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Electrochemical Reduction of Zn (II)L-Amino Acids in N-Methyl Formamide at D.M.E.

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Abstract

Kinetic parameters of Zn (II) with l-lysine, l-aspartic acid, l-glutamic acid, l-arginine, l-tryptophan, l-tyrosine at pH 7.50 ± 0.02 at constant ionic strength $\mu = 0.1$ $NaClO_4$ have been evaluated. The reductions in all the cases were found to be quasi reversible and diffusion controlled. The values of kinetic parameters for the electrode processes α, λ and k^{-}_{s} are obtained using Gelling's treatment[1] and $E^{r}_{1/2}$ values were also evaluated for quasi reversible electrode processes.

Keywords: Electrochemical Reduction; Dropping Mercury Electrode (DME); Zn (II)-Amino Acids Complexes; N-Methyl Formamide; Kinetic Parameters

Introduction

Henyl acetate, phenoxy acetate, p-sulphamido benzoate ion at d.m.e. has been reported earlier[2]. Polarographic study of few metal complexes with l-hydroxy proline was carried out by Filmwala et. al[3]. Kinetic parameters and stability constant of Zn (II) antibiotics streptomycin ternary systems via kinetics of electrode reaction have been studied by Tantuvay Laxmi and F Khan[4]. Complexes of Zn (II) with aspartic acid and also with glycine have also been investigated polarographically in presence of thiourea [5,6]. The stoichiometry and formation constants of various metal ligands complexes have been graphically evaluated using polarographic method[7, 8.]

Kinetic parameters of Zn (II) complexes with various organic acids and esters[9,10] and also with methyl cysteine and penicilamine have been evaluated by polarographically[11]. Stability constant of Zn (II) and Cd (II) complexes with 2-hydroxy propane and 1, 3 diamine, and N, N, N11, N11 Tetra acetic acid have evaluated very recently[12].

In present work the kinetic parameters viz standard rate constant (ks), transfer coefficient (α) and degree of irreversibility (λ) for Zn (II) l-amino acids in different composition of aqueous N-methyl formamide mixture (v/v) have been calculated.

Experimental

Chemicals used were of A.R. grade and solutions were prepared in double distilled water. A conventional type manual (potentiometer make oswal, galvanometer make norish) was used for obtaining current voltage curves. The DME used had the following characteristics m = 1.8 mg/sec. and t=6.0 sec. Triton-X-100 (0.001%) was used to suppress the polarographic maxima. Solutions of Zn (II) complexes were prepared in various percentage of aqueous N-methyl formamide. Oxygen was removed by bubbling purified nitrogen gas through the solution, which was pre saturated with a solution, having the same composition as that of experimental mixture. Sodiumperchlorate solution was used as base electrolyte. Solution containing 1.0 mM of the metal ion with different composition of N-methyl formamide water mixture (v/v) were prepared at constant ionic strength (μ= 0.1).

Results and Discussion

In each case a single well defined wave was obtained during the reduction of Zn (II) complexes at DME. The reduction is found to be diffusion controlled, which is further confirmed from the plots of i_d Vs $\sqrt{h}$ and i_d Vs concentration which were linear and passed through the origin (id = diffusion current, h = height of Hg column).

The plots of log $\frac{i}{i_d - i}$ Vs $E_{.d.e}$ were linear in all cases and the value of slope indicates that the reduction is quasireversible in all cases.

The polarographic characteristics of the reduction of Zn (II) complexes in N-methyl formamide have been summarized in table (1-2).

A constant decrease in id values was found with increase in percentage of N-methyl formamide (20-60%) in all cases. The values of $E^{r}_{1/2}$ have been calculated by applying Gelling's method. The plots of $\left(E+\frac{RT}{nF}\ln\frac{i}{i_d-i}\right)$ vs i, gave smooth curve and the extrapolation of this curve to zero current value gives the $E^{r}_{1/2}$ (fig. 1-6).

Kinetic parameters (α, λ, k_s) have been determined from the plots of log $(z-1)$ vs ξ. Where $\xi = \frac{nF}{2.303R\left(E-E^{r}_{1/2}\right)}$. The plots of log $(z-1)$ vs ξ. are given in Figure (7-24)

In present investigation, it has been observed that, $E_{1/2}$ values of Zn (II) l-aspartic acid, l-lysine, l-glutamicacid complexes shifted towards more cathodic direction with the increase in the percentage of N-methyl formamide (20 – 60%) v/v. which clearly indicates irreversibility of complex formation at electrode. Futher, the ks value of Zn (II) aspartate complex is smaller in comparison to other Zn (II) amino acid complex, which confirms the irreversibility of the electrode process. Higher irreversibility of Zn (II) aspartate complex is due the fact that aspartate form one five membered and one six membered chelate rings. In the case of Zn (II) l-trypthophan, l-tyrosine, l-arginine $E_{1/2}$ shifted towards more anodic direction as the percentage of N-methyl formamide (20–60%) v/v is increased, which suggests easier reduction .The trend of ks values for these complexes is irregular. The irregularity of electrode process (not only) depends upon dielectric constant and viscosity of medium but also on ion pair formation and chemical interaction at the electrode surface.

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Table 1

Polarographic characteristics $E^{r}_{1/2}$ and kinetic parameters for 1.0 mM Zn (II) complexes in N methyl formamide mixtures (μ = 0.1)

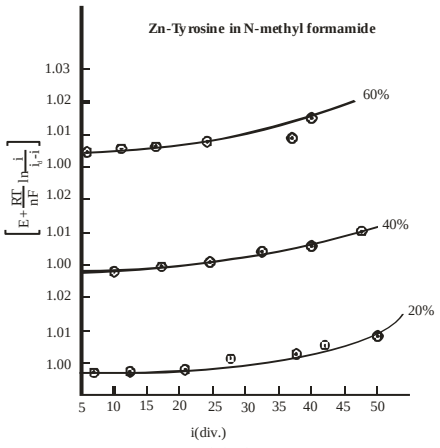
Ligand	% of solvent (v/v)	I_d (μA)	Slope (mV)	$E_{1/2}$ (-V Vs SCE)	$E^{r}_{1/2}$ (-V Vs SCE)	α	λ	$D^{1/2} \times 103$ ($cm^2\ sec^{-1}$)	$k_s \times 10^3$ ($cm\ sec^{-1}$)
l-Arginine	0%	6.525	35	1.032	1.010	0.970	0.278	2.733	0.759
	20%	4.668	44	1.002	0.994	0.989	0.145	1.928	0.281
	40%	4.275	34	0.998	0.995	0.987	0.145	1.765	0.257
	60%	4.725	54	1.000	0.998	0.911	0.217	1.951	0.411
l-Tryptophan	0%	8.662	56	1.023	0.998	0.976	0.242	3.629	0.878
	20%	6.243	30	0.998	0.982	0.986	0.110	2.578	0.285
	40%	5.512	28	0.990	0.987	0.987	0.066	2.276	0.151
	60%	5.231	30	0.986	0.992	0.989	0.290	2.160	0.628
l-Tyrosine	0%	9.225	50	1.020	0.991	0.983	0.291	3.865	1.124
	20%	6.693	32	1.008	0.997	0.985	0.063	2.764	0.149
	40%	5.962	30	1.004	0.998	0.972	0.060	2.462	0.175
	60%	4.893	26	1.002	1.004	0.955	0.042	2.021	0.084

Table-2

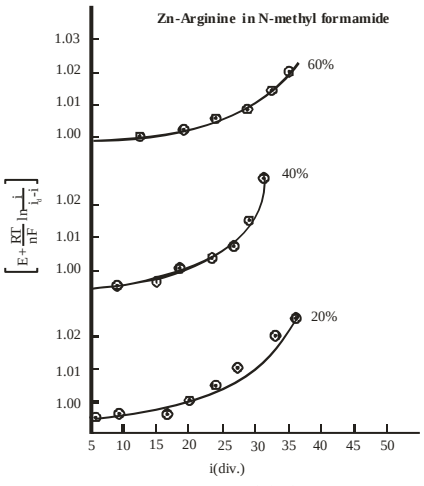
Polarographic characteristics, $E^{r}_{1/2}$ and kinetic parameters for 1.0 mM Zn(II) complexes in aqueous N-methyl formamide mixture (μ = 0.1)

Ligand	% of solvent (v/v)	I_d (μA)	Slope (mV)	$E_{1/2}$ (-V vs SCE)	$E^{r}_{1/2}$ (-V Vs SCE)	α	λ	$D^{1/2} \times 10^{3}$ (cm^2 sec^{-1})	$k_s \times 10^{3}$ (cm sec^{-1})
l-Lysine	0%	7.76	66	1.050	1.007	0.982	0.133	3.262	0.614
	20%	11.362	62	1.030	1.070	0.907	0.201	4.629	0.081
	40%	7.312	70	1.040	1.008	0.982	0.253	3.200	0.810
	60%	5.175	75	1.045	1.005	0.976	0.038	2.137	0.954
l-Aspartic acid	0%	2.250	40	1.140	1.091	0.980	0.279	0.929	0.259
	20%	2.250	46	1.000	1.034	0.985	0.133	0.929	0.225
	40%	2.081	38	1.034	1.030	0.984	0.110	0.859	0.123
	60%	5.175	40	1.040	0.994	0.988	0.105	2.137	0.095
l-Glutamic acid	0%	5.287	40	1.068	1.057	0.979	0.459	2.215	1.072
	20%	4.612	34	1.004	1.001	0.983	0.052	1.719	1.018
	40%	4.837	32	1.008	1.000	0.988	0.110	1.997	0.220
	60%	4.950	30	1.016	1.011	0.985	0.524	2.044	0.091

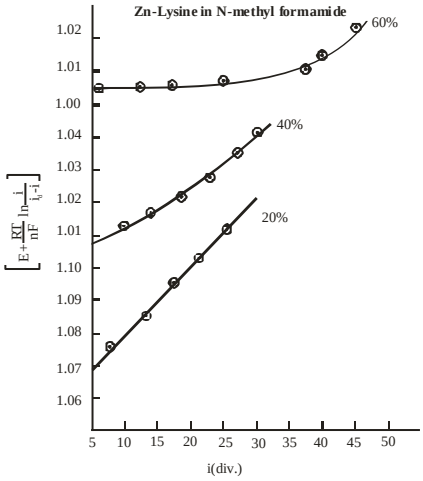
Plots of $\left[E+\frac{RT}{nF}\ln\frac{i}{i_d-i}\right]$ vs i for 1.0 mM Zn(II) complexes in N-mehtylformamide



(Fig.1)



(Fig.2)



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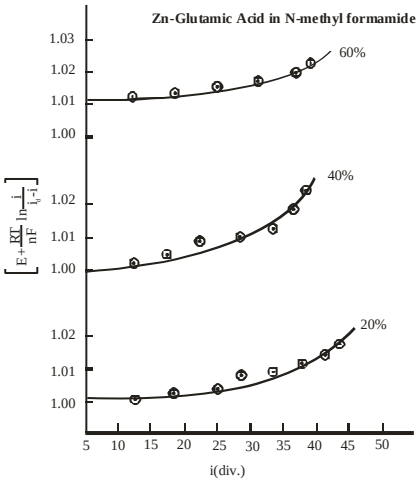
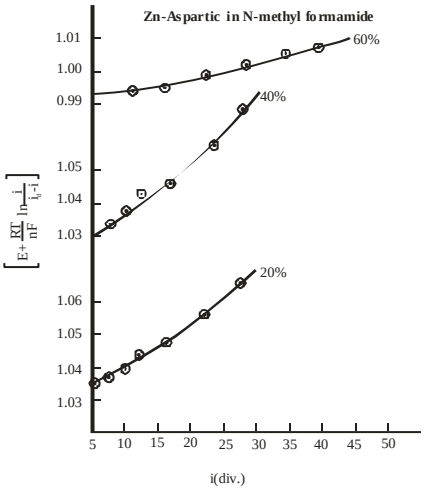
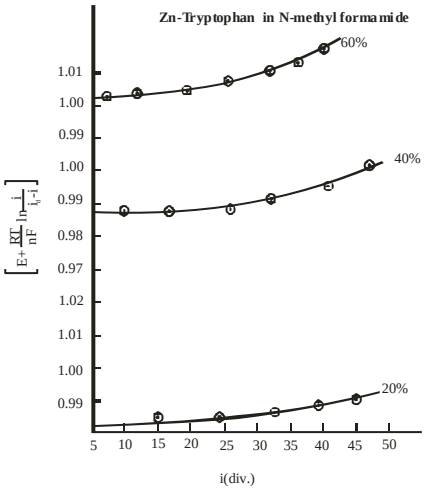


(Fig.4)



(Fig.5)



(Fig.6)

Plots of log (z-1) vs $\frac{nF}{2.303RT}(E\text{-}E^{r}_{1/2})$ in aqueous N-methyl formamide mixture for Zn-*l*-Tyrosine

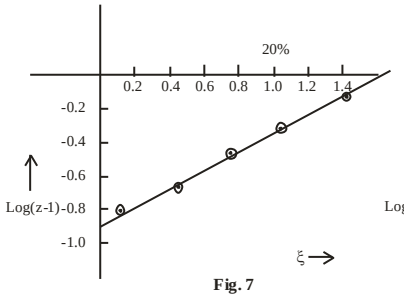


Fig. 7

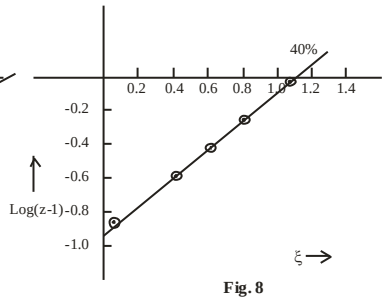


Fig. 8

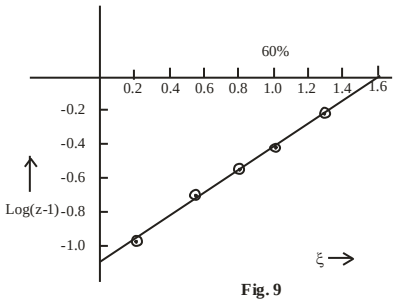


Fig. 9

Plots of log (z-1)$\frac{nF}{2.303RT}$ $(E\text{-}E^{r}_{1/2})$ in aqueous N-methyl formamide mixture for Zn-*l*-Arginine

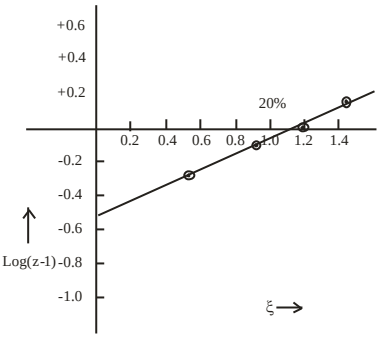


Fig. 10

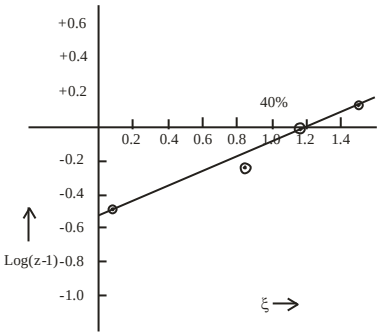


Fig. 11

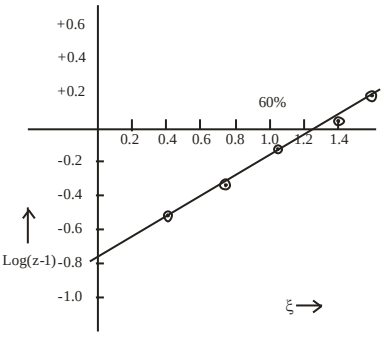


Fig. 12

Plots of log (z-1)$\frac{nF}{2.303RT}$ $(E\text{-}E^{r}_{1/2})$ in aqueous N-methyl formamide mixture for Zn-*l*-Lysine

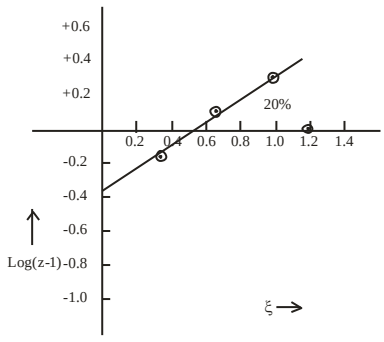


Fig. 13

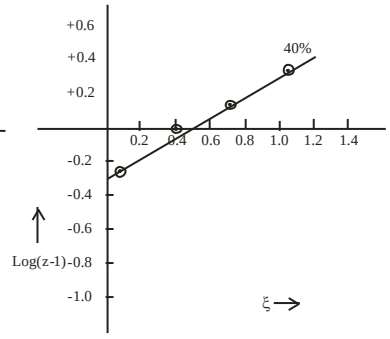


Fig. 14

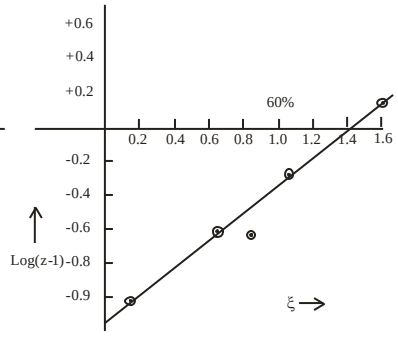


Fig. 15

Plots of log (z-1)$\frac{nF}{2.303RT}$ (E-$E^{r}_{1/2}$) in aqueous N-methyl formamide mixture for Zn-*l*-Glutamic acid

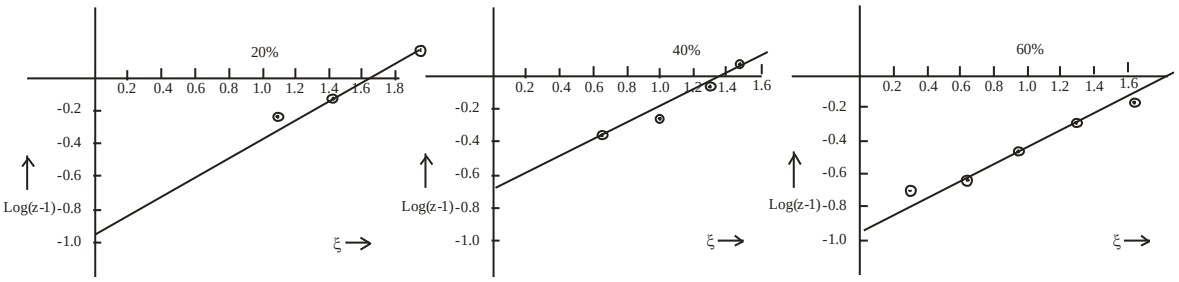


Fig. 16 **Fig. 17** **Fig. 18**

Plots of log (z-1) $\frac{nF}{2.303RT}$ (E-$E^{r}_{1/2}$) in aqueous N-methyl formamide mixture for Zn-*l*-Aspartic acid

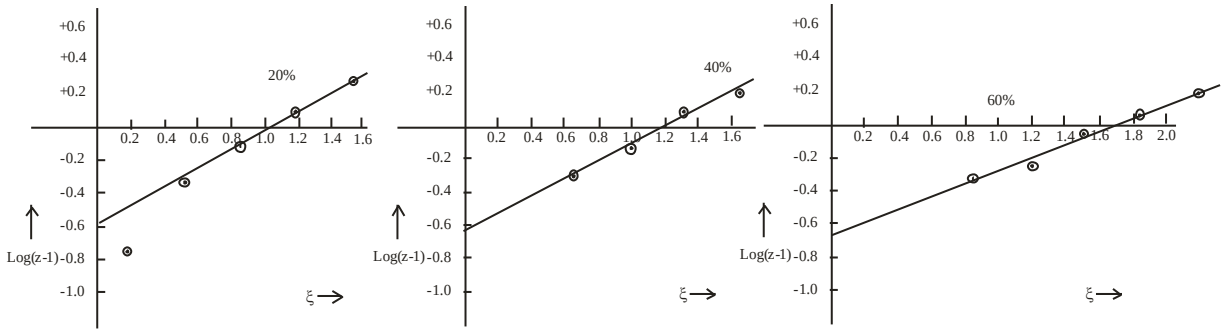


Fig. 19 **Fig. 20** **Fig. 21**

Plots of log (z-1)$\frac{nF}{2.303RT}$ (E-$E^{r}_{1/2}$) in aqueous N-methyl formamide mixture for Zn-*l*-Tryptohan

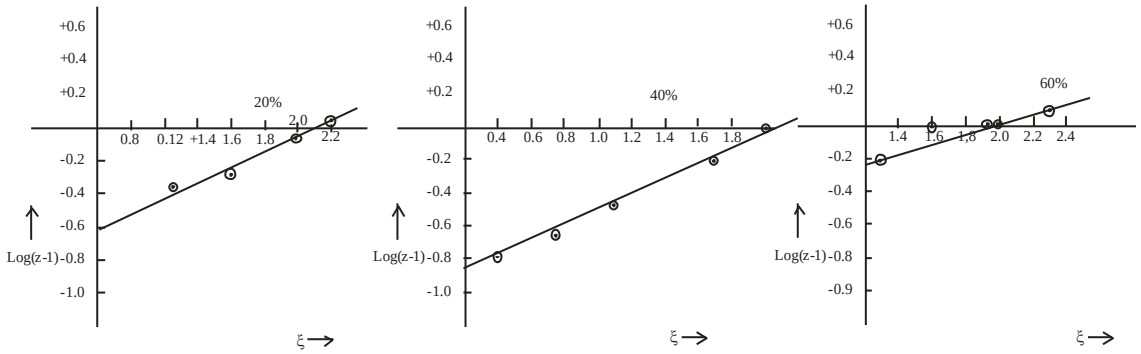


Fig. 22 **Fig. 23** **Fig. 24**