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Study of complexes of cadmium with some L-amino acids and vitamin-C by voltammetric technique

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Abstract: Voltammetric technique was used to study the binary and ternary complexes of cadmium with L-amino acids and vitamin-C (L-ascorbic acid) at pH = 7.30 ± 0.01 , $\mu = 1.0M$ KNO₃ at 25°C and 35°C. Cd (II) formed 1:1:1, 1:1:2 and 1:2:1 complexes with L-lysine, L-ornithine, L-threonine, L-serine, L-phenylglycine, L-phenylalanine, L-glutamic acid and L-aspartic acid used as primary ligands and L-ascorbic acid used as secondary ligand. The trend of stability constant of complexes was 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 ligands. The values of stability constant (log β) varied from 2.23 to 11.33 confirm that these drugs i.e. L-amino acids or in combination with L-ascorbic acid or their complexes could be used against Cd (II) toxicity. The study has been carried out at 35°C also to determine the thermodynamic parameters such as enthalpy change (ΔH), Free energy change (ΔG) and entropy change (ΔS) respectively.

Keywords: voltammetry; thermodynamic parameters; vitamin-C; Cd (II) complexes.

Introduction

The L-amino acids and their compounds are used in biology, pharmacy, industry and laboratory reagents [1-3]. They also control transamination, decarboxylation and metabolism processes in human body. On the other hand, L-ascorbic acid (vitamin-C) is an important drug used against cancer, scurvy and reduced the risk of bronchitis or wheezing [4-6]. It is also an important drug to help the patient to increase the immune system. The person who suffered from AIDS has low concentration of vitamin-C. Vitamin-C is also responsible for the functions of various body components and organs but also keeps in order the immune system [7, 8]. The

deficiency of vitamin-C causes anemia, dental cavities and thyroid insufficiency.

Cd (II) is the one of the toxic metal in the environment to which industrial civilization has exposed itself [9]. Cd (II) contents is fixed in human body but whenever the concentration of Cd increases, the human being suffers from several severe diseases like cancer of the bladder, breast, intestine, leukemic system and sometimes death can also occur. Till now, there is no suitable antidote available for Cd toxicity. At present, H₄EDTA and its derivatives are used for Cd intoxication. Initially they reduce the toxicity of Cd (II) but eventually increase the nephrotoxicity therefore; the uses of these drugs against Cd (II) toxicity are questionable [10]. The present study is related with

the formation of binary and ternary complexes of Cd (II) with selected L- amino acids and ascorbic acid by voltammetric technique with the view that these drugs or their metal complexes could be used against several severe diseases like cancer, AIDS and also metal toxicity.

Experimental

The following chemicals were used for all polarographic experiments: HNO_3 (Sigma), NaOH (Sigma), KNO_3 (Fluka), gelatin (B.D.H.), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (B.D.H.), L-amino acids (Lobachem) and vitamin-C (ascorbic acid) (Fluka) and their solutions were prepared in double distilled water. The purity of L-amino acids was checked by Chromatography method [11]. The concentration of metal, KNO_3 and gelatin in test solution was 0.5 mM, 1.0 M and 0.001% respectively.

The depolarizer and ligands (i.e. amino acid and vitamin-C) were taken in the ratio 1:30:30 in the case of ternary complexes and current – voltage curves were obtained at different pH values. It has been observed that the maximum shift of $E_{1/2}$ was obtained within the pH range 7.10-8.50 but pH 7.30 was selected for studying the complexes in human blood pH [12, 13].

Electrochemical experiments were made by simple DC polarography carried out on a manual polarograph using a (Toshniwal PL-50) polyflex galvanometer. The polarographic cell was of Laitinen and Lingane type in which polarographic capillary of 5.0 cm in length with 0.04 mm in diameter was used. The $m^{2/3} t^{1/6}$ value was $2.40 \text{ mg}^{2/3} \text{ s}^{-1/2}$ at 60.02 cm effective height of mercury. A systronic pH meter 361 was used to measure the pH of the analyte at 7.30 ± 0.01 adjusted by using dilute solutions of HNO_3 or NaOH as required. Potassium dihydrogen phosphate-sodium hydroxide buffer was added to stabilize the pH of the analyte.

Electrochemical measurement was performed in the solutions of physiological ionic strength (1.0 M) KNO_3 as the supporting electrolyte while 0.001% gelatin was the maxima suppressor. The entire study was carried out at 298K and 308 K.

Result and discussion

Electrochemical investigation of Cd (II) complexes with L-amino acids and vitamin-C (L-ascorbic acid) was performed using simple polarography. Cd (II) gives a well defined two electron reversible reduction and diffusion controlled wave in 1.0M KNO_3 at $\text{pH}=7.3 \pm 0.01$ at 25°C [14, 15]. The metal ion and ligands were taken in the ratio 1:30 in binary complexes and 1:30:30 in case of ternary complexes and polarograms were taken at different pH values, it has been observed that the maximum shift of $E_{1/2}$ was obtained at pH range 7.10-8.50 but pH 7.30 was selected for studying the complexes in human blood pH. All the waves of the complexes were reversible and diffusion controlled as clear from the plots between $E_{d.e.}$ vs. $\log (i_d - i) / i$ and i_d vs \sqrt{t} respectively [16].

Binary complexes

[Cd – L - amino acidate] system: The pK values of amino acids were determined by titration method [17]. The concentration of the free ligand was calculated from pK_2 value and pH of test solution. Deford and Hume [18] was used to determine the composition and stability constants of binary complexes of Cd(II) with L-lysine, L-ornithine, L-threonine, L-serine, L-phenylglycine, L-phenylalanine, L-glutamic acid and L-aspartic acid. The values of stability constants of binary complexes were given in Table 1. The study has already been done at $\text{pH} = 8.50$ [19], however the present study has been done at $\text{pH} = 7.30$ to compare the values of stability constants.

[Cd- vitamin-C] complexes: The concentration of vitamin-C (L-ascorbic acid) in the analyte was varied from 50 mM to 200mM in 0.5 mM of Cd (II) in 1.0 M KNO_3 at $\text{pH} = 7.30 \pm 0.01$ at 25°C . Lingane method [20] confirmed the formation of 1:1 and 1:2 complexes of Cd (II) with vitamin-C with stability constants $\log \beta_{01}=2.23$ and $\log \beta_{02}=3.11$ respectively.

Ternary Complexes

[Cd – L-amino acidate – vitamin-C] complexes: The $E_{1/2}$ values became more negative with addition of vitamin-C to [Cd-L-amino acidate] [18] system at $\mu=1.0\text{M}$ KNO_3 and $\text{pH}=7.30 \pm 0.01$ show-

ing the formation of ternary complexes. The concentrations of the secondary ligand were kept constant at 0.025M and 0.05M while the concentration of primary ligand was varied from 0.50mM to 30.0 mM. The current voltage curves were drawn at pH=7.30±0.010. All the waves were found to be reversible and diffusion controlled. The Schaap and McMaster [21] method confirmed the formation of 1:1:1, 1:1:2 and 1:2:1 complexes of Cd (II) with L-

lysine, L-ornithine, L-threonine, L-serine, L-phenylglycine, L-phenylalanine, L-glutamic acid and L-aspartic acid and vitamin-C. The data and plots of $F_{ij}[X, Y]$ against $[X]$ (where F_{ij} is a Schaap and McMaster Function to evaluate the stability constant β_{ij} , $X = \text{L-lysine}$, $Y = \text{vitamin-C}$ and i and j are their stoichiometric numbers respectively} for [Cd-L-lysinate-vitamin-C] system were given in Table 2 and Fig. 1 respectively. These functions

Table 1. Stability constants of ternary complexes, Metal ion Cd(II) = 0.5 mM; μ = 1.0 M; pH = 7.3±0.01; Temperature = 25°C.

Primary Ligand	log β_{01}	log β_{02}	log β_{03}	log β_{10}	log β_{20}	log β_{30}	log β_{11}	log β_{12}	log β_{21}
L-lysine	-	-	-	(3.70) ¹⁸ , 3.65	(6.48) ¹⁸ , 6.37	(9.24) ¹⁸ , 9.19	4.45	-	10.22
L-ornithine	-	-	-	(3.77), 3.70	(6.61), 6.45	(9.42), 9.37	4.61	7.52	10.42
L-threonine	-	-	-	(4.00), 3.72	(7.00), 6.67	(9.50), 9.42	4.95	7.64	10.53
L-serine	-	-	-	(4.07), 3.90	(7.13), 7.00	(9.69), 9.50	5.11	7.86	10.75
L-phenylglycine	-	-	-	(4.10), 4.00	(7.24), 7.15	(9.71), -	5.21	7.95	10.83
L-phenylalanine	-	-	-	(4.17), 4.10	(7.37), 7.25	(9.90), 9.82	5.37	8.17	11.05
L-glutamic acid	-	-	-	(4.30), 4.25	(7.45), 7.38	(10.00), 10.00	5.56	-	11.11
L-aspartic acid	-	-	-	(4.37), 4.30	(7.58), 7.56	(10.24), 10.18	5.72	8.23	11.33
Vitamin-C (ascorbic acid)	2.23	3.11	3.75						

(The values under bracket shows the values of stability constants calculated at pH = 8.50.)

Table 2. Polarographic data and $F_{ij}[X, Y]$ values of [Cd – L-lysinate –vitamin-C] system, Cd(II) = 0. 50mM, μ =1.0M KNO₃, pH = 7.30 ± 0.01, Temp. = 25 °C.

[L-lys] X10 ³ M	[vitamin-C] = 0.025 M (Fixed)						[vitamin-C] = 0.050 M (Fixed)					
	$E_{1/2}^T$ - V vs SCE	log i_m/i_c	$F_{00}[X,Y]$	$F_{10}[X,Y]$ X10 ⁴	$F_{20}[X,Y]$ X10 ⁷	$F_{30}[X,Y]$ X10 ⁷	$E_{1/2}^T$ - V vs SCE	log i_m/i_c	$F_{00}[X,Y]$	$F_{10}[X,Y]$ X10 ³	$F_{20}[X,Y]$ X10 ⁵	$F_{30}[X,Y]$ X10 ⁶
0.50	0.6460	0.0219	114.17	21.60	42.07	173.78	0.6545	0.0219	225.99	42.51	83.74	173.78
1.00	0.6630	0.0295	433.42	42.72	42.16	173.77	0.6715	0.0295	858.17	84.47	83.83	173.77
2.00	0.6800	0.0371	1710.79	85.23	42.33	173.76	0.6890	0.0371	3386.62	168.66	84.00	173.76
3.00	0.6905	0.0449	3848.66	128.08	42.50	173.75	0.6990	0.0449	7609.14	253.19	84.18	173.79
4.00	0.6975	0.0529	6857.50	171.28	42.67	173.74	0.7065	0.0449	13536.16	338.06	84.35	173.78
5.00	0.7030	0.0611	10745.0	214.77	42.85	173.75	0.7120	0.0529	21178.12	423.29	84.53	173.77
6.00	0.7075	0.0693	15529.74	258.73	43.03	173.78	0.7165	0.0529	30545.45	508.86	84.70	173.77
8.00	0.7150	0.0777	27810.80	347.56	43.37	173.77	0.7240	0.0693	54497.83	681.05	85.05	173.76
10.00	0.7205	0.0777	43784.07	437.78	43.72	173.76	0.7295	0.0693	85476.88	854.63	85.39	173.77
20.00	0.7385	0.0864	181955.57	909.75	45.46	173.78	0.7470	0.0777	348690.47	1743.38	87.13	173.78
30.00	0.7495	0.0864	424946.81	1416.47	47.19	173.78	0.7575	0.0864	800080.67	2666.89	88.87	173.78

log A = 0.7881 log B=3.75, log C =8.62, log D= 9.24

log A =1.128 log B=4.95855 log C =9.1225 log D=9.42

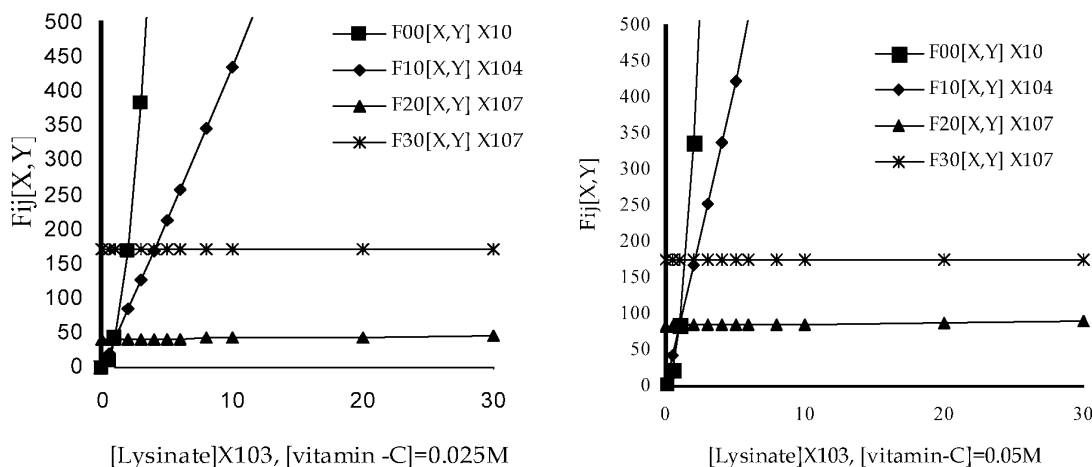


Figure 1. Plot of $F_{ij}[X, Y]$ vs. $[X]$ for $[Cd(II)\text{-}L\text{-lysinate-vitamin-C}]$ system.

were used to determine the stability constant of complexes.

To know the values of β_{11} and β_{12} , the study has been carried out at two constant concentration of secondary ligand $[Y] = [\text{vitamin-C}]$ at 0.025M and 0.05M respectively. The value of stability constants of complexes were given in Table 1. The current voltage curves of $[Cd\text{-}L\text{-lysinate-vitamin-C}]$ at $[\text{vitamin-C}] = 0.025\text{M}$ were given in Fig. 2 and Fig. 3 showed the polarographic experimental set up to study the interaction of Cd (II) with some L-amino acids and vitamin-C.

Comparison of stability of binary and ternary complexes

To compare the stability of binary and ternary complexes, the values of mixing constant $\log K_m$ were calculated by the following equation [21].

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

The values of $\log K_m$ are -0.345, -0.250, -0.105, -0.010, 0.035, 0.130, 0.280, 0.375 respectively, for $\{Cd\text{-}L\text{-lysinate-vitamin-C}\}$, $\{Cd\text{-}L\text{-ornithinate-vitaminC}\}$, $\{Cd\text{-}L\text{-threoninate-vitamin-C}\}$, $\{Cd\text{-}L\text{-serinate-vitamin-C}\}$, $\{Cd\text{-}L\text{-phenylglycinate-vitamin-C}\}$, $\{Cd\text{-}L\text{-phenylalaninate-vitamin-C}\}$, $\{Cd\text{-}L\text{-glutamate-vitamin-}\}$, $\{Cd\text{-}L\text{-aspartate-vitamin-C}\}$ complexes

respectively. The positive values of $\log K_m$ indicate that the ternary complexes are more stable than the binary complexes, while the negative values indicate that the binary complexes are more stable than ternary complexes.

Trend of stability constants of Cd (II) complexes

The sequence of stability constants of complexes with respect to ligands is $L\text{-lys} < L\text{-orn} < L\text{-thr} < L\text{-ser} < L\text{-phg} < L\text{-phe} < L\text{-glu} < L\text{-asp}$. It has been observed that as the size of amino acids increased the stability of its complexes decreased [22]. The stability of L-amino acid complex also depends upon the chelate ring formation and basicities of ligands [23]. In this study, the stability of lysinate complex is minimum owing to the lowest pK value of L-lysine as expected [24]. In case of L-serine and L-threonine, the stability of the latter is less than the L-serine complex owing to the fact that electron withdrawing OH⁻ group is nearer to L-threoninate complex than L-serinate complex, causing greater repulsive forces between metal and OH⁻ group in L-threonine complexes than L-serine complexes [25]. In case of L-phenylglycine and L-phenylalanine, the order of stability is reversed i.e. $L\text{-phenylglycine} < L\text{-phenylalanine}$, this could be attributed to the presence of phenyl group lying at α -carbon atom in L-phenylglycine, whereas it is at β -carbon atom in case of L-

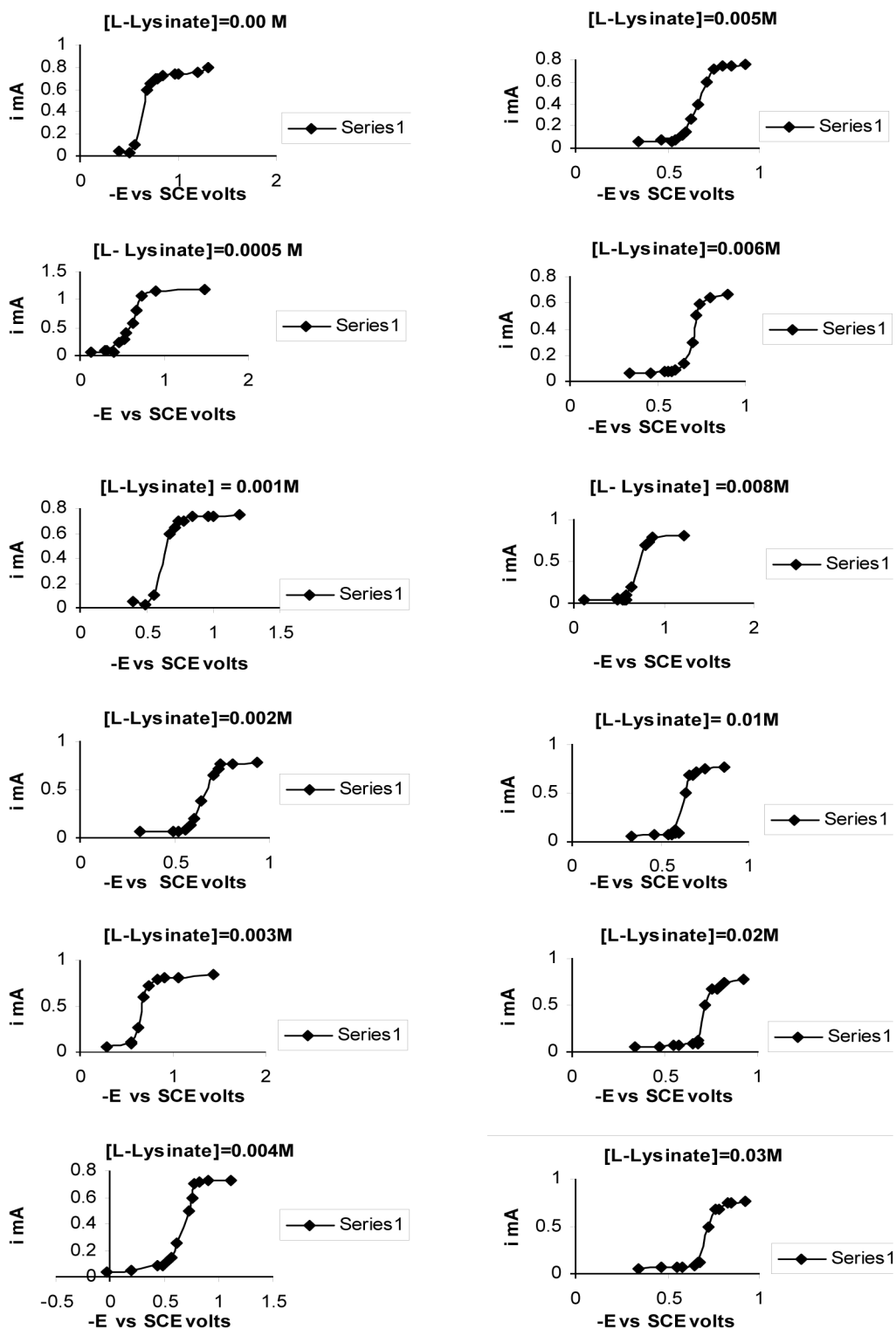


Figure 2. [Cd - L- lysinate - vitamin-C] system, [vitamin-C]=0.025M.

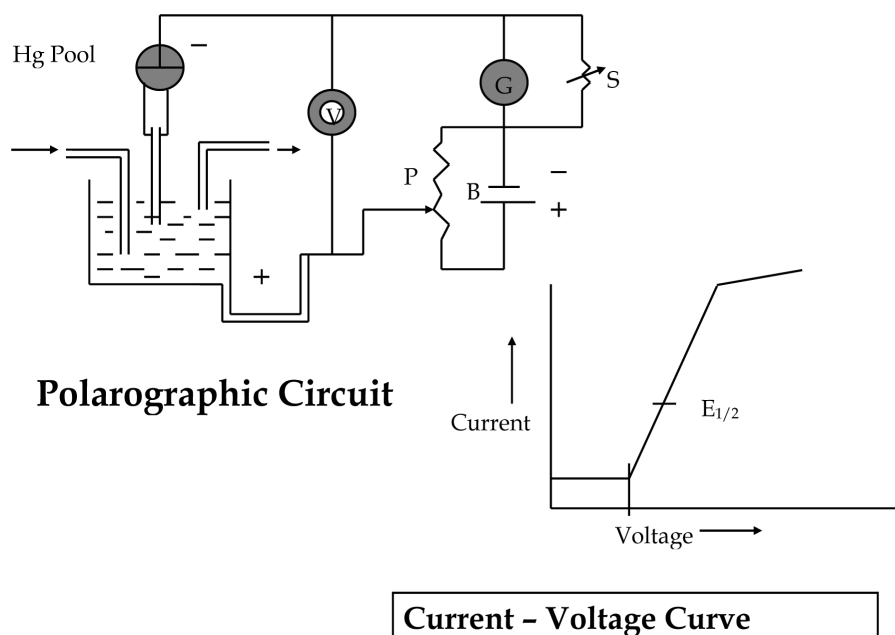


Figure 3. Polarographic set up.

phenylalanine causing greater repulsive forces in the former than in the latter.

The higher stability of L-aspartate complexes than L-glutamate complex is obvious from the chelate ring formation, in these amino acids, the aspartate forms one five and one six-membered ring with the metal while L-glutamate forming one five and one seven-membered ring. As the size of ring in amino acid increases, the stability of complex decreases [26]. The stabilities of L-glutamate and L-aspartate complexes are greater than those of the L-lysinate, L-ornithinate, L-threoninate, L-serinate, L-phenylglycinate and phenylalaninate complexes due to large difference in their basic strength [27]. The same is evident from pK values of L-amino acids [28].

In case of vitamin-C, oxygen of enediol group may take part in bond formation with Cd^{II} , formed a five membered ring [29].

It is clear from the values of stability constant of the complexes that vitamin-C and L-amino acids alone or in combination could be used to reduce the toxicity of Cd^{II} in vivo. One also to consider the quantity of drugs that should not be complexed to the other essential metals present in vivo

and the same could be excreted easily from the body. On the other hand, the person who suffers from AIDS has low concentration of vitamin-C therefore; his resistance can be increased by ascorbic acid therapy.

Thermodynamic parameters

The kind of complex species that can be measured with a mercury electrode depends on thermodynamic aspects [30]. Thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) of the complexes have been calculated by the following equations [31].

$$\Delta H = 2.303R T_1 T_2 (\log K_2 - \log K_1) / T_2 - T_1 \quad (1)$$

$$\Delta G = -2.303 RT \log K \quad (2)$$

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

It is clear from the values of ΔS , ΔG and ΔH in Table 3 that the values of ΔS are more negative at higher temperature and ΔG are less negative at higher temperature confirmed that complexes are not stable at higher temperature [32, 33]. The negative values of ΔH show that reactions are exothermic in nature.

Table 3. Thermodynamic parameters of ternary complexes of [Cd-L-aminoacide-vitamin-C] system.

System	Stability constants			- ΔH K cal./mole			- ΔG K cal./mole			- ΔS K cal./mole		
	$\log\beta_{11}$	$\log\beta_{12}$	$\log\beta_{21}$	$\log\beta_{11}$	$\log\beta_{12}$	$\log\beta_{21}$	$\log\beta_{11}$	$\log\beta_{12}$	$\log\beta_{21}$	$\log\beta_{11}$	$\log\beta_{12}$	$\log\beta_{21}$
	25°C/ 35°C	25°C/ 35°C	25°C/ 35°C	(35°C-25°C) for difference of 10°C			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-L-lysinate - vitamin-C]	4.45	-	9.82	12.1803	-	16.8004	6.0683	-	13.9366	20.5101	-	9.6100
	4.16	-	10.42				5.8631	-	13.8403	20.5103	-	9.6107
[Cd-L-ornithinate- vitamin-C]	4.61	7.521	10.00	13.02031	13.44032	17.6488	6.2865	10.2561	14.2123	22.5967	10.6853	11.5318
	4.3	7.201	10.53				6.0604	10.1491	14.0968	22.5970	10.6858	11.5325
[Cd-L-threoni- nate -vitamin-C]	4.95	7.637	10.12	13.0203	14.2803	17.2204	6.7501	10.4143	14.3607	21.0409	12.9734	9.5963
	4.64	7.297	10.75				6.5396	10.2844	14.2645	21.0412	12.9738	9.5969
[Cd-L-serinate - vitamin-C]	5.11	7.859	10.34	13.4403	14.2803	17.2204	6.9683	10.7173	14.6637	21.7182	11.9565	8.5795
	4.79	7.519	10.83				6.7510	10.5975	14.5777	21.7185	11.9571	8.5802
[Cd-L-phenylglycinate -vitamin-C]	5.21	7.95	10.39	13.0203	13.8603	18.4804	7.1046	10.8411	14.7698	19.8511	10.1316	12.4518
	4.9	7.62	11.05				6.9060	10.7396	14.6451	19.8515	10.1321	12.4525
[Cd-L-phenylalaninate -vitamin-C]	5.37	8.172	10.60	12.6003	14.2803	18.9005	7.3228	11.1441	15.0728	17.7095	10.5243	12.8444
	5.07	7.832	11.11				7.1457	11.0387	14.9441	17.7098	10.5248	12.8451
[Cd-L-glutamate -vitamin-C]	5.56	-	10.65	13.4403	-	19.3205	7.5819	-	15.1529	19.6589	-	13.9847
	5.24	-	11.33				7.3853	-	15.0129	19.6592	-	13.9854
[Cd-L-aspartate - vitamin-C]	5.72	8.231	10.87	13.0203	13.8603	19.3205	7.8001	11.2243	15.4559	17.5174	8.8457	12.9680
	5.41	7.901	9.82				7.6249	11.1356	15.3261	17.5177	8.8463	12.9687

Conclusions

In the present paper, interaction of Cd (II) between L-amino acids and vitamin-C in pH 7.30 ± 0.01 was investigated using simple DC polarography. The results indicated that current voltage curves were reversible and diffusion controlled in 1.0M KNO_3 at pH $= 7.30 \pm 0.01$ at 25°C and 35°C. The stability constants varied from 2.23 to 11.33 which is quite reasonable values therefore, either L-amino acids alone or vitamin-C or in combination or in the form of metal complex could be effective against Cd (II) toxicity and also be very much useful not only to control the aging process but also to prevent the HIV replication in vivo. The negative values of ΔH indicated the exothermic nature of the metal-ligands interaction. The complexes were not stable at higher temperature which was confirmed by the values of μG and μS of complexes at higher temperature.

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