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ELECTROCHEMICAL REDUCTION OF Zn (II) l-AMINO ACIDS SYSTEM IN AQUEOUS FORMAMIDE MIXTURE AT D. M. E.

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ABSTRACT

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

Key words: Electrochemical reduction, Dropping mercury electrode (DME), Zn (II) l-amino acids complexes, Formamide, Kinetic parameters

INTRODUCTION

Zinc produces well developed wave in the presence of various supporting electrolytes and is therefore readily amenable to polarographic reduction[2–5]. Sharma and Gaur[6] have studied the complexes of zinc with pyridines polarographically. A well defined wave of zinc (II) is obtained in thiocyanate medium with nearly same $E_{½}$ values as that of the simple metal ion showing poor complex formation between zinc and thiocyanate ions. Complexes of Zn (II) with aspartic acid and glycine have also been investigated in presence of thiourea[7,8].

Electrochemical behavior of Zn (II) in presence of phenyl acetate, phenoxy acetate and p-sulphamido benzoate ions at dropping mercury electrode has been reported[9]. Polarographic studies of Cu (II) and Zn (II) complexes with glycolate ions have been studied by Jain and Jain[10]. Irreversible diffusion controlled reduction of Zn (II) thiocyanate tartarate and citrate mixed system has been reported by Krishana et al.[11].

Differential pulse polarographic studies of Zn (II), Cu (II) and Pb (II) in DMSO medium and the kinetics of such reduction by varying the concentrations of tetra alkyl ammonium perchlorate have been studied using cyclic voltammetry and chronoamperometry[12]. Mixed ligand complexes of transition metals with heterocyclic amines, halides and pseudohalides have been reported in past years[13].

Non–reversibility of reduction at dropping mercury electrode and subsequent kinetic parameters determination of metal complexes is a unique illustration. Some authors have carried out similar studies earlier[14-15]. The formation constants determination of Zn (II) with acid anion complexes, pyridines and thiocyanate complexes, amino acids and acetic acid complexes and Zn (II)-glutathione complexes have been reported.

Kinetic parameters and stability constant of Zn (II) antibiotics streptomycin ternary systems via kinetics of electrode reduction have been studied by several workers[16-19]. Cyclic voltammetry of mercury electrode in $NaClO_4$ solution containing Zn (II) in absence and presence of N,N' dimethyl thiourea has been carried out by Prezemyslaw[20].

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

EXPERIMENTAL

Chemicals used were of A.R. grade and solutions were prepared in double distilled water. Current-voltage curves were obtained on a conventional type manual (potentiometer Oswal make, galvanometer Norish make) polarograph. The DME used had the 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 formamide. Oxygen was removed by bubbling purified nitrogen gas through the solution, which was presaturated with a solution, having the same composition as that of experimental mixture. Sodium perchlorate solution was used as base electrolyte. Solutions containing 1.0 mM of the metal ion with different composition of dimethyl formamide-water mixture (v/v) were prepared keeping ionic strength ($\mu = 0.1$) constant.

RESULTS AND DISCUSSION

Polarographic characteristics, $E^r_{1/2}$ and kinetic parameters for Zn (II) complexes in aqueous formamide mixtures have been shown in Table 1. In each case, a single well defined diffusion controlled reduction wave was obtained, which was confirmed by the plots of i_d vs $\sqrt{h}$ and i_d vs concentration being linear and passing through the origin (i_d = diffusion current, h = height of Hg column).

Table 1. Polarographic characteristics $E^r_{1/2}$ and kinetic parameters for 1.0 mM Zn (II) complexes in formamide mixtures (μ = 0.1)

Ligand	Comp. solvent (v/v,%)	i_d (mA)	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-Arginine	0	6.525	35	1.032	1.010	0.970	0.278	2.733	0.7590
	20	7.987	50	1.008	1.000	0.981	0.069	3.336	0.2320
	40	7.987	46	1.010	0.999	0.991	0.159	3.298	0.5270
	60	7.200	48	1.012	1.007	0.982	0.544	2.973	0.1640
l-Tryptophan	0	8.662	56	1.023	0.998	0.976	0.242	3.629	0.8780
	20	9.337	30	1.004	1.023	0.940	0.152	3.856	0.5888
	40	7.425	24	1.012	1.010	0.976	0.100	3.066	0.3090
	60	7.087	26	1.014	1.012	0.972	0.080	2.927	0.2345
l-Tyrosine	0	9.225	50	1.020	0.991	0.983	0.291	3.865	1.1240
	20	10.912	28	1.002	0.986	0.992	0.152	4.506	0.6880
	40	8.887	30	1.004	1.000	0.972	0.063	3.670	0.2334
	60	7.537	28	1.006	1.002	0.945	0.048	3.112	0.1499

Ligand	**Comp. solvent (v/v,%)**	**i_d (mA)**	**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	7.760	66	1.050	1.007	0.982	0.133	3.262	0.614
	20	9.337	32	1.002	0.996	0.981	0.121	3.900	0.773
	40	8.662	36	1.010	1.006	0.982	0.060	3.618	0.219
	60	7.875	50	1.014	1.008	0.983	0.048	3.290	0.158
l-Aspartic acid	0	2.250	40	1.140	1.091	0.980	0.279	0.929	0.259
	20	6.975	74	1.024	1.017	0.981	0.231	2.880	0.665
	40	8.212	80	1.040	1.010	0.988	0.192	3.391	0.652
	60	7.313	34	1.044	1.016	0.976	0.061	3.020	0.183
l-Glutamic acid	0	5.287	40	1.068	1.057	0.979	0.459	2.215	1.072
	20	8.437	28	1.008	1.002	0.985	0.073	3.484	0.254
	40	7.200	26	1.010	1.008	0.970	0.121	2.973	0.360
	60	6.750	26	1.020	1.007	0.957	0.160	2.787	0.445

The plots of $\log \frac{i}{i_d - i}$ vs $E_{d.e}$ (applied potential vs S.C.E.) were linear in all cases and the value of slope indicated that the reduction to be quasi reversible.

There is a constant decrease in i_d value with increase in percentage of formamide (20 - 60% v/v) in all the cases. The values of $E^r_{½}$ have been calculated applying Gelling's theoretical treatment. Plots of $\left(E + \frac{RT}{nF} \ln \frac{i}{i_d - i}\right)$ vs i, were smooth curves and the extrapolation of these curves to zero current value gave the $E^r_{½}$ (Fig. 1-6). The $E^r_{½}$ values are shifted towards more negative direction with increase in the percentage of formamide (20-60% v/v).

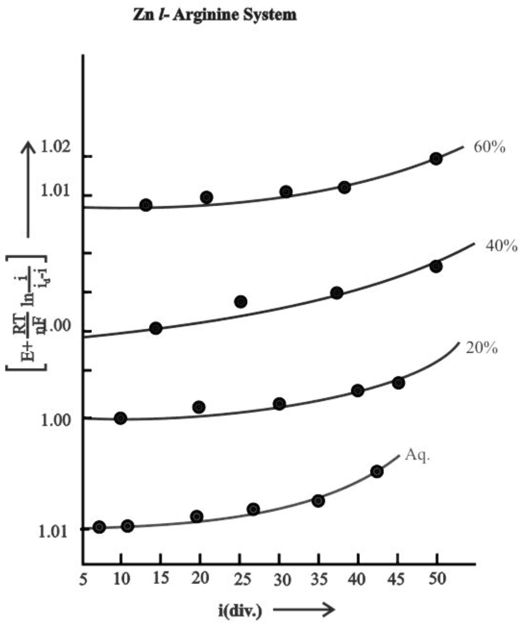
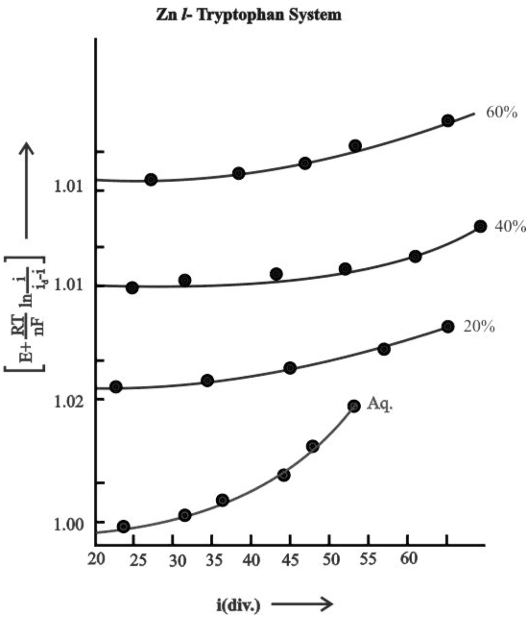


Fig.1



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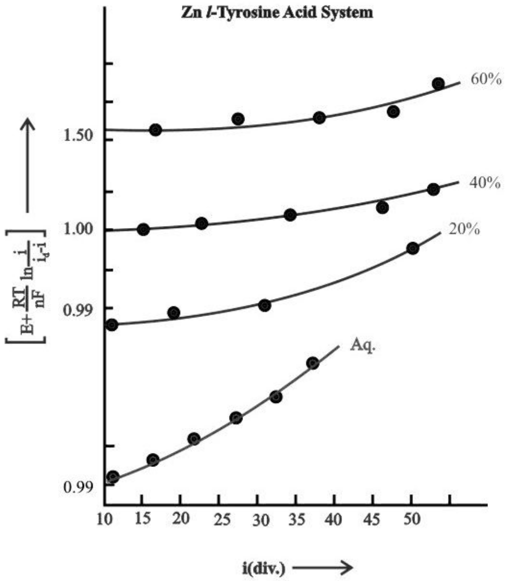

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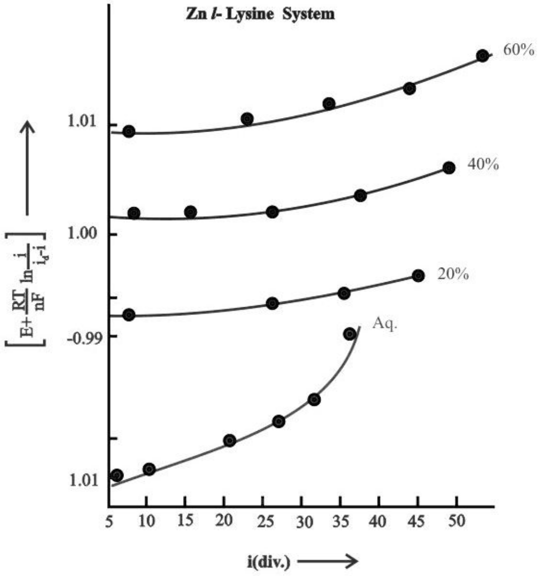

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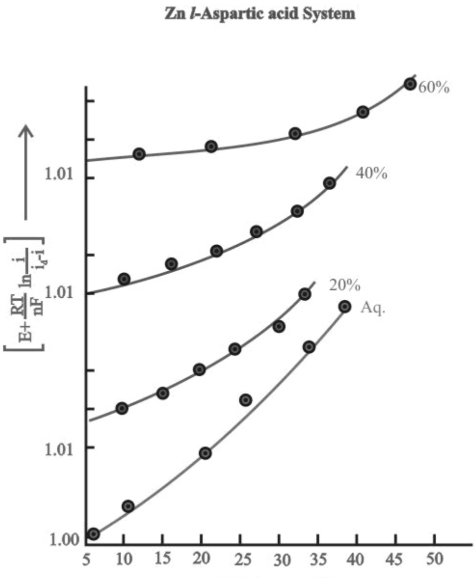


Fig.5

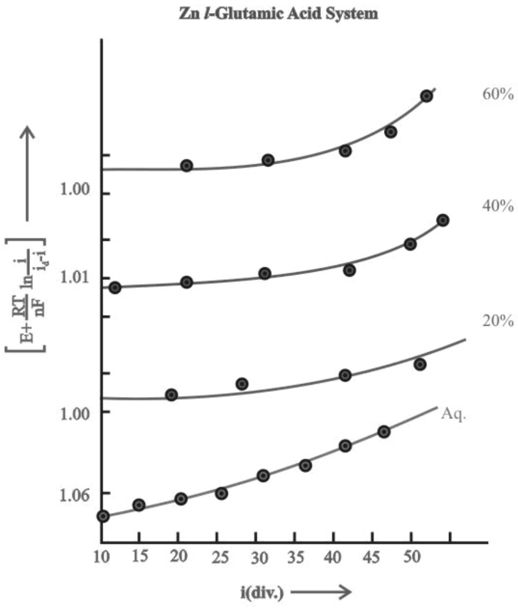


Fig.6

Plots of $\left[\mathbf{E+\frac{RT}{nF}\ln\frac{i}{i_d - i}}\right]$ **v/s i for 1.0 mM Zn(II) complexes in formamide**

In present investigation, it has been observed that $E_{½}$ values shifted towards more cathodic direction with the increase in the percentage of formamide (20-60% v/v). The shift in $E_{½}$ values of Zn (II) *l*-aspartate complex is more when compared with Zn (II) *l*-lysine, *l*-glutamic acid, *l*-arginine, *l*-tyrosine and *l*-tryptophan systems, which clearly indicates more irreversibility of electrode processes. Further greater irreversibility of Zn (II) *l*-aspartate complex is confirmed by the slope values.

Kinetic parameters (α, λ and k_S) have been determined from the plots of log (z–1) vs ξ, where ξ is $\frac{nF}{2.303R\left(E-E^{r}_{1/2}\right)}$.The plots of log (z – 1) vs ξ are given in Figures 7-30. The k_S values suggest the irreversibility of the electrode processes for Zn (II) *l*- arginine complexes show a decrease in forty percentage formamide while it increases in sixty percentage formamide.

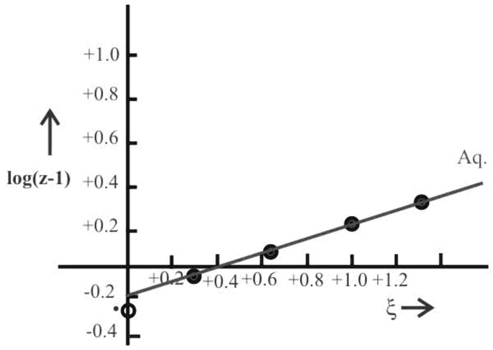
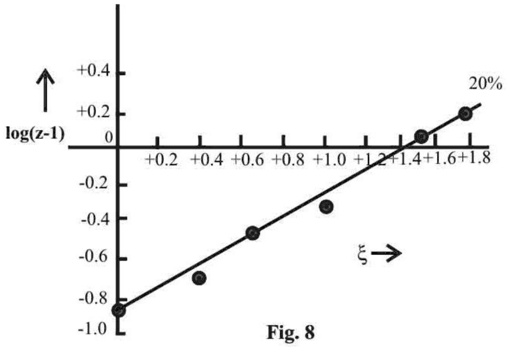


Fig. 7



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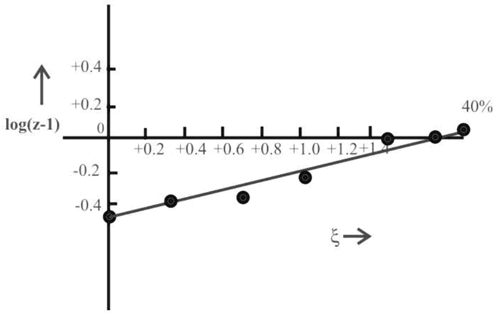

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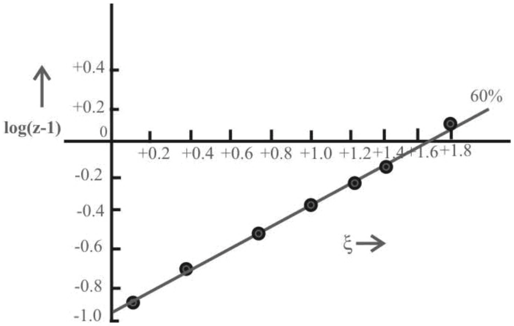

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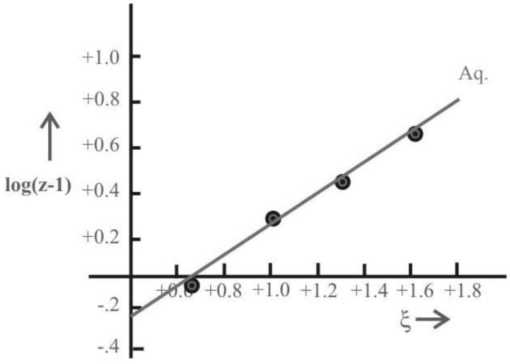

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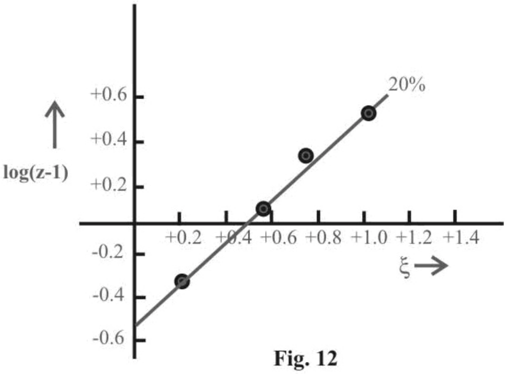

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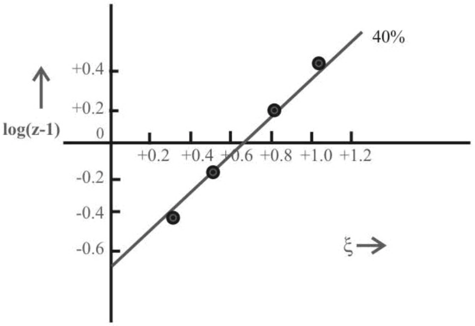
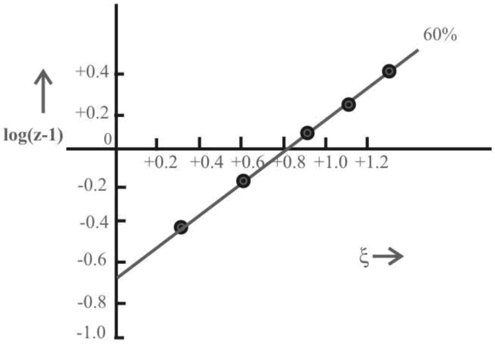


Fig. 13



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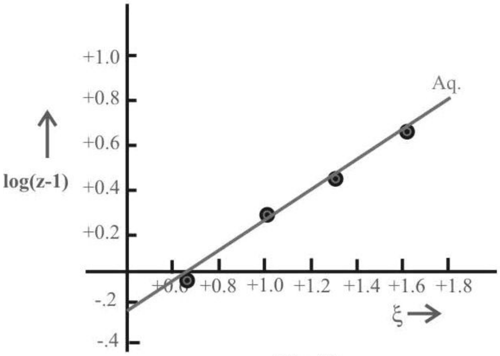

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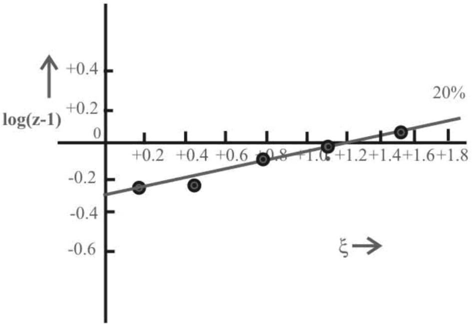

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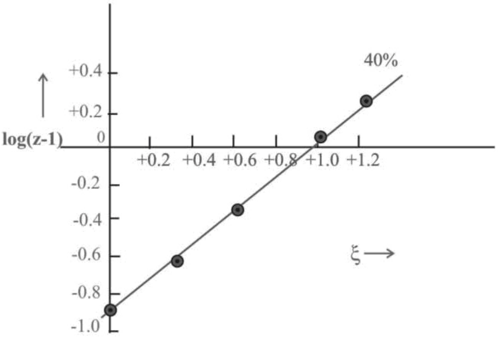
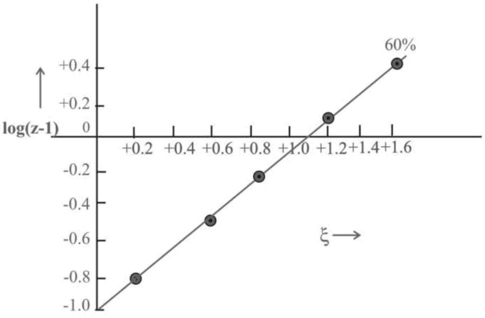


Fig. 17



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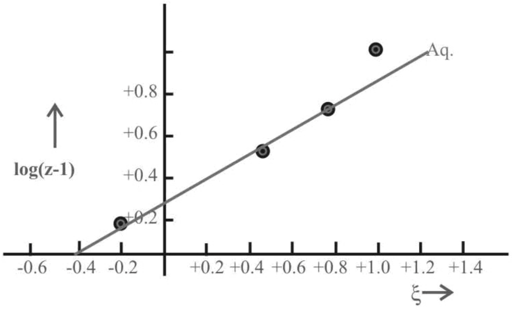


Fig. 19

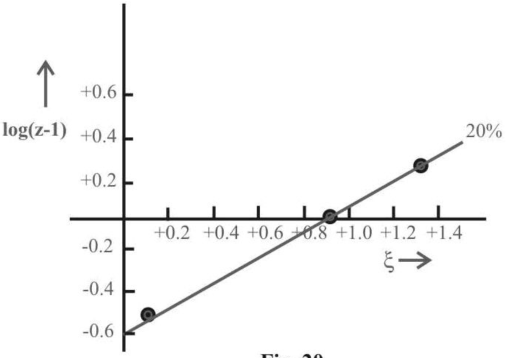
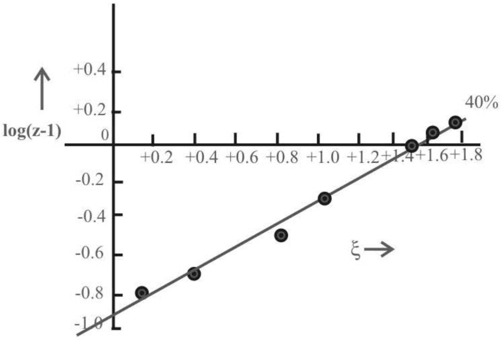


Fig. 20



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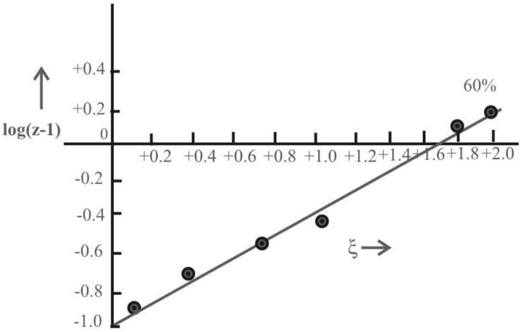

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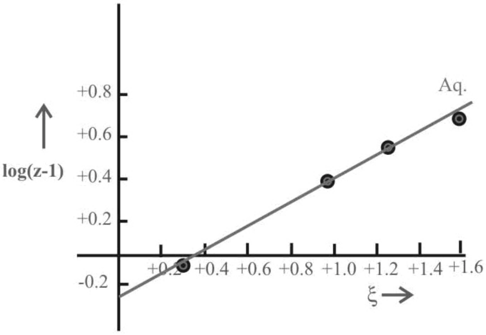

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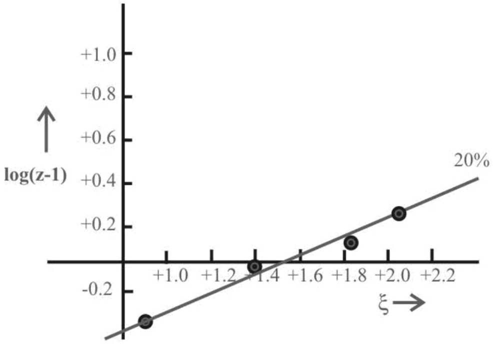

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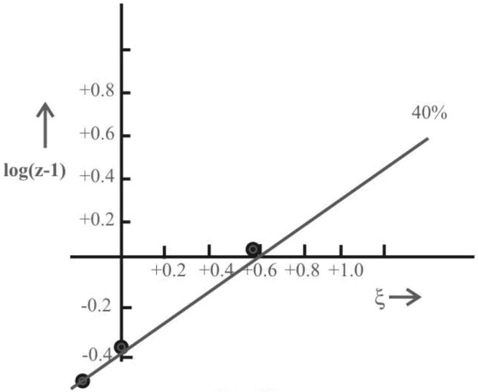

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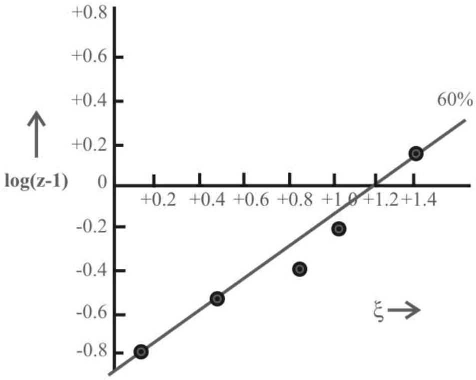

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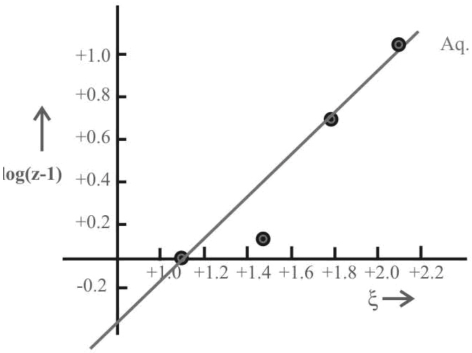

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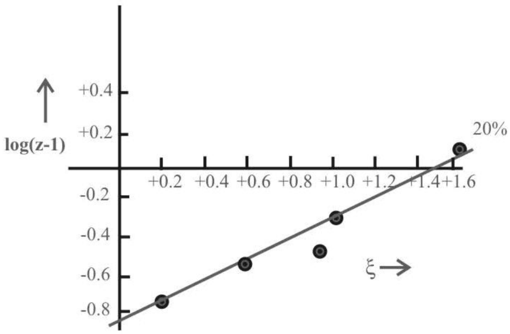

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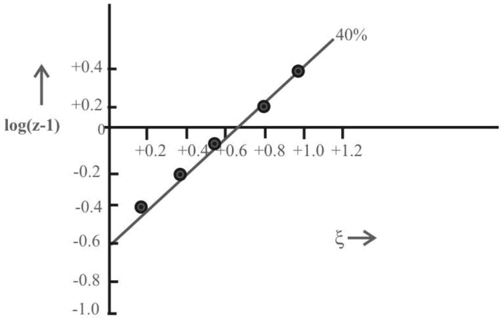

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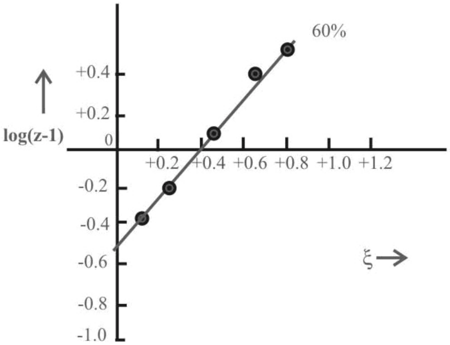

Fig. 30

The variation in polarographic characteristics of the complexes and the irreversibility of the electrode processes with change in solvent composition may be attributed to the properties of the solvent. The structure of double layer also plays the significant role in electrode kinetics. In Zn (II)– *l*-glutamic acid complex, the k_S value increases from (20 - 60 % v/v) formamide mixture, suggesting that irreversibility of the electrode processes decreases.

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