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### Study of Cadmium Complexes of Amino Acids at their Isoionic Points : Cd(II)-Amino Acid & Cd(II)-Thiourea- Amino Acid Systems

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Received 18 February 1980; revised 9 July 1980;  
accepted 28 July 1980

Cadmium(II)-glycine, cadmium(II)- $\beta$ -alanine, cadmium(II)-thiourea-glycine and cadmium(II)-thiourea- $\beta$ -alanine systems have been investigated polarographically at the isoionic points of the amino acids in aqueous medium and at  $25^\circ \pm 0.5^\circ\text{C}$ . Stabilities of Cd(II)-amino acid complexes both in simple and mixed systems are low because of ion pair formation. The mixed ligand complex species have higher stabilities than predicted on statistical considerations. The increased stability may be due to simultaneous  $\pi$ -bonding between Cd(II) and both the ligands.

**S**IMPLE systems as well as mixed ligand systems of glycine (gly) and  $\beta$ -alanine ( $\beta$ -ala) with Cd(II) have been studied<sup>1</sup> at pH above their  $pK_{a_2}$  values because at  $pH > pK_{a_2}$  the  $\text{NH}_3^+$  dissociates making available a lone-pair of electrons on nitrogen of amino group and facilitating chelation to give comparatively more stable complex species<sup>1</sup>. No investigations have been made of the systems at the isoionic points of these ligands and this prompted us to undertake the title investigation. The  $pK_{a_1}$  and  $pK_{a_2}$  of gly are 2.43 and 9.80 and those of  $\beta$ -ala 3.52 and 10.15 respectively. The  $pH = (pK_{a_1} + pK_{a_2})/2$  is the isoionic point. Isoionic points for gly and  $\beta$ -ala are therefore 6.10 and 6.80 respectively. The pH's of all the resulting solutions were maintained at the respective isoionic points. As thiourea was chosen as a secondary ligand for mixed ligand complexation, the Cd(II)-(tu) system was studied only to get the stabilities of Cd(II)-(tu) complexes *in situ*.

All the reagents used were of AR grade. Solutions were prepared in a doubly distilled water. The ionic strength of all the experimental solutions was kept constant at 0.1M with sodium perchlorate.

A Cambridge automatic recording polarograph was used for recording polarograms. No maximum suppressor was found necessary and the polarograms

of the deaerated solutions were recorded at  $25 \pm 0.5^\circ\text{C}$ . SCE was used as reference half-cell.

The dropping mercury electrode had the following characteristics :  $t = 3.0$  sec in 0.5 M KCl (open circuit); and  $m = 1.96$  mg/sec.

**Cd(II)-thiourea system** — In each solution the concentration of Cd(II) (cadmium nitrate) was maintained constant at 1mM while the thiourea concentration was varied from 0.04 to 0.80 M. The  $E_{1/2}$  of Cd(II) ion was  $-0.587$  V which increased in the presence of thiourea to a more negative value indicating complex formation (Table 1). The relationship between  $-(E_{1/2})_c$  and  $\log C_L$  where  $C_L$  is the ligand concentration was not linear but a smooth curve with four segments showing the existence of 1:1, 1:2, 1:3 and 1:4 complex species. The method of DeFord-Hume<sup>2</sup> gave the following values for stability constants:  $\log \beta_{10} = 1.40$ ,  $\log \beta_{20} = 1.70$ ,  $\log \beta_{30} = 1.60$  and  $\log \beta_{40} = 3.30$ . These values are nearly identical to those observed by Lane *et al.*<sup>3</sup> and Migal *et al.*<sup>4</sup>. The slight deviations may be due to the difference in the ionic strength and the media used. The higher value of  $\beta_4$  as compared to  $\beta_1$ ,  $\beta_2$  or  $\beta_3$  may be due to the fact that during the formation of 1:4 complex, the coordination number four of Cd(II) is satisfied.

**Cd(II)-glycine system** — The concentration of glycine was varied from 0.04M to 0.80M. Other conditions were identical to those maintained in the above system. The pH of every solution was kept constant at pH 6.10. The shift of  $E_{1/2}$  of Cd(II) to more negative values (Table 1) by the addition of glycine indicated complex formation. Two complex species 1:1 and 1:3 were detected and their stability constants were  $\log \beta_{01} = 0.78$  and  $\log \beta_{03} = 1.36$ .

**Cd(II)- $\beta$ -alanine system** —  $\beta$ -Alanine concentration was varied from 0.04M to 0.80M maintaining the other conditions same as in the previous systems.

TABLE 1 — SHIFTS IN HALF-WAVE POTENTIAL OF Cd(II) IN THE MIXED LIGAND SYSTEM

[Cd = 1 mM;  $\mu = 0.1$  M (NaClO<sub>4</sub>);  $-(E_{1/2})_s = 0.587$  V]

Ligand (tu) M	$-(E_{1/2})$ (vs. S.C.E.)				
	0.00M gly/ $\beta$ -ala	0.16M gly	0.40M gly	0.12M $\beta$ -ala	0.40M $\beta$ -ala
0.04	0.590	0.595	0.610	0.598	0.613
0.08	0.602	0.607	0.619	0.607	0.622
0.12	0.606	0.612	0.625	0.615	0.627
0.16	0.612	0.619	0.632	0.621	0.633
0.24	0.623	0.631	0.642	0.633	0.644
0.32	0.631	0.639	0.651	0.639	0.653
0.40	0.641	0.646	0.657	0.649	0.660
0.48	0.649	0.653	0.663	0.656	0.666
0.56	0.655	0.659	0.668	0.661	0.672
0.64	0.661	0.663	0.673	0.667	0.677
0.72	0.666	0.668	0.677	0.673	0.682
0.80	0.672	0.672	0.680	0.677	0.686
		$\log A$	$\log B$	$\log C$	$\log D$
		0.30	1.40	1.78	3.26
		0.65	1.60	2.87	3.30
		0.40	1.48	2.00	3.30
		0.95	1.95	2.70	3.55

The pH of each solution was maintained at 6.8. The formation of 1:1, 1:2 and 1:3 complex species was observed with their stability constants  $\log \beta_{01} = 1.06$ ,  $\log \beta_{02} = 0.48$  and  $\log \beta_{03} = 1.73$ .

The low values of stability constants for Cd(II)-gly and Cd(II)- $\beta$ -ala systems are expected because of ion-pair formation. At isoionic point the amino acids predominantly exist as zwitterions. Under these conditions there is probability of ion pair formation. The trend in stability constants  $\beta_i(\text{gly}) < \beta_i(\beta\text{-ala})$  was on expected lines because of higher basicity of  $\beta$ -alanine than that of glycine.

*Cadmium(II)-thiourea-glycine and cadmium(II)-thiourea- $\beta$ -alanine systems* — The two concentrations 0.16M and 0.40M of gly and 0.12M and 0.40M of  $\beta$ -ala at which 1:1 and 1:2 complex species predominated were chosen for the mixed ligand study. The concentration of (tu) was varied. The solutions containing 1mM Cd(II), 0.16M gly and a requisite amount of sodium perchlorate to maintain the ionic strength at 0.1M were used. The same procedure was repeated for gly concentration 0.40M and for two concentrations 0.12 M and 0.40M of  $\beta$ -ala.

In each set a linear relationship was observed between  $E_{d.e.}$  versus  $\log(i/i_a - i)$  with slope values lying in the range 30-33 mV. This showed that the reduction of Cd(II) ion in the absence and in the presence of the ligand was reversible and involved two electrons. The reduction was found to be diffusion controlled from the direct proportionality of  $i_a$  with  $\sqrt{h}$ .

The following observations were made :

- (i) At each gly and  $\beta$ -ala concentration the  $E_{\frac{1}{2}}$  of Cd(II) shifted to a more negative value with increase of (tu) concentration (Table 1).
- (ii) The shift in the  $E_{\frac{1}{2}}$  in the presence of tu-gly and tu- $\beta$ -ala was greater than in the presence of tu alone. This proved the presence of mixed ligand complexes.
- (iii) When all the gly as well as  $\beta$ -ala molecules were replaced the shifts of the  $E_{\frac{1}{2}}$  in the simple and mixed systems nearly coincided (Table 1).

The plot between  $-(E_{\frac{1}{2}})_e$  and  $\log C_L$  for both the gly as well as  $\beta$ -ala concentrations were found to be smooth curves. With the help of Schaap and McMasters method<sup>5</sup> the values of A, B, C and D at both the concentrations of gly as well as  $\beta$ -ala were obtained. These are presented in Table 1.

From these values the stability constants were calculated for all mixed ligand complex species existing in the solutions under the present experimental conditions. These are : (a) for Cd(II)-thiourea-glycine system:  $\log \beta_{12} = 2.20$ ,  $\log \beta_{21} = 2.50$  and (b) for Cd(II)-thiourea- $\beta$ -alanine system :  $\log \beta_{12} = 2.62$ ,  $\log \beta_{21} = 2.84$ .

In both the systems the absence of 1:1:1 mixed complex species was indicated by the negative values of  $\log \beta_{11}$ .

$\log D$  values in the gly and  $\beta$ -ala sets are respectively 3.26 and 3.30; and 3.3 and 3.55 which are

higher than  $\log \beta_{30}$ , the stability constant of the simple  $[\text{Cd}(\text{tu})_3]^{2+}$  complex. This may probably be due to the incomplete dissociation of  $[\text{Cd}(\text{tu})_2(\text{gly})]^+$  and  $[\text{Cd}(\text{tu})_2(\beta\text{-ala})]^+$  complexes under the given conditions.

*Prediction of  $\beta$ -values from the statistical factors* — The statistical factors in the complexation constants were evaluated following the procedure suggested by Watters<sup>6</sup>.

*Cd(II)-thiourea-glycine system* — The predicted values for complexation constants were  $3 \times \beta_{\frac{2}{0}}^{2/3} \times \beta_{\frac{1}{0}}^{1/3}$  for  $[\text{Cd}(\text{tu})_2(\text{gly})]^+$  and  $3 \times \beta_{\frac{1}{0}}^{1/3} \times \beta_{\frac{2}{0}}^{2/3}$  for  $[\text{Cd}(\text{tu})(\text{gly})_2]$  which were  $10^{2.06}$  and  $10^{0.89}$  respectively. The observed values are  $10^{2.5}$  and  $10^{2.2}$ , showing an increase of  $10^{+0.44}$  and  $10^{+1.31}$  respectively.

*Cd(II)-thiourea- $\beta$ -alanine system* — The predicted values for complexation constant were  $3 \times \beta_{\frac{2}{0}}^{2/3} \times \beta_{\frac{1}{0}}^{1/3}$  for  $[\text{Cd}(\text{tu})_2(\beta\text{-ala})]^+$  and  $3 \times \beta_{\frac{1}{0}}^{1/3} \times \beta_{\frac{2}{0}}^{2/3}$  for  $[\text{Cd}(\text{tu})(\beta\text{-ala})_2]$  which were  $10^{2.19}$  and  $10^{1.33}$  respectively. The corresponding experimental values are  $10^{2.84}$  and  $10^{2.62}$  showing an increase of  $10^{+0.65}$  and  $10^{+1.29}$  respectively.

The authors thank Dr A. K. Sundaram of BARC, Bombay for his valuable discussions. Thanks are also due to Prof. K. A. Thakar, and Prof. D. D. Khanolkar for their continued encouragement during the progress of the work. One of the authors (V. G. D.) is thankful to the CSIR, New Delhi for the award of a junior research fellowship.

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#### Stability Constants of Complexes of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) & Cd(II) with 5-Hydroxy-2-methyl-1, 4-naphthoquinone

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Received 28 March 1980; revised and accepted 9 July 1980

Acid dissociation constant of 5-hydroxy-2-methyl-1,4-naphthoquinone and the stability constants of its metal chelates with Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) have been determined in 75% (v/v) ethanol-water mixture at 30° and 0.1 ionic strength by adopting the pH-titration technique of Irving and Rossotti. The stability constants follow the Irving-William order.

NOT much work is reported<sup>1,2</sup> on the chelating ability of 5-hydroxy-2-methyl-1,4-naphthoqui-