

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

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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 Triazole (Tr), Glycine (gly<sup>1-</sup>) and Alanine (ala<sup>1-</sup>) with Cd (II) which make Cd soluble and excrete it through urine. The Stability constants of these complexes [Cd (gly) (Tr)]<sup>+</sup>, [Cd (gly)<sub>2</sub>(Tr)], [Cd (ala) (Tr)]<sup>+</sup>, and [Cd (ala)<sub>2</sub>(Tr)]<sup>+</sup>, are  $\log \beta_{11} = 5.20$ ,  $\log \beta_{21} = 8.556$ ,  $\log \beta_{11} = 5.11$ , and  $\log \beta_{21} = 8.50$  respectively at pH 7.3 and  $25 \pm 0.1^\circ\text{C}$ . 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<sup>1</sup> once in the human body it has been dermatitis to various type of cancer<sup>2</sup>. Although several workers used this technique to study mixed complexes yet this aspect is untouched<sup>3-10</sup>.

### EXPERIMENTAL

All reagents were analytical grade and their solutions were prepared in conductivity water. The ionic strength was maintained constant at  $\mu=1.5$  M using NaNO<sub>3</sub> as supporting electrolyte. The concentration of Cd (II) was maintained at  $1 \times 10^{-9}$  M. Polarogram were obtained<sup>11-12</sup> by means of a manual polarography (Toshniwal CL 02) in

conjunction with Toshniwal polyflex galvanometer (PL 50). All the measurements were made at  $25 \pm 0.1^\circ\text{C}$  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<sub>3</sub>, open circuit):  $m=2.229$  mg/sec,  $t=3.5$  sec,  $m^{2/3} t^{1/6} = 2.10$   $\text{mg}^{2/3} \text{sec}^{-1/2}$ ,  $h_{\text{corr}} = 40$  cm.

### 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 slopes of linear plots of  $\log i/id-i$  vs  $E_{\text{d.m.e}}$  were in the range 30-33 mv and the plots of  $id$  vs  $h_{\text{corr}}^{1/2}$  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<sup>13</sup>. The values of stability constants of simple complexes have been tabulated in Table 1.

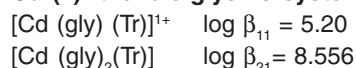
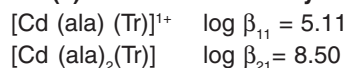
**Mixed system**

Glycine ( $5 \times 10^{-4}$  -  $25 \times 10^{-4}$  M) and alanine ( $4 \times 10^{-4}$  -  $20 \times 10^{-4}$  M) concentration was varied from and that of triazole was kept constant at 0.10M. The  $E_{1/2}$  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).

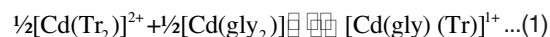
The method of Schaap and McMaster<sup>14</sup> was used to determine the values of the stability constants of mixed complexes. The polarographic characteristics and  $F_{ij}[XY]$  functions of mixed complexes of Cd (II) with triazole, glycine and alanine at fixed [Tr] (0.10 M and 0.20M) are presented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

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



**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)-triazole-glycine system  $[\text{Cd}^{2+}] = 1 \times 10^{-3}\text{M}$ ,  $\mu = 1.5\text{M}$  ( $\text{NaNO}_3$ ),  $\text{pH} = 7.3$ ,  $\text{Temp} = 25 \pm 0.1^\circ\text{C}$  ( $E_{1/2}_s = -0.584$  Volts (S.C.E))**

$[\text{gly}^{1+}]_f \times 10^4 \text{ M}$	$-E_{1/2}$ (S.C.E)	$\log I_m/I_c$	Slope mv	$F_{00}[X,Y]$	$F_{10}[X,Y] \times 10^{-4}$	$F_{20}[X,Y] \times 10^{-7}$	$F_{30}[X,Y] \times 10^{-10}$
<b>Series - I <math>[\text{Tr}]_t = 0.1 \text{ M}</math> (Fixed)</b>							
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
<b>Series - II <math>[\text{Tr}]_t = 0.2 \text{ M}</math> (Fixed)</b>							
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
20.0	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:  $\log A = 1.23$

$\log B = 4.477$

$\log C = 7.778$

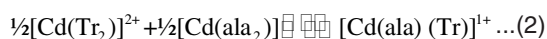
$\log D = 11.11$

Series II:  $\log A = 1.447$

$\log B = 4.60$

$\log C = 8.397$

$\log D = 11.176$



is given by the relation

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

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

shows that

$$\log C = 7.73 \quad \log D = 10.46$$

$$\log C = 7.88 \quad \log D = 10.65$$

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

The mixed complexes exists in solution in

**Table 3: Cd(II)-trizole-glycine-alanine system  $[\text{Cd}^{2+}] = 1 \times 10^{-3} \text{M}$ ,  $\mu = 1.5 \text{M}$  ( $\text{NaNO}_3$ ),  $\text{pH} = 7.3$ ,  $\text{Temp} = 25 \pm 1^\circ \text{C}$  ( $E_{1/2}$ )<sub>s</sub> = - 0.584 Volts (S.C.E)**

$[\text{gly}^{1+}]_f \times 10^4 \text{ M}$	$-E_{1/2}$ (S.C.E)	$\log I_m/I_c$	Slope mv	$F_{00} [X,Y]$	$F_{10} [X,Y] \times 10^{-4}$	$F_{20} [X,Y] \times 10^{-7}$	$F_{30} [X,Y] \times 10^{-10}$
<b>Series - I <math>[\text{Tr}]_t = 0.1 \text{ M}</math> (Fixed)</b>							
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
<b>Series - II <math>[\text{Tr}]_t = 0.2 \text{ M}</math> (Fixed)</b>							
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. $\text{Cd}^{2+} + \text{Tr} + \text{gly}^{1+} \rightleftharpoons [\text{Cd}(\text{Tr})(\text{gly})]^{1+}$	5.201
2. $\text{Cd}^{2+} + \text{Tr} + 2\text{gly}^{1+} \rightleftharpoons [\text{Cd}(\text{Tr})(\text{gly})_2]$	8.556
3. $[\text{Cd}(\text{gly})]^{1+} + \text{Tr} \rightleftharpoons [\text{Cd}(\text{gly})(\text{Tr})]^{1+}$	1.001
4. $[\text{Cd}(\text{Tr})(\text{gly})]^{1+} + \text{gly}^{1-} \rightleftharpoons [\text{Cd}(\text{Tr})(\text{gly})_2]$	3.356
5. $[\text{Cd}(\text{Tr})^{2+} + \text{gly}^{1-} \rightleftharpoons [\text{Cd}(\text{Tr})(\text{gly})]^{1+}$	4.087
6. $[\text{Cd}(\text{Tr}_2)]^{2+} + \text{gly}^{1-} \rightleftharpoons [\text{Cd}(\text{Tr})(\text{gly})]^{1+} + \text{Tr}$	3.422
7. $[\text{Cd}(\text{gly})_2]^{2+} + \text{Tr} \rightleftharpoons [\text{Cd}(\text{Tr}_2)(\text{Tr})]$	1.176
8. $[\text{Cd}(\text{Tr}_3)]^{2+} + 2\text{gly}^{1-} \rightleftharpoons [\text{Cd}(\text{gly})_2(\text{Tr})]^{1+} + 2\text{Tr}$	5.327
9. $[\text{Cd}(\text{gly})_3]^{1+} + \text{Tr} \rightleftharpoons [\text{Cd}(\text{gly})_2(\text{Tr})]^{1+} + \text{gly}^{2-}$	-2.084

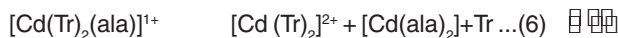
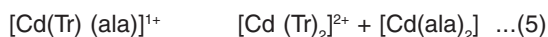
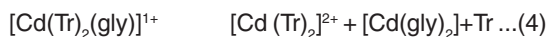
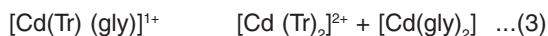
**Table 5: Equilibria involved in Cd (II) -triazole-alanine system and their equilibrium constant (K) values**

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

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

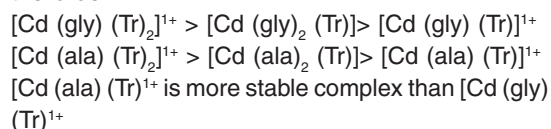
From the above equations it is seen that  $\text{gly}^{1-}$  and  $\text{ala}^{1-}$  can add readily to  $[\text{Cd}(\text{gly})(\text{Tr})]^{1+}$  and  $[\text{Cd}(\text{ala})(\text{Tr})]^{1+}$  than does Tr (Table 4: equilibria 4 and 5 and Table 5: equilibria 4 and 5). Further  $\text{gly}^{1-}$  and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

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



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:



## 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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