TECHNICAL REPORT

KINETICS OF ELECTRODE PROCESS AND FORMATION CONSTANTS OF ZINC-TRIGLYCINE COMPLEXES IN AQUEOUS MEDIUM.

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It has been observed that zinc forms complexes with number of ligands. The tartrate, citrate, acetate, perchlorate, nitrate and chloride complexes of zinc have been studied[1–4] Gaur[5–9] and coworkers have also studied the electrode kinetics of zinc in various complex media. However, very little attention has been paid to the complexes of Zinc with amino acids which are not reversibly reduced at d.m.e. The present paper deals with the determination of kinetic parameters, composition and stability constants of the complex formed between zinc and triglycinate ions.

Reagent grade chemicals were used. The solution of Zn^{+2} was prepared by weighing as Zinc nitrate and standardized as usual. Sodium triglycinate was used as complexing agent. The ionic strength ($\mu = 0.5$) was kept constant by adding requisite amount potassium nitrate Gelatin was used as maxima suppressor. A manual set up of polarograph was used to record polarograms. The d. m. e had the following characteristics. m = 1.274 mg/sec. t = 4.12 Sec. (open circuit), A 'H' type cell saturated with potassium chloride & agar - agar bridge was used. The temperature was kept at 30±0.01°C. Purified nitrogen gas was used for deaeration.

Results and Discussion

A single well defined wave appeared in each case. The plots of i_d versus $\sqrt{h}$ (h is effective hieght of mercury column after applying back pressure) and i_d versus c ($c = [Zn^{+2}]$) were linear and passed through origin, thereby indicating that the reduction was diffusion-controlled. The plots of log $i/(i_d - i)$ versus $E_{d.e}$ were also linear with slopes of the order of 38 mV to 40 mV which were higher than that needed for two - electron—reversible reduction. As the reduction was not reversible, the observed half wave potential could not be used for calculation of stability constants. For this purpose, the reversible $E_{\frac{1}{2}}$ values were determined by Gelling's method[10] which involved plotting of $\left[E + (RT/nF) \log \left(\frac{i}{i_d - i}\right) \right]$ versus i, and extrapolating the curves to zero current values to give $Er_{\frac{1}{2}}$. The reversible half wave potential ($Er_{\frac{1}{2}}$) shifted towards more negative values and the diffusion current decreased with ligand concentration, indicating the formation of complexes between Zn^{+2} and triglycinate ions.

The plot of $Er_{\frac{1}{2}}$ versus - logC_x gave a smooth curve indicating the formation of two or more complex species which are in equilibrium. The DeFord & Hume[11] treatment for stepwise complex formation has been used for calculation of composition and stability constants of complexes formed. The results shows the existence of three complexes viz. $[Zn(Trigly)]^{+}$, $[Zn(Trigly)_2]$ and $(Zn(Trigly)_3]^{-1}$ having log $\beta_1 = 1.5051$, log $\beta_2 = 2.0792$ and log $\beta_3 = 4.1461$ respectively. The relative distribution of Zn^{+2} in various species at different ligand concentrations has also been calculated (Table-1).

As the electrode process is quasi - reversible, the kinetic parameters have been calculated by Gellings method. The plots of log (Z–I) versus $(E - Er_{\frac{1}{2}})$ where linear where Z is defined as

TABLE - 1 Relative distribution of Zn^{+2} simple and complex with the Triglycinate at 300°K. Total Zn^{+2} ion concentration = 0 5 mM

Triglycinate Conc (Moles)	M^{2+}	MX_1^{1+}	MX_2	MX_3^{1-}
0.01	31.9693	10.2301	0.3836	0.4475
0.02	20.8942	13.3723	1.0029	2.3401
0.03	17.6678	16.9611	1.9081	6.6784
0.04	14.7841	18.9349	2.8402	13.2544
0.05	11.4995	18.3992	3.4498	20.1241
0.06	7.1670	13 7733	3.0963	21.6743
0.07	6.1470	13.7693	3.6144	29 5180
0.08	4.3516	11.1401	3.3420	32.1896
0.10	2.5562	8.1799	3.0674	35.7873

$$\log (Z - I) = \log \frac{1.13}{\Lambda\sqrt{\tau_d}} - \frac{(1-\alpha)nF}{2.303RT}(E - E^r_{\frac{1}{2}})$$

$$Z = \text{antilog}\left[\frac{nF}{2.303RT}(E^r_{\frac{1}{2}} - E) - \log\left(\frac{i}{id-i}\right)\right]$$

where R,T, n and F have their usual significance.

From the slopes and intercepts of these plots the values of λ were obtained. The standard rate constant K_s is given by the relation $K_s = \lambda x D^{\frac{1}{2}}$, where D is the diffusion coefficient and is determined from diffusion current data by ilkovic equation. The values of K_s in the case of Zn^{+2} - triglycinate system were found to be of the order of 10^{-3} cm/Sec for complex species and uncomplexed Zn^{+2} in KNO_3 ($\mu = 0.5$) indicating that the irreversibility of electrode process for reduction of Zn^{+2} changes irregularly in the presence of triglycinate ions. The kinetic parameters are given in Table-2.

TABLE - 2 Kinetic parameters for reduction of Zn^{+2} in sodium Triglycinate midum (μ 0.5) at 303°K.

Triglycinate Conc. (Moles)	$E^r_{\frac{1}{2}}$ (-V vs. S.C.E.)	$D^{\frac{1}{2}} \times 10^3$ (m^2Sec^{-1})	λ	$K_s \times 10^3$ Cm Sec^{-1}
0.00	0.9810	4 0920	0.4651	1.90:0
0.01	0.9865	3.9892	0.7806	3.1139
0.02	0.9915	3.8297	1.1025	4.2222
0 03	0.9935	3.7765	0.7368	2.7825
0.04	0.9960	3.7395	0.4695	1.7557
0.05	0.9991	3.7765	0.4389	1.6575
0.06	1.0045	3.5637	0.6567	2.3402
0.07	1.0065	3.6177	0.4578	1.6562
0.08	1.0110	3.4975	0.4472	1.5640
0.10	1.0165	3.1914	0.5853	1.8679

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