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Studies on the Complexation of Transition Metal Ions with Macrocyclic Compounds in Mixed Solvents by Competitive Potentiometry and Polarography

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Complexation of Cu(II), Zn(II), Ni(II), Co(II), Pb(II), Cd(II), Cr(III) and Fe(III) ions with 15-crown-5, benzo-15-crown-5, 18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6, dibenzo-24-crown-8, 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene, 1,4,10-trioxa-7,13-diazacyclopentadecane and cyclam has been investigated in 75% (v/v) DMF + water using the silver(I) ion as an auxiliary cation at 0.05 M ionic strength adjusted with tetrabutylammonium perchlorate (TBAP) by competitive potentiometry. Stability constant values obtained for the metal ion–aza macrocyclic complexes are higher than those for the oxa crowns. Shifts in the peak potential and reduction in the peak current in the differential pulse polarography (DPP) method were also used to determine the stability constants of some of the metal ions with aza and tosylated-aza macrocycles using TBAP as supporting electrolyte in 75% (v/v) DMF + water and 90% (v/v) DMSO + water media. Stability constant values determined both by shifts in the potential and by reduction in the peak current were found to be in good agreement with each other.

Keywords: N ligand; Complexation; Host–guest systems; Voltammetry; Competitive potentiometry

INTRODUCTION

The metal–ion chemistry of macrocyclic ligands has been the subject of great interest since Pedersen first reported the synthesis of a 'crown ether' in 1967 [1]. These macrocyclic compounds are capable of forming complexes with alkali and alkaline earth metal ions by electrostatic attraction and encapsulation into the cavity [2,3]. To understand this host–guest chemistry and the interactions between the macrocyclic ligands and the metal ions, various thermodynamic and kinetic parameters have been studied in the past [4–7]. Studies on oxa polyether–transition metal ion complexation have been reported by us in recent years [8–10]. Stability constants and the interactions of different macrocyclic compounds with different metal ions in non-aqueous media have been reported by many authors [8,11–13]. Pb(II) has been used as an auxiliary ion for studying alkaline metal cation–crown ether complexation in propylene carbonate medium [14]. Gutknecht *et al.* [15] determined the stability constants of cryptate complexes with Ag(I) by potentiometric titration in methanol and several aprotic, polar solvents, and used a silver electrode as an auxiliary electrode in competitive potentiometry to determine the complexation constants of K(I) and Tl(I) with cryptates. Cox *et al.* [16] determined the rates of dissociation of a variety of alkali metal cryptates in methanol by competitive potentiometry. The complexation of lanthanoid trifluoromethanesulfonates by several linear and cyclic polyethers has been investigated by Bunzli *et al.* [17] in propylene carbonate using the Ag(I) ion as a probe. Buschmann [18] used the competitive potentiometric technique in a comparison of different experimental techniques for the determination of the stability constants of alkali, alkaline earth and Ag(I) complexes of polyether, crown ether and cryptand complexes in methanolic solutions. Complexation of some organoammonium ions with crown ethers were studied in pure ethanol by competitive potentiometry using Ag(I) as a probe at different temperatures by Pouretedal and Shamsipur [19].

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Competitive potentiometry for the determination of stability constants of Cu(II) in some mixed solvents using Ag(I) as probe has also been reported by us recently [20].

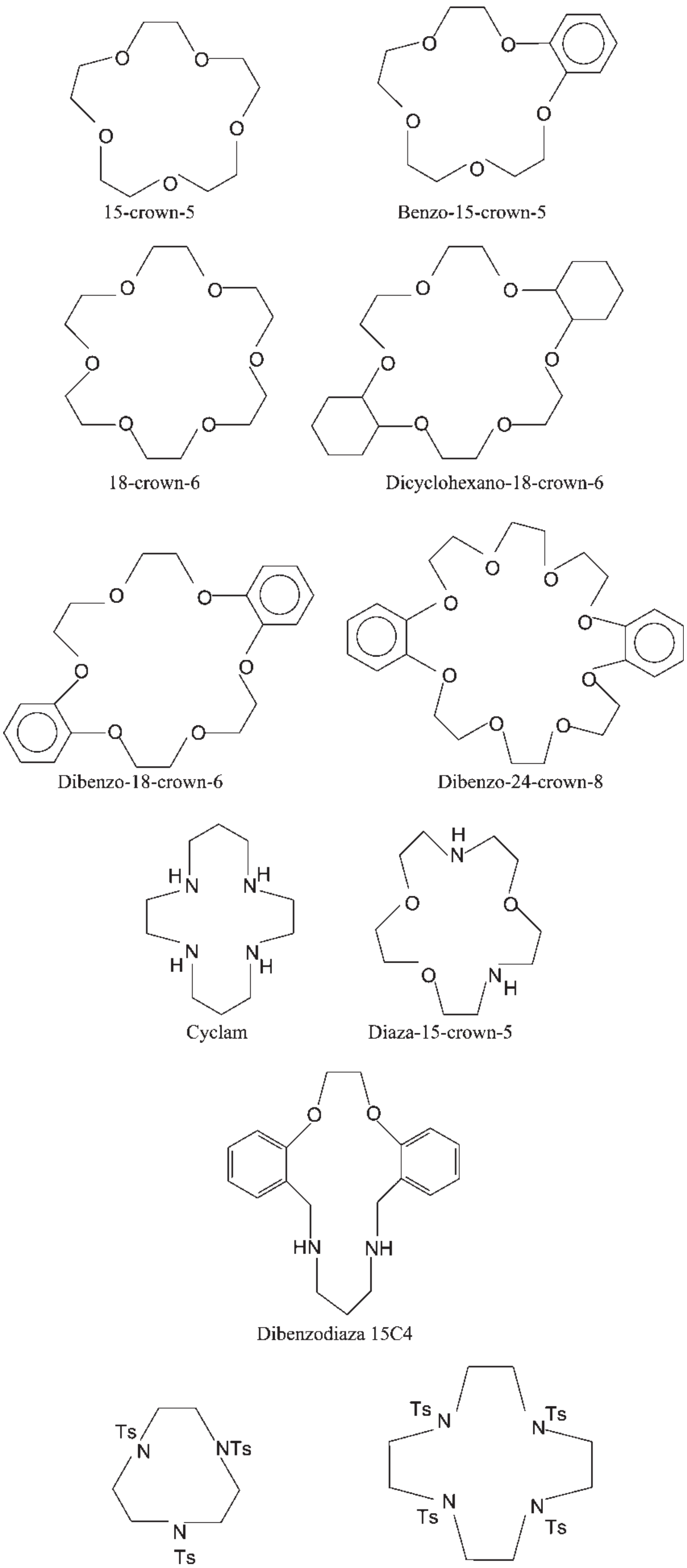
The differential pulse polarography (DPP) method has been used by many workers to study the complexation of metals with macrocyclic compounds. Cukrowski and Luckay [21] used this method for the study of Bi(III) complexes with cyclen and hydroxypropyl derivative of cyclen, and discussed the influence of neutral oxygen donors. In addition to DPP, square-wave polarography has also been used by Rounaghi *et al.* [22] for the determination of stability constants of Pb(II), Tl(II) and Cd(II) with 18-crown-6 in water/propanol, water/acetonitrile and water/dimethylformamide binary systems. Stability constants of Tl(I), Pb(II) and Cd(II) complexes with aza-18-crown-6 in some binary mixed nonaqueous solvents were determined by Monesef *et al.* [23] by monitoring the shifts in half-waves or peak potentials of the polarographic waves of metal ions with ligand concentration. Polarography was further used to determine the stability constants of some divalent metal ions/crown ether complexes in methanol by Chen *et al.* [24] and in 20% propylene carbonate + ethylene carbonate by Samant *et al.* [25]. Complexation of cyclic and acyclic tetraamine polyethers with Cu(II) was studied by Cabbiness and Margerum [26]. Kodama and Kimura studied the kinetics of the complexation of copper, nickel [6,27,28], mercury [29], zinc, lead and cadmium [30] with many cyclic and acyclic aza macrocycles by polarography and an interpretation of the macrocyclic effect was discussed in most of the cases.

The present work is a part of our ongoing research into the complexation behavior of metal–macrocyclic complexes in mixed solvent media. This paper deals with the complexation studies of Ag(I), Co(II), Cu(II), Ni(II), Zn(II), Pb(II), Cd(II), Cr(III) and Fe(III) with the macrocyclic compounds 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-8 (DB24C8), 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (dibenzodiaza15C4), 1,4,10-trioxa-7,13-diazacyclopentadecane (diaza15-C5) and 1,4,8,11-tetraazacyclotetradecane (cyclam) by competitive potentiometry and Cu(II), Cd(II), Zn(II) and Pb(II) complexes with cyclam in 75% (v/v) DMF + water medium by DPP. The shift in the peak potential to the more negative side and a decrease in peak current were used for the estimation of the stability constants. The stability constant values determined by both the shift in potential and the reduction in peak current are in good agreement with each other. In the case of Co(II), Ni(II), Fe(III) and Cr(III), where no shift in peak potential was found within the working potential window, but a significant decrease in peak current was observed, the stability constants were determined by the reduction in peak current. We also attempted a comparative determination of the stability constants of aza and tosylated-aza crowns, namely cyclam and 1,4,7,10-tetratosyl-1,4,7,10-tetraazacyclododecane (tetratosyltetraaza12C4), with Fe(III) and Cr(III) by means of reduction in peak current in 90% (v/v) DMSO + water medium, as tetratosyltetraaza12C4 is insoluble in 75% (v/v) DMF + water. The results of these studies are being explored in the development of chemical sensors.

RESULTS AND DISCUSSION

The structures of all the ligands used in the present study are shown in Fig. 1. Representative potentiometric titration curves of Ag(I) with 15C5 in the absence and presence of Cu(II) in 75% (v/v) DMF + water are presented in Fig. 2. The data in Table I show that, among the oxa crowns, B15C5 forms more stable complexes with the bivalent and trivalent metal ions in the order B15C5 > 15C5 > DCH18C6 > DB18C6 > 18C6, whereas a reverse trend, 18C6 > DB18C6 > DCH18C6 > 15C5 > B15C5, is observed with Ag(I) and Pb(II) complexes. This is because of the larger relative size of Ag(I) (1.26 Å) and Pb(II) (1.20 Å) ions with respect to the other metal ions (taken up for the present study), which get encapsulated easily into the large cavity of 18C6. From the complexation studies it is observed that smaller cations form more stable complexes with benzo-substituted oxa crown ethers. For example, $\log K$ values for Cr(III) (0.64 Å) and Fe(III) (0.64 Å) with B15C5 are 2.93 and 3.42, respectively, whereas the corresponding values with 15C5 are 2.80 and 3.02, respectively (Table I). This may be due to the introduction of side groups, because a slight contraction of the macrocyclic cavity makes it closer to the diameter of the ion, as explained by us in a previous study [8]. The ionic radii of Ni(II), Cu(II), Co(II) and Zn(II) ions are small (0.7–0.8 Å), therefore they form strong complexes with the smallest crown ether B15C5 in the present study.

We have reported studies of the stability constants of silver and copper with macrocyclic compounds in 40% (v/v) ethanol + water [8], 90% (v/v) DMSO + water [9] and 20% (w/w) propylene carbonate + ethylene carbonate [25] media by potentiometry using pure silver/copper wires as indicator electrodes. During the study of Ag(I) and Cu(II) complexation with various macrocycles in 75% (v/v) DMF + water and 75% (v/v) DMSO + water [20], the stability constant values of the metal macrocyclic complexes in the former media are found to be greater than in the latter. This can be explained on the basis of solvation of cations in the media.



15-crown-5

Benzo-15-crown-5

18-crown-6

Dicyclohexano-18-crown-6

Dibenzo-18-crown-6

Dibenzo-24-crown-8

Cyclam

Diaza-15-crown-5

Dibenzodiaza 15C4

Tritosyltriaza-9-crown-3

Tetratosyltetraaza-12-crown-4

FIGURE 1 Structures of the macrocyclic compounds studied.

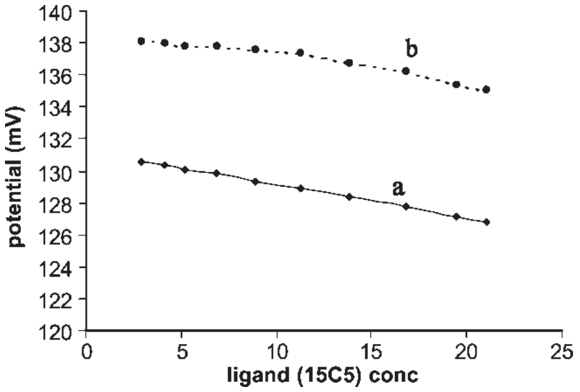


FIGURE 2 Titration curves of Ag(I) (9.27×10^{-4} M) with 15C5 ($2.7–21.0 \times 10^{-4}$ M) in the absence (a) and presence (b) of Cu(II) (2.26×10^{-3} M) in 75% (v/v) DMF + water medium.

The cations are weakly solvated by DMF as compared to DMSO [20]. Moreover, the stability constants of the complexes increases with the increasing concentration of the solvent with the lower donocity number. Comparing the results of our earlier metal ion–macrocycle complexation studies in 75% (v/v) DMSO + water [20] with the present investigation in 75% (v/v) DMF + water, we find that the stability constants of all the complexes are lower in 75% (v/v) DMSO + water than in 75% (v/v) DMF + water. An inverse relationship between the stabilities of the complexes and the donocity number of the solvent was encountered by Amini and Shamsipur while investigating the complexation between dibenzo-30-crown-10 and various monovalent metal ions by conductometry [31] and also by Kashanian and Shamsipur during their study of the complexation of alkali earth metals and macrocyclic compounds by competitive spectrophotometric technique in nonaqueous media [32]. This implies that with increasing solvation strength of the solvent, the values of the stability constants of the resulting complexes decrease [33]. A representative potentiometric titration curve of Ag(I) with 15C5 in the absence and presence of Cu(II) in 75% (v/v) DMF + water is presented in Fig. 2.

Change in potential is not observed during the complexation studies of Ag(I) and tritosyltriaza9C3 using an Ag(I) indicator electrode. 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 [20,34]. Therefore, the competitive potentiometric technique using Ag(I) as a probe could not be used to determine the stability constants of the rest of the metal ions with this ligand. In the case of complexation of Cu(II), Co(II), Ni(II) and Zn(II) with cyclam, the stability constants could not be determined by the competitive potentiometric method (Table I) because silver forms a strong complex with cyclam [9], and this may result in a very low concentration of free Ag(I) ions, falling below the Nernstian range of the indicator electrode used as the probe. Therefore, an attempt was made to determine the stability of these complexes by polarography (Table II).

From the differential pulse polarograms of Zn(II), Cu(II), Cd(II) and Pb(II) cyclam systems in 0.05 M tetrabutylammonium perchlorate (TBAP), it was found that the systems invariably displayed two peaks, one assignable to free metal ions and the other to the metal ion bound to the macrocycle. The peak potential (E_p) values of the metal ions were independent of the concentrations of the macrocycles, but a reduction in the peak current (i_p) was observed with an increase in the concentration of the macrocycle. For Zn(II), Cu(II), Cd(II) and Pb(II), new peaks at fairly negative potentials (less than the half-wave potential of the metal ions) were observed after the addition of the ligand, which further shifts towards a more negative potential with an increase in the concentration of ligand in the solution. Samant *et al.* [25] had observed a similar shift in the peak potential of metal macrocycle complexes with a subsequent increase in the ligand concentration, while investigating the complexation of macrocyclic compounds with metal ions in 20 mass% propylene carbonate + ethylene carbonate. The determination of the stability of complexes by voltammetry is based on the fact that, on complexation, the half-wave potential of the metal ion is shifted to more negative potentials because of the dissociation of the complex, followed by the reduction of the metal ion. The shift

TABLE I Stability constants (log *K*) for metal ion and crown ether complexes in 75% (v/v) DMF + water obtained by competitive potentiometry

Crown ether	Ag(I)*	Cu(II)*	Co(II)	Ni(II)	Zn(II)	Pb(II)	Cr(III)	Fe(III)
15C5	1.94	2.65	2.26	2.43	2.32	3.09	2.81	3.00
B15C5	1.59	3.06	2.96	2.51	2.48	3.51	2.93	3.43
18C6	2.99	2.02	2.17	2.00	1.96	3.94	2.65	2.93
DB18C6	2.04	2.11	2.22	2.09	2.01	3.14	2.74	3.01
DCH18C6	2.11	2.07	3.02	2.12	2.10	3.31	2.89	3.27
DB24C8	2.09	2.06	2.62	1.95	1.97	3.62	3.48	3.72
Diaza15C5	5.66	7.21	4.36	5.49	5.03	5.58	5.42	5.90
Dibenzodiaza15C4	4.85	6.81	4.03	5.06	4.93	5.20	5.03	5.26
Cyclam	8.20	–	–	–	–	7.24	8.95	9.09

In all cases the standard deviation was less than 0.05 for $5 < n < 7$. * Values reported earlier [20]. – Could not be determined.

TABLE II Stability constants (log K) for metal–tetraazacyclotetradecane complexes in 75% (v/v) DMF + water

	Log K	
Metal ion	Determined by shift in E_p	Determined by reduction in i_p
Cu(II)	22.09	22.11
Zn(II)	11.21	11.18
Cd(II)	8.71	8.69
Pb(II)	7.22	7.26
Ni(II)	*	18.15
Co(II)	*	15.15
Fe(III)	*	9.08
Cr(III)	*	8.97

* No shift in potential was observed within the working potential window. In all cases the standard deviation was less than 0.06 for $5 < n < 7$.

in the half-wave potential towards more negative values of the complex ion has also been explained by Khalil *et al.* [35] during a polarographic study of some complexes of Tl(I) with polyoxa macrocyclic ligands in aqueous media. The shift in $E_{\frac{1}{2}}$ to a more negative potential as well as a decrease in peak current of the metal ion in the present investigation can be attributed to complexation of the metal with the macrocycle.

The differential pulse polarograms of Zn–cyclam complexation are given in Fig. 3. It is clearly observed that with the subsequent increase in crown ether concentration in the metal ion solution the E_p shifts to negative potentials. The E_p value of Zn(II) is -1.114 V vs. Ag/AgCl in a solution containing only zinc ions of concentration 1.199×10^{-3} M (Fig. 3a). Figure 3b shows the polarogram obtained in a solution containing 1.199×10^{-3} M Zn(II) and 0.605×10^{-3} M cyclam, and two peaks are observed; the peak at -1.114 V is due to free Zn(II) ions and the peak at -1.380 V to the Zn(II)–cyclam complex. Along with the new peak there is a considerable decrease in the peak height of Zn(II) metal (from 0.915 to 0.505 μA) due to the complexation because of the decrease in free metal ion concentration, whereas the peak height of the complex increases with the addition of cyclam. As shown in Fig. 3c, when the concentration of ligand (1.215×10^{-3} M) exceeds the concentration of the metal ion (1.199×10^{-3} M), a single peak of zinc–cyclam complex is observed at -1.501 V, indicating that all the metal ions are complexed. This indicates 1:1 complexation between the metal ion and the ligand. Earlier studies of transition metal–macrocycles by conductometry in 90% (v/v) DMSO + water have also shown that the complexation is largely in the ratio of 1:1 [9,25]. The first peak appeared continually at the reduction potential of the free metal ions, and the second appeared at more

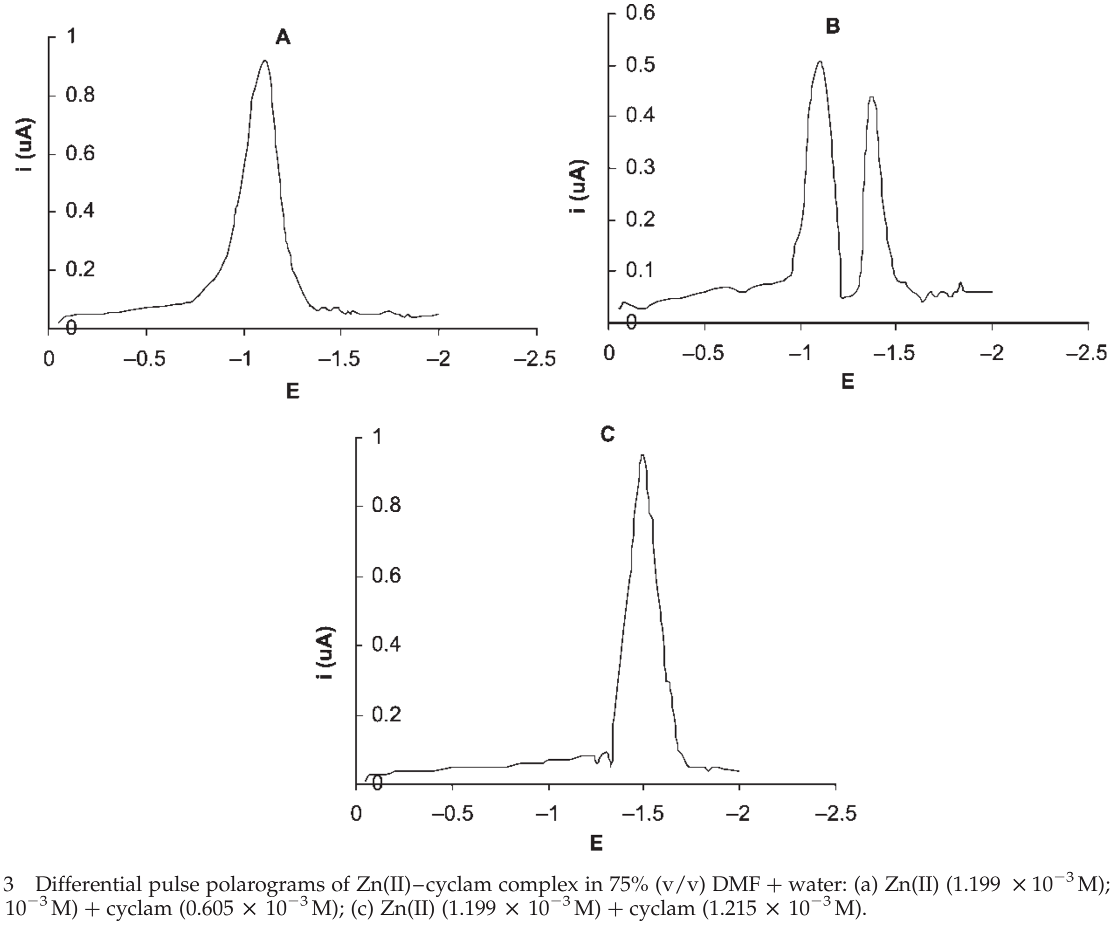


FIGURE 3 Differential pulse polarograms of Zn(II)–cyclam complex in 75% (v/v) DMF + water: (a) Zn(II) (1.199×10^{-3} M); (b) Zn(II) (1.199×10^{-3} M) + cyclam (0.605×10^{-3} M); (c) Zn(II) (1.199×10^{-3} M) + cyclam (1.215×10^{-3} M).

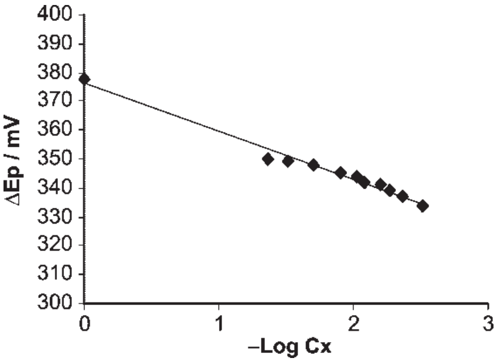


FIGURE 4 Plot of ΔE_p vs. $-\log C_x$ of cyclam–Zn(II).

negative potentials, as reported earlier [29]. The stability constants of these metal–cyclam complexes in the present study were determined by the shift in peak potential as well as by the decrease in peak current of the metal ion after complexation.

To obtain the values of $\log K_p$ and p, plots of ΔE_p vs. $-\log C_x$ were used as described earlier [25,36]. Figure 4 shows a plot of ΔE_p vs. $-\log C_x$ for the cyclam–Zn(II) complex. The derived values of the stability constants are shown in Table II. From the slope of ΔE_p vs. $-\log C_x$, in all of the cases studied, the metal to ligand complexation ratio is found to be in the range of 0.8 to 1.2, indicating 1:1 complexation. However, for the complexation of Ni(II), Co(II), Fe(III) and Cr(III) with cyclam, $\log K$ values could not be calculated as there was no shift in peak potential after addition of the ligands to the metal solutions. Therefore, in these systems the stability constant was calculated only by the reduction in peak current (i_p).

The differential pulse polarograms of Ni(II)–cyclam are shown in Fig. 5. The E_p and i_p values for a solution of Ni(II) of concentration 4.5789×10^{-3} M were found to be -1.43 V and 2.149 μA, respectively, as depicted in Fig. 5, curve (a). After adding 1.2048×10^{-3} M cyclam into the same solution, the polarogram obtained showed neither shift in potential nor formation of any new peak in the working potential range, as obtained in earlier cases. But a reduction in i_p value (1.860 μA) of the metal ion is observed at the same E_p as shown in Fig. 5, curve (b). Further addition of cyclam, 2.4092×10^{-3} M and 4.2162×10^{-3} M, subsequently showed a decrease in the i_p of the metal ion from 1.047 to 0.634 μA, as shown in Fig. 5, curves (c) and (d), respectively. It was noted that when the concentration of cyclam (4.8185×10^{-3} M) exceeded the concentration of the metal ion (4.5789×10^{-3} M), no peak of the metal ion was observed, as shown in Fig. 5, curve (e). This also indicates 1:1 complexation of these metal ions with the macrocycle.

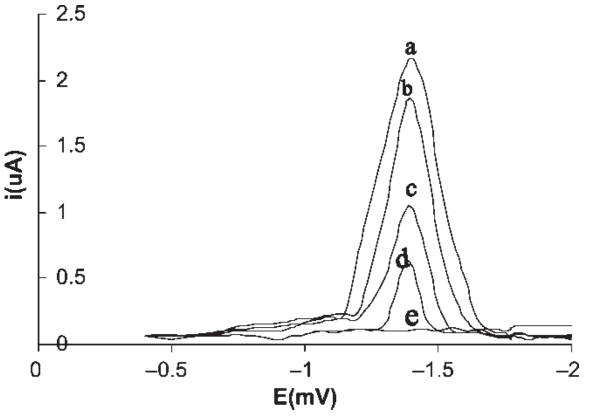


FIGURE 5 Differential pulse polarograms of Ni(II)–cyclam complex in 75% (v/v) DMF + water: (a) Ni(II) (4.5789×10^{-3} M); (b) Ni(II) (4.5789×10^{-3} M) + cyclam (1.2048×10^{-3} M); (c) Ni(II) (4.5789×10^{-3} M) + cyclam (2.4092×10^{-3} M); (d) Ni(II) (4.5789×10^{-3} M) + cyclam (4.2162×10^{-3} M); (e) Ni(II) (4.5789×10^{-3} M) + cyclam (4.8185×10^{-3} M).

The values of $\log K$ for Zn(II), Cu(II), Cd(II) and Pb(II) were also calculated by the reduction in the peak current and it was interesting to note that the values obtained by this method are in good agreement with the values calculated by the shift in peak potential (Table II). Therefore, for Ni(II), Co(II), Fe(III) and Cr(III), where no shift in peak potential was observed after complexation, an attempt was made to determine the stability constants by the reduction in peak current (i_p) (Table II).

The stability constants of Cr(III) and Fe(III) with tetraazacyclotetradecane and tetratosyltetraaza12C4 were also determined by the decrease in peak current of the metal ions with the addition of crown ethers in 90% (v/v) DMSO + water as tetratosyltetraaza12C4 is insoluble in 75% (v/v) DMF + water media. This particular work was undertaken to study the effect of the tosyl group in complexation. Table III shows that the stability constants for both Fe(III) and Cr(III) are slightly greater with tetraazacyclotetradecane than with tetratosyltetraaza12C4. This is possibly because the bulky tosyl group attached to the four nitrogen atoms in the case of tetratosyltetraaza12C4 might hinder the complexation ability of the ligand. During our previous studies of Ag(I) and Cu(II) complexation in 90% (v/v) DMSO + water media we encountered low stability constant values for Ag(I) and Cu(II) with tetratosyltetraaza12C4, whereas with tetraazacyclotetradecane the values were found to be very high [9,20].

TABLE III Stability constants ($\log K$) for Fe(III) and Cr(III) with aza macrocycle complexes in 90% (v/v) DMSO + water (reduction in i_p is considered for calculation)

	Log K	
Metal	Tetraazacyclotetradecane	Tetratosyltetraaza12C4
Fe(III)	8.75	8.12
Cr(III)	8.53	8.06

In all cases the standard deviation was less than 0.06 for $5 < n < 7$.

The stability constant values for the complexes of Pb(II), Cr(III) and Fe(III) with cyclam in 75% (v/v) DMF + water determined by DPP have been found to be in good agreement with the values obtained by competitive potentiometric method (Tables I and II). As tetraazacyclotetradecane and tetratosyltetraaza12C4 can form strong complexes with Fe(III) and Cr(III), these macrocycles have been explored as electroactive materials for developing coated wire ion-selective electrodes (CWISEs) for Fe(III) and Cr(III) ions, respectively [37].

The fact that substitution of 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 [4,7] can be seen in the present study too. Nitrogen-containing crown ethers like cyclam, diaza15C5 and dibenzodiaza15C4 show higher stabilities with all metal ions taken up in the present study. For example, log *K* values of Ag(I) and Cu(II) with diaza15C5 are 5.66 and 7.21, respectively, but the corresponding values with 15C5 are 1.94 and 2.65, respectively (Table I). In the determination of stability constants of some macrocyclic complexes of Ag(I) and Cu(II) in mixed solvents [20] and in methanol [7] by potentiometry, the same trend of complexation was observed. Similarly, from our polarographic studies (Tables II and III) it is also clear that the stability constants for metal- and nitrogen-containing cyclams are very high.

These studies reveal that the stabilities of the metal ions are not dependent only on the ion cavity sizes but also on other factors such as the number and type 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 [38].

MATERIALS AND METHODS

Solvents

Double-distilled, deionized 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. An azeotropic distillation with 10% by volume of dry benzene was carried out with commercially available DMF (S.D. Fine Chem Ltd, India) at atmospheric pressure using a Dean and Stark assembly. The 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 75% (v/v) and 90% (v/v) (±0.05%) of DMSO and DMF, respectively.

Reagents and Standard Solutions

Copper nitrate, silver nitrate, cobalt nitrate, zinc nitrate, lead nitrate, cadmium nitrate chromium nitrate, ferric nitrate and nickel nitrate were reagent-grade chemicals. All salt solutions were standardized before use. 15-Crown-5 (15C5), dicyclhexano-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 (diaza15C5) and 1,4,8,11-tetraazacyclotetradecane (cyclam) were purchased from Fluka (purity ≥ 98%). Benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8) were purchased from Aldrich (purity ≥ 98%) and used as received. Tetratosyltetraaza 12C4 was synthesized by the Richman–Atkins method as described in the literature [39,40] and TBAP was prepared as described [41]. Standard solutions of metal salts were prepared in double-distilled, deionized water. Working solutions were prepared as required by suitable dilution with the same water.

Apparatus

All solutions were prepared using a digital single-pan balance (Mettler Toledo AB204, Switzerland). A Mettler Toledo DL53 autotitrator with automatic temperature compensation (ATC) was used for standardization of metal salt solutions. The silver indicator electrode (DM 141-SC) with an inbuilt Ag/AgCl reference element was used for Ag(I) ions measurements.

The voltammetric system used for the studies was Autolab PGSTAT30, Metrohm Ltd., CH-9100, Switzerland, with (GPES) software installed for analysis. A three-electrode cell comprising dropping mercury as the working electrode (drop size 0.52 mm^2), glassy carbon as a counter electrode and Ag/AgCl as a reference electrode were used for the measurements.

Competitive Potentiometric Measurements for Stability Constant Determination

The ionic strength was adjusted to 0.05 M for all the solutions with TBAP. The silver indicator electrode (DM 141-SC) with inbuilt Ag/AgCl as the reference electrode was used for all measurements involving Ag(I) ions.

The cell potential was measured with varying concentration of silver nitrate solutions to obtain the plot of emf vs. log [Ag^+], which was found to be linear with a slope of 59 ± 1 mV/decade change over the whole working range (10^{-1}–10^{-7} M). The electrode was used to monitor the concentration of silver ions, before and after addition of crown ether solutions, in the presence and absence of metal ions. The emfs were noted after every 2 min. 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 ± 0.3 mV.

The silver ion concentration was calculated from the measured emf of the solution as described in the theory section.

Polarographic Measurements for Stability Constant Determination

A polarogram of the solution containing the supporting electrolyte was run before every measurement and the analyte concentration in the experimental solution was achieved by adding aliquots from the stock solution of the analyte prepared in the supporting electrolyte. For the complexation studies, separate solutions of varying concentration of metal and macrocycles were prepared and polarographic waves were recorded at the dropping mercury electrode. The final working solution was achieved similarly by adding aliquots from the stock solution of the metal and macrocycles in the supporting electrolyte solution. All test solutions were purged with dry nitrogen for at least 10–12 min to remove oxygen.

Theory

Competitive Potentiometry

STABILITY CONSTANTS FOR THE SILVER–CROWN ETHER COMPLEXES

Stability constants of the Ag^+ complexes, K_{Ag}, with various crown ethers, L, in 0.05 M TBAP were determined by potentiometric measurements of Ag^+ ions in a solution of L using the silver indicator electrode considering the following equilibrium [15,19]:

$$Ag^+ + L \overset{K_{Ag}}{\rightleftharpoons} AgL^+ \tag{1}$$

where

$$K_{Ag} = [AgL^+]/[Ag^+][L] \tag{2}$$

STABILITY CONSTANT FOR THE METAL–CROWN ETHER COMPLEXES USING SILVER AS THE PROBE

When the metal ions (M^{n+}) are added to the solution of AgL^+, the following equilibrium exists:

$$M^{n+} + AgL^+ \overset{K_E}{\rightleftharpoons} ML^{n+} + Ag^+ \tag{3}$$

where

$$K_E = [ML^{n+}][Ag^+]/[M^{n+}][AgL^+] \tag{4}$$

At equilibrium, the silver ion concentration was monitored both in the absence and in the presence of the metal ions in the solution of the ligand using the silver indicator electrode with an inbuilt Ag/AgCl reference electrode.

The stability constant K_M of M^{n+} with L for the reaction:

$$M^{n+} + L \overset{K_M}{\rightleftharpoons} ML^{n+} \tag{5}$$

is given by,

$$K_M = [ML^{n+}]/[M^{n+}][L] \tag{6}$$

Combining Eqs (2), (4) and (6) gives

$$K_M = K_E \times K_{Ag} \tag{7}$$

Using this equation the value of K_M is calculated as described earlier [15,19].

Polarography

The basic observation in DPP is that the peak potential of a simple ion is shifted to more negative side by complexation as reported earlier [25].

The peak potential in DPP can be correlated to the stability constant by the following equation:

$$\begin{aligned} \Delta E_p &= (E_p)s - (E_p)c \\ &= (0.05916/n)\log K_p + (0.05916p/n)\log C_x \end{aligned} \tag{8}$$

where (E_p)s is the peak potential of the simple cation, (E_p)c is the peak potential of the complexed cation, C_x is the total ligand concentration, K_p is the stability constant, n is the electron stoichiometry and p is the metal to ligand ratio.

In the present study, the shift in E_p values and also the reduction in peak current were obtained by DPP for Zn(II), Cu(II), Cd(II) and Pb(II) complexes with cyclam in 75% (v/v) DMF + water medium.

Equation (8) indicates that if the plots of ΔE_p vs. $-\log C_x$ are drawn, the intercept will give the value of $(0.05916/n)\log K_p$ and the slope will be $0.05916p/n$, from which K_p and p values for the metal–ligand complex can be calculated [25].

The values of $\log K$ for Zn(II), Cu(II), Cd(II) and Pb(II) were also calculated by the reduction in peak current and were found to be in good agreement with the values calculated by the shift in peak potential. Therefore, for Ni(II), Co(II), Fe(III) and Cr(III), where no shift in peak potential was observed after complexation, an attempt was made to determine the stability constants by reduction in peak current (i_p).

For the determination of the stability constants of the above bivalent metal ion–cyclam complexes by the reduction in peak current, the calibration plot of diffusion current vs. concentration of metal ion was used for the determination of the free metal ion at equilibrium represented by Eq. (5) at different concentrations of the ligand. After determination of the free metal ion, the concentration of metal–ligand complex formed and the concentration of free ligand can be determined successively. The difference of the concentration of total metal ions, C_M, and the free metal ions $[M^{n+}]$ gave the concentration of complexed metal ions $[ML^{n+}]$, while the difference of total ligand and the complexed metal ion gave the concentration of free [L]. These three parameters, viz. the concentration of free metal ion $[M^{n+}]$, metal–ligand complex $[ML^{n+}]$ and free ligand [L] at different concentrations of the ligand and the metal ion in solution are used to determine the stability constants using Eq. (5).

CONCLUSION

Along with the determination of stability constants by competitive potentiometry and polarography by the shift in peak potential value, a successful attempt has been made to determine the stability constants of metal macrocycles by the reduction in peak height of the metal ion with increasing concentration of macrocycles in the metal ion content. Furthermore, from the results of the stability constant values, tetraazacyclotetradecane and tetratosyltetraaza12C4 have been explored as electroactive materials for the preparation of sensors for Fe(III) and Cr(III) ions.

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