Ternary Complexes of Zn^{2+} with some L-Amino acids and Nicotinic acid - A Polarographic Study

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Effects of size, basicity and steric hindrance of the amino acid (primary ligand) on the stability constants of ternary complexes of Zn^{2+} have been ascertained in solution of pH=8.50±0.01 at μ=1.0 $NaClO_4$ at 25°C.

The chelating ability of amino acids and the uses of their compounds in biology, medicine and as laboratory reagents are well known [1-3]. Aspartic acid and glutamic acid play an important role in transamination, decarboxylation cell metabolism and neurotransamination [4-7]. Basicity of the primary ligand and its steric hindrance is likely to affect the stability of the ternary complex but no references could be found. So in this study, the 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 nicotinic acid (vitamine B_5) as the secondary ligand have been reported.

EXPERIMENTAL

A.R. Grade chemicals and doubly distilled water were used to prepare all the solutions. Chromatographic method was used to check the purity of amino acids [8].

A manual polarograph using polyfelx galvanometer (pL-50) was used to record the current-voltage data. The mass flow of mercury in the capillary was 2.4 $mg.sec^{-1}$ at 60.02 cms effective hight of mercury (calculated) [9]. Metal ion concentration was 1.0 mM; ionic strength was maintained at μ = 1.0 M with sodium perchlorate solution while concentration of the ligand varied. A digital type pH meter was used to measure the pH of the test solution (adjusted with dilute solutions of sodium hydroxide or perchloric acid as required). Hydrogen gas was passed through each test solution before recording the current-voltage data. The entire study was carried out at 25°C.

RESULTS AND DISCUSSION

The reduction wave of Zn^{+2} is well defined, two electron, quasi-reversible step. The depolarizer and ligands (i.e L-amino acid and nicotinic acid) were taken in the ratio 1:40 in case of binary complexes and 1:40:40 in case ternary complexes and current-voltage curves were drawn at different pH values. The shift of $E_{1/2}$ was observed to be maximum at pH=8.50; hence pH 8.50±0.01 was selected for the present investigation.

The wave was quasi-reversible and the irreversibility increased with increase in concentration of ligand. Deford and Hume's [10] method modified by Irving [11] has been used to determine the composition and stability constants of complexes with each selected amino acid. The free ligand concentration of amino acid was calculated from pK^{II}_2 values of amino acid, but the analytical concentration of nicotinic acid was taken as ligand concentration in the

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Table 1

Acid dissociation Constants (pK_2^H) and Stability Constants (log ß) of the Various Complex Species

Ligand	acid pK_2^H	log ß of Binary compl. 1:1	1:2	1:3
Lysine	8.95	3.85	6.73	9.3
Ornithine	8.98	3.92	6.85	9.49
Threonine	9	4.34	7.46	9.62
Serine	9.2	4.41	7.59	9.8
Phe.glycine	9.23	4.48	7.73	9.89
Phe.alanine	9.3	4.55	7.86	10.08
Glutamic acid	9.67	5.6	8.9	10.1
Aspartic acid	9.82	5.67	9.03	10.3
Nicotinicacid	-	1.60	2.80	-

calculation. The values of stability constants were given in Table 1.

Ternary Complexes [Zn-L-amino acidate-nicotinic acid]

The $E_{1/2}$ became more negative with the addition of nicotinic acid to the Zn(L-amino acidate) system showing the formation of mixed ligand complex. The waves were quasi-reversible and diffusion controlled; the $(E_{1/2})_a^{rev.}$ were calculated by applying modified Gellings method [12]. Schaap and Memasters' method [13] showed the formation of 1:1:1 and 1:1:2 and 1:2:1 complexes of Zn^{2+} with any selected L-amino acid as primary ligand and nicotinic acid as the secondary ligand. Polarograms were taken at two fixed concentrations (0.025 and 0.05 M) of nicotinic acid while varying the concentration of L-amino acidate from 0.5mM to 50mM and the values of $ß_1$ & $ß_2$ were calculated. Typical data and plots of $F_{ij}[X,Y]$ vs [X] where [X] = L-lysinate ion and [Y] = nicotinic acid are given in Table 2

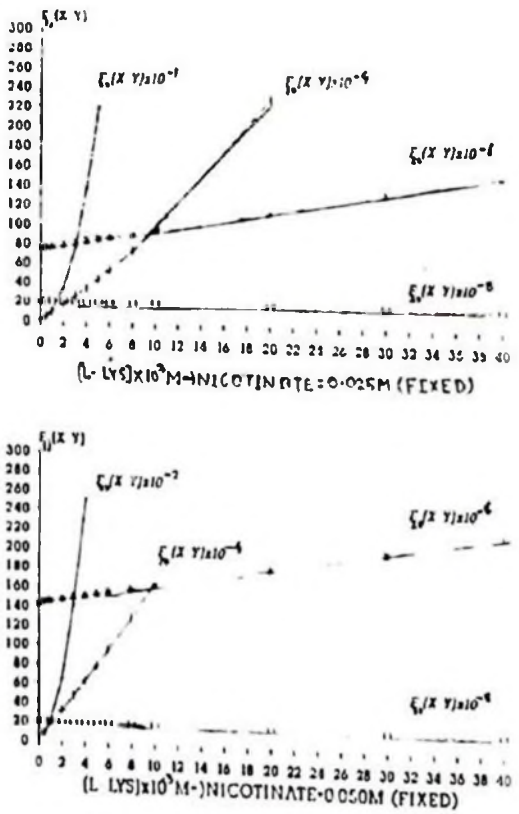


Fig 1 $F_{i,j}[X,Y]$ vs [X] plots
Metal Zn^{2+}; X = Lysinate anion; Y = Nicotinate

Table 2

Polarographic Characteristics of Zinc- L-Lysinate- Nicotinate System

$(E_{1/2})_M$ = -0.989 V vs SCE; μ = 1.0 M $NaClO_4$; pH = 8.50±0.01; Temp. = 25°

[Lycinate]	Nicotinate = 0.025 M			Nicotinate = 0.050 M		
x 10^3 M	$E_{1/2}$	$\Delta E_{1/2}^{rev}$	log I_m/I_c	$E_{1/2}$	$\Delta E_{1/2}^{rev}$	log I_m/I_c
0.50	1.050	0.041	0.00683	1.056	0.050	0.00683
1.00	1.070	0.057	0.00683	1.075	0.065	0.01378
2.00	1.079	0.073	0.01378	1.086	0.082	0.01378
3.00	1.088	0.084	0.01378	1.098	0.092	0.02085
4.00	1.099	0.092	0.01378	1.107	0.099	0.02085
5.00	1.101	0.097	0.02085	1.112	0.105	0.02085
6.00	1.109	0.102	0.02085	1.118	0.100	0.02802
8.00	1.118	0.110	0.02085	1.126	0.117	0.02802
10.00	1.121	0.116	0.02085	1.132	0.123	0.02802
20.00	1.145	0.136	0.02802	1.151	0.142	0.03532
30.00	1.158	0.149	0.02802	1.163	0.154	0.04275
40.00	1.169	0.158	0.03532	1.172	0.162	0.05030
50.00	1.173	0.165	0.03532	1.179	0.169	0.05030
log A=0.37; logB=4.04; logC=7.87; logB=9.29;				logA=0.65; logB=4.35; logC=8.15; logD=9.29		

and Fig.1 respectively. The stability constants of ternary complexes are presented in Table 3. The trend of stability constant obtained is in the order L-lys. <L-orn. <L-threo. <L-ser. <L-phenylgly. <L-phenylala. <L-glu. <L-asp.

Mixing Constants

The values of mixing constant, $\log K_m$ (used to compare the stability of binary and ternary complexes) are calculated by the following equation:

$$\log K_m = \log \beta_{11} - 1/2(\log \beta_{20} + \log \beta_{02})$$

The values are found to be [Zn -lys.-nicotinic acid] -0.645, [Zn -orn.-nicotinic

Table 3

Stability Constants (log ß) of the Various Complex Species

Ligand	log ß of Ternary complex		
	1:1:1	1:1:2	1:2:1
Lysine	4.12	6.78	9.44
Ornithine	4.28	6.96	9.66
Threonine	4.37	7.58	9.95
Serine	4.53	7.73	10.18
Phe.glycine	4.62	7.85	10.11
Phe.alanine	4.78	7.99	10.33
Glutamic acid	5.82	9	10.41
Aspartic acid	5.98	9.12	10.64

acid] -0.55, [Zn -Threo.-nicotinic acid] -0.76, [Zn -ser.-nicotinic acid] -0.665, [Zn -phenylgly. -nicotinic acid] -0.645, [Zn -phenylala.-nicotinic acid] -0.55, [Zn -Glut. -nicotinic acid] -0.03, [Zn -Asp.-nicotinic acid] +0.065, showing ternary complexes are generally more stable than binary complexes.

Higher pK value, indicates higher stability of complexes [14]. The lesser stability of L-threoninate complexes than L-serinate is due to the presence of electron withdrawing OH group nearer to the metal ion resulting in greater repulsive forces in the L-threoninate complexes than in the L-serinate complexes. The constants vary with the size of L-amino acids except in L-phenylglycine and L-phenylalanine. Phenyl group lies on α-carbon atom in L-phenylglycine, whereas, it is at β-carbon atom in L-phenylalanine. This causes reversal in the order of stability. Steric hindrance is greater in the former than in the latter case resulting in greater stability of L-phenylalanine complexes than L-phenylglycine complexes. L-Glutamate complexes are less stable than L-aspartate complexes which might be a result of ring size; L-Gluamate formed five and seven membered rings in the complexes whereas five and six membered rings exist in aspartate complexes. Six membered ring is in any case more stable than five or seven membered rings [14]. The stabilities of the L-glutamate and L-aspartate complexes are greater than the others because of large difference in their basic strengths.

ACKNOWLEDGEMENT

The authors are thankful to the Head, Department of Chemistry, Dr. H.S. Gour University, Sagar, for providing the laboratory facilities.

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