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Electrode Kinetic Studies of Mn(II) Complexes with Some Amino Acids (Glycine, α-Alanine and L-Valine)

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Polarography was used to determine the stability constants (log β) and kinetic parameters of binary complexes of Mn(II) with glycine, α- alanine, L-valine at pH 8.30 ± 0.01 and ionic strength (μ) = 1 M KCl at 300 K. The reduction waves of Mn(II) and its complexes are quasireversible. The trend of stability constants of the complexes and electrode kinetic parameters have been evaluated.

Key Words: Polarography, Mn(II), Complexes, Amino acids.

INTRODUCTION

The complexes of amino acids with transition metals used in cancer therapy, pharmacy and industry[1] are biologically active, thus create considerable interest in their metal complexes. Mixed ligand complexes of transition metals with many amino acids have been studied by many workers[2-8]. Banerjee *et al.*[9] have studied Mn(II) and Zn(II) complexes of vanillin and 4,6-dihydroxypyrimidine polarographically. The electrode kinetics of many metal complexes of amino acids have been studied by many workers[10-13], Zaidi and Khan[14] have studied Mn(II) complexes with amino acids such as L-asparagine, L-glutamine, L-leucine *etc.*, polarographically.

The literature survey reveals no references on the binary complexes of Mn(II) with selected amino acids, hence the study was undertaken using a polarographic technique with the view to determine the stability constants and kinetic parameters of these systems. The present paper describes that DeFord and Hume's method[15] which can be applied in the quasireversible systems with the proper correction done by Gellings method[16] for half-wave potential.

EXPERIMENTAL

Manganese(II) chloride and sodium salts of amino acids were used and their solutions were prepared in conductivity water. Dilute solution of nitric acid and sodium hydroxide were used, as required to adjust the pH by using Toshniwal pH meter. The pH at which the shift of $E_{1/2}$ was maximum, was chosen for the study. The pH values were selected to 8.30 ± 0.01. The ionic strength was maintained constant at μ = 1 using potassium chloride as supporting electrolyte. Triton-X-100 was used as maximum suppressor. Pure nitrogen gas was passed through each test solution before recording the current-voltage data to remove dissolved oxygen. The polarograms were recorded using manually operated polarograph. An H-type cell saturated with potassium chloride agar-agar salt bridge conjunction with a SCE was used. The DME had the following characteristics: m = 2.30 mg/s, t = 3.2 s and h = 40 cm.

RESULTS AND DISCUSSION

Mn(II) gave a well-defined two electrons quasireversible reduction wave in 1 M KCl at pH 8.30 ± 0.01 at 300 K. The plots of i_d *versus* $\sqrt{h_{eff}}$ were linear and passed throgh origin, thereby indicating that the reduction was diffusion controlled. The value of $(E_{1/2})^r$ of Mn(II) was -1.420V *versus* SCE, which by the Gellings method[9] gave $(E_{1/2})^{rev}$ = -1.410 V. Similarly $(E_{1/2})^r$ of complexes for the corresponding concentration of the ligand was also calculated.

Addition of the increasing amount of ligand to the solutions containing 5×10^{-4} M Mn(II) and requisite amount of KCl, shifted the half-wave potential towards cathodic side and this was accompanied by a decrease in the diffusion current. This shows a complexation between metal and ligand.

The plot of $F_0[X]$ and $F_1[X]$ *versus* [X] (amino acid concentration) is a smooth curve and $F_2[X]$ *versus* [X] is a straight line with a slope in each system. The plot of $F_3[X]$ *versus* [X] is again a straight line but parallel to abscissa. These results show the formation of three complexes. The different polarographic measurements and $F_j[X]$ functions values for Mn(II)-amino acid complexes at 300 K have been recorded in Tables 1-3 and shown graphically in Figs. 1-3, respectively.

TABLE-1
POLAROGRAPHIC MEASUREMENTS AND $F_j[X]$
VALUES FOR THE Mn(II)-GLYCINATE SYSTEM
[Mn(II)] = 5×10^{-4} M, $E_{1/2}$ of Mn(II) = -1.410 V *versus* SCE, i_d = 52 div.,
μ = 1 M KCl, pH = 8.30 ± 0.01, Temp. = 300 K

[gly] (mol L^{-1})	$E_{1/2}$	log I_m/I_c	$F_0[X] \times 10^2$	$F_1[X] \times 10^4$	$F_2[X] \times 10^7$	$F_3[X] \times 10^8$
0.001	0.0434	0.0303	0.3082	2.9820	1.4620	20.2000
0.002	0.0581	0.0393	0.9813	4.8565	1.6592	19.9600
0.003	0.0682	0.0383	2.1390	7.0966	1.8588	19.9600
0.004	0.0754	0.0579	3.9065	9.7413	2.0585	19.9625
0.005	0.0815	0.0676	6.4045	12.7890	2.2579	19.9558
0.006	0.0865	0.0825	9.7592	16.2486	2.4606	20.0100
0.007	0.0913	0.0825	14.1488	20.1982	2.6573	19.9614
0.008	0.0952	0.0927	19.5877	24.4721	2.8569	19.9613

The stability constant values for Mn(II)-amino acid complexes at 300 K are given in Table-4.

Kinetic parameters have been calculated by Gelling's method as the electrode process in quasireversible. The plots of log (Z-1) *versus* $(E-E_{1/2})$ were linear where Z is defined as:

TABLE-2
POLAROGRAPHIC MEASUREMENTS AND $F_j[X]$ VALUES
FOR THE Mn(II)-α-ALANINATE SYSTEM
[Mn(II)] = 5 × 10^{-4} M, $E^r_{1/2}$ of Mn(II) = -1.410 V *versus* SCE, i_d = 52 div.,
μ = 1 M KCl, pH = 8.30 ± 0.01, Temp. = 300 K

[ala] (mol L^{-1})	$E^r_{1/2}$	log I_m/I_c	$F_0[X] \times 10^2$	$F_1[X] \times 10^4$	$F_2[X] \times 10^7$	$F_3[X] \times 10^8$
0.001	0.0418	0.0258	0.2695	2.5950	1.2538	17.3800
0.002	0.0564	0.0347	0.8513	4.2065	1.4277	17.3850
0.003	0.0662	0.0439	1.8562	6.1540	1.6014	17.3800
0.004	0.0737	0.0533	3.3888	8.4470	1.7744	17.3600
0.005	0.0798	0.0627	5.5521	11.0842	1.9502	17.4040
0.006	0.0848	0.0775	8.4583	14.0805	2.1227	17.3783
0.007	0.0893	0.0876	12.2633	17.5047	2.2966	17.3800
0.008	0.0934	0.0876	16.8419	21.0398	2.4721	17.4013

TABLE-3
POLAROGRAPHIC MEASUREMENTS AND $F_j[X]$
VALUES FOR THE Mn(II)-L-VALINATE SYSTEM
[Mn(II)] = 5 × 10^{-4} M, $E^r_{1/2}$ of Mn(II) = -1.410 V *versus* SCE, i_d = 52 div.,
μ = 1 M KCl, pH = 8.30 ± 0.01, Temp. = 300 K

[val] (mol L^{-1})	$E^r_{1/2}$	log I_m/I_c	$F_0[X] \times 10^2$	$F_1[X] \times 10^4$	$F_2[X] \times 10^7$	$F_3[X] \times 10^8$
0.001	0.0387	0.0214	0.2098	1.9980	9.4171	10.9710
0.002	0.0529	0.0303	0.6427	3.1635	10.5140	10.9700
0.003	0.0625	0.0393	1.3793	4.5643	11.6231	11.0103
0.004	0.0697	0.0485	2.4594	6.1235	12.7075	10.9687
0.005	0.0759	0.0485	3.9736	7.9272	13.8056	10.9712
0.006	0.0807	0.0676	6.0201	10.0168	14.9015	10.9692
0.007	0.0851	0.0775	0.6569	12.3527	16.0925	11.1036
0.008	0.0889	0.0825	11.7507	14.6758	17.0961	10.9701

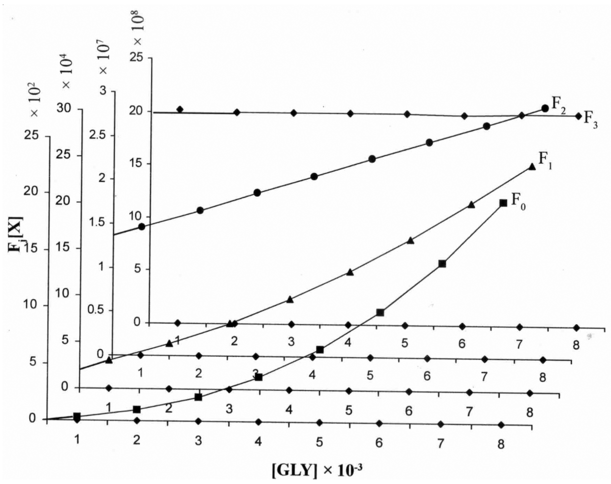

Fig. 1. Plot of $F_j[X]$ *versus* [GLY]: Mn(II)-glycinate system at 300 K

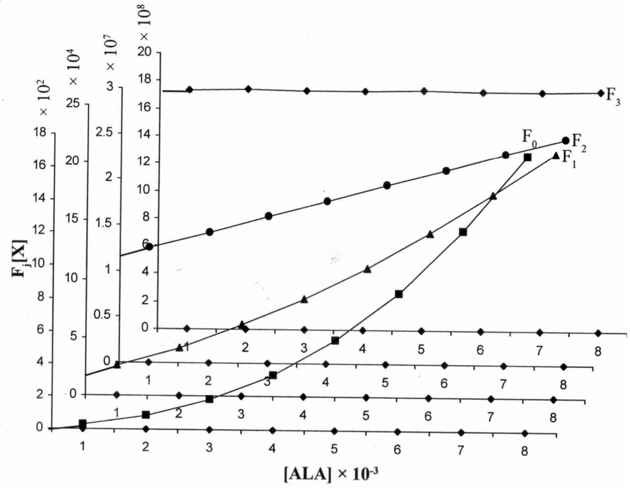

Fig. 2. Plot of $F_j[X]$ *versus* [ALA]: Mn(II)-α-alaninate system at 300 K

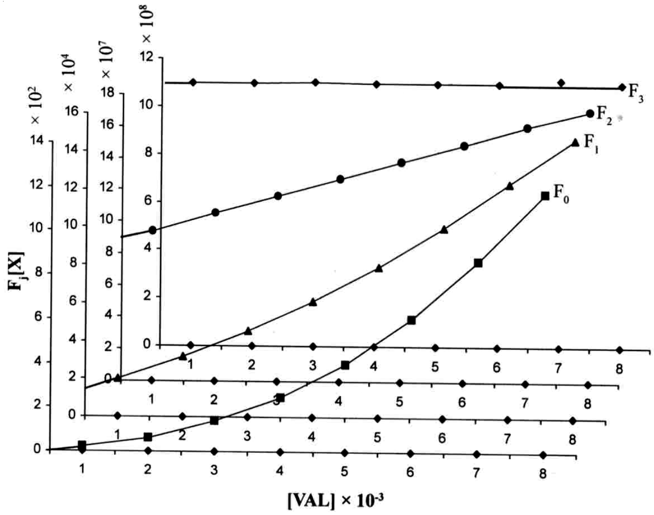

Fig. 3. Plot of $F_j[X]$ *versus* [VAL]: Mn(II)-L-valinate system at 300 K

$$\log(Z-1)=\log\frac{1.13}{\lambda\sqrt{t_d}}-\frac{(1-\alpha)nF}{2.303RT}(E-E_{1/2})$$

$$Z=\text{antilog}\frac{nF}{2.303RT}(E_{1/2}-E)-\log\frac{i}{i_d-i}$$

where R, T, n and F have their usual significance.

The values of λ were calculated from the intercept of these plots. The standard rate constants K_s can be calculated from the relation $K_s = \lambda D^{1/2}$, where D is the diffusion coefficient which can be determined from diffusion current data by Ilkovic equation. The kinetic parameters at 300 K are given in Tables 5-7.

TABLE-4
SUCCESSIVE STABILITY CONSTANTS FOR ML, ML$_2$ AND ML$_3$ COMPLEXES OF Mn(II)-AMINO ACID

Systems	Stability constants		
	log β_1	log β_2	log β_3
Mn(II)-glycinate	4.18	7.10	9.30
Mn(II)-α-alaninate	4.13	7.03	9.24
Mn(II)-L-valinate	4.03	6.92	9.04

TABLE-5
KINETICS PARAMETERS OF Mn(II)-GLYCINATE SYSTEM AT 300 K

[ala] (mol L^{-1})	$D^{1/2} \times 10^{-3}$ (cm^2 s^{-1})	λ	$K_s \times 10^{-3}$ (cm s^{-1})
0.000	4.1748	1.1981	5.0018
0.001	3.8938	1.1898	4.6328
0.002	3.8135	1.1233	4.2837
0.003	3.7836	1.1233	4.2501
0.004	3.6529	1.1104	4.0561
0.005	3.5726	1.1495	4.1067
0.006	3.4522	1.1628	4.0142
0.007	3.4251	1.1363	3.8914
0.008	3.3719	1.1442	3.8581

TABLE-6
KINETICS PARAMETERS OF Mn(II)-α-ALANINATE SYSTEM AT 300 K

[val] (mol L^{-1})	$D^{1/2} \times 10^{-3}$ (cm^2 s^{-1})	λ	$K_s \times 10^{-3}$ (cm s^{-1})
0.000	4.1748	1.1981	5.0018
0.001	3.9339	1.1628	4.5743
0.002	3.8536	1.0977	4.2301
0.003	3.7734	1.0927	4.1232
0.004	3.6931	1.0802	3.9893
0.005	3.6931	1.0802	3.9893
0.006	3.6128	1.0802	3.9025
0.007	3.4924	1.1495	4.0145
0.008	3.3853	1.1311	3.8291

TABLE-7
KINETICS PARAMETERS OF Mn(II)-L-VALINATE SYSTEM AT 300 K

[val] (mol L^{-1})	$D^{1/2} \times 10^{-3}$ (cm^2 s^{-1})	λ	$K_s \times 10^{-3}$ (cm s^{-1})
0.000	4.1748	1.1981	5.0018
0.001	3.9339	1.1628	4.5743
0.002	3.8536	1.0977	4.2301
0.003	3.7734	1.0927	4.1232
0.004	3.6931	1.0802	3.9893
0.005	3.6931	1.0802	3.9893
0.006	3.6128	1.0802	3.9025
0.007	3.4924	1.1495	4.0145
0.008	3.3853	1.1311	3.8291

The stability constants decrease in the order:

Glycine > α-alanine > L-valine

Glycine, due to lack of methyl group, forms more stable complexes than α-alaine and L-valine. A remarkable effect of side-chain on the stabilities of complexes have been observed. It has been observed that if the length of side-chain of an amino acid increases by CH_2 the stability of complex decreases[17]. The steric hindrance it formed least stable complex.

The values of standard rate constant K_s were found to be of the order of 10^{-3} cm/s, at 300 K and slows down as the ligand is added to the solution of simple metal ion. Further it is seen that successive addition of the ligand, effects the rate of reaction which is observed from very small change in the values of diffusion coefficients. The irregular decrease in the K_s values with the increase in ligand concentration, indicates that the irreversibility of electrode process for the reduction of Mn(II) increases in the presence of amino acids.

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