Determination of Copper (II) and Palladium (II) by Polarographic Methods

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Abstract- Schiff base 2–Hydroxy–5–methoxy Benzaldehyde – Tris [HMBT] Ligand is a new chromogenic reagent have not been used so far for the determination of copper and palladium in trace quantities. Effect of p^H on wave height for COPPER-[HMBT] PALLADIUM –[HMBT] systems have been studied at p^H 7-8.5 and 8.5-11.5 for Copper and Palladium respectively in 0.1 m molar $NaNo_3$ and 0.002 % Triton –x–100 which increases the stability of the complex . Effect of Ligand concentration on Copper and Palladium have been studied at P^H 8.5 for Copper and Palladium, Effect of height of mercury column on copper-[HMBT] palladium –[HMBT] at P^H 8.5 , Effect of copper ion concentration and palladium ion concentration on the wave height at P^H 8.5 have been studied.

Index Terms- polarographic ,copper ,palladium ,HMBT ligand.

I. INTRODUCTION

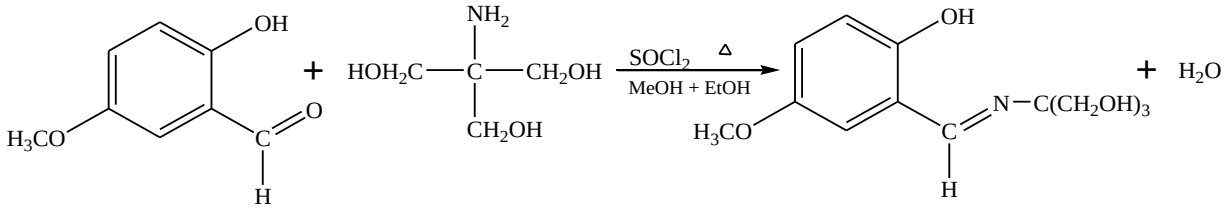
Many number of Schiff bases were synthesized from Tris (Hydroxymethyl) methylamine with different aldehydes and were tested as pharmaceutical intermediates [1,2], bactericides, fungicides [3] and pesticides [4]. Schiff bases prepared by Inoyatov [5] act as effective polymers. Spectrophotometric work [6] on the azomethine of pyridoxal–5'–phosphate–Tris was carried out and determined the formation constant (pKa) values. Vyas *et al.*, [7] published work on polarographic determination of ligand–proton stability constants for Salicylaldehyde–Tris (ST) Schiff base in 50% DMF. Effect of pH, amine concentration and solution composition of pyridoxal–5'–phosphate–Tris was reported by Blazquex *et al.*, [8] employing polarographic technique. ., [9] reported the effect of pH, supporting electrolytes, solvents and acid concentration on the polarographic reduction of ST. Characterization of seven new Schiff bases derived from Tris and various aldehydes was reported [10]. [11,12] reported determination of metal-to-ligand ratio and stability constants of complexes of palladium(II) andcopper(II) in presence of Schiff bases derived from Tris and various ketones in KNO_3 as supporting electrolyte at pH 10.5 in 50% DMF–water medium.

The various metal ions such as Cu(II), Pb(II), Cd(II), Pd(II) and In(III) using HMBT as complexing agent polarographically in $NaNO_3$ as the supporting electrolyte at pH 8.5 in 40 : 60 methanol–water medium. The studies include effect of pH, effect of ligand concentration, effect of height of mercury column and effect of metal ion concentration. The studies were aimed at establishing the complexing ability of 2-Hydroxy-5-methoxy benzaldehyde–Tris and developing a procedure for the determination of various metal ions present individually and in binary mixtures constituting important alloys and ores of industrial importance.

Preparation and Characterization of 2–Hydroxy–5–methoxy Benzaldehyde – Tris [HMBT] Ligand

Preparation of the ligand: 2–Hydroxy–5–methoxy Benzaldehyde – Tris [HMBT]

Equimolar concentrations of Tris (Hydroxymethyl) methylamine **(TRIS)** and 2–Hydroxy–5–methoxy Benzaldehyde were dissolved separately in methanol and refluxed for one hour in methanol & ethanol solvent mixture in presence of few drops of acid catalyst namely $SOCl_2$. The refluxed solution was allowed to cool and kept aside for overnight. White crystalline needles were obtained and the compound was recrystallized. The melting point and yield of the compound were found to be 70–72^0C and 82% respectively.



2-Hydroxy-5-methoxy Benzaldehyde **Tris (Hydroxymethyl) methylamine** **HMBT**

II. Characterization of the Ligand

The characterization of the Schiff base was made by Elemental analysis, Chemical reactions and IR studies. Elemental analysis for Carbon, Hydrogen, Oxygen and Nitrogen present in the Schiff base was obtained from CDRI, Lucknow, India. Chemical analysis for the functional groups i.e., carbonyl (>C=O) and amine (-NH_2) groups was carried out by standard procedure and found to be absent indicating the formation of azomethine.

An infrared spectrum for the derived Schiff base was recorded by KBr Pallet method employing Perkin Elmer IR spectroscopy. Infrared spectrum (Fig. 6) of the azomethine obtained from the reaction of 2–Hydroxy–5–methoxy Benzaldehyde and Tris [HMBT] showed peak at 1650 cm^{-1} indicating the existence of >C=N– group in all compounds. Peaks were also observed in the region of 3370 – 3340 cm^{-1} (broad, OH–stretching), 3200 – 3180 cm^{-1} (broad, phenolic OH), 1600, 1530, 1500, 1450 cm^{-1} (aromatic >C=C< vibrations) and 1230 – 1220 cm^{-1} (C–O stretching coupled phenolic OH deformation). The above IR data clearly suggested that the chemical reaction between the amino and various aldehydic group was taken place resulting in the formation of respective Schiff base compound. The other groups in the compound remain unaffected during conversion into azomethine. The elemental analysis and IR data were tabulated in the Table 1.

III. NMR Spectra

In the present investigation ^1H NMR spectrum was obtained for the ligand HMBT using Gemini – 200MHz ^1H NMR Spectrometer from IICT, Hyderabad, in DMSO–D^6 solvent at room temperature. Important chemical shift values for various protons such as proton of azomethine group, methyl protons of methoxy group, methyl protons of hydroxy methyl group, hydroxyl protons of hydroxy methyl group, proton of aromatic hydroxyl group and aromatic protons present in the compound were summarized in the Table-2.

TABLE-1 Analytical and IR spectral data of [HMBT] Ligand

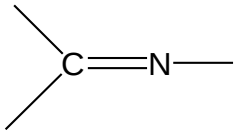
Molecular Formula	$C_{12}H_{17}NO_5$	
Colour	Yellow	
Melting point	70 – 72 °C	
Elemental analysis	**Found (%)**	**Calc. (%)**
Carbon	56.43	56.46
Hydrogen	6.70	6.71
Oxygen	31.32	31.34
Nitrogen	5.47	5.49
Yield	82%	
IR absorption band 	1650 cms^{-1}	

TABLE - 2 ^{1}H NMR spectral data for [HMBT] Ligand in DMSO–D^6

Sl. No.	Different protons in the Ligand	δ Chemical schift in ppm
1	–HC=N (Proton of azomethine group)	7.96
2	–OCH3 (Methyl protons of methoxy group)	3.66
3	–CH_2OH (Methyl protons of hydroxymethyl group)	3.78
4	–CH_2OH (Hydroxyl protons of hydroxymethyl group)	4.62
5	Ar–OH (Hydroxyl Proton of Aromatic hydroxy group)	5.73
6	Aromatic protons	6.64–7.25

IV. RESULTS AND DISCUSSION

i)Polarographic Behaviour of Individual Metal Ions (Cu^{2+}, Pd^{2+}) in Presence of [HMBT]

a)Effect of pH on the Wave height : The main purpose of studying effect of hydrogen ion concentration on polarographic wave is to ascertain the hydrogen ion participation in electrochemical reduction at d.m.e. Further, it is also useful to fix an appropriate pH value at which separation of two or more metal ions is possible present in mixture solutions. In the present study, effect of pH on various metal ions in presence of 0.1M $NaNO_3$ as the supporting electrolyte 0.06M ligand concentration at mercury height of 70.0 cms in 40 **:** 60 methanol–water medium. The pH range studied for Copper and Palladium, was between 5.0–11.5. From $E_{3/4} - E_{1/4}$ value computed from the polarograms of pH studies indicated that, Copper and Palladium reduced reversibly .

TABLE – 3

Effect of pH on Copper – [HMBT] System

$[Cu^{+2}]$ = 1.0 mM
[HMBT] = 0.06M
$[NaNO_3]$ = 0.1 M
Triton –x–100 = 0.002 %

pH	$E_{1/2}$ (–V. vs S.C.E)	$E_{3/4} - E_{1/4}$ (mV)
7.0	0.219	56.82
7.5	0.261	56.80
8.0	0.301	57.78
8.5	0.311	56.84

TABLE – 4

Effect of pH on Palladium – [HMBT] System

$[Pd^{2+}]$ = 1.0 mM
[HMBT] = 0.06M
$[NaNO_3]$ = 0.1 M
Triton –x–100 = 0.002 %

pH	$E_{1/2}$ (–V. vs S.C.E)	$E_{3/4}$ – $E_{1/4}$ (mV)
8.5	0.919	78.98
9.5	0.987	79.92
10.5	1.007	78.90
11.5	1.019	78.98

b) Effect of Ligand concentration

Effect of ligand concentration on polarographic wave is of considerable importance since; it gives whether the polarographic wave is controlled by diffusion alone or depends on some other factors such as kinetic, adsorption or catalytic currents. Further, it also helps to establish the validity of Ilkovic equation. Well defined polarograms obtained with different concentrations of the ligand enables to carryout qualitative determination of metal ions in binary, ternary etc. mixtures constituting important ores and alloys. In addition to the above application, the studies also help to establish the complexation of ligand with various metal ions.,effect of varying concentrations of the HMBT ligand on Copper(II), palladium (II) and in presence of 0.1M $NaNO_3$ as supporting electrolyte and 0.002% of Triton–X–100 as maximum suppressor at pH 8.5. The results indicated that HMBT was able to complex with copper and palladium the metal ions under consideration by the fact that diffusion current **(i_d)** decreased where as half–wave potential **($E_{1/2}$)** shifted towards more negative values with increasing concentration of the ligand Further, the studies also suggested that Lead and Cadmium reduced reversibly at d.m.e

TABLE – 5

Effect of Ligand [HMBT] Concentration on copper

$[Cu^{+2}]$ = 1.0 mM
$[NaNO_3]$ = 0.1 M
pH = 8.5
Triton –x–100 = 0.002 %

[HMBT] (M)	$E_{1/2}$ (–V. vs S.C.E)	i_d (µA)	Slope (mV)
0.005	0.258	6.1042	60.50
0.008	0.264	6.0585	60.50
0.010	0.268	6.0130	61.44
0.020	0.278	5.9674	58.98
0.030	0.287	5.9219	58.98
0.040	0.302	5.7852	57.34
0.050	0.307	5.6941	57.82
0.060	0.311	5.5574	60.50
0.080	0.318	5.4208	58.98
0.100	0.323	5.2841	57.34

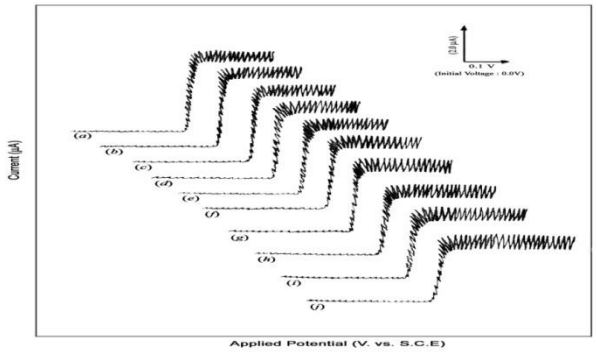


Fig. 1 : Polarograms of 1.0 mM copper ion in a) 0.005 b) 0.008 c) 0.010 d) 0.020 e) 0.030 f) 0.040g) 0.050h) 0.060 i) 0.080 and j) 0.10 M [HMBT] and 0.1M $NaNO_3$ at pH 8.5

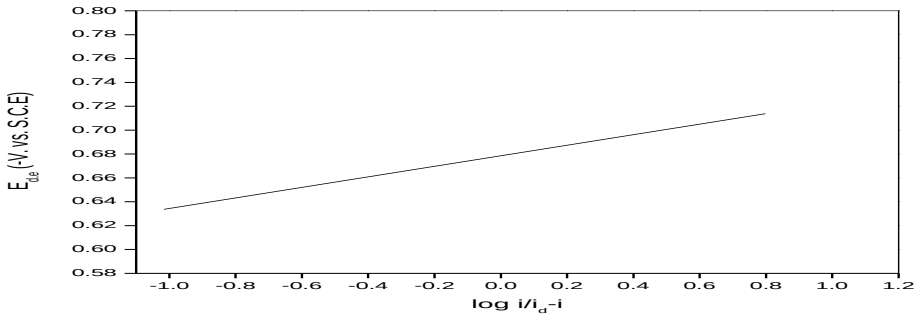


Fig. 2 : A typical log plot of 1.0 mM copper in 0.1 M [HMBT] and 0.1M $NaNO_3$ at pH 8.

TABLE – 6
Effect of Ligand [HMBT] Concentration on Palladium

$[Pd^{2+}]$	=	1.0 mM
$[NH_3+NH_4Cl]$	=	1.0M
pH	=	8.5
Triton –x–100	=	0.002 %

[HMBT] (M)	**$E_{1/2}$** (–V. vs S.C.E)	**i_d** (µA)	**Slope** (mV)
0.005	0.856	5.9174	64.88
0.008	0.868	5.7910	64.49
0.010	0.879	5.6651	64.04
0.020	0.882	5.5392	64.02
0.030	0.885	5.4133	63.90
0.040	0.899	5.3504	64.14
0.050	0.907	5.2874	63.78
0.060	0.919	5.2245	63.22
0.080	0.923	5.0986	63.38
0.100	0.935	4.9727	63.00

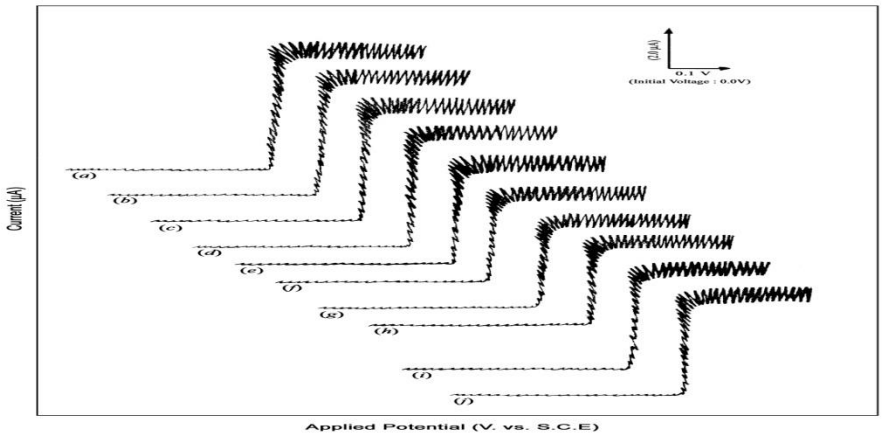


Fig. 3: Polarograms of 1.0 mM Palladium ion in a) 0.005 b) 0.008 c) 0.010 d) 0.020 e) 0.030 f) 0.040g) 0.050h) 0.060 i) 0.080 and j) 0.10 M [HMBT] and 0.1M $NaNO_3$ at pH 8.5

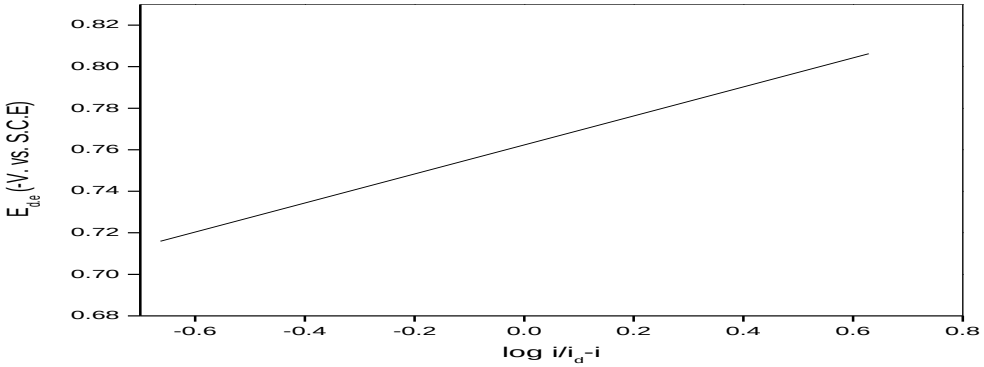


Fig .4 A TYPICAL LOG PLOT OF 1.0 mM Palladium 0.1M [HMBT] AND 0.1M $NaNO_3$ AT P^H 8.5.

c) Effect of height of mercury column :

Effect of height of mercury column on polarographic wave helps to establish the diffusion controlled nature of the electrode reaction at d.m.e by calculating $i_d/\sqrt{h}$ values. In the present studies, in detail the influence of mercury height on diffusion current of metal ions such as copper(II), palladium(II), ions at 1.0 mM concentration (in presence of fixed concentration of HMBT ligand (0.05M), ionic concentration 0.1M $NaNO_3$ except 1.0M as supporting electrolyte and 0.002% of Triton–X–100 as maximum suppressor at pH 8.5. Results indicated that $i_d/\sqrt{h}$ values were constant with in the experimental error (Tables.9,10) suggesting the diffusion controlled nature of all the metal ions under consideration at d.m.e. Mercury height of 70.0 cms was fixed to carry out other studies like effect of pH, effect of ligand concentration and effect of metal ion concentration.

TABLE – 7

Effect of height of Mercury column on copper – [HMBT] System

$[Cu^{+2}]$ = 1.0 mM
[HMBT] = 0.05 M
$[NaNO_3]$ = 0.1 M
[pH] = 8.5
Triton –x–100 = 0.002 %

Height of Mercury Column h(cm)	i_d (μA)	$i_d/\sqrt{h}$
80	6.1250	0.6848
75	5.9296	0.6847
70	5.6941	0.6805
60	5.3105	0.6856

TABLE – 8

Effect of height of Mercury column on palladium–[HMBT] System

$[Pd^{+2}]$ = 1.0 mM
[HMBT] = 0.05 M
$[NH_3+NH_4Cl]$ = 1.0 M
[pH] = 8.5
Triton –x–100 = 0.002 %

Height of Mercury Column h(cm)	i_d (μA)	$i_d/\sqrt{h}$
80	5.6852	0.6350
75	5.5060	0.6362
70	5.2874	0.6320
60	4.9359	0.6377

d) Effect of metal ion concentration

The studies of effect of metal ion concentration on polarographic wave height are of immense importance due to the fact that it establishes diffusion controlled nature of the electrode reaction and the validity of Ilkovic equation. Further, the studies also help us to carryout quantitative determination of metal ions by constructing calibration plots at different concentrations of the depolarizer. Polarographic studies of various metal ions of biological and industrial importance like Copper(II), Lead(II), Cadmium(II),Palladium(II), and Indium(III) . Metal ion concentration was varied from 0.4 mM to 1.2 mM (except for Indium 0.1 mM to 0.5 mM) in presence of complexing agent HMBT (0.05M), 0.1M $NaNO_3$ as supporting electrolyte (except for Palladium1.0M [NH_3+NH_4Cl]) and 0.002% of Triton–X–100 at pH 8.5. Calibration graphs were drawn at different concentrations of metal ion under identical conditions. In all the instances, straight line plots were obtained passing through the origin indicating the validity of Ilkovic equation. Values computed for i_d/c were constant with in the experimental error the metal ions whose half–wave potential difference was more than 0.2 V were selected to carry out quantitative analysis present in binary mixtures constituting different important ores and alloys.

TABLE – 9

Effect of copper ion concentration on the wave height

[HMBT] = 0.05 M
[$NaNO_3$] = 0.1 M
[pH] = 8.5
Triton –x–100 = 0.002 %

[Cu^{+2}] (mM)	**i_d** (μA)	i_d/c
0.4	2.2773	5.6932
0.6	3.4160	5.6932
0.8	4.5449	5.6811
1.0	5.6941	5.6941
1.2	6.8255	5.6879

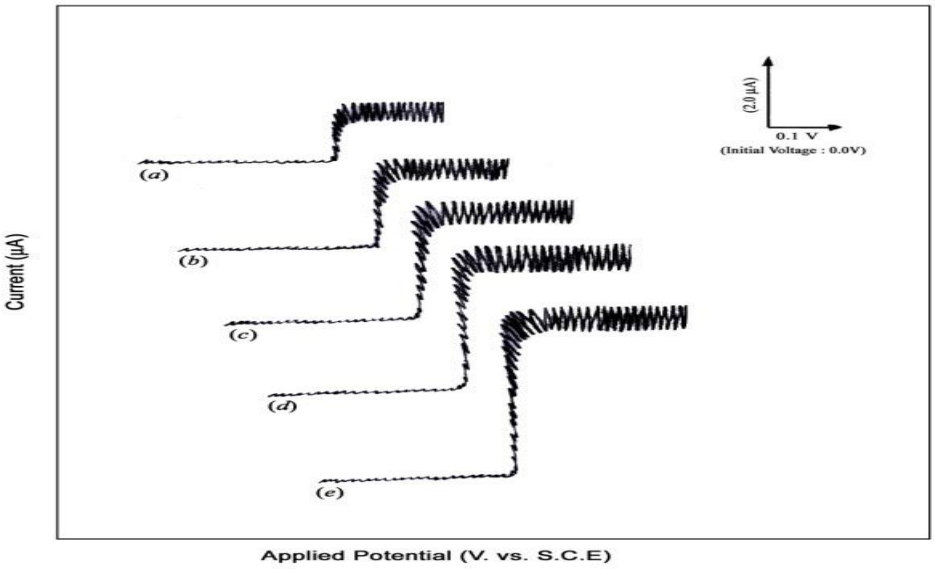


Fig.5: Polarograms a) 0.4 b) 0.6 c) 0.8 d) 1.0 and e) 1.2 mM

Copper ion in 0.050 M HMBT and 0.1M $NaNO_3$ at pH 8.5

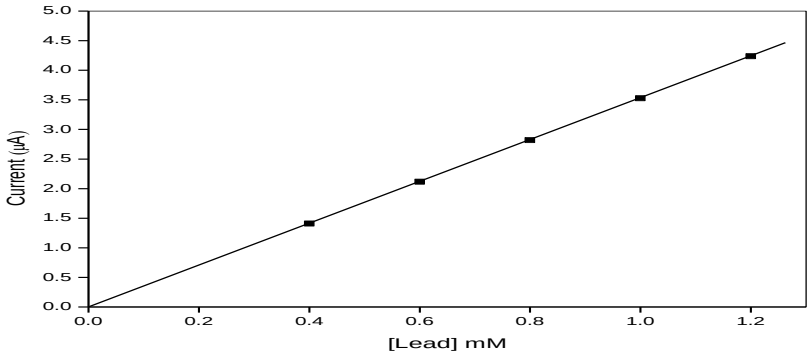


Fig. 6 : Calibration plot of copper ion in 0.05M ligand [HMBT] and 0.1M $NaNO_3$ at pH 8.5

TABLE – 10

Effect of palladium ion concentration on the wave height

[HMBT] = 0.05 M
[NH_3+NH_4Cl] = 1.0 M
[pH] = 8.5
Triton –x–100 = 0.002 %

[Pd^{+2}] (mM)	**i_d** (µA)	**i_d/c**
0.4	2.1144	5.2860
0.6	3.1717	5.2862
0.8	4.2354	5.2943
1.0	5.2874	5.2874
1.2	6.3449	5.2874

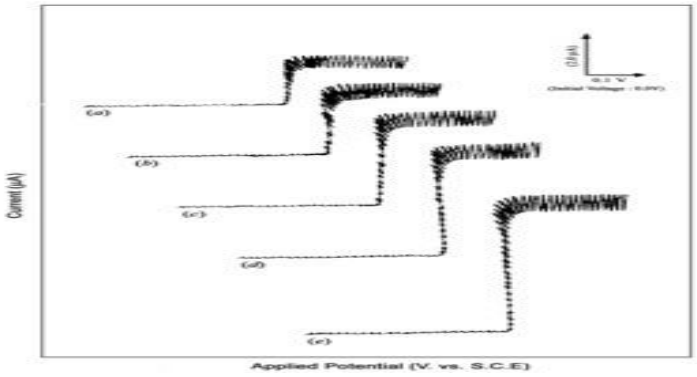


Fig. 7 : Polarograms of a) 0.4 b) 0.6 c) 0.8 d) 1.0 and e) 1.2 mM palladium ion in 0.050MHMBT and 0.1M $NaNO_3$ at pH 8.5

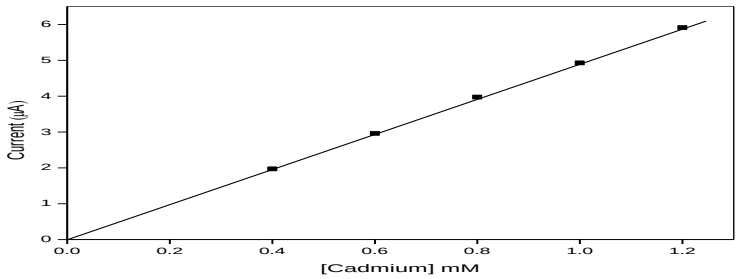


Fig. 8 : Calibration plot of palladium ion in 0.05M ligand [HMBT] and 0.1M $NaNO_3$ at pH 8.5

ii) **Investigation of metal-to-ligand ratio and stability constants of palladium – HMBT reversible system**

Earlier polarographic investigation on palladium in presence of complexing agent HMBT, 0.1M $NaNO_3$ as supporting electrolyte and 0.002% of Triton–X–100 as maximum suppressor at pH 8.5 revealed that palladium undergone reversible electrode reaction at d.m.e. The graph plotted against $E_{½}$ and –log [HMBT] gave a smooth curve showing the existence of various step-wise complex equilibria in solution. The author, therefore, employed Deford and Hume method for the determination of ligand number and formation constants of the palladium–HMBT system.

To start with various $F_0[X]$ functions were determined using the equation

$$\mathbf{F_0[x] = Anti\ log}\left[\frac{0.4343nF}{RT}\Delta E_{½} + \log\frac{I_M}{I_C}\right]$$

Where I_C representing experimental mean value of the diffusion current constant for different complex equilibria. A graph was drawn between $F_0[X]$ and [X] values From the limiting slope of the curve, β_1 value was computed. Secondly, $F_1[X]$ values at different concentrations of the ligand were calculated making use of the following equation

$$\mathbf{F_1[X]} = \left[\frac{F_0[X]-1}{[X]}\right]$$

A plot was constructed between $F_1[X]$ and [X] values The intercept of the curve gave β_1 value and the limiting slope of it represented β_2. $F_2[X]$ functions were then evaluated employing the equation

$$F_2[X] = \left[\frac{F_1[X]-\beta_1}{[X]}\right]$$

A graph was plotted for the obtained values of $F_2[X]$ and [X]values A straight line parallel to X–axis was obtained. The intercept of the graph gave β_2 value. From the results, it was observed that palladium formed 1 **:** 2 complex with HMBT and the step-wise formation constants were found to be $\beta_1 = 0.6 \times 10^2$ and $\beta_2 = 1.675 \times 10^2$. Experimental results were tabulated in the table

TABLE – 11

Effect of Ligand Concentration on copper – [HMBT] System

$[Cu^{+2}]$ = 1.0 mM
$[NaNO_3]$ = 0.1M
pH = 8.5
Triton –x–100 = 0.002 %

[HMBT] (M)	$\mathbf{E_{1/2}}$ (–V. vs S.C.E)	$\mathbf{i_d}$(µA)	**Slope** (mV)	**log [HMBT]**
0.000	0.390	6.0680	–	–
0.005	0.443	3.9030	31.28	–2.3010
0.008	0.450	3.8400	30.72	–2.0969
0.010	0.454	3.7771	29.92	–2.0000
0.020	0.462	3.7142	30.24	–1.6989
0.030	0.468	3.6512	29.32	–1.5228
0.040	0.471	3.5883	29.49	–1.3979
0.050	0.475	3.5253	30.72	–1.3010
0.060	0.479	3.3994	28.90	–1.2218
0.080	0.483	3.3364	29.48	–1.0969
0.100	0.486	3.2105	30.72	–1.0000

$\beta_{Mxj} = 2.0801 \times 10^4$

iii)Calculation of stability constant and ligand number of copper– HMBT system (Lingane method)

Perusal of literature suggested that very little polarographic work on Pb(II) with Schiff bases derived from Tris was reported. Patel *et al.*, [56] reported copper in presence of Salicylaldehyde–Tris (ST) along with various metal ions and determined stability constants for the complex species in aqueous solution using potentiometric technique. Sreenivasulu and his co–workers [153] determined the stability constants of copper with four different Schiff bases derived from Tris and discussed the stability order on the basis of Resonance and Hyperconjugation. Electrochemical studies on copper complexes of Benzoyl acetone–Tris (BAT) was investigated by Babu prasad *et al.*, [248]. Polarographic behaviour of palladium and copper in presence of Ortho Vanillin–Tris (OVT) wasstudied by Hari *et al.*, [318].

In view of limited number of references available on Cu(II) in presence of Schiff bases derived from Tris, the author in the present investigation, therefore, studied polarographic work on Cu(II) in presence of 2–hydroxy–5–methoxy benzaldehyde–Tris (HMBT) in order to understand the complexing ability of the ligand and determined metal-to-ligand ratio as well as stability

constant of the system in 0.1M $NaNO_3$ as supporting electrolyte at pH 8.5. The author prepared the solutions in 40 **:** 60 Methanol–water medium.

Results obtained (Chapter-III; Section-ii) regarding Lead studies in presence of chelating agent HMBT indicated that Lead undergone reversible two electron reduction at d.m.e. Graph drawn between half–wave potential ($E_{1/2}$) and –log [HMBT] gave a straight line (Fig. 36) suggesting the formation of single and stable complex species in solution. Lingane method was, therefore, adopted for the determination of metal–to–ligand ratio and stability constant of copper–HMBT complex using the following equation

$$\Delta E_{1/2} = \frac{0.0591}{n} \log \beta_{mxj} + j \frac{0.0591}{n} \log[X]$$

Where, The symbols represent their usual significance. The coordination number (j) was determined by equating the slope of the plot to $\frac{0.0591}{n}$ j where 'n' representing number of electrons participating in the electrode reaction. The ligand number obtained from the slope of the graph was found to be two. Further, the stability constant of copper–HMBT system was calculated at 0.1 M concentration of the ligand HMBT and was equal to $\beta_{Mxj} = 2.0801 \times 10^4$. Experimental results were tabulated (Table 26).

V. CONCLUSIONS

Determination of traces quantities of elements copper(II) and palladium(II) using HMBT Schiff base is not tedious and do not involve any heating , separation or extraction of the components .Determination of metal ions copper and palladium using HMBT ligand is simple and selective and rapid , can be applicable in determinations in metallurgy ,environmental analysis (air, water, and sea water contaminants),Food analysis ,toxicology and clinical analysis, analysis of drugs and pharmaceutical preparations , determination of pesticide or herbicide residues in the foods and other samples. HMBT is a versatile and new chromagenic reagent for the determination of trace quantities of copper and palladium by polarographic methods .

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