

POLAROGRAPHIC STUDIES OF 3-HYDROXY-3-PHENYL-1-(DICHLORO PHENYL) TRIAZENE WITH Ni (II) COMPLEX

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ABSTRACT

Polarographic studies of Ni (II) - 3-hydroxy-3-phenyl-1-(dichloro phenyl)triazene (HPDCT) complex has been done in aqueous medium. It is observed that Ni (II) forms 1:2 complexes with HPDCT and the electrochemical reduction of the complex is diffusion controlled in nature between pH 6.5 to 7. Well defined waves are obtained and the $E_{1/2}$ shifts to more negative side with the addition of HPDCT. The log β value have been calculated using Lingane method and a 2 electron reduction mechanism is proposed. The present studies are first attempt to study electro chemical behavior of Ni(II)-3-hydroxy-3-phenyl-1-(dichloro phenyl) triazene complex.

Keywords: Polarography, Ni(II)- Hydroxytriazene complexes, electrochemical behavior.

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INTRODUCTION

Polarography is a well established electrochemical technique for the study of electro chemical behavior of transition metal complexes. Hydroxytriazenes are well known analytical reagent for transition metal determination.²⁻⁵ We have reported similar studies using D.C. Polarography earlier⁶⁻⁷. Further there are some reports on similar compounds from other places.⁸⁻¹³ In view of this a method has been developed to study nickel Hydroxytriazene complexes using polarography. The complex composition as well as stability constant for new hydroxytriazene system have been worked out.

EXPERIMENTAL

Synthesis of 3-hydroxy-3-Phenyl-1-(2,5-dichloro phenyl)triazene (HPDCT)

Hydroxytriazenes are synthesized in following steps:

Step-1

Synthesis of phenyl hydroxylamine : In a one litre beaker (0.1 mol) of nitrobenzene 5 g of NH_4Cl 100 ml water and 50 ml $\text{C}_2\text{H}_5\text{OH}$ were mixed, stirred mechanically with constant heating. 20g Zn dust was added in small lots such that the temperature of reaction mixture remained at about 60°C . Addition of Zn dust was completed in 40 min. The reaction mixture was stirred mechanically for another 15min. The solution of hydroxylamine was filtered under suction and washed with hot water. The filtrate was taken in a beaker and kept in freezer and used as such for coupling with diazotized product.

Step-2 Diazotization

Diazonium salt of 2,5-dichloro aniline: In a 500 ml beaker 0.1mol (17.2 ml) of 2,5-dichloro aniline was dissolved in warm mixture of 25 ml of concentrated HCl and 25 ml of water. After constant stirring the mixture was kept in a freezer to cool. In another beaker 6.9 g of NaNO_2 was dissolved in 20 ml of distilled water and kept in the freezer. The beaker which contained 2,5-dichloro aniline solution was put in an ice bath to maintain temperature between 0 to 5°C . To this NaNO_2 solution was added drop by drop with continuous stirring. The diazotized product so obtained was directly used for coupling.

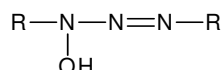
Step-3 Coupling

Coupling the compounds obtained in step(a) and (b) was done at 0-5°C, under mechanical stirring with occasional addition of sodium acetate to maintaining pH at about 5. The compound 3-hydroxy-3-phenyl-1-(2,5-dichlorophenyl) triazene was obtained as yellowish fluffy powder after crystallization from ethanol.

The purity and characterization of the compound was ascertained using following physico chemical techniques: CHN and FTIR Spectra.

IR Spectral analysis

IR Spectra of the synthesized hydroxytriazene were recorded to characterize the compound. Following bands were observed 1489 cm⁻¹ (N-N), 1732 cm⁻¹ (N=N), 3086 cm⁻¹ (C-H), 3252 cm⁻¹ (OH), 1391 cm⁻¹ (C-N), 763 cm⁻¹ (C-Cl), which are characteristics of Hydroxytriazene.



Thus it was found that compound is in pure state.

Polarographic study of nickel (II) complexes with hydroxytriazenes

A Systronics polarograph 1632 was used for obtaining current voltage curves. Metal solution (1mM) was prepared using NiSO₄.7H₂O and ligand solution was prepared by dissolving requisite quantity of HPDCT (.01 M) in double distilled water. Citric acid and Na₂HPO₄ solutions were used as buffer to maintain pH. Ionic strength was kept constant by using KCl as supporting electrolyte, Gelatin (0.002%) was used as maximum suppressor. The capillary had following characteristics t=1 drop/sec. IR drop correction were applied. The polarographic study of Ni(II)-HPDCT has been done at D.M.E in aqueous medium. Solution was deaerated by purging oxygen free nitrogen for 20 min.

Determination of half wave potential of Ni(II) with HPDCT

A 1×10⁻³ M Ni(II) solution in N/10 KCl has been used to obtain polarograms of Ni(II). This showed an E_{1/2} at 0.25 v/s SCE. The polarogram of Ni(II) hydroxytriazene showed the half wave potentials shifted towards more negative value with increasing concentration of ligand indicating complex formation and the diffusion current was found to decrease regularly with increase of HPDCT concentration. Thus it is established that Ni(II) formed complex with HPDCT.

Determination of stability constant of the complex

Ni(II) hydroxytriazene complex solution gave a well defined reversible wave in various concentrations of ligand at constant ionic strength. The shift of E_{1/2} towards more negative value with increase of ligand's concentration and decrease in diffusion current indicated complex formation. The Lingane's¹ equation was used to calculate the overall stability constant of complex formed in the system. The equation used was-

$$\Delta E_{\frac{1}{2}} = \frac{.0591}{n} \log \beta_{MXJ} + J \frac{.0591}{n} \log C_x \quad (1)$$

Here,

Δ E_{1/2} = Difference of half wave potentials of simple metal ion and complexed ion.

log β = overall stability constant

C_x = Concentration of hydroxytriazene

n = Number of transferred electrons

J = Co-ordination number.

Values of stability constant (log β) for each complex were calculated using Lingane's equation mentioned above. Results obtained are given in Table-2.

RESULTS AND DISCUSSION

Results of the polarographic studies of Ni (II) complex with hydroxytriazene have been reported in tables II and also presented graphically. It is clear from this table and plots that Ni(II) forms fairly stable complexes with hydroxytriazenes mentioned above. In case of this complex study co-ordination no. (J) has been found to be six.

Table-1: Physical Characteristics, M.P., CHN values of the Reagent

Molecular formula	Color and shape of the crystals	Solvent used	Elemental analysis				M.P. (°C)
				% Carbon	% Hydrogen	% Nitrogen	
C ₁₂ H ₉ N ₃ OC ₂	Yellow colored microcrystals	Ethanol	Th.	41.86	4.65	24.41	81
			Exp.	41.90	4.61	24.40	

Thus number of ligand molecules attached to each metal ion comes out to be two as ratio of J to n. Looking to the bidentate nature of hydroxytriazene ligand it seems that four co-ordination number of metal ion are satisfied by two ligand molecules and remaining co-ordination sites may have been satisfied by water molecules via bonding. Thus the tentative structure of Ni –HPDCT complex can be proposed as-

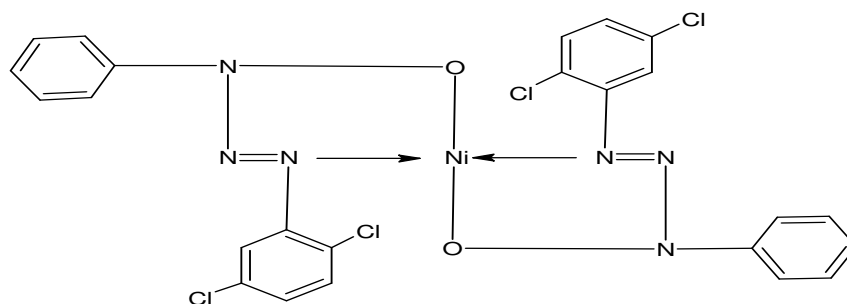


Fig.-1: Tentative structure of Nickel (II) complex of hydroxytriazenes having square planar geometry

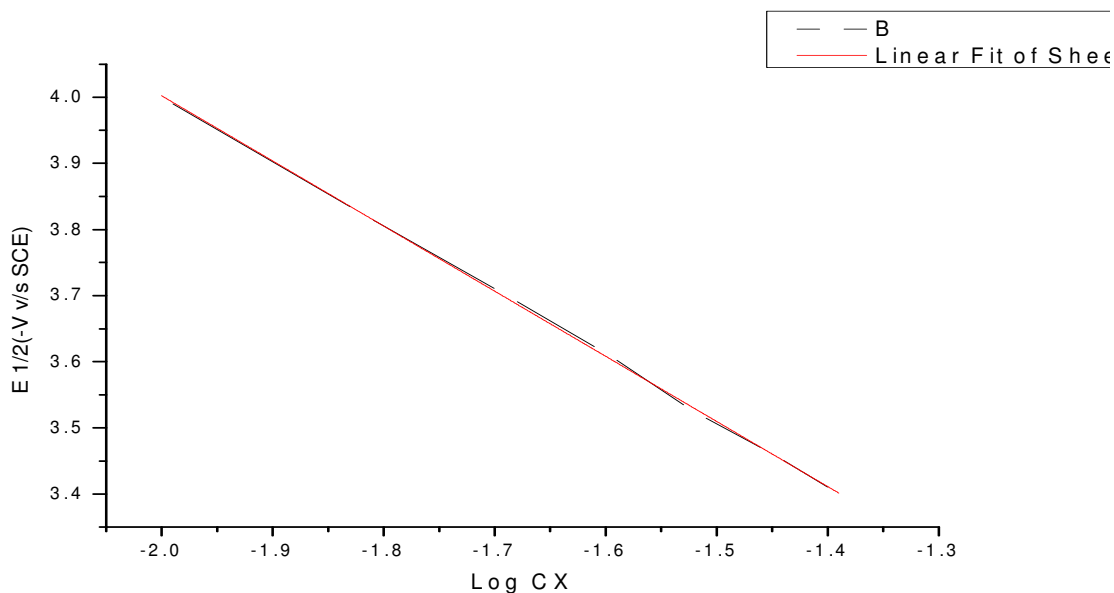


Fig.-2

Table-2: Polarographic characteristics of hydroxytriazene 3-hydroxy-3-Phenyl-1-(2,5-dichloro phenyl)triazene (HPDCT)

S.No.	Cx	Log Cx	E _{1/2}	Log β
1.	0.010	-2.0000	4.0	9.02
2.	0.015	-1.8239	3.9	11.55
3.	0.020	-1.6989	3.8	11.72
4.	0.025	-1.602	3.7	11.87
5.	0.030	-1.5228	3.6	11.93
6.	0.035	-1.4559	3.5	11.90
7.	0.040	-1.3979	3.4	11.81

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