POLAROGRAPHIC CHARACTERISTICS AND THERMODYNAMICS APPLIED IN [Cd - L-AMINO ACIDATES - VITAMIN-B7] TERNARY SYSTEM

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ABSTRACT

The present work describes the complexe formation of the Cd (II) with amino acids (L-glutamine, L-asparagine, L-valine, L-leucine, α-alanine and glycine) as primary ligands and vitamin-B7 (β-biotin) as secondary ligand by polarographic technique. The Cd (II) formed 1: 1: 1, 1: 1: 2 and 1: 2: 1 complexes at pH = 7.30 ± 0.01, μ = 1.0 M KNO_3. The Cd (II) showed the two electrons reversible reduction wave with diffusion controlled nature. The trend of the stability constants of the complexes with respect to primary ligand was L-glutamine < L-asparagine < L-valine < L-leucine < α-alanine < L-glycine. The thermodynamic parameters like enthalpy, free energy, and entropy change is also determined. The results showed that the complexes were lesser stable at high temperature and formed with the evolution of heat.

Keywords: [Cd-L-amino - acids-vitamin-B_7] complexes, Cd complexes.

INTRODUCTION

The metal such as Cd ((II) are required for biological processes such as oxygen transport, electron transfer, and catalysis and also necessary to maintain body function to optimize growth, reproductive performance, and immune response[1-3]. The minerals mis-regulation leads to many serious diseases such as oxidative stress diabetes, amyotrophic lateral sclerosis, cancer, inflammatory, neurodegenerative, and potential to various toxic effects etc.[4-10]. In addition to these, toxic effects are reduced with the ligands therapy. The bioactive amino acids and vitamin-B7 complexes with the Cd (II) are also used to prevent excess metal accumulation and toxicity[11].

Amino acid side chain groups are involved in various biological functions such as the molecular recognition and catalytic activity of the enzyme active center and formation of an environment with the metal ions used to in medicinal fields[12]. Weak interactions involving functional groups of coordinated amino acids in metal complexes may mimic the modes and effects of the interactions in metalloproteins. Complexes of amino acids and vitamins with metal ions have great importance because of their physiological and pharmacological activities. Some of the research work reported antitumor activities[13-14].
Biotin is act as cofactor and coenzyme involved in vital biological process such as fatty acid synthesis, gluconeogenesis, amino acids metabolism, and carbon dioxide fixation reaction[15]. Therefore the combination of the amino acids and vitamin-B7 with Cd (II) are used to reduce the metal toxicity. The coordination chemistry of the Cd (II) metal ion has shown too significant for the organisms on complexation with the bioactive ligands by chelating nitrogen and oxygen donor ligands[16]. In the present work, we report the complex formation between Cd^{2+} and some L-amino acids and β-biotin with the aim to ascertain the effects of size and basicity of ligand on the stability of complexes.

MATERIAL AND METHODS

Reagents

All chemicals were of reagent grade and used without further purification and their solutions were prepared in double distilled water. The concentrations of Cd (II), L-amino acids and vitamin-B7 (biotin) were taken in the ratio of 1: 40: 40 and the pH of the analytes were fixed at 7.30 ± 0.01 which were adjusted with the required amount of HCl or sodium hydroxide as needed. The pH of the analyte was stabilized by the addition of potassium dihydrogen phosphate buffer.

Instruments

The polarograms were obtained on a manual polarograph using polyflex galvanometer (PL-50). The polarographic cell was of Laitinen and Lingane[17] type in which capillary of 5.0 cm in length with 0.04 mM in diameter was used. The value of $m^{2/3}\ t^{1/6}$ was 2.40 $mg^{2/3}s^{1/2}$ at 60.02 cm. The pH of the analyte was measured using digital pH Meter Model (l11-101 E).

Polarographic procedure

In complex formation of [Cd - L-amino acidate - vitamin-B7] system, the concentrations of primary ligands i.e. L-amino acids varied from 0.5 mM to 30.0 mM at 0.025 M and 0.050 M (fixed) concentration of secondary ligand (vitamin- B7). The concentrations Cd (II), KNO_3 and gelatin (as suppressor) in the analyte were 0.50 mM, 1.0 M and 0.001 % respectively. The $E_{1/2}$ became more negative with the addition of secondary ligand (vitamin- B7) to binary complexes of the [Cd - L-amino acids] system that showed ternary complex formation of 1: 1: 1, 1: 1: 2 and 1: 2: 1 complexes. Cd (II) showed the well-defined two electron reversible reduction wave with half-wave potential -0.586 V vs. S. C. E. at pH = 7.30 ± 0.01 and μ = 1.0 M KNO_3 at 25ºC and 35º C[18].

RESULTS AND DISCUSSION

The values of stability constant were given in Table 1 and the polarographic characterstics data and plots of Fij [X, Y] against [X]{Where Fij is a Schaap and McMaster[19] function to evaluate the stability constant βij, X = glycine, Y = vitamin-B7 and i and j are their stoichiometric numbers respectively} for [Cd -glycine - vitamin-B7] system were given in Table 2 and Figure 1 respectively, to determine the values of function F_{00}, F_{10}, F_{20} and F_{30}.The comparisons of the stability of binary and ternary complexes by the values of log K were given by the following equation[20]

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

The calculated values are as follows 0.463, 0.447, 0.436, 0.620, 0.606 and -0.277 respectively for [Cd -glycinate - vitamin-B7], [Cd - α-alaninate - vitamin-B7], [Cd - L- leucinate - vitamin-B7], [Cd - L-valinate - vitamin-B7], [Cd -L-asparaginate – vitamin-B7] and [Cd - L-glutaminate -vitamin-B7] systems respectively. The positive values of logKm confirmed that the ternary complexes are more stable than their corresponding binary complexes and the negative values showed that the binary complexes are more stable than the corresponding ternary complexes.

The trend of stability constant of the complexes followed as L-glutamine < L- asparagine < L-valine < L-leucine < α-alanine < L-glycine. The increase of stability constants of metal complexes with amino acids can be explained on the basis of side chain[21]. The amino acids act as bidentate ligands which bond through COOH and amino groups to Cd (II) metal and form five member chelate ring system[22]. The β-biotin coordinates through the oxygen and nitrogen atoms of ureidyl group with Cd (II) metal ion[23-24]. The glycine complexes formed with the maximum stability because there is no methyl group[25] whereas the L-glutamine formed complexes of minimum stability due to its lesser basicity[26] with Cd (II) ion. But in case of the L-valine and L-leucine the order of the stability is reversed due to higher basicity of L-leucine than L-valine[27]. It is cleared from the values of stability constants that the complexation of the amino acids and vitamin with the Cd (II) complexes are used to in metal toxicity and in oxidative stress.

Thermodynamics parameters

The thermodynamic stability of complexes is also ascertained. The values of thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG), and entropy change (ΔS) of complexes were given in Table 3

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which showed that these complexes were lesser stable at higher temperature[28]. The values of ΔH of complexes showed that there is greater interaction between metal and ligands. As the composition of complex changes, the value of enthalpy varied. The values of $E_{1/2}$ of complexes with increase of concentration also supported this Fig. 2, Table 2). The negative values of enthalpy confirmed that the complexes are formed with the evolution of heat. The negative values of ΔH indicated that the complexes were formed with the evolution of heat. The thermodynamic parameters of complexes were calculated by the following equations[29].

$$\Delta H = 2.303\ RT_1T_2\ (\log \beta_2 - \log \beta_1) / T_2 - T_1 \quad \text{----- (i)}$$
$$\Delta G = -2.303\ RT \log \beta \quad \text{----- (ii)}$$
$$\Delta G = \Delta H - T\Delta S \quad \text{---- (iii)}$$

Table1. Stability constant of [Cd -L-amino acidate - vitamin-B_7] system.

Primary ligands	logβ_{01}	log β_{02}	log β_{03}	log β_{10}	log β_{20}	log β_{30}	log β_{11}	log β_{12}	log β_{10}
L-glycine	_	_	_	4.30	7.60	9.64	4.71	8.00	9.73
a-alanine	_	_	_	4.23	7.46	9.43	4.60	7.98	9.66
L-leucine	_	_	_	4.17	7.35	9.34	4.53	7.81	_
L-valine	_	_	_	4.11	7.21	9.16	4.45	7.68	9.50
L-asparagine	_	_	_	4.07	7.18	9.10	4.32	7.56	9.42
L-glutamine	_	_	_	4.00	7.04	8.91	_	7.45	9.32
vitamin- B_7 [β-Biotin]	2.01	2.86	_	_	_	_	_	_	_

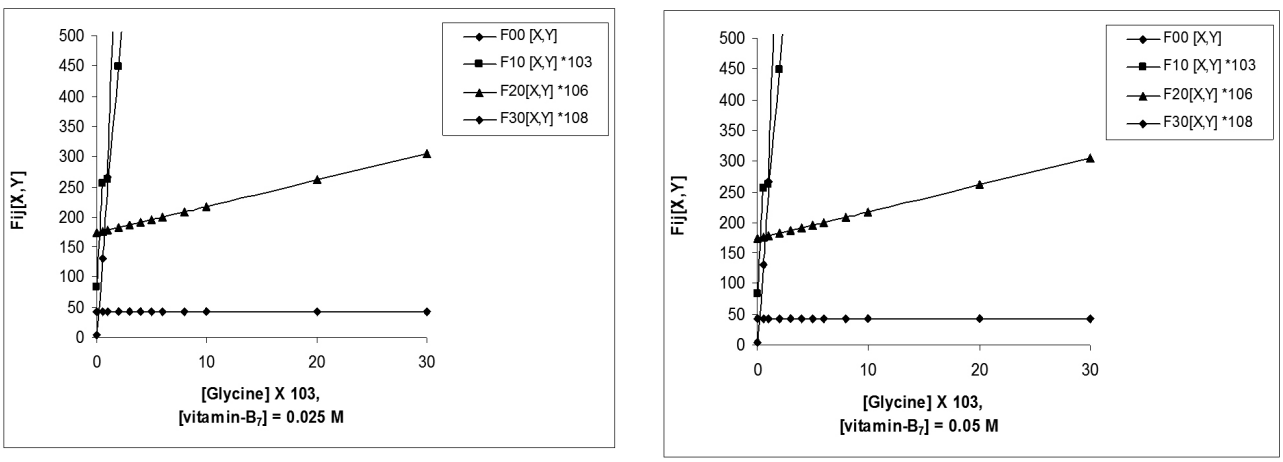

Fig.1: Plots of Fij[X, Y] vs. [X] for [Cd - L-amino acids - vitamin- B_7] system.

Table2. Polarographic characteristics and $F_{ij}[X, Y]$ values for the [Cd - glycinate - vitamin B_7] system Cd (II) = 0.5mM, μ = 1.0M KNO_3, pH = 7.30± 0.01, Temp. = 25ºC.

	(vitamin- PP)= 0.025M						(vitamin- PP) = 0.050M					
[gly]x 10^{-3}M	$E_{1/2}^r$ –V vs. SCE	logI_m/I_c	F_{00}[X,Y]	F_{10}[X,Y] x10^3	F_{20}[X,Y] x10^6	F_{30}[X,Y] x10^7	$E_{1/2}^r$ -V vs. SCE	logI_m/I_c	F_{00}[X,Y]	F_{10}[X,Y] x10^3	F_{20}[X,Y] x10^6	F_{30}[X,Y] x10^7
0.00	0.586	-	4.011	83.73	174.07	43.65	0.586	-	7.93	272.52	308.33	43.65
0.50	0.648	0.0073	131.81	255.59	176.25	43.65	0.661	0.0073	358.07	700.29	310.51	43.65
1.00	0.660	0.0073	266.18	262.17	178.44	43.66	0.667	0.0147	593.14	585.22	312.69	43.66
2.00	0.673	0.0147	902.68	449.33	182.8	43.65	0.682	0.0222	1821.21	906.64	317.06	43.65
3.00	0.682	0.0222	1943.74	645.24	187.67	43.66	0.691	0.0222	3718.34	1236.8	321.43	43.66
4.00	0.689	0.0299	3403.55	849.89	191.54	43.67	0.697	0.0299	6310.65	1575.68	325.79	43.65
5.00	0.695	0.0378	5320.18	1063.23	195.9	43.66	0.703	0.0378	9624.53	1923.32	330.16	43.66
6.00	0.699	0.0457	7716.21	1285.36	200.27	43.67	0.707	0.0457	13685.77	2279.64	334.52	43.65
8.00	0.707	0.0457	14047.83	1755.48	208.97	43.66	0.714	0.0457	24156.59	3018.58	343.26	43.66
10.00	0.713	0.0539	22611.35	2260.73	217.7	43.66	0.719	0.0539	37931.13	3792.32	351.98	43.65
20.00	0.733	0.0621	106214.69	5310.53	261.34	43.65	0.738	0.0621	163841.66	81916.87	395.96	43.66
30.00	0.745	0.0621	277034.03	9324.33	305.02	43.65	0.750	0.0621	403535.53	13450.92	439.28	43.65
log A = 0.60, log B = 4.92, log C = 8.24 log D = 9.64							log A = 0.89, log B = 5.43, log C = 8.49, log D = 9.64					

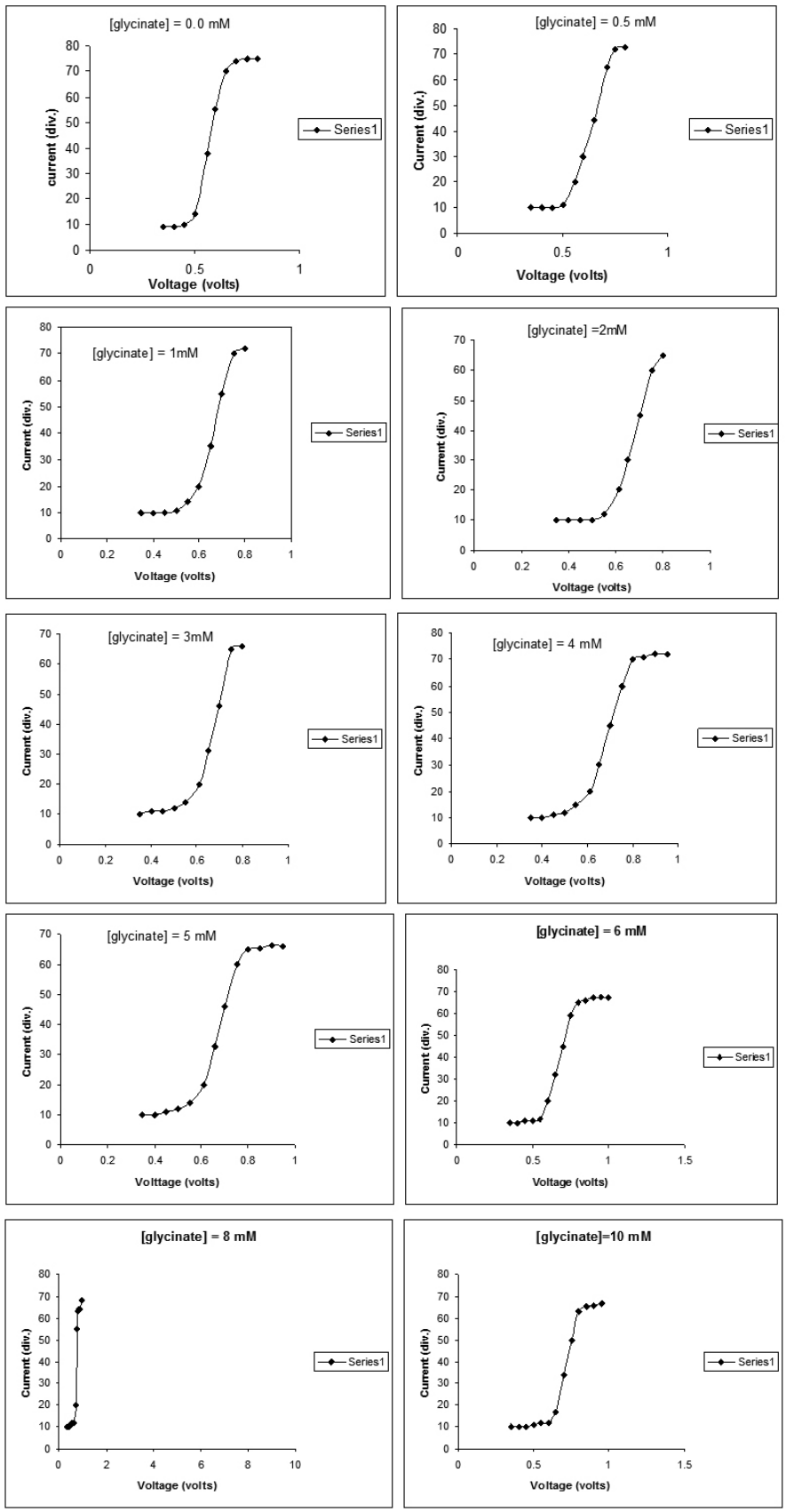

Fig.2: Current – Voltage curves for [Cd – L-amino acids – β-biotin] system, [β-biotin] = 0.025M (fixed).

Table3. Thermodynamic Parameters of [Cd -L-amino acidates - vitamin- B_7] ternary system Cd (II) = 0.5mM, μ = 1.0M KNO_3, pH = 7.30± 0.01, Temp. = 25ºC/35°C.

system	Stability Constant			-ΔH			-ΔG			-ΔS		
	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$	$\log \beta_{11}$	$\log \beta_{12}$	$\log \beta_{21}$
	25°C/ 35°C	25°C/ 35°C	25°C/ 35°C	(35ºC-25ºC) for difference of 10ºC			25°C/ 35°C	25°C/ 35°C	25°C/ 35°C	25°C/ 35°C	25°C/ 35°C	25°C/ 35°C
[Cd - gly-vit.-B_7]	4.71	8.00	9.73	16.3804	18.9004	20.1605	6.4428	10.9093	13.2684	16.3599	18.8647	20.1167
	4.32	7.55	9.25				6.0886	10.6409	13.0369	16.3606	18.8659	20.1181
[Cd-α-ala-vit.B_7]	4.60	7.98	9.66	16.8004	15.9604	17.6404	6.2778	10.8820	13.1729	16.7805	15.9244	17.5967
	4.20	7.60	9.24				5.9195	10.7114	13.0228	16.7812	15.9256	17.5981
[Cd-L-leu-vit.-B_7]	4.53	7.81	_	15.5404	18.0604	_	6.1714	10.6501	_	15.5207	18.0255	_
	4.16	7.38	_				5.8631	10.4013	_	15.5213	18.0266	_
[Cd - L-val - vit.-B_7]	4.45	7.68	9.50	14.7003	15.1204	17.2204	6.0683	10.4729	12.9548	14.6809	15.0857	17.1774
	4.10	7.32	9.09				5.7785	10.3168	12.8114	14.6809	15.0869	17.1788
[Cd - L-asn - vit.-B_7]	4.32	7.56	9.42	13.4403	14.2803	18.0604	5.8910	10..3093	12.8457	13.4214	14.2462	18.0179
	4.00	7.22	8.99				5.7376	10.1759	12.6705	13.4220	14.2473	18.0192
[Cd - L-gln - vit.-B_7]	_	7.45	9.32	_	14.2803	17.2204	_	10.1593	12.7093	_	14.2467	17.1783
	_	7.11	8.91				_	15.0208	12.5577	_	14.2478	17.1796

CONCLUSION

The paper suggested that L-amino acidates coordinate bidentate towards the metal ion and to form a planar five membered chelate ring and bonded through the amino nitrogen and COOH with the Cd (II) ion. The stability constant may be used to reduce metal toxicity, oxidative stress and nephrotoxicity. The thermodynamics parameters showed that the complexes were lesser stable at high temperature and formed with the evolution of heat.

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