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Study of Electrode Kinetics of Zn^{2+}–L-Amino Acids–γ-Picoline Mixed System

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Polarography was used to determine the stability constants ($\log\beta$) of ternary complexes of Zn^{2+} with L-lysine, L-ornithine, L-threonine, L-serine, L-phenylglycine, L-phenylalanine, L-glutamic acid, and L-aspartic acid as primary ligands and γ-picoline as secondary ligand at pH = 8.50±0.01 and ionic strength μ = 1.0 mol dm^{-3} $NaClO_4$ at 25 °C. The waves of Zn and its complexes were quasireversible. Zn formed 1 : 1 : 1, 1 : 1 : 2, and 1 : 2 : 1 complexes. The kinetic parameters viz. the standard rate constant (k), degree of irreversibility (λ), and charge transfer coefficient (α) were also determined. The trend of the stability constants of Zn^{2+} complexes with these amino acids and γ-picoline is L-lysine < L-ornithine < L-threonine < L-serine < L-phenylglycine < L-phenylalanine < L-glutamic acid < L-aspartic acid, which is explained on the basis of the sizes and basicities of the primary ligands.

The chelating ability of amino acids with various metal ions has been long known.[1—3] The complexes of amino acids with transition metals are used in cancer therapy, pharmacy, and industry.[4,5] Amino acids are biologically active, thus creating considerable interest in their metal complexes. Whenever the concentration of various essential metals increases in blood and serum, as a result of uptake of polluted water or infected food, human beings suffer from several disease, such as cancer of the bladder, breast, intestine, leukemic system, ovary, pancreas, prostate, lungs, rectum or skin. The concentration of these metals can be reduced in vivo by ligand (L-amino acid) therapy.[6]

On the other hand, the kinetic parameters viz. the standard rate constant (k), transfer cofficient (α), and degree of irreversibility (λ) are very useful for studying the nature of electrode processes.

A survey of the literature has revealed that no reference is available regarding the ternary complexes of Zn^{2+} with selected L-amino acids as primary ligands and γ-picoline as a secondary ligand, by any method; hence, the authors studied these ternary complexes using a polarographic technique, with the view to determine the stability constants and kinetic parameters of these ternary systems.

Experimental

Zinc chloride (Aldrich, USA), $NaClO_4$ (Fluka, Switzerland), L-amino acids (BDH), and γ-picoline (Fluka) were used, and their solutions were prepared in conductivity water. The purity of amino acids was checked by chromatography.[7] The concentrations of the metal ion and $NaClO_4$ in the test solution were 0.5 mmol dm^{-3} and 1.0 mol dm^{-3}, respectively. γ-Picoline was used without further purification. Pure hydrogen gas was passed through each test solution before recording the current–voltage data.

Current–voltage measurements were made on a manual polarograph using a (Toshniwal PL-50) polyflex galvanometer. The capillary characteristics were $m^{2/3}t^{1/6}$ = 2.40 mg$^{2/3}$ S$^{-1/2}$ at a 60.02 cms (calculated) effective height of mercury. An Elico (LI-120) pH meter was used to measure the pH values of the solutions, which were adjusted to 8.50±0.01 with dilute solution of NaOH or $HClO_4$, as required. The temperature was maintained constant at 25 °C.

Results and Discussion

Zn–L-Amino Acidate–γ-Picoline Complexes: Zn^{2+} gave a well-defined two-electron quasireversible reduction wave in 1.0 mol dm^{-3} $NaClO_4$ at pH = 8.50±0.01 at 25 °C. The value of $(E_{1/2})^{\text{quasireversible}}$ of Zn^{2+} was −1.010 V vs. SCE, which by the Gellings method[8] gave $(E_{1/2})^{\text{reversible}} = -0.989$ V. Similarly, $(E_{1/2})^{\text{reversible}}$ from $(E_{1/2})^{\text{quasireversible}}$ of complexes for the corresponding concentration of the ligand was also calculated. In all cases, the irreversiblity increased along with an increase in the concentration of the ligand. The depolariser and ligands (L-amino acids and γ-picoline) were used in the ratio 1 : 40 : 40, and current–voltage curves were obtained for different pH values; it has been observed that the maximum shifts of $E_{1/2}$ could be obtained at pH 8.50±0.01; therefore, this range of pH was selected for the present study. The free-ligand concentrations of L-amino acids were calculated based on their pK^{H}_{2} (e.g. L-lysine $H^{+}{}_3N(CH_2)_4CH(NH_2)COO^{-} + H_2O \overset{K_2^H}{\rightleftharpoons} H_3O^{+} + H_2N(CH_2)_4CH(NH_2)COO^{-}$, p$K^{H}_{2}$ = 8.95) and the experimental pH of the study. The Schaap and McMaster method[9] was used to study ternary complex formation. In ternary complexes, the concentration of L-amino acid varied from 0.50 mmol dm^{-3} to 50.00 mmol dm^{-3}. For calculations of β_{11} and β_{12}, a study was carried out at 0.025 and 0.050 mol dm^{-3} of γ-picoline. The quasireversible nature of the waves was confirmed based on the kinetic parameters given in Table 2. The data and plots are of the Schaap and McMaster function,[9] values of

F_{ij}[X,Y] vs. [X] {where i & j are stoichiometric numbers for the primary ligand X (i.e. L-amino acids) and secondary ligand Y (i.e. γ-picoline), respectively; [ ] stands for concentration)} are given in Table 1 and Fig. 1, respectively. Plots of log $(Z-1)$ vs. $(E^{\mathrm{r}}_{1/2}-E)$[10] for Zn and its complexes are given in Figs. 2 and 3, respectively. The parameter, which is a measure of degree of irreversibility (Z), is given by the following equation:[10]

$$Z = \text{antilog}\,\{nF/2.303RT(E^{\mathrm{r}}_{1/2}-E)\} + \log i_{\mathrm{d}} - i/i.$$

Comparison of Stability of Complexes: The value of the mixing constant, $\log k_{\mathrm{m}}$, which is a measure of comparing the stability of binary and ternary complexes, can be calculated by the following equation:[11]

$$\log k_{\mathrm{m}} = \log \beta_{11} - 1/2[\log \beta_{20} + \log \beta_{02}].$$

The values of $\log k_{\mathrm{m}}$ are −0.465, −0.353, 0.570, −0.468, −0.463, −0.361, 0.070 and 0.176, for [Zn–L-lys.–γ-pic.], [Zn–L-orn.–γ-pic.], [Zn–L-threo.–γ-pic.], [Zn–L-ser.–γ-pic.], [Zn–L-phenylgly.–γ-pic.], [Zn–L-phenylala.–γ-pic.], [Zn–L-glu.–γ-pic.], and [Zn–L-asp.–γ-pic.] systems, respectively (Table 3). The positive values of $\log k_{\mathrm{m}}$ indicate that the ternary complexes are more stable than their parent binary complexes, while the negative values indicate that binary complexes are more stable than their ternary complexes.[11]

It is clear from the values of the standard rate constant

Table 1. Polarographic Characteristics and F_{ij}[X,Y] Values for the Zn^{2+}–L-Lysinate–γ-Picoline System
$[Zn^{2+}] = 0.5$ mmol dm^{-3}, $\mu = 1.0$ mol dm^{-3} NaClO$_4$, pH = 8.50±0.01, Temp = 25 °C

	$[\gamma-\text{picoline}]=0.025$ mol dm^{-3}(fixed)						
[L-lys] × 10^{-3}	$(E_{1/2})^{\mathrm{q.r.}}$ V vs. SCE	$(\Delta E_{1/2})^{\mathrm{r.}}$ V	$\log \frac{I_{\mathrm{m}}}{I_{\mathrm{c}}}$	F_{00}[X,Y] × 10^{-1}	F_{10}[X,Y] × 10^{-4}	F_{20}[X,Y] × 10^{-7}	F_{30}[X,Y] × 10^{-9}
0.00	1.010	—	—	—	—	—	—
0.50	1.066	0.0516	0.0068	5.67	10.19	16.43	1.98
1.00	1.078	0.0669	0.0137	19.08	18.50	16.53	1.99
2.00	1.099	0.0837	0.0208	71.46	35.44	16.73	1.99
3.00	1.107	0.0937	0.0280	158.89	52.77	16.93	1.99
4.00	1.114	0.1011	0.0280	282.58	70.50	17.13	1.99
5.00	1.121	0.1067	0.0353	443.72	88.62	17.33	1.99
6.00	1.132	0.112	0.0427	643.50	107.15	17.53	1.99
8.00	1.139	0.1186	0.0503	1163.76	145.39	17.92	1.99
10.00	1.142	0.1246	0.0503	1852.93	185.23	18.32	1.99
20.00	1.160	0.1434	0.0579	8166.52	408.29	20.31	1.99
30.00	1.177	0.1550	0.0579	20135.36	671.15	22.30	1.99
40.00	1.182	0.1632	0.0658	38953.43	973.82	24.29	1.99
50.00	1.189	0.1697	0.0737	65814.74	1316.28	26.28	1.99

$(E_{1/2})^{\mathrm{q.r}} \pm 0.0003$

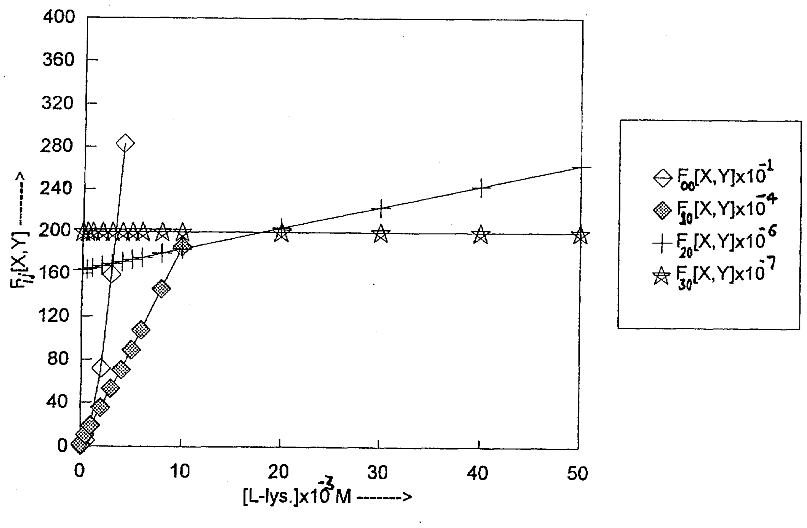
$\log A = 0.76$, $\log C = 8.21$,
$\log B = 4.29$, $\log D = 9.30$.

	$[\gamma-\text{picoline}]=0.050$ mol dm^{-3}(fixed)						
[L-lys] × 10^{-3}	$(E_{1/2})^{\mathrm{q.r.}}$ V vs. SCE	$(\Delta E_{1/2})^{\mathrm{r.}}$ V	$\log \frac{I_{\mathrm{m}}}{I_{\mathrm{c}}}$	F_{00}[X,Y] × 10^{-1}	F_{10}[X,Y] × 10^{-4}	F_{20}[X,Y] × 10^{-7}	F_{30}[X,Y] × 10^{-9}
0.00	1.010	—	—	—	—	—	—
0.50	1.077	0.0616	0.0068	12.42	21.61	32.22	1.98
1.00	1.090	0.0763	0.0137	39.43	37.82	32.30	1.99
2.00	1.106	0.0925	0.0208	142.67	70.53	32.50	1.99
3.00	1.116	0.1024	0.0280	312.51	103.63	32.70	1.99
4.00	1.125	0.1094	0.0353	550.16	137.13	32.90	1.99
5.00	1.134	0.1151	0.0353	856.81	171.03	33.10	1.99
6.00	1.136	0.1196	0.0427	1233.64	205.33	33.20	1.99
8.00	1.150	0.1268	0.0503	2202.66	275.13	33.70	1.99
10.00	1.156	0.1324	0.0579	3466.76	346.51	34.10	1.99
20.00	1.170	0.1508	0.0579	14547.96	727.31	36.09	1.99
30.00	1.182	0.1616	0.0658	34439.20	1147.91	38.08	1.99
40.00	1.189	0.1696	0.0658	64334.47	1608.32	40.07	1.99
50.00	1.195	0.1755	0.0819	105427.79	2108.52	42.06	1.99

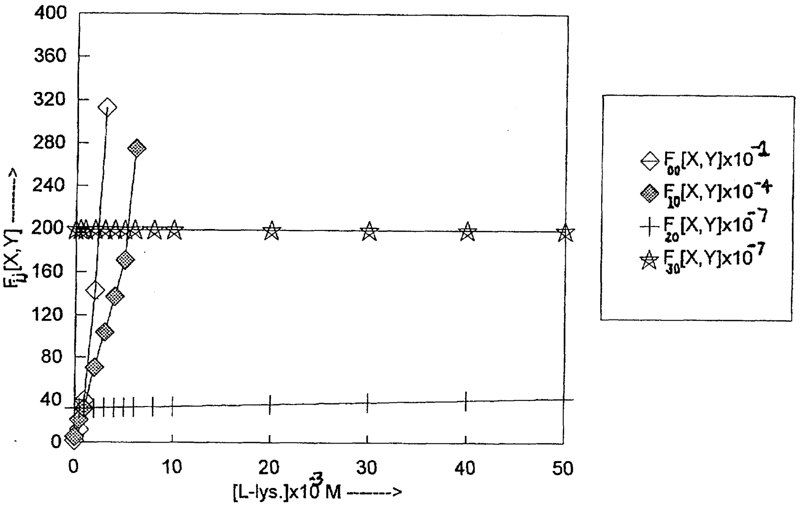
$(E_{1/2})^{\mathrm{q.r}} \pm 0.0003$

$\log A = 1.20$, $\log C = 8.50$,
$\log B = 4.74$, $\log D = 9.30$.

$(E_{1/2})^{\mathrm{q.r}} = (E_{1/2})^{\mathrm{quasireversible}}$, $(\Delta E_{1/2})^{\mathrm{r.}} = (\Delta E_{1/2})^{\mathrm{reversible}}$.



γ-Picoline=0.025M (Fixed)



γ-Picoline=0.050M (Fixed)

Fig. 1. Zn–L-lysinate–γ-picoline system.

Table 2. Kinetic Parameters of Zn^{2+}–L-Lysinate–γ-Picoline System
$[Zn^{2+}] = 0.5$ mmol dm^{-3}, $\mu = 1.0$ mol dm^{-3} $NaClO_4$, pH = 8.50±0.01, Temp = 25 °C

	[γ-picoline]=0.025 mol dm^{-3}(fixed)						[γ-picoline]=0.050 mol dm^{-3}(fixed)					
[L-Lys.] × −3	$(E_{1/2})^r$	Slope	α	γ	$D_{1/2}$	k	$(E_{1/2})^r$	Slope	α	γ	$D_{1/2}$	k
	V vs. SCE	mV			$10^3 cm^2 s^{-1}$	$\times 10^3 cm\, s^{-1}$	V. vs SCE	mV			$\times 10^3 cm^2 s^{-1}$	$\times 10^3 cm\, s^{-1}$
0.00	0.989						0.989					
0.50	1.040	40.0	0.478	1.18	4.32	5.10	1.050	42.5	0.503	1.18	4.32	5.10
1.00	1.055	37.5	0.509	1.05	4.25	4.47	1.065	37.5	0.465	1.32	4.25	5.63
2.00	1.072	40.0	0.478	1.18	4.18	4.94	1.081	42.5	0.494	1.05	4.18	4.40
3.00	1.082	40.0	0.462	1.25	4.11	5.14	1.091	40.0	0.444	1.32	4.11	5.45
4.00	1.090	37.5	0.490	1.05	4.11	4.33	1.098	37.5	0.519	1.18	4.04	4.77
5.00	1.095	37.5	0.499	1.18	4.04	4.77	1.104	45.0	0.514	1.05	3.04	4.25
6.00	1.100	42.5	0.509	1.05	3.98	4.18	1.108	40.0	0.499	1.05	3.98	4.18
8.00	1.107	37.5	0.499	1.18	3.91	4.61	1.115	45.0	0.494	1.05	3.91	4.11
10.00	1.113	40.0	0.478	1.05	3.91	4.11	1.121	42.5	0.471	1.05	3.84	4.04
20.00	1.132	40.0	0.519	1.18	3.84	4.53	1.139	45.0	0.494	1.18	3.84	4.53
30.00	1.144	42.5	0.519	1.18	3.84	4.53	1.150	40.0	0.494	1.05	3.77	3.97
40.00	1.152	40.0	0.499	1.11	3.77	4.20	1.158	42.5	0.438	1.05	3.77	3.97
50.00	1.158	40.0	0.519	1.05	3.70	3.89	1.164	45.0	0.503	1.11	3.63	4.05

$(E_{1/2})^r \pm 0.0001$—± 0.0003, $\alpha \pm 0.0002$, $\lambda \pm 0.002$, $k \times 10^3 \pm 0.03$, $(E_{1/2})^r \pm 0.0001$—± 0.0003, $\alpha \pm 0.0002$, $\lambda \pm 0.002$, $k \times 10^3 \pm 0.03$.

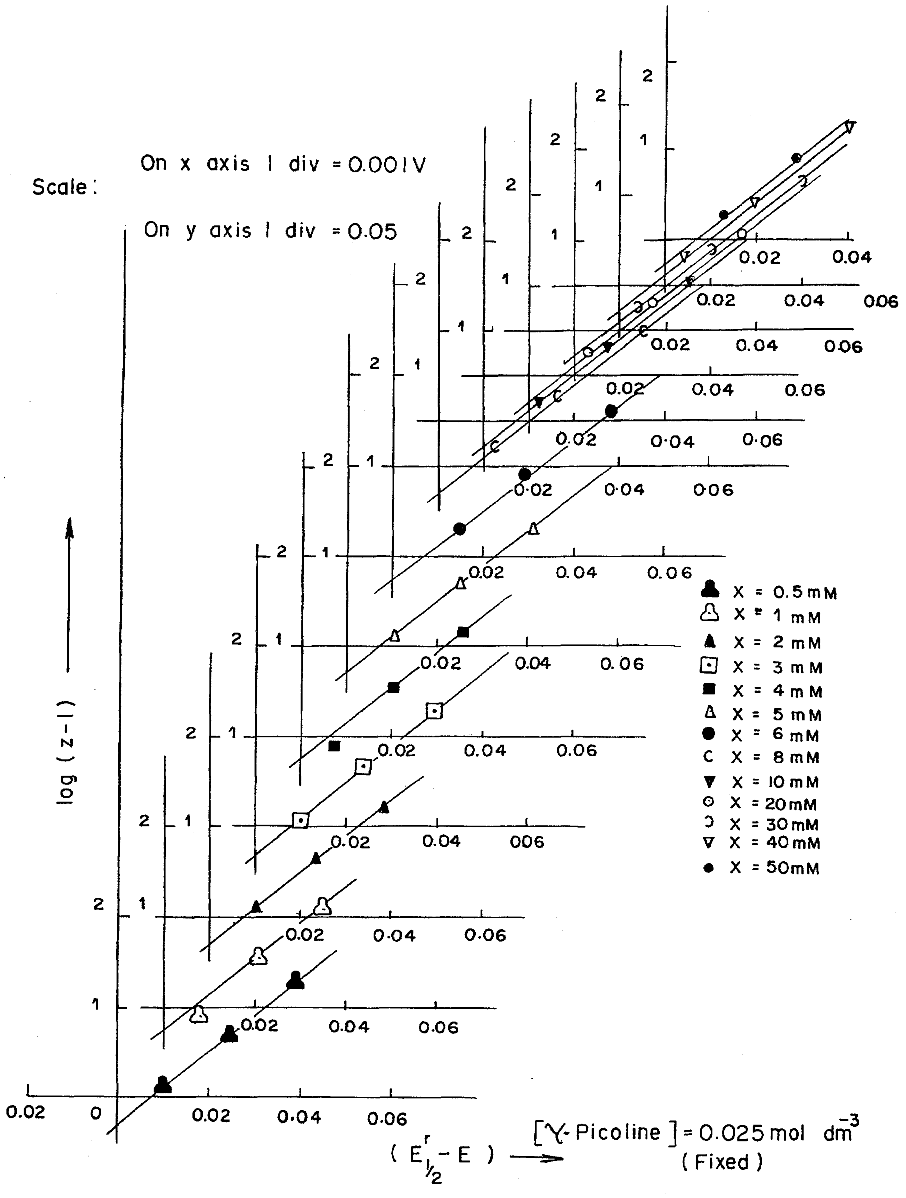


Fig. 2. Zn–L-lysinate–γ-picoline system.

Table 3. Stability Constants of Zn^{2+}–L-Amino Acidate–γ-Picoline System
$[Zn^{2+}] = 0.5$ mmol dm^{-3}, $\mu = 1.0$ mol dm^{-3} $NaClO_4$, pH = 8.50±0.01, Temp = 25 °C

		Binary complexes[16]							
Ligands	pK_2^H	$\log\beta_{01}$	$\log\beta_{02}$	$\log\beta_{10}$	$\log\beta_{20}$	$\log\beta_{30}$	$\log\beta_{11}$	$\log\beta_{12}$	$\log\beta_{21}$
L-Lysine	8.95	—	—	3.85	6.75	9.30	4.71	7.26	9.80
L-Ornithine	8.98	—	—	3.92	6.86	9.49	4.87	7.51	—
L-Threonine	9.00	—	—	4.34	7.46	9.62	4.96	7.93	10.16
L-Serine	9.20	—	—	4.41	7.59	9.80	5.12	8.18	10.40
L-Phenylglycine	9.23	—	—	4.48	7.73	9.89	5.20	8.35	10.64
L-Phenylalanine	9.30	—	—	4.55	7.86	10.08	5.36	8.60	—
L-Glutamic acid	9.67	—	—	5.60	8.90	10.10	6.32	9.66	10.81
L-Aspartic acid	9.82	—	—	5.67	9.02	10.30	6.48	9.91	11.04
γ-Picoline[17]	—	1.90	3.60	—	—	—	—	—	—

$\log\beta_{10}\pm0.01$—±0.02, $\log\beta_{20}\pm0.02$, $\log\beta_{30}\pm0.01$, $\log\beta_{11}\pm0.01$, $\log\beta_{12}\pm0.02$, $\log\beta_{21}\pm0.02$.

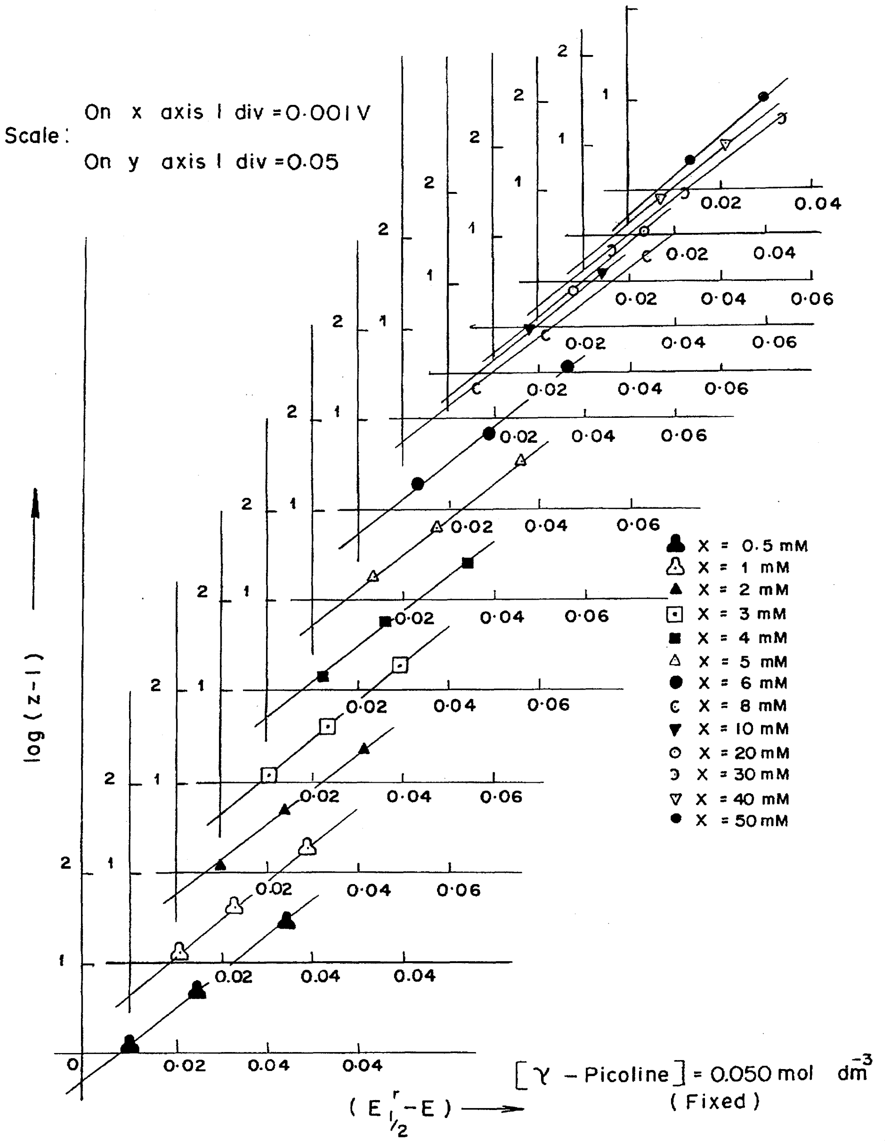


Fig. 3. Zn–L-lysinate–γ-picoline system.

(k) (Table 2) of Zn and its complexes, which are in the order of 10^{-3} cm s^{-1}, that the electrode processes were quasireversible.[12] The charge-transfer coefficient (α), signifies the fraction of the applied voltage, which favors the cathodic reaction $M^{2+}+2e \rightarrow M$ (Where M stands for the reduced species), also has the expected values.[13] The values of the standard rate constant confirmed that the reduction of electroactive species at the surface of the dropping mercury electrode is not fast.

The sequence of the stability constants of complexes with respect to the ligands is L-lysine < L-ornithine < L-threonine < L-serine < L-phenylglycine < L-phenylalanine< L-glutamic acid < L-aspartic acid. It has been observed by us that as the size of the amino acid increased, the stability of its complex decreased.[14]

In this study, the stability of the lysinate complex is minimum, owing to the lowest pK value of L-lysine. As the pK values decrease, the stability constants of the complexes decrease.[15] In the case of L-serine and L-threonine, the stability of the L-threonine complex is smaller than that of the L-serine complex, owing to the fact that the electron-withdrawing –OH group, which is nearer in the L-threonine complex than L-serine complex, causes greater repulsive forces between the zinc and the –OH group in L-threonine complexes than in L-serine complexes. The effect of the size on the stability of complexes was observed in all of the selected amino acids, except for in the case of the L-phenylglycine and L-phenylalanine complexes, where the order of the stability constants is reversed i.e. L-phenylglycine < L-phenylalanine. This can be explained by the fact that the presence of the phenyl group lies at the α-carbon atom in L-phenylglycine, while it is on the β-carbon atom in the case of L-phenylalanine, causing, greater repulsive forces in the former case than in the latter one.

The higher stability of L-aspartate complexes than that of L-glutamate complexes is obvious based on the result of the chelate-ring formation of these amino acids with the metal ion. As the aspartate formed one five- and one six- membered ring with the metal ion, while L-glutamate forms one six- and one seven- membered ring with the metal ion. As the size of the ring increases, the stability of complexes decreases.[14] The stabilities of the L-glutamate and L-aspartate complexes are higher than that of the L-lysinate, L-ornithinate, L-threoninate, L-serinate, L-phenylglycinate, and L-phenylalaninate complexes, because of the large differences in their basicities.

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