Stability and some Structural Aspects in Complex Formation between Zinc(II) and Amino Acids and Propionic Acid : A Polarographic Study

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A few complexes of amino acids with zinc have been reported in the literature[1]. Recently, Zn^{II} complexes with a number of amino acids as primary ligands and acetic acid as secondary ligand have been reported from the author's laboratory[2]. Gergely[3] reported the mixed-ligand complex of Zn with amino acids using different techniques. In the present investigation, Zn^{II} complexes with L-lysine, L-ornithine, L-threonine, L-serine, L-phenylglycine, L-phenylalanine, L-glutamic acid and L-aspartic acid as primary ligands and propionic acid as a secondary ligand have been reported with the views to ascertain the effects of size, basicity and steric hindrance on the solution stability of binary and ternary complexes of Zn^{II} polarographically, for which no reference could currently be found out in the literature.

Results and Discussion

Zn^{II} gave a well-defined two-electron quasireversible reduction wave[4] in 1.0 M NaClO$_4$ at pH 8.50 ± 0.1. The metal and ligand (i.e. amino acid and propionic acid) were taken in the ratio 1 : 40 in case of binary and 1 : 40 : 40 in case of ternary complexes and the current-voltage curves have been drawn at different pH values. The maximum shifts of $E_{1/2}$ has been observed at pH 8.50 ± 0.1, hence this pH was selected for the present study.

Zn-propinate system : This system was studied at pH 8.50 ± 0.1 and μ = 1.0 M (NaClO$_4$) at 25°. The waves were quasireversible and dif-

fusion-controlled. The irreversibility increased with increase of concentration of propionic acid. Modified Gellings's method[5] have been applied to calculate the $E_{1/2}^r$ from $E_{1/2}$ vs SCE. Lingane's method[6] revealed the formation of 1 : 1 and 1 : 2 complexes of Zn^{II} with propionic acid with stability constant log β_{01} = 2.58 and log β_{02} = 3.98, respectively.

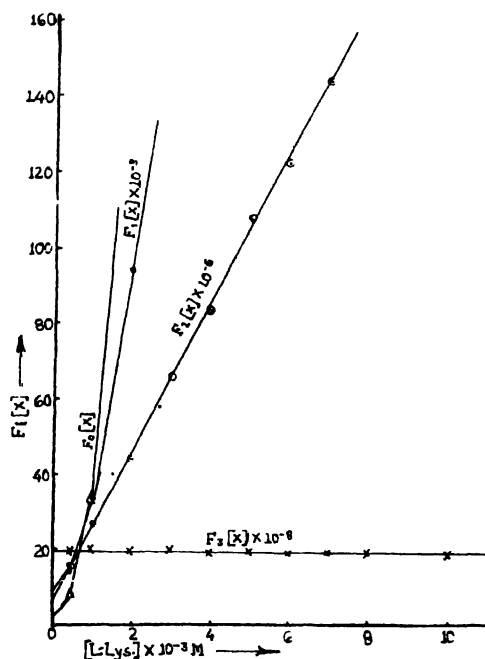*Zn-L-aminoacidate system* : This system has also been studied at pH 8.50 ± 0.1 and μ =

Fig. 1. Zinc-L-lysinate system.

TABLE 1—POLAROGRAPHIC CHARACTERISTICS OF Zn^{II}-L-LYSINATE SYSTEM AT 25°

μ = 1.0 M (NaClO$_4$), pH = 8.50 $\pm$ 0.1

Sl. no.	[L-Lys.] $\times 10^3 M$	$-E_{1/2}$ V vs SCE	$-E^r_{1/2}$	$\Delta E_{1/2}$	$\log \dfrac{I_m}{I_c}$	$F_{00}[X,Y]$ $\times 10^{-3}$	$F_{10}[X,Y]$ $\times 10^{-6}$	$F_{20}[X,Y]$ $\times 10^{-8}$	$F_{30}[X,Y]$ $\times 10^{-8}$
1.	0.00	1 01	0.989	–	–	–	–	–	–
2.	0.50	1.036	1.016	0.027	0 006 83	8.327	14 65	15.15	19.51
3.	1.00	1.055	1 034	0 045	0.006 83	33.85	32.85	26.77	20 38
4.	2.00	1.078	1 056	0.067	0.013 7	190.97	94.99	43.95	19 28
5.	3.00	1.094	1.071	0.082	0.013 7	314 58	204.17	65 81	20 14
6.	4.00	1.105	1 081	0.092	0.020 8	1 361.69	340.17	83.27	19 47
7.	5.00	1 115	1.09	0.101	0.020 8	2 745.61	548.92	108.37	20.59
8.	6 00	1.122	1.096	0.107	0.028 0	4 455.33	742.38	122.55	19 52
9.	7.00	1.129	1.102	0 113	0.028 0	7 110 82	1 015.59	144.08	19.81
10.	8.00	1.135	1.107	0 118	0.035 3	10 676 28	1 334 41	165.91	20 06
11.	10.00	1.144	1.115	0.126	0.035 3	19 913.15	1 991.21	198.41	19.30

$\log \beta_{10}$ = 3.85, $\log \beta_{20}$ = 6.73, $\log \beta_{30}$ = 9.30.
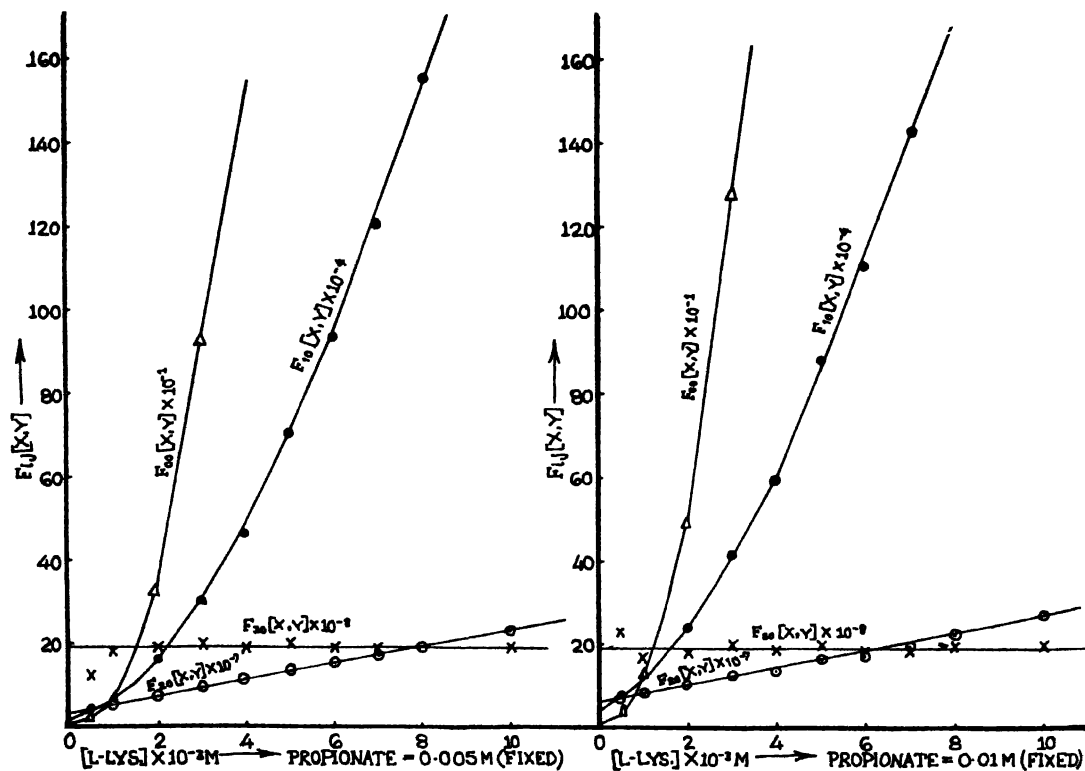

Fig. 2(a). Zinc-L-lysinate-propionate system.

1.0 M (NaClO$_4$) at 25°. The free ligand concentrations of amino acids were calculated from its pK_2^H values. The waves were quasireversible at lower concentrations, but at higher concentrations of ligands, irreversibility increased. Gellings's method has been applied to calculate of $E^r_{1/2}$ values. The composition and stability constants have been determined by DeFord and Hume method as modified by Irving[7]. The data and plots for [Zn-L-lysinate] system are given in Table 1 and Fig. 1 respectively.

*Zn-L-amino acidate-propionate system* : This system has also been carried out at pH 8.50

± 0.1 at μ = 1.0 M (NaClO$_4$). The waves were quasireversible and diffusion-controlled and the $E^r_{1/2}$ values were calculated by applying modified Gelling's method. Schapp and McMaster revealed the formation of 1 : 1 : 1, 1 : 1 : 2 and 1:2 : 1 complexes of Zn^{II} with L-lysine, L-ornithine. L-threonine, L-serine, L-phenylglycine, L-phenyla-
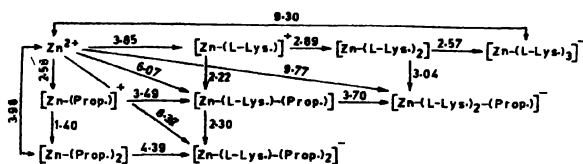
Scheme 1. [Zn-L-Lys.-Prop.] system.

lanine, L-glutamic acid and L-aspartic acid as primary ligands and propionic acid as secondary ligand. For the calculation of β$_{11}$ and β$_{12}$, the system was studied at two fixed concentrations
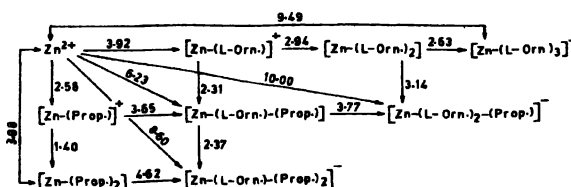
Scheme 2. [Zn-L-Orn.-Prop.] system.

TABLE 2–STABILITY CONSTANTS* OF TERNARY SYSTEMS OF Zn^{II} WITH L-AMINO ACIDS AND PROPIONIC ACID

pH = 8.50 ± 0.1, μ = 1.0 M (NaClO$_4$), Temp. = 25°

System	log β$_{11}$	log β$_{12}$	log β$_{21}$
[Zn- L-Lys.-Prop.]	6.07	8.37	9.77
[Zn-L-Orn.-Prop.]	6.23	8.60	10.0
[Zn-L-Threo.-Prop.]	6.27	8.69	10.09
[Zn-L-Ser.-Prop.]	6.43	8.91	10.31
[Zn-L-Phenylgly.-Prop.]	6.50	9.10	10.48
[Zn-L-Phenylala.-Prop.]	6.66	9.32	10.70
[Zn-L-Glut.-Prop.]	6.67	9.59	10.83
[Zn-L-Asp.-Prop.]	6.83	9.81	11.05

*Original values upto 4th. decimal place.

TABLE 2(a)–POLAROGRAPHIC CHARACTERISTICS AND F_{ij} [X,Y] VALUES FOR ZINC-L-LYSINATE-PROPIONATE SYSTEM

μ = 1.0 M (NaClO$_4$), pH = 8.50 ± 0.1, Temp. = 25°

Sl. no.	[L-Lys] × 10^3M	−$E_{1/2}$ vs SCE	−$E^r_{1/2}$	$\Delta E_{1/2}$	log $\frac{I_m}{I_c}$	$F_{00}[X,Y]$ × 10^{-1}	$F_{10}[X,Y]$ × 10^{-4}	$F_{20}[X,Y]$ × 10^{-7}	$F_{30}[X,Y]$ × 10^{-8}
Propionate = 0.005 M (fixed) :									
1.	0.00	1.01	0.989	–	–	–	–	–	–
2.	0.50	1.052	1.029	0.040	0.006 83	2.29	3.95	4.14	12.40
3.	1.00	1.068	1.044	0.055	0.0013 7	7.49	7.18	5.30	17.79
4.	2.00	1.088	1.063	0.074	0.0013 7	32.95	16.31	7.22	18.49
5.	3.00	1.102	1.076	0.087	0.0020 8	92.23	30.64	9.58	20.21
6.	4.00	1.112	1.085	0.096	0.0028 8	185.97	46.41	11.13	19.03
7.	5.00	1.121	1.093	0.104	0.0028 0	352.66	70.47	13.72	20.39
8.	6.00	1.128	1.099	0.110	0.0028 0	562.86	93.75	15.31	19.65
9.	7.00	1.134	1.104	0.115	0.0035 3	845.08	120.68	16.97	19.21
10.	8.00	1.140	1.109	0.120	0.0035 3	1 247.67	155.92	19.25	19.66
11.	10.00	1.149	1.117	0.128	0.0042 7	‹ 2 367.11	236.68	23.48	19.96

log A = 0.50, log B = 4.27, log C = 7.55 log D = 9.30

|									
Propionate = 0.01 M (Fixed) :									
1.	0.00	1.01	0.989	–	–	–	–	–	–
2.	0.50	1.062	1.038	0.049	0.006 83	4.62	8.08	7.68	23.45
3.	1.00	1.076	1.051	0.062	0.0013 7	12.93	12.35	8.11	16.02
4.	2.00	1.094	1.068	0.079	0.0020 8	49.45	24.43	10.09	17.93
5.	3.00	1.107	1.080	0.091	0.0020 8	128.06	42.49	12.75	20.80
6.	4.00	1.116	1.088	0.099	0.0028 0	238.87	59.57	13.83	18.30
7.	5.00	1.125	1.096	0.107	0.0028 0	445.53	88.99	16.95	20.88
8.	6.00	1.131	1.101	0.112	0.0035 3	668.97	111.39	17.86	18.91
9.	7.00	1.137	1.106	0.117	0.0035 3	1 004.57	143.43	19.88	19.10
10.	8.00	1.143	1.111	0.122	0.0042 7	1 483.13	185.32	22.63	20.15
11.	10.00	1.152	1.119	0.130	0.0042 7	2 766.30	276.57	27.23	20.72

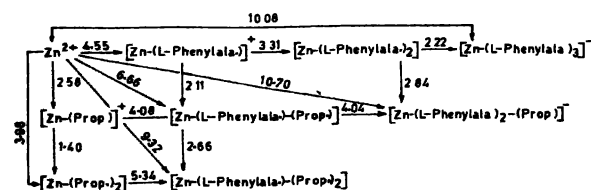log A = 0.76, log B = 4.63, log C = 781, log D = 9.29
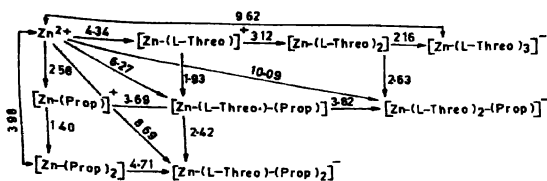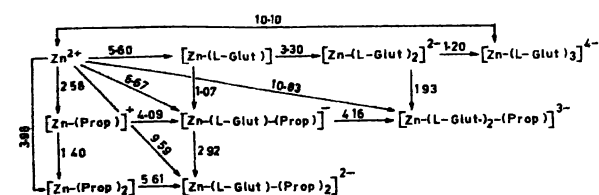
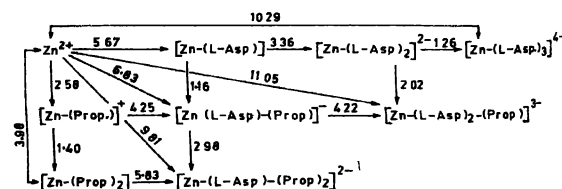Scheme 3. [Zn-L-Threo.-Prop.] system
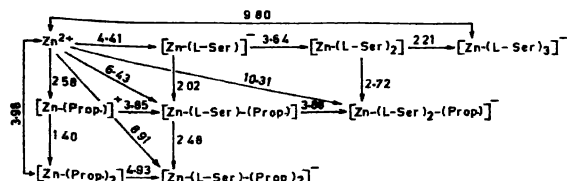
Scheme 4. [Zn-L-Ser -Prop] system
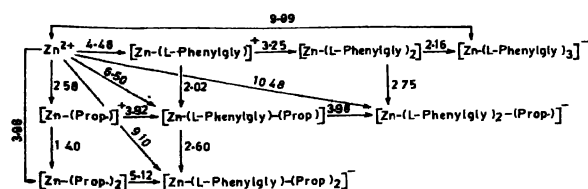
Scheme 5. [Zn-L-Phenylgly -Prop] system

Scheme 6. [Zn-L-Phenylala.-(Prop.)] system.

Scheme 7 [Zn-L-Glut.-Prop.] system.

of propionate ions (i.e. 0.005 and 0.01 M) while varying the concentrations of L-aminoacidate from 0.5 to 10.0 mM, and current-voltage curves were drawn. The data and plots[8] ($F_{ij}|X,Y|$ vs $|X|$, where

Scheme 8. [Zn-L-Asp.-Prop] system

$|X|$ = L-lysinate ions and $|Y|$ = propionate ions, are given in Table 2(a) and Fig. 2(a) respectively Equilibria of all the ternary systems are given in Schemes 1–8 respectively. The values of stability constants are presented in Table 2.

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

From the above equation[9], the calculated values of log K_m are 0.715, 0.810, 0.550, 0.645, 0.645, 0.740, 0.230 and 0.325 for Zn-L-lys.-prop., Zn-L-orn.-prop., Zn-L-threo.-prop., Zn-L-ser.-prop., Zn-L-phenylgly-prop., Zn-L-phenylala.-prop., Zn-L-glut-prop. and Zn-L-asp.-prop. systems respectively, showing that the ternary complexes are more stable than the binary ones. The trend of stability constants of complexes with respect to the binary and ternary complexes is L-lysine < L-ornithine < L-threonine < L-serine < L-phenylglycine < L-phenylalanine < L-glutamic acid < L-aspartic acid, which can be explained on the basis of size, basicity and steric hindrance of the amino acids[10]. It has been observed that if the size of amino acid increases, the stability of complexes decreases by a constant factor, definitively, log β^{*}_{RSB} e.g [Zn-(L-lys.)]$^{+}$, [Zn-(L-lys)$_2$] and [Zn-(L-lys.)$_3$]$^{-}$ have lesser stability than [Zn-(L-orn.)$_2$]$^{+}$, [Zn-(L-orn.)$_2$] and [Zn-(L-orn.)$_3$]$^{-}$ by, log β_{RSB10} = 0.0694, log β_{RSB20} = 0.1333 and log β_{RSB30} = 0.1875, respectively. This effect of size has also been observed in other L-amino acids except in L-phenylglycine and L-phenylalanine, where the order obtained was reversed, i.e. L-phenylglycine < L-phenylalanine This reversal in order of stability is due to the presence of phenyl group at α-carbon atom in L-phenylglycine whereas it is at β-carbon atom in L-phenylalanine. Therefore, the steric hindrance is greater in the former than in the latter, resulting

greater stability of L-phenylalanine complex than L-phenylglycine ones. It is clear from the values of stability constant that the stability of L-lysinate complexes is minimum which might be a result of lowest pK values of L-lysine. As the pK value decreases, the stability of complexes also decreases[11]. The lesser stability of L-threoninate complexes than L-serinate is due to the nearer presence of electron-withdrawing OH⁻ group to the metal ion in the case of the former than in the later, resulting a greater repulsive forces in the L-threoninate complexes than in the L-serinate ones. The higher stability of L-aspartate complexes than the L-glutamate ones is obvious from the chelate ring formation of these amino acids as the aspartate formed one five- and one six-membered ring with the metal while L-glutamate formed one six- and one seven-membered ring. As the size of ring increases, stability of complexes decreases[11]. The greater stabilities of the L-glutamate and L-aspartate complexes than those of the L-lysinate, L-ornithinate, L-threoninate, L-serinate, L-phenylglycinate, L-phenylalaninate complexes are due to the large differences in their basic strength.

In case of the ternary complexes, the stabilities of [Zn-(L-lys.)-(prop.)], [Zn-(L-lys.)₂-prop.)]⁻ and [Zn-(L-lys.)-(prop.)₂]⁻ are lesser than [Zn-(L-orn.)-(prop.)], [Zn-(L-orn.)₂-(prop.)]⁻ and [Zn-(L-orn.)-(prop.)₂]⁻ by a constant factor, definitively, log $\beta^{**}_{RST_{21}}$ i.e. log $\beta_{RST_{11}}$ = 0.1600, log $\beta_{RST_{12}}$ = 0.2222 and log $\beta_{RST_{21}}$ = 0.2222 respectively. This is true in the case of other ternary complexes also except in [Zn-(L-phenylgly.)-(prop.)] and [Zn-(L-phenylala.)-(prop.)] where the order found was reversed.

The sequence of stability of the ternary complexes being same in the binary complexes, can be explained on the basis of size, basicity and steric hindrance of amino acids. The factor log β^{*}_{RSB} and log β^{**}_{RST} are given by the equations,

$$\log \beta^{*}_{RSB} = \frac{(Z+4)\ im}{12\ (Z+5)}$$

and

$$\log \beta^{**}_{RST} = \frac{(Z+4)\ (i+j)m}{10\ (Z+5)}$$

where Z, i, j and m are the charge of the complex, stoichiometric number for primary ligand, secondary ligand and metal ion respectively, representing the complex equilibria,

$$Zn + i\ [\text{L-aminoacidate}] + j\ [\text{propionate}] =$$
$$[\text{Zn-(L-aminoacidate)}_i - (\text{propionate})_j]$$
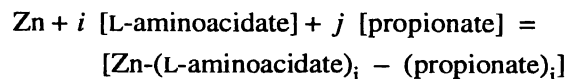
log β_{RSB} and log β_{RST} represent the reduction factors, reduce the stabilities of binary and ternary complexes, if the size of an amino acid increased by CH_2.

Experimental

All the solutions were prepared in double-distilled water. The purity of amino acids were checked by chromatographic method[12]. In the test solution, the concentrations of metal and NaClO₄ were 1.0 m M and 1.0 M respectively. The concentration of ligand varied from 0.5 to 10 mM in each case.

A Toshniwal Polyflex PL-50 galvanometer was used to record the current-voltage data. The characteristics of capillary were $m^{2/3}t^{1/6}$ = 2.40 mg s⁻¹ at 60.01 cm (calculated) effective height of mercury[13]. Hydrogen gas was passed through each test solution before recording the current-voltage data. Sodium perchlorate solution was used to maintain the ionic stregth (μ) at 1.0 M. A needle type LI-10 pH meter was used to measure the pH of the test solution at 8.50 ± 0.1 which was adjusted with dilute solution of NaOH or HClO₄ as required. The entire study was carried out at 25°.

Acknowledgement

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