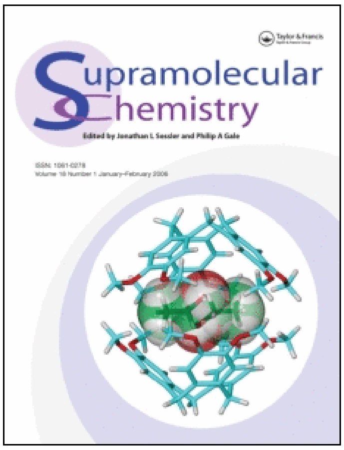

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Stability Constants of Some Macrocyclic Complexes of Ag(I) and Cu(II) in Mixed Solvents by Potentiometry

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Stability constants of complexes of Ag(I) and Cu(II) perchlorates and nitrates with some macrocyclic compounds in 90 and 75% (v/v) DMSO + water and 75% (v/v) DMF + water media have been determined by potentiometry. Silver and copper wires, and Coated Wire Ion Selective Electrodes (CWISE) were used as indicator electrodes. It was observed that complexation is stronger when the salt is present as a perchlorate than when it is as a nitrate. For both cations the stability constant values in 75% (v/v) DMF + water were somewhat higher than in 75% (v/v) DMSO. The macrocyclic effect due to cyclization of linear amine tosylates has been observed. Competitive potentiometry has been utilized to compare some of the results.

Keywords: Potentiometry; Coated wire ISE; Silver; Copper; Macrocyclic compounds

INTRODUCTION

Ever since Pedersen synthesized and studied cyclic polyethers, interest in this field has increased [1]. 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]. The greatest use of crown ethers and other macrocyclic compounds has been in the field of Ion Selective Electrodes (ISEs) [4]. Several aza macrocycles and thia macrocycles [5–8] have been tested for their use in the fabrication of Cu(II) and Ag(I) ISEs. We have recently reported Coated Wire Ion Selective Electrodes (CWISEs) for Ag(I) [9] and Cu(II) [10] based on cyclam and 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene respectively. Stability constants for the 1:1 complexes of 22 cyclic polyethers with several cations in water and in methanol have been determined by potentiometry with cation-selective electrodes by Frensdorff [11]. A complexation reaction of 18C6 with Ag(I) in methanol, ethanol, acetonitrile, propylene carbonate, acetone, dimethylformamide and dimethyl sulfoxide has been studied in terms of the strength of solvation of the silver ion and stability constants by Buschmann and Schollmeyer [12]. Stability constants for the 1:1 lanthanum(III)–chromotrope-2B complex by a graphical method using novel membrane electrode and coated wire electrodes have been determined by Chattopadhyaya *et al.* [13]. A thiopentone–Cu(II) precipitate-based Cu(II)-ion-selective electrode have been developed to determine the stability constant of the Cu(II) complex with 4-(2-pyridylazo)resorcinol [14]. pH and EMF measurements of the chelation of Cu(II) cation by 18C6 and hydroxybenzene in aqueous solution have been carried out with a Cu(II)/Cu ISE by Junquera *et al.* [15]. 1:1 Complexation of alkali metal and silver ion with some crown ethers in methanol, isopropanol, *n*-butanol, acetonitrile, acetone propylene carbonate and alcohols has been studied by Kolthoff *et al.* [16] using cation-selective electrode. Coetzee *et al.* [17] have reviewed the applications of potentiometric ion sensors in the characterization of nonaqueous solvents. A heterogeneous ion selective electrode based on a nickel complex of 1,4,8,11-tetraazacyclotetradecane was calibrated in 20% DMF solution and was used to determine the stability constant of a nickel sulphosalicylic acid complex [18]. Gokel *et al.* [19] have developed a competitive technique based on ISE to determine the stability constants for Ca(II) with crown ethers in methanol. A similar approach to

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competitive potentiometry was taken by Pouretedal and Shamsipur [20], Cox *et al.* [21] and Bunzli and Pilloud [22] using Ag(I) as an auxiliary cation.

We have already reported the stability constants of silver and copper with macrocyclic compounds in 40% (v/v) ethanol + water [23,24], 90% (v/v) DMSO + water [25], and 20% (w/w) propylene carbonate + ethylene carbonate [26] media by potentiometry using pure silver/copper wires as indicator electrodes. The present study was undertaken to demonstrate the utility of CWISEs and to provide a quantitative comparison of the stabilities of the macrocyclic complexes in 90% (v/v) DMSO + water, 75% (v/v) DMSO + water and 75% (v/v) DMF + water media.

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 [27]. Media containing DMSO and DMF ensure the solubility of most of the macrocyclic compounds and so this solvent was chosen for the present study. Also, the results in sulfur-containing DMSO are compared with nitrogen-containing DMF media. Further, some complexes of copper were studied by competitive potentiometry using silver ion as a probe [20] and the values obtained were compared with copper CWISE potentiometry. The effects of anions, donor atoms and solvent compositions are also discussed herein.

Complexation by tosyl derivatives of aza crown ethers (which are intermediates in the synthesis of aza crown ethers) has been rarely studied [28]. In the present work, complexation of tosyl derivatives such as *N*,*N*′,*N*″-tritosyldiethylenetriamine, *N*,*N*′,*N*″,*N*‴-tetratosyltriethylenetetramine and their cyclic analogs 1,4,7-tritosyl-1,4,7-triazacyclononane (tritosyltriaza 9C3) and 1,4,7,10-tetratosyl-1,4,7,10-tetraazacyclododecane (tetratosyltetraaza 12C4) with Ag(I) and Cu(II) has also been studied.

RESULTS AND DISCUSSION

Silver [9] and copper [10] CWISEs were used to determine the stability constants of silver and copper macrocyclic complexes in 90% (v/v) DMSO + water medium by potentiometry, which were comparable with earlier values determined by using pure silver and copper as indicator electrodes [25,29]. The results obtained for the stability constant values ($K_{ML}{}^{n+}$) of silver and copper complexes, in 90% (v/v) DMSO + water are given in Table I. A comparative study of perchlorate and nitrate salts was done in 90% (v/v) DMSO + water and 75% (v/v) DMSO + water (Tables I and II). In both the cases it was found that the stability of perchlorates is slightly higher than that of the nitrates. The CWISEs were also used to determine the stability constants of silver and copper (nitrates) with macrocycles in 75% DMF + water medium (Table III). Stability constants by competitive potentiometry of some copper complexes are reported in 75% (v/v) DMF + water (Table IV) and the values are quite comparable to those obtained by CWISE (Table III).

From the complexation studies it is observed that Cu(II) forms a more stable complex with benzo-substituted oxa crown ethers in all the media. The introduction of side-groups causes a slight contraction of the macrocyclic cavity making it closer to the diameter of the ion. Most stable complexes of Cu(II) are formed with B15C5 having the order B15C5 > 15C5 > DCH18C6 > DB18C6 > 18C6 in all the media. In contrast, a reverse trend i.e. 18C6 > DB18C6 > DCH18C6 > 15C5 > B15C5 is observed in the case of Ag(I) complexes, because the diameter of the monovalent silver ion is larger than that of the divalent copper ion and it is encapsulated easily into the large cavity of 18C6. It is noticed in the present work that the stability of Ag(I) and Cu(II) with oxa crowns in 90% (v/v) DMSO + water is slightly higher than in 75% (v/v) DMSO + water

TABLE I Stability constants (log $K_{ML}{}^{n+}$) for the silver and copper ion macrocyclic complexes obtained by CWISE potentiometry in 90% (v/v) DMSO-water*

	90% DMSO + water (salts as perchlorates)		90% DMSO + water (salts as nitrates)	
Macrocycle	log $K_{ML}{}^{n+}$ Ag(I)	log $K_{ML}{}^{n+}$ Cu(II)	log $K_{ML}{}^{n+}$ Ag(I)	log $K_{ML}{}^{n+}$ Cu(II)
15C5	1.49	2.26	1.31	2.09
B15C5	1.41	2.35	1.37	2.29
18C6	2.18	2.01	2.05	1.91
DB18C6	2.09	2.05	1.95	1.89
DCH18C6	2.02	2.11	1.93	2.02
DB24C8	1.71	1.69	1.63	1.53
Diaza 15C5	5.23	6.31	5.11	6.02
Dibenzodiaza 15C4	4.19	5.93	4.10	5.61
Tritosyltriaza 9C3	–	6.09	–	5.87
Tetratosyltetraaza 12C4	2.11	7.54	2.04	7.33
N,*N*′,*N*″-Tritosyldiethylenetriamine	–	–	–	–
N,*N*′,*N*″,*N*‴-Tetratosyltriethylenetetramine	–	–	–	–

*In all cases the standard deviation was less than 0.05 for $5 < n < 9$. – No change in EMF observed.

TABLE II Stability constants ($\log K_{\mathrm{ML}}{}^{n+}$) for the silver and copper ion macrocyclic complexes obtained by potentiometry in 75% (v/v) DMSO + water*

	75% DMSO + water (salts as perchlorates)		75% DMSO + water (salts as nitrates)	
Macrocycle	$\log(K_{\mathrm{ML}}{}^{n+})$ Ag(I)	$\log(K_{\mathrm{ML}}{}^{n+})$ Cu(II)	$\log(K_{\mathrm{ML}}{}^{n+})$ Ag(I)	$\log(K_{\mathrm{ML}}{}^{n+})$ Cu(II)
15C5	1.25	2.05	1.12	2.02
B15C5	1.18	2.14	1.02	2.08
18C6	1.92	1.73	1.88	1.63
DB18C6	1.84	1.91	1.76	1.72
DCH18C6	1.88	1.94	1.72	1.78
DB24C8	1.64	1.55	1.44	1.35
Diaza 15C5	5.52	6.58	5.22	6.33
Dibenzodiaza 15C4	4.66	6.34	4.26	5.98

*In all cases the standard deviation was less than 0.05 for $5 < n < 9$.

(Tables I and II). This is attributed to the hydrogen-bonding capability of water molecules, which decreases the stability of the complexes as the hydrogen atoms of the water form bonds with the oxygen atoms of the macrocyclic compounds. Therefore, with the increase of water content in the medium, the stability constant values decrease in the case of oxa crowns. For instance, the $\log K$ values for Ag–18C6 complexes in water and DMSO are 1.6 and 6.21 respectively [30]. A similar observation was found for K–18C6 in mixture of dioxane + water [31]. As the ratio of dioxane:water is increased from 2:8 (v/v) to 8:2 (v/v), the stability of the K–18C6 complex is increased from 2.47 to 4.21. While dealing with nitrogen-containing crown ethers in the above media, an opposite trend was observed. The $\log K$ values of both Ag and Cu decrease with the increase in DMSO content in the medium (Tables I and II). This is consistent with the observation that the values for the Ag(I) and Cu(II) complexes with Diaza15C5 in pure water are 5.85 and 7.17, respectively, while the $\log K$ for these complexes in pure DMSO are 5.17 and 4.37 [30]. A comparison of the $\log K$ values of perchlorate and nitrate salts in 90% (v/v) DMSO + water and 75% (v/v) DMSO + water (Tables I and II) shows that the stability of the perchlorates is slightly higher than that of the nitrates. This could be because of the larger size of the perchlorate ion, which helps in greater dissociation of the metal salt and the cation can react more easily with the crown ether than the smaller nitrate ion, as observed earlier [23,24]. This is also evident from the fact that the metal perchlorates show practically no association in 40% (v/v) ethanol + water and 90% (v/v) DMSO + water, whereas some significant association is observed in the case of metal nitrates [23–25].

From Tables II and III it is found that the $\log K_{\mathrm{Ag}}$ and $\log K_{\mathrm{Cu}}$ values in 75% (v/v) DMF + water are somewhat greater than those in 75% (v/v) DMSO + water. This could be because of greater solvation of the cations by DMSO. A similar trend is also observed in the case of the alkali metal complexes. For example, the $\log K$ values of Na–18C6 in pure DMF, DMSO and water are 2.31, 1.41 and 0.82, respectively [30]. This implies that because of greater solvation of the cation, the stability in the particular medium decreases (in the case of water there is also competition due to hydrogen bonding). From our earlier studies it was found that the $\log K_{\mathrm{ML}}{}^{n+}$ values for silver and copper complexes in 90% (v/v) DMSO + water [25] are lower compared to those in pure propylene carbonate (PC) and 20 wt% propylene carbonate + ethylene carbonate (EC) [20]. Thus, the solvation of cations also influences the stabilities of the complexes formed. With increasing

TABLE III Stability constants ($\log K_{\mathrm{ML}}{}^{n+}$) for the silver and copper (nitrates) ion macrocyclic complexes determined by CWISE potentiometry in 75% (v/v) DMF + water*

Macrocycle	$\log K_{\mathrm{ML}}{}^{n+}$ Ag CWISE	$\log K_{\mathrm{ML}}{}^{n+}$ Cu CWISE
15C5	1.95	2.67
B15C5	1.56	3.08
18C6	2.97	2.03
DB18C6	2.06	2.13
DCH18C6	2.14	2.11
DB24C8	2.11	2.09
Diaza 15C5	5.69	7.13
Dibenzodiaza 15C4	4.88	6.79
Tritosyltriaza 9C3	–	6.58
Tetratosyltetraaza 12C4	†	†
N,N′,N″-Tritosyldiethylenetriamine	–	–
N,N′, N″,N‴-Tetratosyltriethylenetetramine	–	–

*In all cases standard deviation was less than 0.05 for $5 < n < 9$. – No change in EMF observed. †Not soluble in 75% DMF + water.

TABLE IV Results of competitive potentiometry for the determination of stability constants ($\log K_{\mathrm{ML}}{}^{n+}$) for the silver and copper (nitrates) ions in 75% (v/v) DMF + water*

Macrocyclic	$\log K_{\mathrm{Ag}}$	$\log K_{\mathrm{Cu}}$
15C5	1.94	2.65
B15C5	1.59	3.06
18C6	2.99	2.02
DB18C6	2.04	2.11
DCH18C6	2.11	2.07
DB24C8	2.09	2.06
Diaza 15C5	5.66	7.21
Dibenzodiaza 15C4	4.85	6.81
Tritosyltriaza 9C3	–	–
Tetratosyltetraaza 12C4	†	†
N,*N*′,*N*″-Tritosyldiethylenetriamine	–	–
N,*N*′, *N*″, *N*‴-Tetratosyltriethylenetetramine	–	–

*In all cases standard deviation was less than 0.05 for $5 < n < 9$. – No change in EMF observed. †Not soluble in 75% DMF + water.

solvation strength of the solvent the values of the stability constants of the resulting complexes decrease [32]. The fact that the strength of solvation of the metal ion is responsible for the stability of complexes formed was further studied by Buschmann and Schollmeyer [12] during the complexation of silver ions with 18C6 in different solvent media. The $\log K$ values of Ag–18C6 were found to be 7.10, 1.56 and 2.44 in PC, DMSO and DMF, respectively, and for acetonitrile it was found to be <1. The observation was explained on the basis of the solvation of the Ag(I) ion.

It is a well-known fact that substitution of a sulfur and/or nitrogen atom in the coronand ring of the crown compound increases the affinity of the ligand towards transition metal ions and decreases its affinity towards alkali and alkaline earth metal ions [30]. Being soft acids, the transition metal ions form stronger coordination bonds with softer bases like sulphur/nitrogen than with oxygen in macrocyclic compounds. For instance, the stability of the Pb-monoaza 15C5 complex in 95% methanol + water is significantly higher ($\log K = 6$) than that of the cyclic polyoxa analogue, 15C5, either in pure water ($\log K = 2.76$) or in pure methanol ($\log K = 3.36$) [30]. Ag and Cu too, being transition metal ions, show higher stability with the aza crowns than the oxa crowns in the media studied in the present work. For example, in 90% (v/v) DMSO + water, the $\log K$ values of diaza15C5–Ag(I) and diaza15C5–Cu(II) are 5.23 and 6.31, respectively. Moreover, the $\log K$ values of 15C5–Ag(I) and 15C5–Cu(II) are 1.49 and 2.26, respectively, in the same medium (Table I). Frensdorff also observed that the substitution of N or S for oxygen reduces the affinity for alkali ions like Li^+, Na^+, K^+ and Cs^+ but strengthens the complexing of Ag^+, dealing with complexation in aqueous medium [11].

It can be summarized that the stabilities of these ions are not solely dependent on the ion/cavity sizes, but also on other factors like the number of the binding sites in the ring, the types of binding sites in the ring, the groups attached to the ring, the solvent and the extent of solvation of the ion, and the binding sites and the electrical charge of the ion.

While dealing with tosylated compounds, it was observed that there is no change in EMF in the case of open-chain compounds, indicating that no noticeable complexation takes place with *N*,*N*′,*N*″-tritosyldiethylenetriamine and *N*,*N*′,*N*″,*N*‴-tetra tosyltriethylenetetramine. In contrast, tritosyltriaza 9C3 and tetratosyltetraaza 12C4 show good stability with Cu(II). This can be attributed to the macrocyclic effect. Macrocyclic ligands form more stable complexes with metal ions than their open-chain analogues with the same donor groups. For example, there is more than a 10^6-fold increase in the stability constant of Ni(II) with cyclam ($\log K = 22.2$), as compared to its acyclic analog ($\log K = 15.8$) [33]. The macrocyclic effect has been studied by Cabbiness and Margerum in Cu(II) and amine complexes [34]. The macrocyclic tetraamine-Cu(II) complex was found to be 10,000 times more stable than the Cu(II) complex of the noncyclic counterpart. The kinetics of solvated Cu(II) reacting with a series of open and closed macrocyclic polyether chain have been explained on the basis of the solvent effect, macrocyclic as well as the ring size effect, by Diaddario *et al.* [35]. Kodama and Kimura have studied the complexation of some transition metals with cyclic and acyclic macrocyclic structures by polarography and have reported evidence for the macrocyclic effect [36,37]. They have also noticed the macrocyclic effect while dealing with Cu(II)–cyclen ($\log K = 24.8$), which is nearly 10^5-fold greater than its acyclic analogue ($\log K = 20.0$) [37]. Tritosyltriaza 9C3 does not form a complex with Ag(I), but shows appreciable stability with Cu(II) (Tables I and III). This is due to the smaller cavity size of the macrocycle as compared to the large Ag(I) ion and the hindrance by bulky tosyl groups. But Cu(II), being a smaller ion, fits into the cavity.

The *p*-tolylsulphonyl group attached to the nitrogen atom prevents the protonation of nitrogen and also decreases the solubility of the macrocyclic compound in water [29]. Because of this the tosyl derivatives have significant advantages when used in chemical sensors. Wickstorm *et al.* have used 13-(*p*-tolylsulphonyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane in ISEs [28] and Srivastava *et al.* have used tritosyltriaza 9C3 and tetratosyltetraaza 12C4 for the development of chemically modified electrodes [38]. Therefore, in light of the present studies of tosylated compounds an attempt is being made to explore these products for the development of different electrochemical sensors [39].

MATERIALS AND METHODS

Solvents

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 hours 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. An azeotropic distillation with 10% by volume of dry benzene was carried out with the commercially available DMF (S. D. Fine Chem Ltd, India) at atmospheric pressure with the help of Dean and Stark apparatus. Dry DMF thus obtained was held over molecular sieves 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. Appropriate volumes of the organic solvents were mixed with water to give 90% (v/v) and 75% (v/v) (± 0.05%) of DMSO and DMF, respectively.

Reagents and Standard Solutions

Nitrates of copper(II) and silver(I), tetrahydrofuran (THF), dibutyl phthalate and potassium nitrate were analytical grade chemicals, purchased from S. D. Fine Chem Ltd (India) and were used as such. Copper(II) and silver(I) perchlorates were prepared by general methods described elsewhere [40]. Polyvinyl chloride (PVC), 15-crown-5 (15C5), dicyclohexano-18-crown-6 (DCH18C6), 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (dibenzodiaza 15C4), 1,4,10-trioxa-7,13-diazacyclopentadecane (diaza 15C5) and 1,4,8,11-tetraazacyclotetradecane (cyclam) were purchased from Fluka (Switzerland). Benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8) were purchased from Aldrich (USA) and were used as supplied. *N*,*N*′,*N*″-Tritosyldiethylenetriamine and *N*,*N*′,*N*″,*N*‴-tetratosyltriethylenetetramine, 1,4,7-tritosyl-1,4,7-triazacyclononane (tritosyltriaza 9C3) and 1,4,7,10-tetratosyl-1,4,7,10-tetraazacyclododecane (tetratosyltetraaza 12C4) were synthesized by the Richman–Atkins method as described in the literature [41,42]. The analytical data for the compounds synthesized in the present work are comparable with those reported in the literature [41,42]. Standard solutions of metal salts were prepared in double-distilled deionised water. Working solutions were prepared as required by suitable dilution with the same water. All the compounds used in the present work are sufficiently soluble in 90% (v/v) DMSO + water, 75% (v/v) DMF + water and 75% (v/v) DMSO + water mixtures, so as to provide a stock solution of 0.01 M, except for the tetratosylated macrocyclic compounds, which are soluble only in 90% (v/v) DMSO + water.

Preparation of Membranes and Electrodes

Equal volumes of equimolar solutions of macrocyclic compound and metal salt were mixed in an appropriate solvent and kept overnight for precipitation. The precipitate obtained the next day was filtered, washed and dried at room temperature to obtain the ionophore. A slurry of 5% w/w ionophore, 33% PVC, and 62% diethyl phthalate plasticizer was made in THF. To prepare the electrode, a platinum wire was coated by dipping it several times in the slurry until a bead was formed and was kept for drying in air for 24 h as described earlier [9,10].

Apparatus and EMF Measurements

All solutions were prepared using a digital single-pan balance (Mettler Toledo AB204, Switzerland). A CyberScan 2500 pH meter (Eutech Instruments, Singapore) having ± 0.1 mV accuracy with a SCE as reference electrode and KNO_3 salt bridge were used for potential measurements. All measurements were carried out at 25°C with cell of the type:

SCE//M^{n+}+ligand/ion-selective membrane (bead)/Pt wire.

Procedure for Potentiometry

A silver indicator electrode (DM 141–SC) with an inbuilt Ag/AgCl reference element was used for measurement of Ag(I) ions. The EMFs were noted every 2 minutes. The potentials recorded were the average of the last two observations, which normally agreed to within ± 0.1 mV and the measured cell potentials were reproducible to ± 0.5 mV. In competitive potentiometry this silver indicator electrode was used to monitor the silver ion concentration in the presence and absence of copper ions.

A pure copper wire (purity > 99.95%) and the CWISEs in conjunction with an SCE were used for measurement of EMFs using a Eutech CyberScan 2500 pH/ion meter. The EMFs were recorded every 2 minutes as above.

Stock solutions of copper/silver nitrates and perchlorates and crown ethers were prepared in 90% (v/v) DMSO + water, 75% (v/v) DMF + water and 75% (v/v) DMSO + water mixtures. Experimental solutions were prepared by appropriate dilution of the stock solutions to the required concentrations.

Theory

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

$$\begin{array}{ccc} M^{n+} \;+\; L \rightleftharpoons & ML^{n+} & \\ \alpha[M]_t \quad [L]_t-(1-\alpha)[M]_t & (1-\alpha)[M]_t & (1) \end{array}$$

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

$${K'_{ML}}^{n+} = [ML]\,{f_{ML}}^{n+}/[M]\,{f_M}^{n+}[L]\,f_L \qquad (2)$$

where [ML], [M] and [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 ${f_{ML}}^{n+}$ are unknown, is given by

$$\begin{aligned} {K_{ML}}^{n+} &= {K'_{ML}}^{n+}{f_M}^{n+}/{f_{ML}}^{n+} = [ML]/[M][L] \\ &= (1-\alpha)/\alpha[L] \qquad (3) \end{aligned}$$

where f_L has been taken as unity, which is responsible for the electrically neutral macrocyclic compounds at this low concentration. So, by knowing $[M]_t$ and $[L]_t$, the stability constant is given by

$${K_{ML}}^{n+} = (1-\alpha)/(\alpha\{[L]_t - [M]_t(1-\alpha)\}) \qquad (4)$$

As the ionic strength and thus presumably the activity coefficient were constant, the EMF difference within any particular run could be taken to reflect concentration ratios. Since the calibration showed the indicator electrode to behave ideally, the ideal Nernst slope was used to give the following relations.

$$\alpha = 10^{-\Delta V/59.16} \quad \text{for silver} \qquad (5)$$

$$\alpha = 10^{-\Delta V/29.58} \quad \text{for copper} \qquad (6)$$

where ΔV is the difference between the EMF of the metal salt solution and that of the same concentration of metal salt + macrocyclic compound solution (in millivolts).

By use of this value of α in Eq. (4), ${k_{ML}}^{n+}$ is obtained.

To evaluate the stability constants of metal crown ether complexes by competitive potentiometry, the concentration of silver ions is monitored with and without addition of the metal ion.

CONCLUSION

The results obtained from the current study indicate that even though the match between the radii of the cations and the macrocyclic ligand plays an important role in complexation, it is not the only factor governing the stability of complexes. The substitution of oxygen donor atoms of crown ethers by nitrogen affects the complexation of the transition metal ions, even in solvents other than water. The solvation of metal ions also affects the stability of the complexes. The macrocyclic effect due to cyclization is quite pronounced, even in case of tosyl derivatives.

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