Effects of Size, Basicity and Steric Hindrance on the Stability of Binary and Ternary Complexes of Cadmium with some Amino Acids and α-Picoline - A Polarographic Study

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Polarographic technique was used to study mixed ligand complex formation of Cd with L-tyrosine, L-arginine, L-methionine, L-hydroxytrytophane, L-tryptophane, L-hydroxyproline, L-proline and L-histidine as primary ligands and α-picoline as secondary ligand in media of 1.0 M KNO_3 and pH 8.50±0.01 at 25°C. Three mixed ligand complexes were identified. The sequence of stability constant was explained on the basis of basicity of the ligands, steric hindrance and nature of bonding between the depolariser and ligands.

Amino acids are well known chelating agents and play important role in biology, pharmacy and industry [1-3]. Hence there is considerable interest in their metal complexes. A survey of literature reveals no systematic polarographic study on ternary complexes of Cd with L-amino acids as primary ligands and α-picoline as secondary ligand. The present study examines the nature of bonding between the metal & these ligands and the effect of basicity & steric hinderance of ligands on the solution stability of the complexes.

EXPERIMENTAL

The purity of L-aminoacids (Lobachem) was checked by chromatographic method [13]. α -Picoline (Fluka, Switzerland) was used without further purification. Solutions were prepared in double distilled water.

A Toshniwal manual polarograph in conjuction with a sensitive polyflex galvanometer (PL-50) was used to record the current - voltage data. Each test solution was deaerated by bubbling pure hydrogen gas before recording current-voltage data. The pH of the test solutions was measured with an Elico-digital pH meter model L-I-120 fitted with glass and saturated calomel electrode and was maintained at 8.50±0.01 with the dilute solutions of NaOH or HNO_3 as required. All measurements were made at 25°C.

RESULTS AND DISCUSSION

Cd^{2+} is reversibly reduced at d.m.e. giving a well-defined, diffusion controlled, two electron, polarographic wave. The metal and ligands were taken in the ratio of 1:40 for binary complexes and 1:40:40 in case of ternary complexes. Polarograms were taken at different pH values of the solutions. It was observed that shift in half wave potential was maximum at pH=8.50±0.01.

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Therefore, this pH was selected for the present investigation. Ionic strength was maintained at 1.0 M with KNO_3. All measurements were carried out at 25°C. In all cases a single, reversible and diffusion controlled wave was observed.

Cd - L-Aminoacidate System

The results in these systems have already been reported [5]. The free ligand concentrations of L-amino acid have been calculated using pK_2^{II}[6], pH of the test solutions and the amount of ligand added. The stability constant values are included in Table 1.

Cd - α-Picoline System

Binary complexes of Cd was investigated in order to obtain stability constants. The concentration of α-picoline varied from 10 mM to 100 mM. Lingane's method [4] gave the values of the stability constant of 1:1 and 1:2 complexes. The values are cited in Table 1.

Cd -L-Aminoacidate- α-Picoline System

Study was carried out with 0.025 M and 0.05 M α-picoline in the medium and varying concentrations (from 0.5 mM to 50 mM) of L-aminoacidate and C-V curves were drawn. In all cases, a single, well-defined, reversible and diffusion controlled wave was obtained. In each of the mixed systems, the half wave potential shifted to more negative side on increasing concentrations of L-amino acids. The polarographic data are indicated in Table 2.

Schaap and McMaster method [8] was applied to calculate the stability constants.

Table 1

Acid dissociation Constants (pK_2^{II}) and Stability Constants (log ß) of the Various Binary Complex Species

Ligand	acid pK_2^{II}	log ß of Binary compl. 1:1	1:2	1:3
Tyrosine	9.11	3.54	6.11	9.00
Arginine	9.10	3.60	6.30	9.11
Methionine	9.20	3.69	7.00	9.23
Hyd.tryptohane	9.32	3.74	7.39	9.41
Tryptophane	9.40	4.44	7.51	9.91
Hyd.proline	10.20	4.62	8.21	11.11
Proline	10.60	4.70	8.72	11.80
Histidine	9.20	5.40	9.67	12.00
α -Picoline	-	1.60	2.81	-

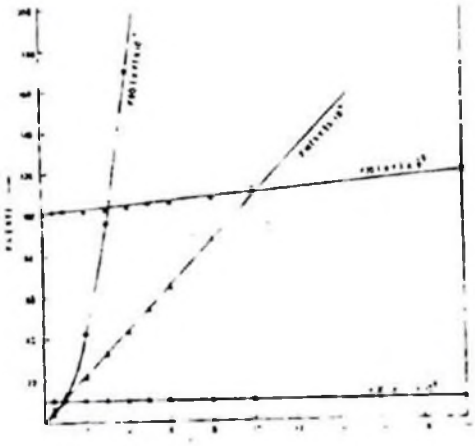


Fig1. Cd-L-Tyrosinate- α Picoline System
$F_{(x,y)}$ *vs* Tyrosine concentration
[α Picoline] = 0.025 M (fixed)

The plot for [Cd-L-Tyrosinate-α -Picoline] system have been given in Fig.1 as typical of all systems. Three complexes (1:1:1, 1:1:2 and 1:2:1 ratio) were indicated. All the values of stability constants are listed in Table 3.

The equilibria for Cd-L-aminoacidate -α-picoline system are shown in schemes I to VIII (numerical values are log K values).

Table 2

Polarographic Characteristics of Cadmium L-Tyrosinate- α-Picoline System

The dropping mercury electrode had the following characteristics :
$m^{2/3}t^{1/6}$=2.40 mg. sec^{-1} at mercury height 60.02 cm (calculated).
$(E_{1/2})_M$ = -0.586 V *vs* SCE; μ = 1.0 M KNO_3; pH = 8.50±0.01; Temp. = 25°

[L-Tyros.]	α-Picoline = 0.050 M			α-Picoline = 0.025 M		
x 10^3 M	$E_{1/2}$	$\Delta E_{1/2}$	log I_m/I_c	$E_{1/2}$	$\Delta E_{1/2}$	log I_m/I_c
0.50	0.638	0.0525	0.0144	0.629	0.0435	0.0144
1.00	0.654	0.0685	0.0219	0.645	0.0597	0.0219
2.00	0.671	0.0850	0.0294	0.662	0.0768	0.0219
3.00	0.681	0.0950	0.0294	0.673	0.871	0.0294
4.00	0.688	0.1029	0.0371	0.680	0.0943	0.0371
5.00	0.694	0.1087	0.0371	0.686	0.1002	0.0371
6.00	0.701	0.1129	0.0529	0.690	0.1045	0.0529
8.00	0.706	0.1202	0.0610	0.697	0.1118	0.06105
10.00	0.708	0.1229	0.0693	0.703	0.1175	0.0693
20.00	0.729	0.1439	0.0777	0.722	0.1364	0.0693
30.00	0.740	0.1548	0.0777	0.733	0.1475	0.0777
40.00	0.748	0.1625	0.0863	0.741	0.1558	0.0777
50.00	0.754	0.1667	0.0863	0.748	0.1622	0.0863

log A=0.6627; logB=1.1473; logC=8.3010; logB=9.0;

logA=0.3802; logB=3.7972; logC=8.0; logD=9.0

Table 3

Stability Constants (log ß) of the Various Cadmium Ternary Complex Species

m = 1.0 M KNO_3 pH = 8.50±0.01, Temp. = 25°C

Ligand	log ß of Ternary complex		
	1:1:1	1:1:2	1:2:1
Tyrosine	4.10	6.60	9.60
Arginine	4.26	6.85	9.75
Methionine	4.37	7.25	9.85
Hyd.trypt.	4.45	7.65	10.01
Tryptopha	4.60	7.80	10.20
Hyd.prol.	4.72	8.40	11.30
Proline	4.80	8.90	11.90
Histidine	5.75	9.90	12.25

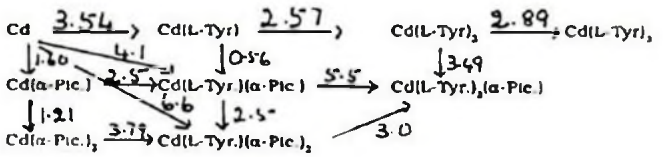
For a comparison of stabilities of simple and mixed complexes, it is convenient to evaluate the logarithm of constant K_m by the following relation:

$$\log K_m = \log ß_{11} - 1/2 [\log ß_{20} + \log ß_{02}]$$

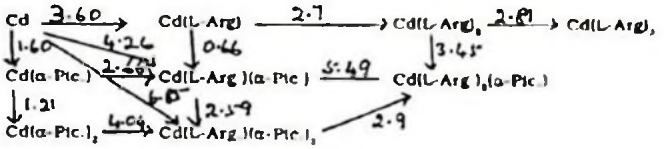
The values of $\log K_m$ are -0.36, -0.185, -0.535, -0.65, -0.56, -0.79, -0.965, -0.49 respectively for [Cd.L-tyr.α-pic], [Cd.L-arg.α-pic.], [Cd.L-met.α-pic], [Cd.L-hydroytryp.α-pic.], [Cd.L-tryp.α-pic], [Cd.L-hydroxypro.α-pic.], [Cd.L-pro.α-pic.] and [Cd.L-his.α-pic.] system. The negative values of $\log K_m$ indicates that the parent binary complexes are more stable as compared to the mixed complexes.

Structure and Strenth of Complex

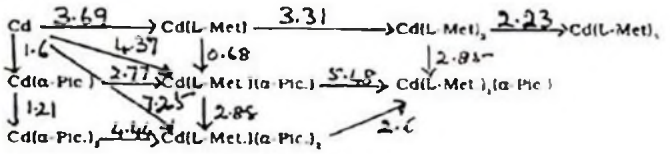
Scheme I Cd. L-Tyrosinate. α-Picoline System



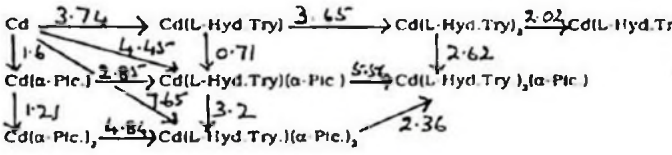
Scheme II Cd. L-Arginate. α-Picoline System



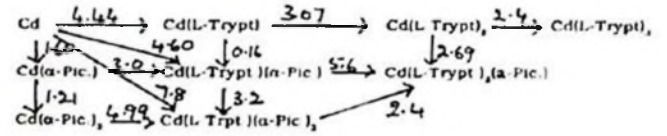
Scheme III Cd. L-Methioninate. α-Picoline System



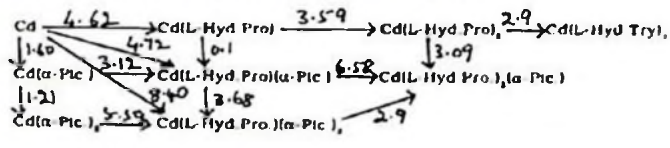
Scheme IV Cd. L-Hydroxy tryptophanate. α-Picoline System



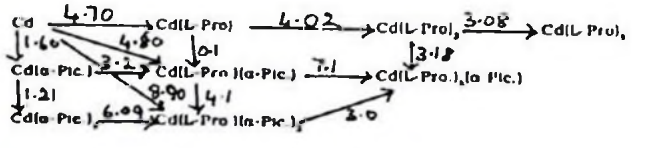
Scheme V Cd. L-Tryptophanate. α-Picoline System



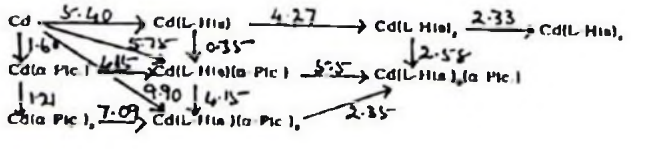
Scheme VI Cd. L-Hydroxy Prolinate. α-Picoline System



Scheme VII Cd. L-Prolinate. α-Picoline System



Scheme VIII Cd. L-Histidinate. α-Picoline System



α-Amino and carboxylic groups of L-tyrosine bind with the metal ion [9-10], whereas the phenylhydroxyl group does not take part in coordination under the experimental conditions. In L-arginine, there are one distart $-NH_2$ and one guanidine group which cause a large asymmetry and therefore, shift in half wave potential values is larger than in L-tyrosine.

Amino and carboxylic groups of L-arginine also bind with metal ion. Owing to the fact that L-arginine may be written as H_2N-C(=NH_2)-NH-CH_2-CH_2-CH_2-CH(NH_2)COOH. this extended chain molecule is folded in such a way that the positively charged (=NH_2) group comes adjacent to α amino group. Therefore, Cd^{2+} cation is repelled by the adjacent positive charge. This results in a lesser stability of its complexes than L-methionine complexes.

L-Methionine contains α-amino and carboxylic groups and reactive -S group, in its molecule but the values and stability constants show that -S does not take part in complex formation under the experimental conditions.

The aromatic α-amino acids, L-hydroxytryptophane and L-tryptophane, can bind through amino and carboxylic groups. However, there is a possibility of hydrogen bonding between the indolic -NH and 'O' of carboxylic group, affecting the stability of complexes.

L-Hydroxyprorline and L-proline have α-imino groups and carboxylic groups. However only α-imino nitrogen takes part in complex formation [11] and is responsible for the higher stability of their complexes than the other L-amino acids complexes.
In L-histidine, amino nitrogen and imidazole nitrogen takes part in complex formation making six membered ring and imidazole ring. The chelate complex with imidazole nitrogen is the most stable complex. This could be the reason behind the maximum stability of L-histidine complexes amongst the complexes of the chosen L-amino acids.

α-Picoline binds with the metal ion through nitrogen of the pyridine ring [12].

The trend of stability constants of complexes is found to be: L-tyrosine < L-arginine < L-methionine < L-hydroxytryptophane < L-tryptophane < L-hydroxyproline < L-proline < L-histidine which is in accordance with the nature of bonding, basicities and steric hindrance of these ligands.

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