M}^{n+}}^0/\text{S cm}^2 \text{ mol}^{-1}$			
		15C5	B15C5	18C6	DCH18C6
$\text{Ni}^{II}$	50.8	80.7	86.2	82.6	86.4
$\text{Co}^{II}$	46.1	49.1	47.4	48.2	48.2
$\text{Cu}^{II}$	54.7	57.7	56.7	65.1	63.5
$\text{Zn}^{II}$	47.0	74.6	49.0	65.6	70.5
$\text{Mn}^{II}$	41.0	42.8	43.0	44.6	46.2
$\text{Ag}^I$	28.7	24.4	23.5	22.8	18.0

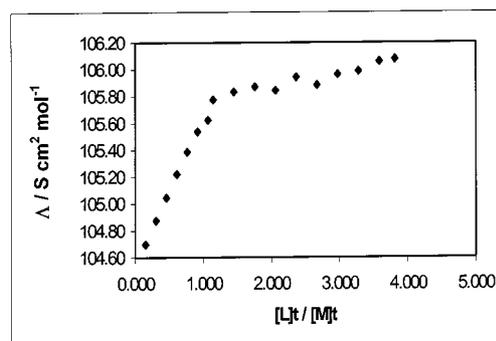


Figure 1. Plot of  $\Lambda$  vs.  $[L]_t/[M]_t$  for 15C5- $\text{Cu}(\text{ClO}_4)_2$  system

Figure 1 and 2 show plots of  $\Lambda$  vs.  $[L]_t/[M]_t$  for  $\text{Cu}^{\text{II}}$  and  $\text{Ag}^{\text{I}}$  with 15-crown-5, respectively, and they are representative of other metal ions and crown ethers.

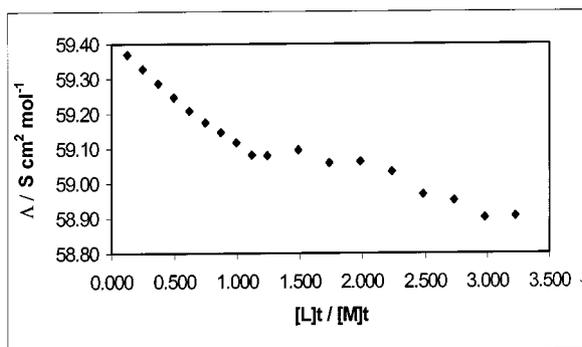


Figure 2. Plot of  $\Lambda$  vs.  $[L]_t/[M]_t$  for 15C5– $\text{AgClO}_4$  system

It was observed that the  $\Lambda$  value increases with an increase in the  $[L]_t/[M]_t$  ratio for all the systems involving the divalent transition metal ions, whereas a decrease in  $\Lambda$  values was observed in systems involving silver ions. This can be explained on the basis of the solvation sphere. The divalent transition metal ions have a high charge-to-radius ratio, on account of which they are highly solvated. On complexation, however, the crown ether molecule replaces the solvation sheath around the metal ion and, as a result, the moving entity becomes less bulky and more mobile. The silver ion, on the other hand, is relatively large and has a lower charge-to-radius ratio; hence it is solvated to a lesser extent. When complexed with crown ether it becomes bulkier causing a decrease in its mobility and also in the  $\Lambda$  values. The curves show a break point at  $[L]_t/[M]_t \approx 1$ , which indicates the formation of 1:1 complexes between the crown ethers and the metal ions. In the case of Ag-15C5 and Ag-B15C5 a slight break is also observed at  $[L]_t/[M]_t \approx 2$ , which hints at the formation of 2:1 sandwich complexes. However, in this paper we are confining our discussions to 1:1 complexes.

The values of the stability constants as  $\log K_{\text{ML}^{n+}}$  for the divalent metal ions (arranged in the order of increasing ionic radii) and silver complexes, obtained by conductometry and potentiometry, are given in Table 2 and 3, respectively.

Table 2. Stability constants ( $\log K_{\text{ML}^{n+}}$ ) for the metal ion–crown ether complexes by conductometry; figures in brackets indicate standard deviations ( $6 \leq n \leq 9$ )

Metal ion	15C5 <sup>[a]</sup>	B15C5 <sup>[a]</sup>	18C6 <sup>[a]</sup>	DCH18C6 <sup>[a]</sup>
$\text{Ni}^{\text{II}}$	1.95 (0.05)	2.01 (0.05)	1.65 (0.03)	1.74 (0.03)
$\text{Co}^{\text{II}}$	1.90 (0.08)	2.01 (0.06)	1.80 (0.06)	1.82 (0.09)
$\text{Cu}^{\text{II}}$	2.10 (0.05)	2.33 (0.08)	1.88 (0.07)	1.95 (0.04)
$\text{Zn}^{\text{II}}$	1.82 (0.04)	2.01 (0.08)	1.59 (0.04)	1.60 (0.04)
$\text{Mn}^{\text{II}}$	1.97 (0.03)	1.98 (0.03)	2.76 (0.03)	2.88 (0.05)
$\text{Ag}^{\text{I}}$	1.35 (0.04)	1.16 (0.01)	2.06 (0.02)	1.89 (0.01)

<sup>[a]</sup>  $\log (K_{\text{ML}^{n+}}/\text{mol dm}^{-3})$ .

Table 3. Stability constants ( $\log K_{\text{ML}^{n+}}$ ) for the metal ion–crown ether complexes by potentiometry; figures in brackets indicate standard deviation ( $6 \leq n \leq 9$ )

Metal ion	15C5 <sup>[a]</sup>	B15C5 <sup>[a]</sup>	18C6 <sup>[a]</sup>	DCH18C6 <sup>[a]</sup>
$\text{Cu}^{\text{II}}$	2.04 (0.04)	2.32 (0.10)	1.85 (0.04)	1.95 (0.08)
$\text{Ag}^{\text{I}}$	1.37 (0.03)	1.15 (0.01)	2.07 (0.02)	1.87 (0.01)

<sup>[a]</sup>  $\log (K_{\text{ML}^{n+}}/\text{mol dm}^{-3})$ .

Among the divalent ions it is observed that copper happens to form more stable complexes, which may be explained on the basis of its larger size relative to the other ions. However, the lower stability of zinc complexes remains unexplained. Also, as there is not much difference in the ionic radii of the divalent metal ions studied, one cannot establish a clear relationship based on the cavity sizes and the ionic radii alone. Other factors such as extent of solvation, entropy changes, changes in the conformations, etc. also need to be considered. Among the crown ethers studied, it is observed that the substituent bearing crown ethers forms more stable complexes with the divalent ions. This may be due to the contraction of the cavity size, making it closer to the diameter of the ions. As a result, the most stable complexes are formed with B15C5, the order being  $\text{B15C5} > \text{15C5} > \text{DCH18C6} > \text{18C6}$ . In the case of silver the opposite trend is observed, mainly because the diameter of the silver ion is much larger, the order being  $\text{18C6} > \text{DCH18C6} > \text{15C5} > \text{B15C5}$ .

It is clear that the  $\log K_{\text{ML}^{n+}}$  values for copper and silver complexes in this medium are low relative to those in pure propylene carbonate (PC) and 20wt% propylene carbonate + ethylene carbonate (EC). For example, in PC  $\log K_{\text{ML}^{n+}}$  values for Ag–18C6 and Ag–DCH18C6 are 5.78 and 4.86, respectively,<sup>[6]</sup> and in 20wt% PC + EC they are 4.92 and 4.93, respectively.<sup>[7]</sup> The copper complexes in 20wt% PC + EC, with 15C5 and B15C5 show a  $\log K_{\text{ML}^{n+}}$  of 4.20 and 3.78, respectively.<sup>[7]</sup> This can be attributed to the strong solvating properties and hydrogen bonding capability of water and ethanol molecules. The hydrogen bonds of these molecules and the ether oxygen atoms decrease the complexing ability of crown ethers, whereas the  $\log K_{\text{ML}^{n+}}$  values for the divalent metal ions in 40% ethanol + water are nearly the same as those observed in methanol,<sup>[14]</sup> which has hydrogen bonds and a lower dielectric constant. The stability constants for Ag-B15C5 and Ag-18C6 complexes in a 90% (v/v) ethanol + water mixture<sup>[20]</sup> were found to be 3.47 and 3.58, respectively, whereas in pure ethanol<sup>[21]</sup> the values for Ag-15C5 and Ag-18C6 are 3.12 and 3.36, respectively. A comparison of these values shows the effect of hydrogen bonding. Water, being a strongly hydrogen bonding solvent, decreases the stability of the complexes, and as the percentage of water decreases, the stability increases. Similar observations were found in dioxane + water mixtures.<sup>[22]</sup> As the ratio of dioxane/water was increased from 2:8 (v/v) to 8:2 (v/v), the stability of the K-18C6 complex increased from 2.47 to 4.21. However, the transition metal complexes are less stable than the alkali metal complexes in

a similar medium (e.g. methanol)<sup>[8]</sup> and this can be explained on the basis of the “Hard and Soft, Acid-Base” (HSAB) concept.<sup>[12,23,24]</sup> The transition metal ions being soft acids would form stronger coordination bonds with sulfur/nitrogen-containing polyethers, which are softer bases than oxygen.

The limiting molar conductivities (Table 1) of the transition metal ion complexes do not show any particular trend, except that they are higher than those of the solvated ions, whereas in the case of silver complexes they are lower than those of the solvated ions.

## Conclusion

The results obtained show that crown ethers form complexes with transition metal ions, although weak ones, in protic polar media and it is observed that the stabilities are not solely dependent on the ion/cavity sizes. The close agreement between the results obtained by conductometry and potentiometry is remarkable as it gives an accurate indication of the stabilities of the complexes.

## Experimental Section

**Solvents:** Double distilled, deionised water was used for the preparation of all solutions. Triple distilled ethanol (over molecular sieves), containing less than 0.2% water (as determined by Karl Fischer titration), was used to prepare the ethanol-water mixtures. Both the solvents were stored in sealed containers to prevent atmospheric contamination. Appropriate volumes of ethanol and water were mixed to give the 40% (v/v) solvent mixture.

**Reagents:** Silver perchlorate was prepared as described in the literature<sup>[25]</sup> and standardized by titration against sodium chloride on a DL 53 autotitrator. The other metal perchlorates were prepared from their respective carbonates by the general methods described elsewhere<sup>[26]</sup> and were standardized by titration against EDTA on a DL 53 autotitrator. The crown ethers, 15-crown-5 (Fluka), benzo-15-crown-5 (Aldrich), 18-crown-6 (Aldrich) and dicyclohexano-18-crown-6 (Fluka) were used as received.

**Apparatus:** A Mettler Toledo DL53 autotitrator with automatic temperature compensation (ATC) was used for the standardization of metal salt solutions and potentiometric and conductivity measurements. The probes used were: silver electrode with Ag/AgCl reference electrode (DM 141-SC) and conductometric sensor (Inlab 710). An Elico, digital pH-mV meter (model LI-120) was used for emf measurements of cells involving Cu<sup>II</sup>, in conjunction with a saturated calomel electrode (SCE).

**Procedure for Conductometry:** All measurements were done at 25 ± 0.1 °C, using a conductometric sensor Inlab 710 (with ATC), which was calibrated regularly with Mettler Toledo standard solutions. All molar conductivities were calculated after correcting for the solvent conductivity.

**Method 1. Determination of  $K_A$  of the Transition Metal Perchlorates:** Pure solvent mixture was placed in the cell and the conductance was measured. A step-by-step increase in the metal ion concentration was effected by means of the autotitrator. The conduc-

tivity was measured after each addition, followed by mixing, and the most stable reading over a span of 10 minutes was taken.

**Method 2. Determination of  $K_{ML^{++}}$ :** The metal perchlorate solution ( $\approx 1 \times 10^{-3} M$ ) was placed in the cell and the conductivity was measured. The crown ether solution ( $\approx 0.02 M$ ) was added to the cell in small increments until the total concentration of the crown ether was approximately 2–3 times as large as that of the metal perchlorate. The conductivity was measured after each addition as above.

**Method 3. Determination of  $\Lambda_0$  of MLCIO<sub>4</sub>:** A crown ether solution ( $\approx 2 \times 10^{-3} M$ ) was placed in the cell and the conductance of the solution was measured. Then, a step-by-step increase in the concentration of metal perchlorate was effected as mentioned above until the concentration of metal perchlorate became approximately twice as large as that of the crown ether.

**Procedure for Potentiometry:** The silver indicator electrode (DM 141-SC) with an inbuilt Ag/AgCl reference element was used for all measurements involving Ag<sup>I</sup> ions. As a general procedure, the emfs were recorded every 2 minutes. The potentials recorded were the average of the last two observations, which normally agreed to within ±0.1 mV; the measured cell potentials were reproducible to ±0.5 mV.

A pure copper wire (purity >99.95%) in conjunction with the SCE was used for measurement of emfs along with an Elico, digital pH-millivoltmeter. As a general procedure, the emfs were recorded every 2 minutes. The potentials recorded were the average of the last two observations, which normally agreed to within ±1 mV; the measured cell potentials were reproducible to ±3 mV.

Stock solutions of silver/copper perchlorates and crown ethers were prepared in a 40% ethanol + water mixture. The experimental solutions were prepared by appropriate dilution of the stock solutions to the required concentrations.

The dielectric constant and viscosity of 40%(v/v) ethanol + water were interpolated from previous data<sup>[17,27]</sup> using data fitting software (Numerical Methods Toolkit)<sup>[28]</sup> and were found to be 58.41 and 2.29 cP, respectively.

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