



POLAROGRAPHIC STUDIES ON INTERACTION OF 3-HYDROXY-3-p-TOLYL-1-p-SULFONATO (SODIUM SALT) PHENYLTRIAZENE WITH Ni (II) IN AQUEOUS MEDIUM

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ABSTRACT

Polarographic studies of Ni (II) - 3-hydroxy-3-p-tolyl-1-p-sulfonato (sodium salt) phenyltriazene (HTST) have been done in aqueous medium. Ni (II) forms 1:2 complexes with HTST and the electrochemical reduction of the complex is diffusion controlled in nature between the pH 6.5 to 7. Well defined waves are obtained and the $E_{1/2}$ shifts to more negative side with the addition of HTST. The reduction mechanism indicates two electron reversible reduction processes and the stability constant $\log \beta$ value found is 10.99.

Keywords: 3-Hydroxy-3-p-tolyl-1-p-sulfonato (sodium salt) phenyltriazene, Polarographic reduction.

INTRODUCTION

In the present work complex formation of Ni (II) with 3-hydroxy-3-p-tolyl-1-p-sulfonato (sodium salt) phenyltriazene (HTST) have been examined polarographically and stability constants are in very good agreement with results of spectrophotometric studies on this system.

EXPERIMENTAL

Synthesis:

3-hydroxy-3-p-tolyl-1-p-sulfonato (sodium salt) phenyltriazene has been synthesized as per reported method⁴. In this method p-nitro toluene (13.7 ml) was reduced with Zn dust (20 g) in the presence of NH_4Cl (5.3 g) at 40-60°C to obtain phenyl hydroxylamine. The diazotized product was obtained by adding sodium nitrite (6.9 g) to sulphanilic acid (17.3 g) dissolved in 20 ml HCl and 100 ml water in small lots at 0-5°C under constant mechanical stirring. The diazonium compound was coupled with phenyl hydroxylamine at 0-5°C under mechanical stirring with occasional addition of sodium acetate solution for maintaining pH close to 5 during coupling process. After complete addition of diazonium salt NaCl was added in sufficient quantity for salting out. The hydroxytriazene was obtained as light yellow needle shape crystals after crystallization from double distilled water. Its purity was checked by m.p. determination and CHN analysis. M.P. was found 170°C. The theoretical and experimental values of %C, %N and %H were found to be (Th.) 40.90, 11.01, 2.91 and (Exp.) 40.31, 11.22, 2.90 respectively. Further the compound was subjected to IR spectral analysis which yielded the characteristics bands reported for hydroxytriazenes⁵ and their values for $\nu_{\text{O-H}}$, $\nu_{\text{N-H}}$, $\delta_{\text{N-H}}$ and $\delta_{\text{N-OH}}$ are 3450, 3190, 1590 and 940 respectively. The IR spectra confirmed their presence establishing purity of compound.

Apparatus and solutions:

A Systronics Polarograph 1632 was used for obtaining current- voltage curves. Metal solution (1mM) was prepared using nickel sulphate heptahydrate and ligand solution was prepared by dissolving HTST (.01M) in double distilled water. Citric acid and Na_2HPO_4 solutions were used as buffer to maintain pH of test

solution. Ionic strength was kept constant by using KCl as supporting electrolyte. Gelatin (.002%) was used as maximum suppressor.

The D.M.E. had the following characteristics: $m = 1.35 \text{ mg/sec.}$; $t = 1 \text{ sec / drop.}$

The electrochemical behaviour of Ni (II) – HTST has been studied at d.m.e. in aqueous medium. Solution was deaerated by purging of oxygen free nitrogen through the polarographic cell for about 20 minutes. Temperature was maintained at 298 K.

Study of Ni (II) – HTST System:

Solutions of Ni (II) 1 mM mixed with various concentrations of HTST were prepared from the stock solution and polarographed. The shift of half-wave potentials towards a more negative value with increasing concentration of ligand indicated complex formation and the diffusion current was found to decrease regularly with increase of HTST concentration. To avoid any precipitation, the polarographic behaviour of Ni (II) – HTST system has been studied in a solution containing a ten fold excess of ligand.

RESULTS AND DISCUSSION

A single well defined wave was obtained for Ni (II) – HTST system between pH 6.5 to 7. Diffusion controlled nature of each wave was verified from i_d Vs C and i_d Vs \sqrt{h} plot. Where i_d = diffusion current in μA

C = conc. In m mole lit^{-1}

h = height of mercury column.

Slope of the linear plots of $\log\left(\frac{i}{i_d - i}\right)$ Vs E_{de} was found to be in the range of 30-32 mV, thereby

showing the reversible nature of reduction process involving two electrons.

Determination of coordination number:

The plot of half wave potential $E_{1/2}$ Vs $\log C_x$ (where C_x = concentration of ligand in m mole lit^{-1}) have been found to be a straight line showing the formation of most stable complex. The coordination number (J) of the metal in the complex is obtained from the slope of this plot, as may be expressed by:

$$\frac{d\left(E_{\frac{1}{2}}\right)_c}{d \log C_x} = -J \frac{.0591}{n}$$

Where n = no. of electrons involved (here $n = 2$). The value of j as determined by slope is 4. This shows that the complex composition is in 1:2 (M: L) ratio.

Determination of stability constant:

The stability constant $\log \beta$ of the Ni (II) – HTST complex has been determined by classical method of Lingane¹, as this method is applicable for maximum coordination number and for the stability constant of highest complex formed. The $\Delta E_{1/2}$ has a linear correlation with ligand concentrations; which shows that there is only one complex formed in the solution. The following equation has been used to calculate the stability constant of the complex studied.

$$\Delta E_{\frac{1}{2}} = \frac{.0591}{n} \log \beta + j \frac{.0591}{n} \log C_x$$

Here,

$\Delta E_{\frac{1}{2}}$ = Difference of half wave potentials of simple metal ion and complexed ion.

n = Number of transferred electrons

$\log \beta$ = Stability constant of complex formed.

j = Coordination number

C_x = Concentration of ligand

The value of $\log \beta$ has been found to be 10.99. Which is in good agreement with the results of similar hydroxytriazene - Ni (II) complexes studied spectrophotometrically by earlier authors²⁻³. The data are given in Table-1.

Table-1: Polarographic study of Ni (II) – HTST system in aqueous medium.
[Ni²⁺]: 1mM; pH =6.5

S.No.	C _x	Log C _x	E _{1/2} (-V vs. SCE)	Log β
1	00.00		1.190	
2	0.010	-2.0000	1.290	11.38
3	0.015	-1.8239	1.295	10.85
4	0.020	-1.6980	1.300	10.52
5	0.025	-1.6020	1.325	10.98
6	0.030	-1.5228	1.335	11.00
7	0.035	-1.4559	1.340	10.90
8	0.040	-1.3979	1.355	10.67
9	0.045	-1.3467	1.375	11.65

Thus, from this observation the average value of $\log \beta$ is found 10.99.

CONCLUSION

Above studies have included a new reagent for the polarographic studies of nickel complexes in addition to spectrophotometric studies. This is a new development for quantitative analysis of nickel.

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