

Cadmium(II)-Thiourea-Glutamate Mixed Ligand System: A Polarographic Study

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The stability constants of simple and mixed ligand complexes of thiourea (tu) and glutamate (glu) with Cd(II) have been determined polarographically in aqueous medium at pH 6.8 and ionic strength of 1.0 M (NaClO₄). The overall stability constants for the simple complexes are: $\log \beta_1 = 1.30$, $\log \beta_2 = 2.30$, $\log \beta_3 = 2.17$ and $\log \beta_4 = 3.74$ with thiourea and $\log \beta_1 = 4.00$, $\log \beta_2 = 7.00$ and $\log \beta_3 = 10.17$ with glutamate at $25 \pm 0.5^\circ\text{C}$. Three mixed complexes, viz. $[\text{Cd}(\text{tu})(\text{glu})]^+$, $[\text{Cd}(\text{tu})_2(\text{glu})]^+$ and $[\text{Cd}(\text{tu})_2(\text{glu})]^+$ are formed with their respective stability constants: $\log \beta_{11} = 5.86$, $\log \beta_{12} = 8.69$ and $\log \beta_{21} = 6.42$. The negative value of β_{22} indicates the absence of $[\text{Cd}(\text{tu})_2(\text{glu})_2]$ complex species.

Mixed ligand complex formation between thiourea and glycine/ β -alanine with Cd(II) at the isoionic point of the amino acids has been earlier reported from our laboratory¹. As an extension of our earlier work, the mixed ligand complexation of Cd(II) with thiourea (tu) and glutamate (glu) has been studied polarographically in aqueous medium at pH 6.8.

All the chemicals used were of AR grade and used as such. Sodium perchlorate was used as the supporting electrolyte and also to keep the ionic strength constant at 1.0 M. No maximum suppressor was found necessary. The solutions were prepared in air-free conductivity water.

Polarograms of thoroughly deaerated solutions were recorded at $25 \pm 0.5^\circ\text{C}$ with a Cambridge automatic recording polarograph using a saturated calomel electrode (SCE) as the reference electrode. pH measurements were made on a Digital pH-meter model L120 (Elico Hyderabad). The cell resistance was found to be low in all the cases. Half-wave potentials were obtained from log plots. The d.m.e. had the following characteristics: $t = 3.0$ sec and $m = 1.92$ mg/sec.

Stability constants of Cd(II)-thiourea and Cd(II)-glutamate binary complexes

Reduction of Cd(II) in the presence and absence of ligands was found to be reversible, since the slopes of the plots $\log (i/i_d - i)$ versus $E_{d.e.}$ were always in the range of (32 ± 2) mV. That the reduction is diffusion-controlled is indicated by the linear plots of i_d versus $\sqrt{h}$ (effective) which passed through the origin. The

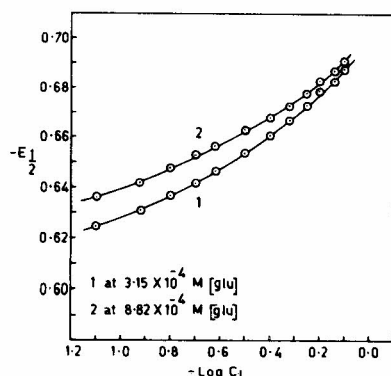
half-wave potentials of Cd(II) shifted to more negative values on increasing ligand concentration indicating complex formation. Since plots of $E_{1/2}$ versus $-\log C_L$ (C_L = ligand concentration) were smooth curves, it indicated the formation of more than one complex species. De Ford and Hume method was used to calculate the overall stability constants of the consecutive complexes. The concentration of glutamate ion was calculated from the concentration and pK_2 value of glutamic acid, determined at the same ionic strength and pH of the solution. The concentration of thiourea was taken as the analytical concentration. The normal state of thiourea² (tu) is considered to be a zwitterion, while glutamic acid³ (glu) is present in the form HL^- at pH 6.80.

The binary systems were studied only in order to get the data under identical conditions maintained for mixed systems. The observed values of stability constants of binary complexes of Cd(II) are: $\log \beta_1 = 1.30$, $\log \beta_2 = 2.30$, $\log \beta_3 = 2.17$ and $\log \beta_4 = 3.74$ with thiourea; and $\log \beta_1 = 4.00$, $\log \beta_2 = 7.00$ and $\log \beta_3 = 10.17$ with glutamate. The values in the case of thiourea are nearly identical with the reported values⁴. Slight deviations observed may be due to the difference in ionic strength and media used. The stability constant values of Cd(II) complexes with glutamate are found to be higher than those of thiourea system. The overall stability constant of the complex species $\text{Cd}(\text{glu})_2$, (7.00) is nearly identical with the reported value⁵ (7.10). However, it is not possible to compare the values of stability constants with those obtained by other workers using potentiometric and polarographic methods since the experimental conditions are widely different.

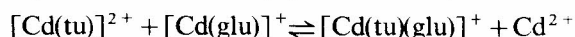
Cd(II)-thiourea-glutamate system

Polarograms were recorded with solutions containing 1 mM Cd(II), constant [glutamate] (3.15×10^{-4} M and 8.82×10^{-4} M in sets 1 and 2 respectively) and varying [thiourea] at pH 6.80. The two constant concentrations of glutamate were so chosen that at the lower value 1:1 and at higher value 1:2 complex species predominated in the simple systems. The ionic strength of all the experimental solutions was kept constant at 1.0 M (NaClO₄). On increasing the concentration of thiourea, the half-wave potentials of Cd(II) shifted towards more negative values and the shift was found to be more marked than in the simple systems.

Similar observations were recorded at higher concentrations of glutamate ion. In both the sets (1)

Fig. 1—Plot of $-E_{1/2}$ versus $-\log C_L$

and (2) of the mixed ligand systems, the reduction waves were found to be well-defined, reversible and diffusion-controlled in the presence and absence of the ligands. The plots of $-E_{1/2}$ versus $-\log C_L$ are smooth curves at both the concentrations of glutamate (Fig. 1). Schaap and McMasters⁶ method was applied to determine the overall stability constants of the mixed ligand complexes. The stability constant values of the three mixed ligand complexes, viz. $[\text{Cd}(\text{tu})(\text{glu})]^+$, $[\text{Cd}(\text{tu})(\text{glu})_2]$ and $[\text{Cd}(\text{tu})_2(\text{glu})]^+$ are found to be $\log \beta_{11} = 5.87$, $\log \beta_{12} = 8.69$ and $\log \beta_{21} = 6.42$. The negative value of β_{22} indicated the absence of $[\text{Cd}(\text{tu})_2(\text{glu})_2]$ mixed complex species. The average value of $\log E$ is 3.91 respectively, which is nearly identical with the value of the parent complex $[\text{Cd}(\text{tu})_4]^{2+}$. The stability of mixed ligand complexes can be compared with those of simple complexes. The equilibrium constant (K) for the reaction



is given by the relation

$$\Delta \log K = \log \beta_{11} - (\log \beta_{10} + \log \beta_{01})$$

The value of $\Delta \log K$ for the above reaction has been estimated as 0.57, which suggests that the mixed ligand complex species are more stable than the parent mono complexes.

The values of mixing constant K_m (equilibrium constant) and stabilization constant, K_s , calculated are found to be 1.22 and 0.92 indicating that the mixed complexes are more stable than the concerned simple bis complexes.

Prediction of β values from the statistical factors

It is known^{7,8} that for a mixed ligand system in which three mixed ligand complexes are formed, it is possible to predict on statistical basis, the values of the formation constants $\pi_{11} = 2(4/9 \beta_{02} \times \beta_{20})^{1/2}$; $\beta_{12} = 3 \times \beta_{30}^{1/3} \times \beta_{03}^{2/3}$; and $\beta_{21} = 3 \times \beta_{30}^{2/3} \times \beta_{03}^{1/3}$. The observed values of the stability constants of mixed ligand complexes with the predicted values obtained from the above equations are as follows:

Constant	Observed	Predicted	Increase
β_{11}	$10^{5.87}$	$10^{4.78}$	$10^{1.09}$
β_{12}	$10^{8.69}$	$10^{7.99}$	$10^{0.70}$
β_{21}	$10^{6.42}$	$10^{5.32}$	$10^{1.10}$

It is observed that the mixed ligand complexes have higher stabilities than would be predicted on statistical considerations. Such increases may be due to some weak bonding between unlike bound ligands, formation of π -bond between metal and both the ligands and the coordination tendencies of $\text{Cd}(\text{II})$ ion and the basicity of oxygen and nitrogen of the ligands.

The results were further tested by applying Van Panthaleon Van Eck equation⁹ and the formation of π -bond between metal and ligand was established from the deviations observed in the linear relationship of $\log K_N$ versus $(N-1)$ where N represents the coordination number.

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