

Polarographic Study of L-Tryptophan Complexes of Zn(II), Ni(II) & Co(II)

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Ni(II) yields a single irreversible and diffusion-controlled wave in the presence of tryptophan at pH 7 and $\mu = 0.1$ (NaClO₄). However, Zn(II) and Co(II) afford two waves of which the first is diffusion-controlled and irreversible and the second one is kinetically controlled. Zn(II) forms two consecutive complexes [Zn(Trypt)]⁺ and [Zn(Trypt)₂] with stability constants $\log \beta_1 = 9.0$ and $\log \beta_2 = 14.7$ while both Ni(II) and Co(II) form a single complex, viz. [Ni(Trypt)]⁺ and [Co(Trypt)]⁺ with stability constants $\log \beta = 7.2$ and 4.72 respectively.

A SURVEY of literature reveals that polarographic studies on complex formation of Zn(II) and Co(II) with L-tryptophan do not appear to have been undertaken so far, though a few reports are available on the polarographic behaviour of Ni(II)-tryptophan system. Chandra and Srivastava¹ reported that the reduction of Ni(II)-tryptophan system at d.m.e. resulted in a single irreversible wave in the presence of KCl, the wave exhibiting a positive shift in $E_{1/2}$ with increasing [DL-tryptophan]. But in borax and Kolthoff buffers a negative shift in $E_{1/2}$ was noticed. Lal and Christian² studied Ni(II)-DL-tryptophan system in 0.1 M KNO₃ and reported that the reduction occurred in two irreversible steps due to the formation of two complexes in sluggish equilibrium with each other. However, Lal and Christian did not take into consideration the role of the pH in complex formation, and the pH at which their investigations were made was not mentioned. Their calculations of stability constants also suffered from a serious error in that they did not take into consideration the free [ligand] i.e. tryptophanate ion concentration in the calculations. It was therefore worthwhile to study the polarographic behaviour of Zn(II), Ni(II), and Co(II) at pH 7 in the presence of increasing [L-tryptophan] with special reference to the determination of the composition and stability constants of the complexes formed.

All the chemicals used were of reagent grade and their stock solutions were prepared in conductivity water. The concentration of Zn(II) and Co(II) was kept at 1×10^{-3} M in each case while that of Ni(II) was kept at 5×10^{-4} M. NaClO₄ solution was used to keep the ionic strength constant at 0.1 M.

The concentration of tryptophanate ion was calculated from pH of the solution and pK_a values of L-tryptophan ($pK_1 = 2.28$ and $pK_2 = 9.72$). Triton X-100 (2×10^{-3} %) was used as maxima suppressor in the case of Ni(II) and Co(II). Since no maximum was encountered with Zn(II), the addition of Triton X-100 was avoided. Polarograms of the deaerated solutions were taken on a manual set-up (Toshniwal polarograph model CIO2 in con-

TABLE 1 — POLAROGRAPHIC CHARACTERISTICS OF Zn(II)-L-TRYPTOPHAN SYSTEM

[Zn ²⁺] = 1×10^{-3} M; $\mu = 0.1$ M (NaClO ₄); pH = 7					
[L-Tryptophan] $\times 10^3$ (M)	[X ⁻] $\times 10^3$ M	$-E_{1/2}^r$ (V, vs SCE)	$-E_{1/2}^r$ (V, vs (SCE)	i_d (μ A)	Slope (mV)
0	0	1.070	1.060	7.04	44
10	2.404	1.210	1.190	5.10	80
20	3.908	1.220	1.200	4.25	85
30	5.728	1.230	1.210	3.96	82
40	7.638	1.235	1.216	3.69	89
50	9.550	1.240	1.220	2.64	82

[X⁻] = Tryptophanate ion concentration.

junction with Toshniwal polyflex galvanometer, model PL-50) at $25 \pm 0.01^\circ$ C. Saturated calomel electrode (SCE) was used as a reference electrode. The d.m.e. had the following characteristics (in 0.1 M NaClO₄, open circuit) : For Zn(II) system : $m = 1.44$ mg/sec, $t = 4.87$ sec, $m^{2/3} t^{1/6} = 1.66$ mg^{2/3} sec^{-1/2}; $h_{\text{corr}} = 61.9$ cm; for Ni(II) and Co(II) systems : $m = 1.67$ mg/sec; $t = 4.04$ sec; $m^{2/3} t^{1/6} = 1.778$ mg^{2/3} sec^{-1/2} $h_{\text{corr}} = 63.0$ cm. The number of electrons (n) involved in the reduction processes was determined by millicoulometric method of DeVries and Kroon³. This gave the value of $n = 2$ at pH 7 in each case.

Zn(II)-L-tryptophan system — The polarograms of the solution containing 1×10^{-3} M Zn(II) and 10×10^{-3} M L-tryptophan at different pH values, indicated that the negative shift in $E_{1/2}$ was maximum at pH 7 and hence this pH was chosen to study the complex formation. Well-defined diffusion-controlled quasireversible wave appeared in the absence of tryptophan. On the addition of tryptophan in the concentration range 0.0 to 5×10^{-2} M two waves appeared in each case—the first being diffusion-controlled and totally irreversible⁴⁻⁷ while the other being kinetically controlled. Lal and Christian³ and recently Zutshi and Gupta⁹ suggested a method for determining the composition and stability constants of consecutively formed complex species undergoing irreversible reduction at d.m.e. This consisted of determining the value of reversible half-wave potential ($E_{1/2}^r$) by Gellings' method¹⁰. This method has been followed and the $E_{1/2}^r$ values as a function of [(tryptophanate)⁻] are presented in Table 1.

The plot of $E_{1/2}^r$ versus $\log [(tryptophanate)^-]$ was a smooth curve, thereby indicating the formation of successive complexes. DeFord and Hume's¹¹ method as modified by Irving¹² was applied for the calculation of composition and stability constants of the complexes. The values of $F_1 [X]$ functions at different [(tryptophanate)⁻] were determined. Two complex species, viz. [Zn(Trypt)]⁺ and [Zn(Trypt)₂] with stability constants $\log \beta_1 = 9.0$ and $\log \beta_2 = 14.70$ are formed.

Ni(II)-L-tryptophan system — The polarograms of Ni(II)-tryptophan system at different pH values were taken and based on these, pH 7 was chosen to study complex formation. At different concentration of L-tryptophan a single well-defined diffusion-controlled irreversible wave appeared with shift in $E_{1/2}$ to more negative potentials thereby indicating complex formation between Ni(II) and L-tryptophan. The linear plot of $E_{1/2}$ versus $\log [(tryptophanate)^-]$ indicated the formation of a single complex. The composition and stability constant were determined following the method of Tamamushi and Tanaka¹³. The value of coordination number j , comes out to be 1. The composition of the complex is, therefore, $[Ni(Trypt)]^+$ with stability constant $\log \beta = 7.2$. The results are in contrast to those of Lal and Christian², stability constants $\beta_1 = 1.0 \times 10^3$, $\beta_2 = 1.5 \times 10^7$ and $\beta_3 = 6.8 \times 10^9$.

Co(II) — tryptophan system — As in Zn(II) and Ni(II) system, pH 7 was chosen to study complex formation. At different ligand concentrations two waves appeared, of which the first was diffusion-controlled and irreversible and the second one was kinetically controlled. The $E_{1/2}$ of the first wave got shifted to more negative potential with increasing $[(tryptophanate)^-]$. This shows that the first wave is due to the reduction of Co(II)-tryptophan complex.

The plot of $E_{1/2}$ versus $\log [(tryptophanate)^-]$ was linear, indicating the formation of single complex. The method of Tamamushi and Tanaka¹³ has been applied to determine the composition and stability constant of the complex. The value of the coordination number, j , comes out to be 1. The composition of the complex is, therefore, $[Co(Trypt)]^+$ with stability constant $\log \beta = 4.72$.

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References

- CHANDRA, S. & SRIVASTAVA, S. N., *Indian J. Chem.*, **7** (1969), 829.
- LAL, S. & CHRISTIAN, G. D., *J. prakt. Chem.*, **313** (1971), 99.
- DEVRIES, T. & KROON, J. L., *J. Am. chem. Soc.*, **75** (1953), 2484.
- MEITES, L., *Polarographic techniques* (Interscience, New York), 1965, 232.
- GOTO, R. & TACHI, I., *Proc. Intern. Polarogr. Congr. Prague*, **1** (1951), 69.
- DELAHAY, P., *J. Am. chem. Soc.*, **73** (1951), 4944.
- KIVALO, P., OLDHAM, K. B. & LAITINEN, H. A., *J. Am. chem. Soc.*, **75** (1953), 4148.
- LAL, S. & CHRISTIAN, G. D., *J. prakt. Chem.*, **1** (1971), 99.
- ZUTSHI, KAMALA & GUPTA, K. C., *Indian J. Chem.*, **16A** (1978), 453.
- GELLINGS, P. J., *Z. elektrochem. Bur. Bunsenges Phys. Chem.*, **66** (1962), 477, 481, 788; **67** (1953), 167.
- DEFORD, D. D. & HUME, D. N., *J. Am. chem. Soc.*, **73** (1951), 5321.
- IRVING, H., *Advances in polarography*, edited by I. S. Longmuir, Vol. I (Pergamon Press, London), 1960, 42.
- TAMAMUSHI, R. & TANAKA, N., *Bull. chem. Soc., Japan*, **22** (1949), 227.

Polarographic Studies on the Effect of Increasing Concentrations of Some Complex Forming Agents on the Kinetics of the Irreversible Electrode Reactions of Co(II), Dioxouranium(VI), In(III) & Th(IV)

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The polarographic behaviour of Co(II), dioxouranium(VI), In(III) and Th(IV) has been studied at 25°C in the presence of increasing concentrations of some complex forming agents, viz. sulphosalicylate (SSA^{2-}), tartrate ($Tart^{2-}$) and $EDTA^{2-}$. The reduction of all the depolarizers has been found to be diffusion-controlled and irreversible. Koutecky's treatment has been applied to calculate the rate constant ($k_{t,h}$) at various potentials in the presence of increasing concentrations of the ligands. The values of the kinetic parameters (αn_a and $k_{f,h}^\circ$) have been calculated as a function of the concentration of ligand.

MANY metal complexes are irreversibly reduced and several methods¹⁻⁵ have been proposed for the determination of their composition and stability constants. Several other workers⁶⁻¹⁶ have put forward methods for studying the kinetics of the irreversible reduction of metal complexes at d.m.e. However, in these methods the influence of the varying concentration of complexing agent on the electrical double layer or on the kinetics of electrode reaction of depolarizer has not been taken into account. We report here a polarographic study on the influence of increasing concentration of some complex forming agents on the kinetics of the electrode reactions of Co(II), dioxouranium(VI), In(III) and Th(IV). This influence has been studied on the basis of the variations observed in the values of the parameters, αn_a and $k_{f,h}^\circ$, and also in terms of the value of $k_{t,h}$ at a selected potential (which lies between the foot and the plateau of the wave). The following complex forming agents (ligands) have been used: 5-sulphosalicylic acid (sodium salt), tartrate (as sodium potassium tartrate) and EDTA (disodium salt of ethylenediaminetetraacetic acid).

Stock solutions of $UO_2(NO_3)_2 \cdot 6H_2O$ (AR, BDH), $In(NO_3)_3 \cdot 3H_2O$ (E. Merck, G.R.), $Th(NO_3)_4$ (M & B England), and $Co(NO_3)_2 \cdot 6H_2O$ (AR, BDH) were prepared in conductivity water. EDTA (disodium salt) and sodium potassium tartrate were of AR (BDH) grade. 5-Sulphosalicylic acid (sodium salt) was of GR (E. Merck) grade.

The concentration of each of the depolarizers in the final solution to be polarographed was maintained at 1.0×10^{-3} M. The polarograms of the solutions were obtained in the presence of increasing concentrations of the complexing agents at $25 \pm 0.1^\circ C$ and at a constant ionic strength and pH by using a manual polarograph (Toshniwal CL02) in conjunction with polyflex galvanometer (Toshniwal PL 50). Purified nitrogen was used for removing the dissolved oxygen. The potentials were measured against a saturated calomel electrode (S.C.E.). Triton X-100 (1.0×10^{-3} %) was used as the maxima suppressor.