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Study of (Cd (II) -amino acids-triazole) system as a tool in removal of excess cadmium from human blood (A polarogrpahic aproach)

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ABSTRACT

The excess of Pb & Cd in human blood, causing stone problem and cancer in gall bladder is conspicuous among the residents of Ganga belt. We have studied mixed ligand complexes of Trizole (Tr), Glycine (gly^{1-}) and Alanaine (ala^{1-}) with Cd (II) which make Cd solubel and excrete it through urine. The Stability constants of these complexes $[Cd (gly) (Tr)]^+$, $[Cd (gly)_2(Tr)]$, $[Cd (ala) (Tr)]^+$, and $[Cd (ala)_2(Tr)]^+$, are $\log \beta_{11} = 5.20$, $\log \beta_{21} = 8.556$, $\log \beta_{11} = 5.11$, and $\log \beta_{21} = 8.50$ respectievly at pH 7.3 and 25±0.1°C. The value of stability constant is determined by polarographic method.

Key words: Polarography, mixed ligand complexes, stability constants.

INTRODUCTION

Soil pollution with heavy metals such as Cd (II) is a problem of concern. Contamination comes from local sources, mostly industry, power plants, irrigation with polluted water sewage and fertilizers. Cd (II) has a half life of ten years[1] once in the human body it has been dermatitis to various type of cancer[2]. Although several workers used this technique to study mixed complexes yet this aspect is untouched[3-10].

EXPERIMENTAL

All reagents were analytical grade and their solutions were prepared in conductivity water. The ionic strength was maintained constant at μ=1.5 M using $NaNO_3$ as supporting electrolyte. The concentration of Cd (II) was maintained at 1×10^{-3}M. Polarogram were obtained[11-12] by means of a manual polarography (Toshniwal CL 02) in conjunction with Toshniwal polyflex galvanometer (PL 50). All the measurements were made at 25±0.1°C and pH 8.2. A saturated calomel electrode (S.C.E) was used as reference electrode. The d.m.e had the following characteristics (in 0.1M $NaNO_3$, open circuit): m=2.229 mg/sec, t=3.5 sec, $m^{2/3}\, t^{1/6} = 2.10\ mg^{2/3}\ sec^{-1/2}$, h_{corr}= 40cm.

RESULTS AND DISCUSSION

The reduction of Cd (II) in triazole, glycine and alanine was found to be reversible and diffusion controlled. The same was true for the mixed system. The slops of linear plots of log i/id-i vs $E_{d.m.e}$ were in the range 30-33 mv and the plots of id vs $h^{½}_{corr}$ were linear and passed through the origin. The stability constants of simple complexes of Cd (II) with triazole, glycine and alanine were determined separately prior to the study of mixed ligand system. Identical conditions were maintained in both the simple and mixed systems.

Simple system

The simple systems of Cd(II) with triazole, glycine and alanine were studied by the method of Deford and Hume[13]. The values of stability constants of simple complexes have been tabulated in Table 1.

Mixed system

Glycine (5×10^{-4} - 25×10^{-4} M) and alanine (4×10^{-4} - 20×10^{-4} M) concentraiton was varied from and that of triazole was kept constant at 0.10M. The $E_{½}$ values were greater compared to those obtained in the absence of triazole thereby showing the formation of mixed complexes. The system was repeated at another concentration of triazole (0.20M).

The method of Schaap and McMaster[14] was used to determine the values of the stability constants of mixed complexes. The polarographic characteristics and $F_{ij}[XY]$ functions of mixed complexes of Cd (II) with triazole, glycine and alanine at fixed [Tr] (0.10 M and 0.20M) are presented in Tables 2 and 3.

The stability constants of the mixed complexes were calculated from the constants A, B, C and D. Three mixed complexes as are formed in each mixed system.

Cd (II)- triazole-glycine system

$[Cd (gly) (Tr)]^{1+}$ $\log \beta_{11} = 5.20$
$[Cd (gly)_2(Tr)]$ $\log \beta_{21} = 8.556$

Cd (II) - triazole-alanine system

$[Cd (ala) (Tr)]^{1+}$ $\log \beta_{11} = 5.11$
$[Cd (ala)_2(Tr)]$ $\log \beta_{21} = 8.50$

The mixing constant KM (equilibrium constant) for the reactions.

$$½[Cd(Tr_2)]^{2+} + ½[Cd(gly_2)] □ □□ [Cd(gly)\ (Tr)]^{1+} \quad ...(1)$$

Table 1: Stability constants of triazole, glycine and alanine with Cd(II)

Contents	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
Triazole	1.113	1.778	3.184
Glycine	4.20	7.38	10.64
Alanine	4.14	7.34	10.09

Table 2: Cd(II)-trizole-glycine system $[Cd^{2+}] = 1\times10^{-3}$M, μ = 1.5M ($NaNO_3$), pH = 7.3, Temp = 25±.1°C $(E_{½})_s$ = - 0.584 Volts (S.C.E)

$[gly^{1+}]_f$ $\times10^4$ M	$-E_{½}$ (S.C.E)	log I_m/I_c	Slope mv	F_{00} [X,Y]	$F_{10}[X,Y] \times10^{-4}$	F_{20} [X,Y] $\times 10^{-7}$	F_{30} [X,Y] $\times10^{-10}$
Series - I $[Tr]_t$ = 0.1 M (Fixed)							
5.0	0.635	0.05697	31	60.57	8.71	11.42	10.84
10.0	0.652	0.06105	31	229.87	21.28	18.28	12.28
15.0	0.665	0.06105	31	632.81	14.05	25.36	12.90
20.0	0.675	0.06517	32	1392.19	68.75	32.87	13.43
25.0	0.683	0.06932	31	2621.13	98.05	38.02	12.80
Series - II $[Tr]_t$ = 0.2 M (Fixed)							
5.0	0.644	0.06932	31	125.63	19.52	31.04	12.08
10.0	0.661	0.06932	31	472.31	44.43	40.43	15.43
15.0	0.672	0.08203	32	1145.69	74.51	47.00	14.66
20.00	0.681	0.08203	32	2309.61	114.08	55.04	15.02
25.0	0.688	0.09950	32	4147.82	164.79	64.31	15.72

Series I:	log A = 1.23	log B = 4.477	log C = 7.778	log D = 11.11
Series II :	log A = 1.447	log B = 4.60	log C = 8.397	log D = 11.176

$$\tfrac{1}{2}[Cd(Tr_2)]^{2+} + \tfrac{1}{2}[Cd(ala_2)] \rightleftharpoons [Cd(ala)(Tr)]^{1+} \quad ...(2)$$

is given by the relation

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

These works out to be +1.135 for reaction 1 and +0.551 for reaction 2. The positive values shows that

log C = 7.73 log D = 10.46

log C = 7.88 log D = 10.65

the mixed complexes $[Cd(gly)(Tr)]^{1+}$ and $[Cd(ala)(Tr)]^{1+}$ are more stable than simple complexes $[Cd(Tr)_2]^{2+}$, $[Cd(ala)_2]$.

The mixed complexes exists in solution in

Table 3: Cd(II)-trizole-glycine-alanine system $[Cd^{2+}] = 1\times10^{-3}$M, μ = 1.5M ($NaNO_3$), pH = 7.3, Temp = 25±.1°C $(E_{½})_s$ = - 0.584 Volts (S.C.E)

$[gly^{1+}]_f$ ×10^4 M	$-E_{½}$ (S.C.E)	log I_m/I_c	Slope mv	F_{00} [X,Y]	F_{10}[X,Y] ×10^{-4}	F_{20} [X,Y] × 10^{-7}	F_{30} [X,Y] ×10^{-10}
				Series - I $[Tr]_t$ = 0.1 M (Fixed)			
5.0	0.628	0.04103	31	33.84	47.10	52.75	-
10.0	0.640	0.04103	31	86.20	89.00	78.75	3.09
15.0	0.649	0.04490	32	175.32	133.60	89.66	2.97
20.0	0.656	0.05293	32	308.09	183.18	98.29	2.76
25.0	0.662	0.06932	33	510.57	247.78	110.89	2.84
				Series - II $[Tr]_t$ = 0.2 M (Fixed)			
5.0	0.633	0.04496	31	50.42	66.05	75.12	-
10.0	0.644	0.06105	31	123.23	124.07	110.08	4.26
15.0	0.653	0.06932	32	253.27	191.05	129.20	4.43
20.00	0.661	0.06932	33	472.31	280.19	152.61	4.78
25.0	0.667	0.08203	33	776.10	376.05	170.02	4.70

Series I:	log A = 1.176	log B = 4.41	log C = 7.73	log D = 10.46
Series II :	log A = 1.38	log B = 4.556	log C = 7.88	log D = 10.65

Table 4: Equilibria involved in Cd (II) -triazole-glycine system and their equilibrium constant (K) values

Equilibrium	LogK
1. $Cd^{2+}+Tr+gly^{1+}$ $[Cd(Tr)(gly)]^{1+}$	5.201
2. $Cd^{2+}+Tr+2gly^{1+}$ $[Cd(Tr)(gly)_2]$	8.556
3. $[Cd(gly)]^{1+}Tr$ $[Cd(gly)(Tr)]^{1+}$	1.001
4. $[Cd(Tr)(gly)]^{1+}gly^{1-}$ $[Cd(Tr)(gly)_2]$	3.356
5. $[Cd(Tr)^{2+}+gly^{1-}$ $[Cd(Tr)(gly)]^{1+}$	4.087
6. $[Cd(Tr)_2)]^{2+}gly^{1-}$ $[Cd(Tr)(gly)]^{1+}+Tr$	3.422
7. $[Cd(gly)_2]+Tr$ $[Cd(Tr)_2(Tr)]$	1.176
8. $[Cd(Tr)_3)]^{2+}2gly^{1-}$ $[Cd(gly)_2(Tr)]^{+}+2Tr$	5.327
9. $[Cd(gly)_3)]^{1-}+Tr$ $[Cd(gly)_2(Tr)+gly^{2-}$	-2.084

Table 5: Equilibria involved in Cd (II)-triazole-alanine system and their equilibrium constant (K) values

Equilibrium	LogK
1. $Cd^{2+}+Tr+ala^{1+} \rightleftharpoons [Cd(Tr)(ala)]^{1+}$	5.110
2. $Cd^{2+}+Tr+2ala^{1+}$ $[Cd(Tr)(ala)_2]$	8.550
3. $[Cd(ala)]^{1+}Tr$ $[Cd(ala)(Tr)]^{1+}$	0.970
4. $[Cd(Tr)(ala)]^{1+}ala^{1-}$ $[Cd(Tr)(ala)_2]$	3.390
5. $[Cd(Tr)^{2+}+ala^{1-}$ $[Cd(Tr)(ala)]^{1+}$	3.997
6. $[Cd(Tr)_2)]^{2+}ala^{1-}$ $[Cd(Tr)(ala)]^{1+}+Tr$	3.332
7. $[Cd(ala)_2]+Tr$ $[Cd(Tr)_2(Tr)]$	1.160
8. $[Cd(Tr)_3)]^{2+}2ala^{1-}$ $[Cd(ala)_2(Tr)]^{+}+2Tr$	5.316
9. $[Cd(ala)_3)]^{1-}+Tr$ $[Cd(ala)_2(Tr)+ala^{2-}$	-1.590

the equilibria shown in table 5 and 6. The log values of equilibrium constants are given for each equilibrium.

From the above equations it is seen that gly^{1-} and ala^{1-} can add readily to $[Cd(gly)(Tr)]^{1+}$ and $[Cd(ala)(Tr)]^{1+}$ than does Tr (Table 4: equilibria 4 and 5 and Table 5: equilibria 4 and 5). Further gly^{1-} and ala^{1-} can replaced Tr from complexes $[Cd(gly)_2(Tr),]$ $[Cd(gly)(Tr)_2]^{1+}$, $[Cd(ala)_2(Tr)]$ and $[Cd(ala)(Tr)_2]^{1+}$ (Table 4: equilibrium 6-8 and Table 5: equilibria 6-8) but not the vice versa for this shows that gly^{1-} and ala^{1-} is strong ligand than Tr.

The equilibrium constant (log values) for the following disproportion reactions.

$[Cd(Tr)(gly)]^{1+}$ $[Cd(Tr)_2]^{2+} + [Cd(gly)_2]$ ...(3)

$[Cd(Tr)_2(gly)]^{1+}$ $[Cd(Tr)_2]^{2+} + [Cd(gly)_2] + Tr$ ...(4)

$[Cd(Tr)(ala)]^{1+}$ $[Cd(Tr)_2]^{2+} + [Cd(ala)_2]$ ...(5)

$[Cd(Tr)_2(ala)]^{1+}$ $[Cd(Tr)_2]^{2+} + [Cd(ala)_2] + Tr$ ...(6)

works out to be -1.932, -5.170 and -1.591, -4.262 for the disproportion reactions 3, 4, 5 and 6 respectively. The large negative log values for the equilibrium constants show that the formation of mixed complexes is strongly favoured over simple ones.

The stability of the mixed complexes follow the order:

$[Cd(gly)(Tr)_2]^{1+} > [Cd(gly)_2(Tr)] > [Cd(gly)(Tr)]^{1+}$

$[Cd(ala)(Tr)_2]^{1+} > [Cd(ala)_2(Tr)] > [Cd(ala)(Tr)]^{1+}$

$[Cd(ala)(Tr)]^{1+}$ is more stable complex than $[Cd(gly)(Tr)]^{1+}$

CONCLUSIONS

The values of stability constant shows that the soluble mixed ligand complexes of Cd (II) with triazole, glycine and alanine are stable. So triazole, glycine and alanine can from the soluble complexes with the cadmium present in the human blood and they can excrete it through urine.

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