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Complexation of macrocyclic compounds with mono-, di- and tri-valent transition and heavy metal ions in 90% (v/v) DMSO + water medium

Vijaykumar S. Ijeri, Ashwini K. Srivastava [1],*

Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (E), Mumbai 400098, Maharashtra, India

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Abstract

Stability constants in 90% (v/v) DMSO + water mixture were evaluated for the complexes of Ag(I), Co(II), Cu(II), Mn(II), Ni(II), Zn(II), Pb(II), Cr(III) and Fe(III) with the macrocyclic compounds, namely, 15-crown-5, benzo-15-crown-5, 18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6, dibenzo-24-crown-8 and dicyclohexano-24-crown-8 by conductometric titrations. A potentiometric study of complexes of Ag(I) and Cu(II) was also undertaken to compare the results with those obtained by conductivity measurements, which were found to be in good agreement with each other. In addition, complexation studies of Ag(I) and Cu(II) with 1,4,8,11-tetraazacyclotetradecane, 1,4,10-trioxa-7,13-diaza-cyclopentadecane, 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene and 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane were carried out by potentiometry to study the effect of the heteroatom, nitrogen. The complexation studies indicate 1:1 complex formation between the metal ion and crown ether, and the log $K_{\mathrm{ML}}{}^{n+}$ values are in the range 1–20. The limiting molar conductivities of the metal ions and their crown ether complexes were also determined.

Keywords: Macrocyclic compounds; Transition metal ions; Complexation; Conductometry; Potentiometry

1. Introduction

With the discovery of crown ethers [1], the focus on complexation through covalent interactions shifted to that of non-covalent interactions. These macrocyclic compounds are capable of forming complexes with alkali and alkaline earth metal ions via electrostatic attraction and encapsulation into the cavity [2,3]. As pointed out in our earlier papers [4,5], the literature till now has plenty of examples on the complexation behaviour of lanthanides, alkali and alkaline earth metal ions with crown ethers in various solvents. The complexation of transition metal ions has been studied mainly with respect to aza and thia crown ethers, but not with oxa crown ethers. Our earlier papers [4,5], largely dealt with the complexation behaviour of transition metal ions, viz. Ag(I), Co(II), Cu(II), Mn(II), Ni(II), Zn(II) and Pb(II) with oxa crown ethers in 40% (v/v) ethanol + water.

Transition metal ions are essential micro-nutrients/minerals to humans, animal and plants, and the macrocyclic compounds, by accepting the metal ions in a more or less 'lock and key' fashion, mimic in a relatively uncomplicated way the very complicated functions of biological materials such as enzymes. It is this mimicry that excites the scientists. The study of various macrocyclic compounds in different solvents or solvent-mixtures may indicate new approaches for developing pharmaceutical systems or a way to cross the blood–organ barrier. So, the object of the present work was to study the complexation behaviour of Ag(I), Co(II), Cu(II), Mn(II), Ni(II), Zn(II), Pb(II), Cr(III) and Fe(III) with 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DCH18C6), dibenzo-24-crown-

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* Corresponding author. Tel.: +91-22-2652-6091x353; fax: +91-22-2652-8547.

E-mail address: aks@mail.mu.ac.in (A.K. Srivastava).

[1] akschbu@yahoo.com

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8 (DB24C8) and dicyclohexano-24-crown-8 (DCH24C8) in 90% (v/v) dimethylsulphoxide (DMSO) + water medium by conductometry. Aqueous DMSO is used as a cryoprotective agent in chemistry, biology and/or as a physiological substrate and has also been proposed as a pharmaceutical or pharmacological substrate [6]. Also, as this particular composition prevents the hydrolysis of Cr(III) and Fe(III) salts, ensured the solubility of the benzo and dibenzo compounds and interestingly lies on the maxima of the viscosity curve of DMSO + water mixtures, it was chosen for the present study. The complexation of Ag(I) and Cu(II) have been studied by potentiometry as well, to compare the results obtained by conductometric measurements. In addition Ag(I) and Cu(II) complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam), 1,4,10-trioxa-7,13-diaza-cyclopentadecane (diaza 15C5), 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (dibenzodiaza 15C4) and 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (dibenzyldiaza 18C6) have also been studied potentiometrically to evaluate the effect of nitrogen atom as these metal ions are directly amenable to potentiometric studies.

2. Experimental

2.1. Solvent

Double distilled, deionised water was used for preparation of all solutions. Commercially available DMSO (99% pure, Spectrochem, India) was held over sodium hydroxide for 3 h at 90 °C and distilled twice at reduced pressure. Finally, a third distillation was carried out without any additive, under reduced pressure. The middle fraction, comprising about 80% was collected and used. Both the solvents were stored in sealed containers to prevent atmospheric contamination. Appropriate volumes of DMSO and water were mixed to give 90 vol.% ($\pm 0.05\%$) solvent mixture.

2.2. Reagents

Mn(II) perchlorate hexahydrate (Fluka), Cr(III) perchlorate hexahydrate (Fluka) and Fe(III) perchlorate nonahydrate (Fluka) were used as such after standardisation. The other metal perchlorates were prepared from their respective carbonates/oxides by the general methods described elsewhere [7–9] and were dried in vacuum to get the anhydrous salts. All salt solutions were standardised before use.

The crown ethers, 15-crown-5 (Fluka), benzo-15-crown-5 (Aldrich), 18-crown-6 (Aldrich), dibenzo-18-crown-6 (Aldrich), dicyclohexano-18-crown-6 (Fluka), dibenzo-24-crown-8 (Fluka), dicyclohexano-24-crown-8 (Fluka), 1,4,8,11-tetraazacyclotetradecane (Fluka), 1,4,10-trioxa-7,13-diaza-cyclopentadecane (Fluka), 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (Fluka) and 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Fluka) were used as received.

2.3. Apparatus

A Mettler Toledo DL53 autotitrator with automatic temperature compensation (ATC) was used for standardisation of metal salt solutions and conductivity measurements. The probe used was conductometric sensor (Inlab 710). The potentiometric measurements were carried out using the silver indicator electrode DM 141-SC.

An Eutech Cyberscan 2500 pH/ion meter readable to ±0.1 mV with a saturated calomel electrode (SCE) as reference electrode was used in conjunction with a pure copper wire (purity $\geq 99.9\%$) as indicator electrode, for electrode potential measurements.

2.4. Procedure for conductometry

All measurements were done at 25 ± 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 solvent conductivity and the methods have been described before [4,5].

2.5. Procedure for potentiometry

A pure copper wire (purity $> 99.95\%$) in conjunction with SCE was used for measurement of emfs using an Eutech Cyberscan 2000 pH/ion meter. As a general procedure, the emfs were recorded every 2 min. The potentials recorded were the average of the last two observations, which normally agreed to within ±0.2 mV and the measured cell potentials were reproducible to ± 1 mV. Similarly, the silver indicator electrode (DM 141-SC) was used for Ag(I) systems [4,5].

Stock solutions of copper/silver perchlorates and crown ethers were prepared in 90% DMSO + water mixture. Experimental solutions were prepared by appropriate dilution of the stock solutions ($\sim 10^{-2}$ M) to the required concentrations ($\sim 10^{-4}$–10^{-3} M).

The stability constants ($K_{\mathrm{ML}}{}^{n+}$) of Ag(I)/Cu(II) complexes with macrocyclic compounds were calculated by the following equation [4,5]:

$$K_{\mathrm{ML}}{}^{n+} = (1-\alpha)/(\alpha\{[L]_{\mathrm{t}} - [M]_{\mathrm{t}}(1-\alpha)\}) \qquad (1)$$

where $[M]_{\mathrm{t}}$, $[L]_{\mathrm{t}}$ and α are the total concentration of cation, the total concentration of ligand and the fraction of uncomplexed cation, respectively.

As an example, for silver complexation, the determination of α is based on the measurement of the emf of the cell:

$$\text{Ag/AgCl reference electrode//Ag}^+ + \text{Ligand/Ag}^+ \text{ in 90\% DMSO} + \text{water}$$

The conductance and potentiometric studies on Ag(I) and Cu(II) perchlorates in this medium, show that it is completely dissociated and the silver electrode behaves linearly over the range 1×10^{-1}–10^{-7} M. So, the difference (ΔE) 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:

$$\alpha = 10^{-\Delta E/59.96} \text{ for Ag(I)} \qquad (2)$$

$$\alpha = 10^{-\Delta E/29.58} \text{ for Cu(II)} \qquad (3)$$

Using these values of α, $K_{\mathrm{ML}}{}^{n+}$ is obtained from equation 1.

The relative permitivity and viscosity of 90 vol.% DMSO+water were interpolated from previous data [10] using data fitting software (Numerical Methods Toolkit) [11] and were found to be 56.2 and 2.75 mPa s, respectively.

3. Theory

The Fuoss and Edelson method as used earlier [4,5,12] was used to treat the conductance data of the divalent metal perchlorates. The method consists of evaluating the limiting equivalent conductance, Λ_0, and the first step association constant, K_A, of an electrolyte of the type MX_2. The equations used for calculation of stability constants have been described [4,5,12] earlier. The limiting ionic conductance ($\lambda^0{}_{\mathrm{ML}}{}^{n+}$) value of the metal–crown ether complex is obtained by using $\lambda^0{}_{\mathrm{ClO4^-}} = 19.3$ S cm^2 mol^{-1}. This value was obtained [7] indirectly from the limiting molar conductivities of tetrabutylammonium iodide, sodium tetraphenylboride, NaI, $NaNO_3$, $AgNO_3$ and $AgClO_4$ by treatment of the conductivity data in this medium by the Fuoss 1978 equation [13,14]. As all conductance equations [15] (even simple freehand extrapolations) give essentially the same values for Λ_0, the limiting molar conductivities of trivalent ions were obtained from extrapolation of experimental data [7] by regression method using MICROSOFT EXCEL.

4. Results and discussion

On treatment of the conductance data of the divalent metal perchlorates by the Fuoss–Edelsen equations, it was found that none of them showed any association in this solvent mixture. Only Pb(II), which was used as a nitrate salt showed an association constant of 28.3. We had noted similar observations in 40% ethanol+water [4,5,7], which has nearly the same dielectric constant (58.4). However, significant association is observed for these metal perchlorates in pure DMSO [16], which has a lower dielectric constant (46.4). From these observations we can safely assume that the metal perchlorates are completely dissociated in media of dielectric constants greater than 50, and such media could give us a clearer picture of complexation behaviour. The values of the limiting molar conductivities, $\lambda^0{}_{\mathrm{M}}{}^{n+}$ of the metal ions derived from the Fuoss–Edelson plots are given in Table 1 along with the limiting molar conductivities of the complexes. Figs. 1 and 2 show plots of Λ versus $[L]_t/[M]_t$ for Cu–15C5 and Ag–18C6 systems which are representative of other metal ions and crown ethers. It was observed that the Λ value increases with an increase in $[L]_t/[M]_t$ ratio for all the systems involving the divalent and trivalent metal ions. This has been explained [4] on the basis of solvation sphere. The divalent and trivalent transition 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 ion, on the other hand, is relatively larger and has a lower charge to radius ratio. Hence, it is solvated to a lesser extent. When complexed with larger crown ethers it becomes bulkier causing a decrease in its mobility and also in the Λ values. But, this is not the case with Ag–15C5 and Ag–B15C5 systems, which show curves of type Fig. 1, as the crown ether molecule is relatively small. An interesting point to be noted here is that, all the Pb(II) and Ag(I)–crown ether systems in 40% ethanol+water, showed [5,7] curves of the type in Fig. 2 but in 90 vol.% DMSO+water, all the Pb(II)–crown ether systems give curves of the type in Fig. 1, suggesting that the lead ions are more solvated in 90% DMSO+water. The curves show a break point at $[L]_t/[M]_t \approx 1$, which indicates the formation of 1:1 complexes between crown ethers and the metal ions.

The values of stability constants as log $K_{\mathrm{ML}}{}^{n+}$ for the metal ions obtained by conductometry and potentiometry are given in Tables 2 and 3, respectively. Among the divalent transition metal ions it is observed that copper happens to form more stable complexes with 15C5 and B15C5, which may be explained on the basis of closeness of match between the ionic diameter and cavity size. As there is not much difference in the ionic radii among the divalent metal ions studied here (as compared with alkali/alkaline earth metal ions), one cannot establish a clear relationship based on the cavity sizes and the ionic radii alone. Other factors like, extent of solvation, entropy changes, changes in the conformations, directional nature of the bonds, etc. also need to be considered. As expected, the complexation of diva-

Table 1
Limiting molar conductivities of M^{n+} and ML^{n+}

$\lambda^0{}_M{}^{n+}$ (S cm^2 mol^{-1})		$\lambda^0{}_{ML}{}^{n+}$ (S cm^2 mol^{-1})						
Metal ion	Solvated metal ion	15C5	B15C5	18C6	DB18C6	DCH 18C6	DB24C8	DCH 24C8
Ag(I)	10.4	11.6	11.2	9.8	9.5	9.2	9.0	8.8
Co(II)	21.6	23.8	23.4	22.8	22.4	22.2	22.0	21.8
Cu(II)	24.6	25.7	25.4	25.3	25.1	25.0	24.8	24.8
Mn(II)	19.4	21.9	21.6	21.4	21.1	20.9	20.6	20.3
Ni(II)	20.8	22.6	22.1	21.8	21.6	21.4	21.3	21.1
Zn(II)	20.6	22.8	22.5	22.4	22.1	21.8	21.5	21.2
Pb(II)	22.5	25.3	25.1	24.7	24.3	24.1	23.7	23.5
Cr(III)	33.9	36.5	36.2	35.8	35.5	35.2	34.8	34.6
Fe(III)	42.5	45.4	45.1	44.7	44.2	44.0	43.5	43.2

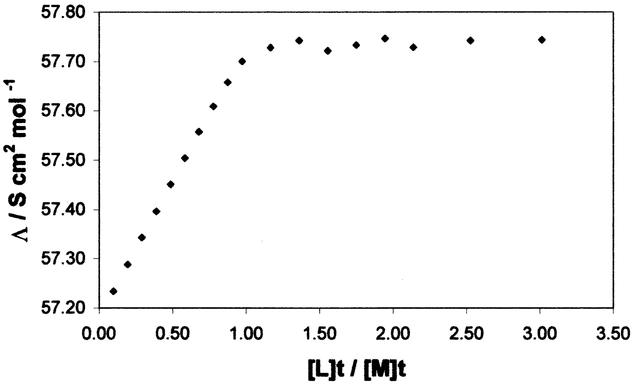

Fig. 1. Plot of Λ vs. $[L]_t/[M]_t$, for 15C5–Cu(ClO$_4$)$_2$ system.

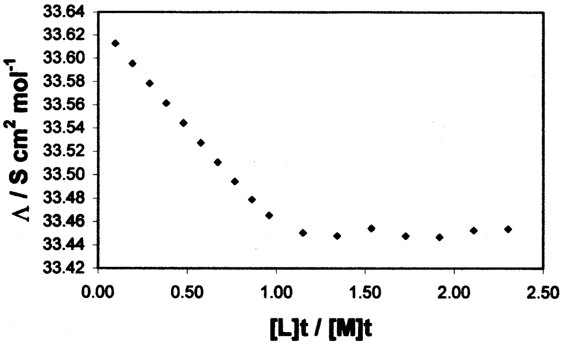

Fig. 2. Plot of Λ vs. $[L]_t/[M]_t$ for 18C6–AgClO$_4$ system.

lent metal ions with DB24C8 and DCH24C8 is the least in all cases due to the large difference in the relative sizes of ions and me crown ethers. Among the crown ethers studied, it is observed that the substituent bearing crown ethers form more stable complexes with these 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, most stable complexes are formed with B15C5, the order being B15C5 > 15C5 > DCH18C6 > DB18C6 ≈ 18C6 > DCH24C8 > DB24C8 for Ni(II), Co(II), Cu(II) and Zn(II). In case of silver and lead the order is 18C6 > DCH18C6 > DB18C6 > DCH24C8 > DB24C8 > 15C5 > B15C5. Here too [5,7], Pb(II) shows greater stability than Ag(I) due to higher charge density. Also, it is observed that there is little difference in the stabilities among the 18C6 ethers and 24C8 ethers for most of the metal ions studied. This is due to the flexibility of the larger rings to accommodate the metal ion.

In contrast to the above, the trivalent ions form more stable complexes with DB24C8 and DCH24C8 even though there is no close match in their ionic sizes and the cavity sizes. This could be due to the flexibility of the larger crown ethers that are able to wrap around the smaller ion, giving a stronger complex or due to the ion being encapsulated into the cavity along with its solvation sphere. However, in the latter case, it would lead to a decrease in the conductivity of the complex giving a curve of the type Fig. 2. But as the nature of the curve obtained was that of the type Fig. 1, it can be concluded that the crown ether molecule replaces the solvent molecules around the ion by wrapping around it, giving a more stable complex. These wrap-around complexes are not expected in case of 15C5 or 18C6, as they are smaller and hence more rigid.

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 was obtained (Fig. 3). Table 3 gives the stability constants of Ag(I) and Cu(II) complexes with the aza macrocyclic compounds obtained by potentiometry. The introduction of two nitrogen atoms in 15C5 causes an increase in stability by about 4 U and in case of cyclam, with four nitrogen atoms the stability is increased by about 18 U. The large increase in stability of copper/silver complexes on substitution of oxygen by nitrogen atoms demonstrates that the bonding in such complexes are of both types—electrostatic and covalent, whereas, in case of alkali/alkaline earth metal ion complexes with oxa crown ethers there is only electrostatic bonding.

Table 2
Stability constants (log $K_{ML}{}^{n+}$) for the metal ion–crown ether complexes by conductometry

Metal ion	log $K_{ML}{}^{n+}$						
	15C5	B15C5	18C6	DB18C6	DCH 18C6	DB24C8	DCH 24C8
Ag(I)	1.42 (0.02)	1.38 (0.02)	2.11 (0.02)	2.02 (0.04)	2.09 (0.04)	1.75 (0.03)	1.80 (0.04)
Co(II)	1.98 (0.04)	2.17 (0.04)	1.83 (0.05)	1.89 (0.06)	1.95 (0.03)	1.54 (0.04)	1.64 (0.03)
Cu(II)	2.25 (0.04)	2.39 (0.05)	1.98 (0.04)	2.01 (0.04)	2.05 (0.05)	1.74 (0.03)	1.76 (0.03)
Mn(II)	2.11 (0.03)	2.19 (0.03)	2.65 (0.02)	2.69 (0.05)	2.88 (0.04)	1.85 (0.03)	1.98 (0.04)
Ni(II)	2.02 (0.05)	2.15 (0.02)	1.66 (0.02)	1.69 (0.05)	1.71 (0.03)	1.55 (0.03)	1.61 (0.03)
Zn(II)	1.94 (0.03)	2.14 (0.02)	1.61 (0.02)	1.65 (0.03)	1.72 (0.03)	1.57 (0.03)	1.63 (0.03)
Pb(II)	2.85 (0.02)	2.53 (0.03)	3.87 (0.03)	3.36 (0.02)	3.55 (0.03)	2.97 (0.04)	3.14 (0.03)
Cr(III)	2.40 (0.04)	2.53 (0.02)	2.16 (0.02)	2.33 (0.02)	2.46 (0.03)	3.16 (0.02)	3.23 (0.02)
Fe(III)	2.78 (0.02)	3.15 (0.03)	2.54 (0.03)	2.76 (0.03)	2.96 (0.03)	3.45 (0.02)	3.63 (0.04)

Figures in parentheses indicate standard deviation ($6 \leq n \leq 9$).

Table 3
Stability constants (log $K_{ML}{}^{n+}$) for the silver/copper ion-macrocycle complexes by potentiometry

Macrocycle	log $K_{ML}{}^{n+}$	
	Ag(I)	Cu(II)
15C5	1.45 (0.03)	2.23 (0.03)
B15C5	1.37 (0.04)	2.37 (0.03)
I8C6	2.15 (0.03)	1.93 (0.03)
DB18C6	1.98 (0.03)	2.04 (0.04)
DCH18C6	1.99 (0.05)	2.08 (0.03)
DB24C8	1.75 (0.03)	1.76 (0.02)
DCH24C8	1.78 (0.03)	1.79 (0.04)
Cyclam	7.88 (0.04)	20.66 (0.03)
Diaza15C5	5.12 (0.02)	6.64 (0.03)
Dibenzodiaza 15C4	4.22 (0.03)	5.98 (0.02)
Dibenzyl diaza 18C6	4.45 (0.03)	5.25 (0.03)

Figures in parentheses indicate standard deviation ($5 \leq n \leq 8$).

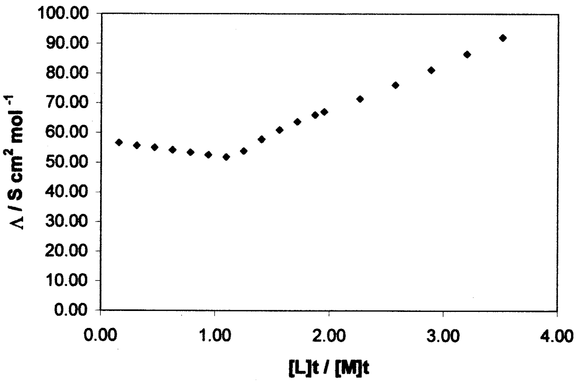

Fig. 3. Plot of Λ vs. $[L]_t/[M]_t$ for cyclam–$Cu(ClO_4)_2$ system.

It is seen that the log $K_{ML}{}^{n+}$ values for the crown ether–transition metal ion complexes in this medium are more or less same as in 40% ethanol+water [4], though the percentage of water is only 10% and the effect of competing hydrogen bonds is lesser. However, due to the drastic reduction of water content and absence of the other protic solvent (ethanol), one would expect a much larger value of stability constant which is not so. This is because the solvent DMSO being more basic, solvates the cations more strongly than water or ethanol and as a result the replacement of the solvent molecules around the cation by the crown ether would be energetically expensive. This effect is observed for almost all metal ions with oxa-crown ethers, for instance the log $K_{ML}{}^{n+}$ values for Ag–18C6 complexes in water, DMSO and propylene carbonate (PC) are 1.6, 6.21 and 7.10, respectively, for Cs–DCH18C6 complexes in water, DMSO and PC are 1.25, 2.20 and ~4, respectively [17].

Also, it is seen that the log $K_{ML}{}^{n+}$ values for copper complexes in this medium are low as compared with those in 20 wt.% propylene carbonate+ethylene carbonate (EC), which are aprotic and poor solvating agents. For example, the copper complexes in 20 wt.% PC+EC, with 15C5 and B15C5 show a log $K_{ML}{}^{n+}$ of 4.20 and 3.78, respectively [8], whereas in 90% DMSO+water, the values are 2.25 and 2.39, respectively. This can be attributed to the strong solvating properties of DMSO and hydrogen bonding capability of water molecules. The hydrogen bonds of water molecules and the ether oxygen atoms coupled with the strong solvation by DMSO decrease the complexing ability of crown ethers.

However, the transition metal ion complexes with oxa crown ethers are less stable than the alkali metal ion complexes within a same medium (e.g. methanol) [17] and this can be explained on the basis of 'Hard and Soft, Acid–Base' (HSAB) concept [4,5,18,19]. The transition metal ions being soft acids would form stronger coordination bonds with sulfur/nitrogen containing polyethers, which are softer bases than oxygen. In case of diaza 15C5 and dibenzodiaza 15C4 with two nitrogen atoms each, the stabilities were found to be increased by about 4 U though they have nearly the same cavity size as that of 15C5. The stability constants of Cu–diaza 15C5 complexes in water and DMSO were found to be 7.17 and 4.37, respectively [17], and in the present work, 6.64, which shows that the solvation effects on the cation are more pronounced in case of complexation via covalent interactions, whereas in case of oxa-crown ethers, where the complexation is mainly non-covalent, the effect of hydrogen bonding is more important. Dibenzyldiaza 18C6 shows a lesser stability as it has a larger size, but cyclam shows the highest stability as it has four nitrogen atoms and also its cavity size is closer to that of the copper ion. A similar increase in stability is observed for the silver complexes of aza macrocycles. A decrease in the stability by about 2 U [17] is observed in this medium as compared with that in water and can be attributed to the strong solvating power of DMSO. Similar studies in DMSO + acetonitrile [20] have shown that an increase in acetonitrile percentage leads to an increase in the stability of the 1,10-diaza-18-crown-6 complexes. This kind of behaviour is also observed for the cryptates of smaller transition ions like Cu(II) and Zn(II), and is attributed to the covalent character of the bonds between the transition cations and the heteroatoms of the ligand [21]. The interesting fact to note is that, the stabilities of the oxa crown ether complexes are slightly greater in DMSO + water as compared with those in ethanol + water mixture [4,7], whereas, the stabilities of the aza crown ether complexes are slightly lesser in DMSO + water as compared with those in ethanol + water mixture [5,7]. So, it seems appropriate to extend the same explanation for the lower stability of Pb(II) complexes in DMSO + water medium as compared with that in water or ethanol + water, i.e. it has partially covalent interactions.

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

5. Conclusion

The results obtained, show that the oxa crown ethers form weak complexes with transition metal ions, in protic polar media, but stronger complexes are formed with aza crown ethers, and it is observed that the stabilities are not solely dependent on the ion/cavity sizes. The solvation of cations, the presence of heteroatoms in the coronand ring and the nature of bonding (covalent/non-covalent) affect the stabilities to a large extent. 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. The strong complexes formed with aza macrocycles have been utilised in the fabrication of Chemically Modified Electrodes for electrocatalytic determination of ascorbic acid [22] and Ion Selective Electrodes for copper [23].

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