

# Complexation of Macrocyclic Compounds with Metal Ions: 1. Cd(II), Pb(II), Co(II), Mn(II), and Ag(I) Ions in 40 vol % Ethanol + Water Medium

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Stability constants in 40 vol % ethanol + water mixture were evaluated for the complexes of Cd(II) and Pb(II) with the macrocyclic polyethers 15-crown-5, benzo-15-crown-5, 18-crown-6, and dicyclohexano-18-crown-6 by conductometric titrations. Complexation studies of Ag(I) with 1,4,8,11-tetraazacyclotetradecane and 1,4,10-trioxa-7,13-diazacyclopentadecane were carried out by potentiometry to study the effect of nitrogen substituent. In addition, the stabilities of complexes of Co(II), Mn(II), and Ag(I) with oxygen-containing crown ethers were determined using the nitrate salts and were found to be lower than those obtained by using perchlorate salts in our previous study. A potentiometric study of complexes of Ag(I) was also undertaken to compare the results with those obtained by conductivity measurements, which were found to be in good agreement with each other. The complexation studies indicate 1:1 complex formation between the metal ion and macrocycle, the  $\log K_{ML}^{n+}$  values being in the range 1–9. The limiting molar conductivities of the metal ions and their crown ether complexes were also determined.

## Introduction

Ever since 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> interest in this field has increased. Present studies involve the synthesis of new macrocyclic compounds, newer methods of study,<sup>4</sup> interpretations of the complexation behavior,<sup>5</sup> and applications. As mentioned earlier,<sup>6</sup> the complexation behavior of lanthanides, alkali, and alkaline earth metal ions<sup>7,8</sup> with crown ethers have been extensively studied in various solvents and the complexation of transition metal ions has been studied mainly with respect to aza and thia crown ethers, as they are softer ligands. Few studies have been made on the complexation behavior of transition metal ions with oxygen containing crown ethers.<sup>6,9</sup> Studies relating to the effect of anion on the formation constants of the complexes are rare.<sup>10</sup>

The object of the present work was to study the complexation behavior of Co(II), Mn(II), Cd(II), Pb(II), and Ag(I) with 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), and dicyclohexano-18-crown-6 (DCH18C6). In addition, silver complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,4,10-trioxa-7,13-diazacyclopentadecane (diaza15C5) were also studied in 40 vol % ethanol + water. This is a continuation of our research studies in this medium. Aqueous alcohol is widely used as a physiological substrate and also in alcoholic beverages. On the basis of our previous complexation studies<sup>6</sup> with transition metal perchlorates in 40 vol % ethanol + water medium, we successfully fabricated a chemically modified electrode (CME) and developed a method for the trace analysis for copper<sup>9</sup> in alcoholic beverages. In this study we have used nitrate salts of Co(II), Mn(II), and Ag(I) for comparison and some other possible applications. In addition,

the complexation of Ag(I) have been studied by potentiometry, to compare the results obtained by conductometric measurements.

## Experimental Section

**Solvent.** Double distilled, deionized water was used for preparation of all solutions. Triple distilled ethanol (once over calcium oxide followed by twice over molecular sieves), containing less than 0.2% water, by volume (as determined by Karl Fischer titration), was used to prepare the ethanol + water mixture. Both of the solvents were stored in sealed containers to prevent atmospheric contamination. Appropriate volumes of ethanol and water were mixed to give 40 vol % ( $\pm 0.05\%$ ) solvent mixture.

**Reagents.** Cobalt nitrate, lead nitrate, silver nitrate, cadmium nitrate, and manganese nitrate were of reagent grade and were recrystallized once from double-distilled water. Stock solutions of the metal salts were prepared and standardized by titrating against EDTA and sodium chloride (for silver nitrate) on the DL 53 autotitrator, before use.

The crown ethers, 15-crown-5 (Fluka), benzo-15-crown-5 (Aldrich), 18-crown-6 (Aldrich), dicyclohexano-18-crown-6 (Fluka), 1,4,8,11-tetraazacyclotetradecane (Fluka), and 1,4,10-trioxa-7,13-diazacyclopentadecane (Fluka) were of reagent grade (purity  $\geq 98\%$ ) and used as received.

**Apparatus.** A Mettler Toledo DL53 autotitrator with automatic temperature compensation (ATC) was used for standardization of metal salt solutions and potentiometric and conductivity measurements. The probes used were silver electrodes with Ag/AgCl reference electrode (DM 141-SC) and conductometric sensor with ATC (Inlab 710).

**Procedure for Conductometry.** All measurements were done as before<sup>6</sup> at  $25.0 \pm 0.1$  °C, using the conductometric sensor Inlab 710 (with ATC), which was calibrated regularly with the Mettler Toledo standard solutions. All molar conductivities were calculated after correcting for the

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solvent conductivity. The uncertainty in the measurement of conductivities was  $\pm 0.1 \mu\text{S}$ .

**Method 1. Determination of  $K_A$  of the Divalent Metal Nitrates.** 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. After each addition, followed by mixing, the system was allowed to stabilize and a reading, which did not change, by  $\pm 0.2 \mu\text{S}$  over a span of 10 min. was recorded.

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

**Method 3. Determination of  $\Lambda_0$  of  $MLX_n$ .** A crown ether solution ( $\sim 2 \times 10^{-3} \text{ M}$ ) was placed in the cell, and the conductance of the solution was measured. Then a step-by-step increase in the concentration of metal nitrate was effected as mentioned above until the concentration of metal nitrate 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 electrode was used for all measurements involving Ag(I) ions. As a general procedure, the electromotive forces (emf's) were recorded every 2 min. The potentials recorded were the average of the last two observations, which normally agreed to within  $\pm 0.1 \text{ mV}$ , and the measured cell potentials were reproducible to  $\pm 0.5 \text{ mV}$ .

Stock solutions of silver nitrate and crown ethers were prepared in a 40% ethanol + water mixture. Experimental solutions ( $\sim 10^{-3}$  to  $10^{-4} \text{ M}$  with respect to  $\text{AgNO}_3$ ) were prepared by appropriate dilution of the stock solutions to the required concentrations.

The relative permittivity and viscosity of 40 vol % ethanol + water were interpolated from previous data<sup>11,12</sup> using data fitting software (Numerical Methods Toolkit)<sup>13</sup> and were found to be 58.41 and 2.29 mPa·s, respectively.

## Theory

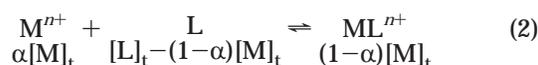
The conductance data of the divalent metal nitrates were treated by the Fuoss and Edelson method.<sup>14</sup> The method consists of evaluating the limiting molar conductance,  $\Lambda_0$ , and the first step association constant,  $K_A$ , of an electrolyte  $\text{MX}_2$  in 40 vol % ethanol + water based on the equilibrium



where  $\text{M} = \text{Cd, Co, Pb, Mn}$  and  $\text{X} = \text{NO}_3$ . The equilibrium leading to the neutral species  $\text{MX}_2$  is neglected in this method.

The treatment of conductance data for silver nitrate was done by using the Shedlovsky function.<sup>11</sup> The equations<sup>6,15</sup> used for calculation of stability constants are described briefly as follows:

**Conductometric Study of Crown Ether Complexation with Metal Nitrates.** The complexation of a metal ion (M) with crown ether (L) may be represented as



where  $[\text{M}]_t$ ,  $[\text{L}]_t$ , 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

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

where  $[\text{ML}]$ ,  $[\text{M}]$ , and  $[\text{L}]$  are the concentrations of complexed cation, uncomplexed cation, and uncomplexed crown ether, respectively, while  $f_{ML}^{n+}$ ,  $f_{M}^{n+}$ , 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

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

where  $f_L$  is assumed to be unity.

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

$$\kappa = k_{MX_n} + k_{MLX_n} \quad (5)$$

where  $k_{MX_n}$  and  $k_{MLX_n}$  are the conductivities of metal nitrate and metal crown ether nitrate, respectively. The respective molar conductivities are given by

$$\Lambda_{MX_n} = k_{MX_n}/[\text{M}] = k_{MX_n}/\alpha[\text{M}]_t \quad (6)$$

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

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

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

The correction for the viscosity changes is neglected, as the crown ether concentration was kept low. Using eqs 4 and 8 one obtains

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

where  $[\text{L}] = [\text{L}]_t - \{[\text{M}]_t(\Lambda_{MX_n} - \Lambda)/(\Lambda_{MX_n} - \Lambda_{MLX_n})\}$ . The  $\Lambda_{MLX_n}$  value is estimated from the  $\Lambda$  values at the point of large  $[\text{L}]_t$  to  $[\text{M}]_t$  ratio. By use of the  $\Lambda_{MLX_n}$  value, the  $K_{ML}^{n+}$  value in eq 9 is 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

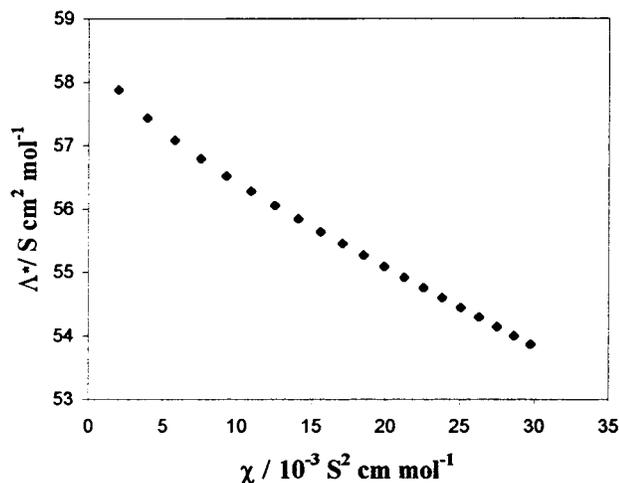
$$[\text{M}]_t = [\text{M}^{n+}] + [\text{ML}^{n+}] \quad (10)$$

$$[\text{L}]_t = [\text{L}] + [\text{ML}^{n+}] \quad (11)$$

On combination of eq 4 with eqs 10 and 11, the following quadratic equation is obtained

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

The  $[\text{M}^{n+}]$  value is obtained from eq 10 using the  $[\text{ML}^{n+}]$  value calculated from eq 12 at a particular concentration of metal nitrate  $[\text{M}]_t$  and crown ether  $[\text{L}]_t$ . The  $k_{MX_n}$  value in eq 5 at this  $[\text{M}^{n+}]$  point can be obtained from the  $\Lambda_{MX_n}$  vs  $[\text{MX}_n]^{1/2}$  plot. Then the  $\Lambda_{MLX_n}$  value at the corresponding  $[\text{ML}^{n+}]$  point can be calculated from eqs 5 and 7 using this



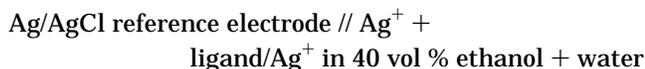
**Figure 1.** Plot of  $\Lambda^*$  vs  $\chi$  for  $\text{Pb}(\text{NO}_3)_2$  in 40 vol % ethanol + water.

$k_{\text{MX}_n}$  value and organized in the form of a  $\Lambda_{\text{MLX}_n}$  vs  $[\text{MX}_n]^{1/2}$  plot. The limiting molar conductance ( $\Lambda_0$ ) of the metal–crown ether nitrate is determined by extrapolation of the plot generated in the above manner. The limiting ionic conductivity ( $\lambda_{\text{ML}^{n+}}^0$ ) of the metal–crown ether complex is obtained<sup>16</sup> by using  $\lambda_{\text{NO}_3^-}^0 = 28.8 \text{ S cm}^2 \text{ mol}^{-1}$ .

**Potentiometric Study of Crown Ether Complexation with Silver Nitrate.** The stability constant ( $K_{\text{ML}^{n+}}$ ) for  $\text{Ag}(\text{I})$  with crown ether, using eqs 2 and 4, is given by

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

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



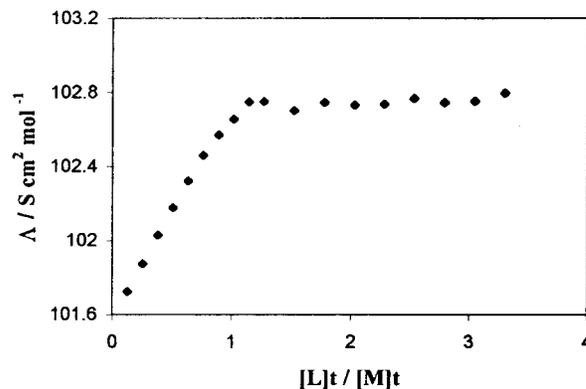
The conductance and potentiometric studies on  $\text{AgNO}_3$  in 40 vol % ethanol + water show that it is completely dissociated and the silver electrode behaves linearly over the range  $1 \times 10^{-1}$  to  $1 \times 10^{-6}$  M. So, the difference ( $\Delta E$ ) between the emf of the salt solution 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

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

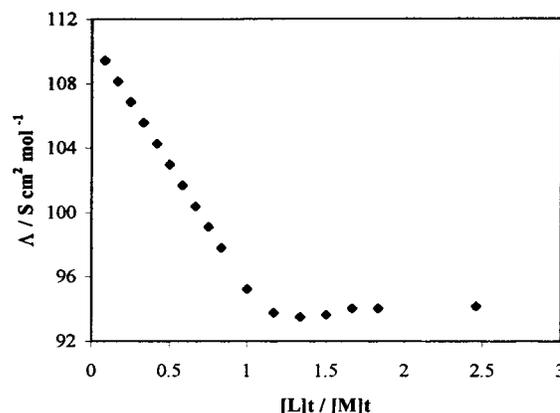
By use of this value of  $\alpha$  in eq 13,  $K_{\text{ML}^{n+}}$  is obtained.

## Results and Discussion

On treatment of the conductance data of the divalent metal nitrates and silver nitrate by Fuoss–Edelson and Shedlovsky equations, respectively, it was found that all of them showed a slight association. This result is in contrast to our previous<sup>6</sup> observations using perchlorate salts wherein practically no association was found. Figure 1 shows a representative Fuoss–Edelson plot, which is a plot<sup>14</sup> of  $\Lambda^*$  vs  $\chi$ . From this plot, the limiting molar conductivities and the association constants were obtained. The plot is nonlinear as the concentration increases. This is because of the failure of the approximation used in the treatment.<sup>14–16</sup> The values of  $K_\Lambda$  are obtained from a tangent in the region of the  $\chi$  value before divergence from a straight line and are found to be 21.9, 9.9, 6.5, and 11.4 for cobalt, manganese, cadmium, and lead nitrates, respectively. The association constant for silver nitrate as deter-



**Figure 2.** Plot of  $\Lambda$  vs  $[\text{L}]_t/[\text{M}]_t$  for the 15C5– $\text{Co}(\text{NO}_3)_2$  system.



**Figure 3.** Plot of  $\Lambda$  vs  $[\text{L}]_t/[\text{M}]_t$  for the 18C6– $\text{Pb}(\text{NO}_3)_2$  system.

**Table 1. Limiting Molar Conductivities of the Solvated Metal Ions ( $\lambda_{\text{M}^{n+}}^0$ ) and of Complexed Metal Ions ( $\lambda_{\text{ML}^{n+}}^0$ )**

metal ion	$\lambda_{\text{M}^{n+}}^0 / \text{S cm}^2 \text{ mol}^{-1}$ solvated metal ion	$\lambda_{\text{ML}^{n+}}^0 / \text{S cm}^2 \text{ mol}^{-1}$			
		15C5	B15C5	18C6	DCH18C6
Cd(II)	43.8	46.7	46.0	45.6	45.1
Pb(II)	58.8	58.0	57.4	55.3	54.8

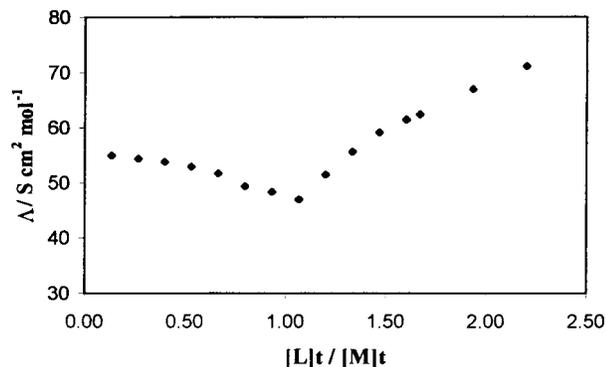
mined by the Shedlovsky equations was found to be 1.1. The derived values of limiting molar conductivities  $\lambda_{\text{M}^{n+}}^0$  and  $\lambda_{\text{ML}^{n+}}^0$  for Cd(II) and Pb(II) are given in Table 1. The values for other metal ions have been reported earlier.<sup>6</sup> Figures 2 and 3 show plots of  $\Lambda$  vs  $[\text{L}]_t/[\text{M}]_t$  for Co(II) and Pb(II) with 15-crown-5 and 18-crown-6, respectively, which are representative of other metal ions and crown ethers. It was observed that the  $\Lambda$  value increases with an increase in  $[\text{L}]_t/[\text{M}]_t$  ratio for all the systems involving the Co(II), Mn(II), and Cd(II) whereas a decrease in  $\Lambda$  values was observed in systems involving silver and lead ions. This has been explained<sup>6</sup> on the basis of a solvation sphere. The divalent metal ions have a high charge-to-radius ratio on account of which they are highly solvated. But on complexation, 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 and lead ions, on the other hand, are relatively larger and have lower charge-to-radii ratio. Hence, they are 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  $[\text{L}]_t/[\text{M}]_t \approx 1$ , which indicates the formation of 1:1 complexes between crown ethers and the metal ions.

The values of 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 conductom-

**Table 2. Stability Constants ( $\log K_{ML^{n+}}$ ) for the Metal Ion–Crown Ether Complexes by Conductometry<sup>a</sup>**

metal ion	$\log K_{ML^{n+}}$			
	15C5	B15C5	18C6	DCH18C6
Co(II)	1.66 (0.04)	1.86 (0.02)	1.42 (0.04)	1.53 (0.02)
Mn(II)	1.71 (0.02)	1.88 (0.01)	2.55 (0.02)	2.82 (0.01)
Cd(II)	2.07 (0.06)	1.83 (0.03)	3.66 (0.03)	3.37 (0.04)
Pb(II)	2.87 (0.05)	2.68 (0.05)	6.94 (0.04)	6.83 (0.02)
Ag(I)	1.26 (0.01)	1.08 (0.01)	1.97 (0.01)	1.86 (0.01)

<sup>a</sup> Figures in parentheses indicate standard deviation ( $6 \leq n \leq 9$ ).

**Figure 4.** Plot of  $\Lambda$  vs  $[L]_t/[M]_t$  for the cyclam–AgNO<sub>3</sub> system.

etry are given in Table 2. Among the divalent ions it is observed that lead happens to form more stable complexes with 18C6, which may be explained on the basis of its larger relative size that fits into the cavity and also a partial covalent interaction. However, the stabilities of silver complexes are low (even though its ionic radius is closer to that of 18C6), for silver ion being monovalent exerts lesser electrostatic attraction. Similar behavior was observed in the case of 18C6 complexes of K(I) and Ba(II) in aqueous medium<sup>17</sup> with barium showing much higher stability. But the stability and selectivity are low in all cases for complexes of 15C5, which could be due to the combination of two unfavorable factors, viz. (i) a lesser number of interaction sites and (ii) though the cavity is well adapted to smaller cations, the latter are more strongly solvated than the larger cations. Among the crown ethers studied, it is observed that the substituent bearing crown ethers form more stable complexes with the smaller ions. This may be due to the contraction of the cavity size, making it closer to the diameter of the ions. As a result, relatively more stable complexes of Co(II) are formed with B15C5, the order being B15C5 > 15C5 > DCH18C6 > 18C6. In the case of silver, cadmium, and lead the opposite trend is observed, mainly because their diameters are much larger, the order being 18C6 > DCH18C6 > 15C5 > B15C5. However, Mn(II), which has an ionic diameter slightly greater than that of Co(II), forms more stable complexes with 18C6 rather than 15C5.

The conductometric experiments with cyclam and diaza-15C5 showed 1:1 complexation, but the data could not be used for calculation of stability constants as these compounds caused a change in the pH of the system and a "V"-shaped curve (Figure 4) was obtained. Hence, only the complexation of silver ions with aza macrocycles was studied, as they are amenable to measurements by direct potentiometry. Table 3 gives the stability constants of Ag(I) complexes with crown ethers and aza macrocyclic compounds obtained by potentiometry. The introduction of two nitrogen atoms in 15C5 causes an increase in stability by about 4 units, and in the case of cyclam, with four

**Table 3. Stability Constants ( $\log K_{ML^{n+}}$ ) for the Silver Ion–Macrocycle Complexes by Potentiometry<sup>a</sup>**

macrocycle	$\log (K_{ML^{n+}})$	macrocycle	$\log (K_{ML^{n+}})$
15C5	1.26 (0.01)	DCH18C6	1.84 (0.02)
B15C5	1.08 (0.01)	cyclam	8.36 (0.03)
18C6	1.99 (0.01)	diaza15C5	5.83 (0.04)

<sup>a</sup> Figures in parentheses indicate standard deviation ( $5 \leq n \leq 8$ ).

nitrogen atoms the stability is increased by about 7 units even though the cavity size is smaller. Similar behavior was observed with Ag–18C6 and Ag–diaza18C6 ( $\log K_{ML^{n+}} = 1.6$  and 7.8, respectively) in aqueous medium.<sup>18,19</sup> With copper complexes too, it was observed that the enthalpy of reaction between Cu(II) and 15C5 or 18C6 was too small to be measured by calorimetry indicating weaker complexation, but with pyridino-18-crown-6 the  $\log K$  was found to be 4.63.<sup>20</sup> Also, it is observed that the stability of perchlorates<sup>6</sup> is slightly greater than that of the nitrate salts. For example, the stabilities of 15C5–Co(II) perchlorate and 15C5–Co(II) nitrate are 1.90 and 1.66, respectively. This can be attributed to the larger size of the perchlorate anion that helps in greater dissociation of the salt and the cation is freer to react with the crown ether. This is also evident from the values of association constants of the nitrates and perchlorates. A strongly chelating anion can pull out the cation from the cavity of the crown ether by a strong interaction, thereby decreasing its stability. Therefore, one cannot establish a clear relationship based on the cavity sizes and the ionic radii alone. Other factors such as nature of donor atoms, associated anion, extent of solvation, entropy changes, changes in the conformations, directional nature of the bonds, etc., also need to be considered. For example, in the case of Co(II)–DCH18C6 complexes it was found (by IR and magnetic moment data) that only three oxygen atoms of the ring were involved in bonding with each cobalt cation.<sup>19</sup> The effect of anion is important from the point of view of fabrication of sensors as they compete with the macrocyclic ligands to complex with the metal ion. For example, with CMEs for Hg(II) based on crown ethers, the best response was observed in acetate medium and no response was observed in chloride medium,<sup>21</sup> whereas with CMEs based on thia crown ethers it was possible to accumulate Ag(I) from a perchlorate medium rather than from an acetate medium.<sup>22</sup> The stabilities in this medium are lower than those in pure ethanol or solvent mixtures containing higher percentage of ethanol, as observed earlier.<sup>6</sup> For example, the stability constants for Ag–B15C5 and Ag–18C6 complexes in 90% (v/v) ethanol + water mixture<sup>23</sup> were found to be 3.47 and 3.58, respectively, whereas in pure ethanol<sup>24</sup> the values for Ag–15C5 and Ag–18C6 are 3.12 and 3.36, respectively. This has been attributed<sup>6</sup> to the strong solvating properties and hydrogen bonding capability of water and ethanol molecules. A comparison of these values with the results presently obtained shows the effect of hydrogen bonding (though a slight discrepancy is observed, i.e., stability in 100% ethanol is slightly lower than that in 90 vol % ethanol + water, which can be attributed to the different electrolytes used to maintain the ionic strengths). This example also brings out the importance of the influence of electrolytes used to maintain the ionic strengths. Therefore, for a detailed comparison it is necessary to maintain all parameters identical.<sup>25</sup> 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 found in dioxane + water

mixtures<sup>25</sup> and methanol + water mixtures<sup>26</sup> have been discussed before.<sup>6</sup> Similarly, the stability of Pb–18C6 is greater in 40% ethanol + water by about 2–3 units than in water.<sup>27</sup> However, the transition metal ion complexes are less stable than the alkali metal ion complexes within the same medium<sup>20,27</sup> and this can be explained on the basis of the “hard and soft, acid–base” (HSAB) concept.<sup>28–30</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 increase in stability of silver complexes on substitution of oxygen by nitrogen atoms demonstrates that the bonding in such complexes is of both types (electrostatic and covalent), whereas in the case of alkali/alkaline earth metal ion complexes with oxa crown ethers there is only electrostatic bonding.

The limiting molar conductivities (Table 1) of Co(II), Mn(II), and Cd(II) complexes do not show any particular trend except that they are higher than that of the solvated ions, whereas in the case of silver and lead complexes they are lower than that of solvated ions.

## Conclusion

The results obtained show that crown ethers form weak complexes with transition metal ions in protic polar media, and it is observed that the stabilities are not solely dependent on the ion/cavity sizes. The anions associated with the metal ions also have considerable effect on the formation of complexes. 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. Strong complexation of Pb(II) with 18C6 was observed due to greater charge density and close match of the ionic diameter and the cavity size. This observation has been made use of in the development of a method based on CMEs for trace analysis of lead in alcoholic beverages.<sup>31</sup> The nature of donor atoms in the coronand ring has a strong effect on the stabilities of complexes. The strong complex formed between silver and cyclam has been used<sup>32</sup> to construct coated wire ion selective electrodes for analysis of Ag(I).

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