POLAROGRAPHIC STUDY OF MIXED COMPLEXES OF Zn(II) WITH ETHYLENEDIAMINE AND TARTRATE

Jyoti Sharma, Arvind Kumar, A.L.J. Rao* and B.K. Puri**

Department of Chemistry, Delhi University, Delhi - 110007

** Department of Chemistry, Punjabi University, Patiala (Punjab)*

*** Department of Chemistry, I.I.T., Hauz Khas, New Delhi - 110016.*

Zn(II)-ethylendiamine-tartrate system has been studied polarographically at constant pH 6.90 and ionic strength, μ = 0.6 M (KCl) in aqueous solution at 30 ± 0.1 C. The reduction of the simple and mixed complexes is reversible and diffusion controlled. The application of Schaap and Mc-Master's method leads to the formation of the mixed complex [Zn (ethylenediamine) (tartrate)] with log β_{11} = 9.71.

The polarographic behaviour of zinc has been studied in various electrolytes and complexing agents[1-3]. Literature reveals that there are only a few references for the polarogrphic behaviour of mixed ligand complexes of zinc [4-6]. In the present communication, zinc (II) in ethylenediamine (en), tartrate ($Tart^{-2}$) and ethylendiamine-tartrate systems has been studied polarographically.

EXPERIMENTAL

All chemicals used were of analytical reagent grade and their stock solutions were prepared in conductivity water. Ethylenediamine (en) and tartrate ($Tart^{-2}$) were used as ligands. The ionic strength was maintained constant at = 0.6 M using KCl. Triton-X-100 (0.002%) was used as the maximum supressor.

Polarograms in all the cases were recorded at 30 ± 0.1°C using a manual poalrograph (Toshniwal CL02). A saturated calomel electorde (SCE) was used as the reference electrode and connected to the polarographic cell through a potassium chloride agar-agar bridge. The dropping mercury electrode (dme) had the following characteristics: $m^{\frac{2}{3}}t^{\frac{1}{6}}$= 2.01 at h = 30.0 cms in 0.1M KCl solution with open circuit. The number of electrons (n) involved in the reduction process was determined by the millicoulometric method [7].

RESULTS AND DISCUSSION

A series of polarograms of reduction of Zn(II) in en and Tart separately was found to be reversible and diffusion controlled. The slopes of linear plots of log $[i/(i_d - i)]$ vs-E_{de} were of the order of 30±1 mV. Stability constants of simple complexes of Zn(II) with en and $Tart^{-2}$ were determined prior to the study of the mixed ligand systems in the same medium. Same conditions were maintained in the mixed system also. The concentration of ligand species is calculated using analytical concentration of the ligand, pH of the medium and pK value of the ligand.

Simple Complexes

A plot of E 1/2 vs log [en] was a smooth curve indicating the formation of successive complexes. Application of DeFord and Hume's method[8] showed the formation of two successive complexes, $[Zn(en)]^{2+}$ & $[Zn(en)_2]^{2+}$ with stability constants log β_{10} = 6.09 and log β_{20} =11.215 respectively. Similarly zinc was found to form two complexes with tartrate viz [Zn(Tart)] and $[Zn(Tart)_2^{2-}]$ with stability constants log β_{01} = 4.14 and log β_{02} = 5.46 respectively.

TABLE 1

POLAROGRAPHIC CHARACTERISTICS AND F(X,Y) FUNCTIONS FOR ZINC-ETHYLENEDIAMINE-TARTRATE MIXED SYSTEM
Zn = 0.5 mM, μ = 0.6M (KCl), pH = 6.90,
TEMPERATURE = 30 ± 0.1 C

[en] M	$\Delta E_{1/2}$ V vs SCE	Log $\frac{I_s}{I_c}$	$F_{00}(X,Y)$ X 10^{-8}	F_{10} (X,Y) X 10^{-9}	F_{20} (X,Y) x 10^{-11}
Series : 1		$[Tart^{2-}]$ = 0.04 M (fixed)			
0.02	0,242	0.0172	1.19	3.95	1.87
0.04	0.256	0.0114	3.43	8.50	2.09
0.06	0.266	0.0231	7.60	12.00	1.96
0.08	0.274	0.0291	14.23	17.29	2.13
0.10	0.278	0.0439	20.04	19.61	1.94
Series : 2		$[Tart^{2-}]$ = 0.08 M (fixed)			
0.02	0.250	0.0056	2.14	-	-
0.04	0.265	0.0172	6.94	1.40	3.5
0.06	0.275	0.0435	15.88	2.48	4.0
0.08	0.282	0.0376	26.80	3.22	3.9
0.10	0.288	0.0303	41.07	4.07	4.0

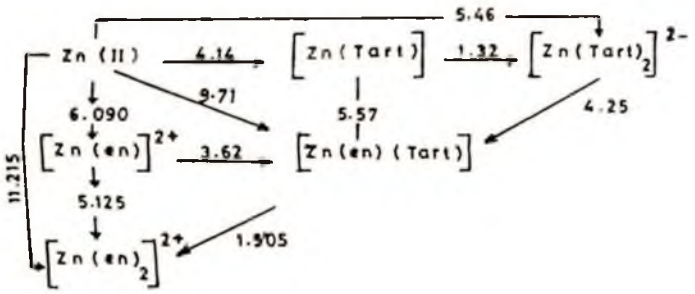
Series 1 : log A = 17.602. log B = 8.301,
log C = 11.30, log β_{11} = 9.641
Series 2 : log A = 8.00, log B = 8.69,
log C = 11.588 log β_{11} = 9.790
Mean, log β_{11} = 9.715

Mixed Ligand Complexes

The [en] was varied from 0.02-0.1 M keeping [Tart] constant at 0.04 M in one set of experiments (series 1) and 0.08 M in the the second set (series 2). In all the cases, a well defined, diffusion controlled and reversible two electron step appeared.

The $E_{1/2}$ values were found to be more negative than those obtained in the absence of $Tart^{-2}$ showing the formation of mixed complexes. Schaap and McMaster's method[9] was used for the determination of composition and stability constants of the mixed complexes. From the plots of F(X,Y) (where X = en and Y = Tart) data vs [en], the intercept values for constants A,B and C were obtained (Table 1).

It is inferred that Zn(II) forms a mixed 1:1:1 complex [Zn(en)(Tart)] with stability constant $\log \beta_{11} = 9.71$. The results of this study under these conditions are summarized below. The numerical values shown are the log of equilibrium constants of the reactions indicated.



The mixing constant $K_m^{[10]}$ for the reaction[10]

$1/2\ [Zn(en)_2]^{2+} + 1/2\ [Zn(Tart)_2]^{2-} \longrightarrow [Zn(en)(Tart)]$ is given by the relation

$\log K_m = \log \beta_{11} - 1/2\ [\log \beta_{02} - \log \beta_{20}]$

The value of $\log K_m^*$ comes to be +1.373 which confirms that the mixed complex is more stable than the binary complexes $[Zn(Tart)_2]^{2-}$ and $[Zn(en)_2]^{2+}$

ACKNOWLEDGEMENT

Sincere thanks of the authors are due to U. G.C. For providing the financial assistance to one of us (J.S.) and also to Dr. N.K. Kaushik for useful discussion.

REFERENCES

1. L. Meites, *Polarographic Techniques, (Interscience, New York)* (1965.

2. A.L.J. Rao and B.K. Puri, *Analyst (London)*, 96 (1971) 364; *Z. Anal. Chem.* 254 (1971) 362.

3. B.K. Puri and Ashok Kumar, *India J. Chem.* 22A (1983) 1071; *J. Indian Chem. Soc.*, 60 (1984) 1034.

4. P.K. Migal and E.P. Koptemko, *Zh. Neorg. Khim;* 19 (1974) 2313.

5. R. Sundaresan and A.K. Sunderam, *Indian J. Chem.* 13 (1975) 299.

6. Krishna, R. Kulshrestha, P. Sharma and Mukhtar Singh, *J. Electrochem. Soc. India* 33 (1984) 267.

7. T. Devries and J.L. Kroon, *J.Am.Chem. Soc.*, 75 (1953) 2489.

8. D.D. DeFord and D.N. Hume, *J.Am.Chem. Soc.*, 73 (1951) 5321.

9. W.B. Schapp and D.L. McMaster, *J. Am. Chem. Soc.*, 83 (1961) 4699.

10. R. Sundaresan and A.K. Sundaram, *Proc Ind. Acad. Sci.* 79A (1974) 161; S.L Jain, J. Kishan and R.C. Kapoor, *Ind. J. Chem.* 18A (1979) 133.