Polarographic methods for the determination of Copper (II) and Cadmium (II) using Schiff base as chromogenic reagent

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Abstract- Schiff base, 1-[2,4–dihydroxy phenyl] ethanone [RPT] Ligand is a new chromogenic reagent have not been used so far for the determination of copper and cadmium in trace quantities. Effect of pH on wave height for Cu-[RPT] and Cd-[RPT] systems have been studied at pH 6.5-11.0 in 0.1 M $NaNO_3$, and 0.002 % Triton -X-100 which increases the stability of the complex. Effects of Ligand concentrations, height of mercury column, metal ion concentrations on Copper and Cadmium on wave height at pH 10.0 have been studied. The author also investigates metal-ligand ratio and stability constants of cadmium-RPT by reversible system.

Index Terms- polarographic, Schiff base, copper, cadmium, NMR, IR and Lingane method.

I. Introduction

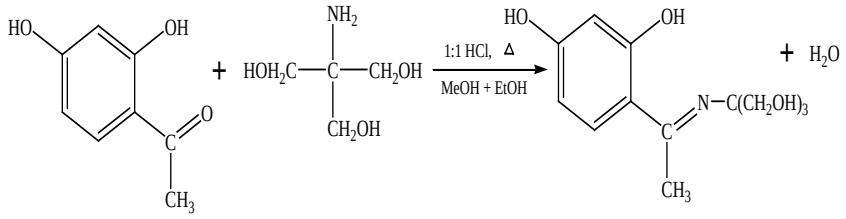
Many number of Schiff bases were synthesized from Tris (Hydroxymethyl) methylamine with different aldehydes and were tested as pharmaceutical intermediates [1,2], bactericides, fungicides [3] and pesticides [4]. Schiff bases prepared by Inoyatov [5] act as effective polymers. Spectrophotometric work [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].[11-14] reported determination of metal-to-ligand ratio and stability constants of complexes of cadmium(ll) and copper(Il) 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 metal ions such as Cu(II) and Cd(II), using RPT as complexing agent polarographically in $NaNO_3$ as the supporting electrolyte at pH 10.0 in 40 : 60 rnethanol-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 1–[2,4–dihydroxy phenyl] ethanone–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 1–[2,4–dihydroxy phenyl] ethanone [RPT] Ligand :

II. Preparation of the Ligand

Equimolar concentrations of Tris (Hydroxymethyl) methylamine (TRIS) and 1–[2,4–dihydroxy phenyl] ethanone were dissolved separately in methanol and refluxed for one hour in methanol & ethanol solvent mixture in presence of few drops of acid catalyst namely $SOC1_2$. 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 133-134°C and 74% respectively.



resacetophenone **Tris (Hydroxymethyl) methylamine** **RPT**

III. 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 earned 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. The Infrared spectrum of the compound (RPT) formed between Tris(hydroxymethyl) methyl amine and resacetophenone showed peak at 1630 cm^{-1} indicating the existence of >C=N– group in the compound. The Peaks were also observed in the region of 3340 – 3330 cm^{-1} (broad, strong, OH-stretching), 3190–3180 cm^{-1} (broad, medium, phenolic OH), 1600, 1580, 1500, 1480 cm^{-1} (aromatic >C=C< vibrations) and 1220 cm^{-1} (small, medium, >C=O stretching coupled phenolic -OH deformation). The above IR data clearly suggested that the chemical reaction between the amino group of Tris and the carbonyl group of resacetophenone resulting in the formation of respective Schiff base compound. The elemental analysis and IR data were tabulated in the Table-1.

IV. NMR spectra

In the present investigation ^1H NMR spectrum was obtained for the ligand RPT 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 methyl proton attached to azomethine group, methyl protons of hydroxy methyl group, hydroxyl protons of hydroxy methyl group, hydroxyl protons of aromatic hydroxy group and aromatic protons present in the compound were summarized in the Table-2.

TABLE – 1
Analytical and IR spectral data of [RPT] Ligand

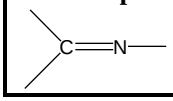
Molecular Formula	$C_{12}H_{17}NO_5$	
Colour	White crystalline needles	
Melting point	133 – 134 °C	
Elemental analysis	**Found (%)**	**Calc. (%)**
Carbon	56.45	56.46
Hydrogen	6.69	6.71
Oxygen	31.32	31.34
Nitrogen	5.48	5.49
Yield	74%	
IR absorption band 	1630 cms^{-1}	

TABLE – 2
^1H NMR spectral data for [RPT] Ligand in DMSO–D^6

Sl. No.	**Different protons in the Ligand**	**δ Chemical shift in ppm**
1	H_3C–C=N (methyl protons attached to azomethine group)	3.38
2	–CH_2OH (Methyl protons of hydroxymethyl group)	3.80
3	–CH_2OH (Hydroxyl protons of hydroxymethyl group)	4.57
4	Ar–OH (Hydroxyl Protons of Aromatic hydroxy group)	5.91
5	Aromatic protons	6.52 – 7.61

V. RESULTS AND DISCUSSION

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

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 at 0.1M ligand concentration at mercury height of 70.0 cms in 40 : 60 methanol– water medium. The pH range studied for Copper and Cadmium was between 6.5-11.0. From $E_{3/4} - E_{1/4}$ value computed from the polarograms of pH studies indicated that, Copper and Cadmium reduced reversibly as shown in Table 3&4 respectively.

TABLE – 3
Effect of pH on Copper – [RPT] system

$[Cu^{2+}]$ = 1.0 mM
[RPT] = 0.1M
$[NaNo_3]$ = 0.1M
Triton –x–100 = 0.002%

pH	$\mathbf{E_{1/2}}$ (–V.Vs S.C.E)	$\mathbf{E_{3/4} – E_{1/4}}$ (mV)
6.5	0.225	54.80
8.0	0.301	54.60
9.0	0.371	54.80
10.0	0.390	54.80
11.0	0.405	53.92

TABLE – 4
Effect of pH on Cadmium – [RPT] system

$[Cd^{2+}]$ = 1.0 mM
[RPT] = 0.1M
$[NaNo_3]$ = 0.1M
Triton –x–100 = 0.002%

pH	$\mathbf{E_{1/2}}$ (–V.Vs S.C.E)	$\mathbf{E_{3/4} – E_{1/4}}$ (mV)
6.5	0.631	30.90
8.0	0.635	30.90
9.0	0.665	30.44
10.0	0.725	28.90
11.0	0.760	27.96

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. In view of the above advantages, the author in the present investigations studied effect of varying concentrations of the RPT ligand on copper(II) and cadmium (II) in the presence of 0.1 M $NaNO_3$ as supporting electrolyte and 0.002% of Triton-X–100 as maximum suppressor at pH 10.0. The results indicated that RPT was able to complex with copper and cadmium ions under consideration by the fact that diffusion current (id) decreased where as half-wave potential (E½) shifted towards more negative values with increasing concentration of the ligand as shown in Fig1-4 and Table-5-6. Further, the studies also suggested that copper and cadmium reduced reversibly at d.m.e.

TABLE – 5
Effect of Ligand – [RPT] concentration on Copper

$[Cu^{2+}]$ = 1.0 mM
$[NaNO_3]$ = 0.1M
pH = 10.0
Triton –x–100 = 0.002%

[RPT] (M)	$\mathbf{E_{1/2}}$ (–V.Vs S.C.E)	$\mathbf{i_d}$ (µA)	**Slope** (mV)

0.02	0.355	7.7150	59.76
0.03	0.359	7.3480	58.62
0.04	0.361	7.0975	57.54
0.05	0.364	7.0143	57.74
0.06	0.367	6.6800	57.54
0.08	0.386	6.2626	57.52
0.10	0.390	5.8445	57.44
0.20	0.404	5.3440	57.48
0.40	0.419	5.0100	57.52
0.50	0.424	4.5925	57.48
0.60	0.427	4.1750	57.44
0.80	0.433	3.7575	57.42
1.00	0.437	3.3401	57.42

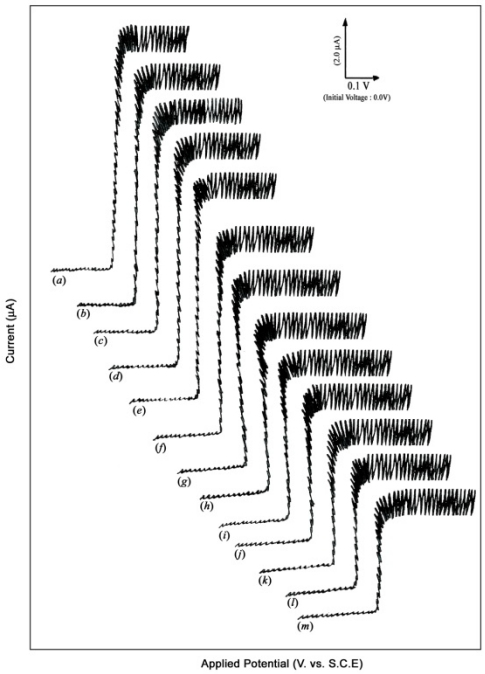


Fig. 1 : Polarograms of 0.2 mM copper ion in a) 0.02 b) 0.03 c) 0.04 d) 0.05 e) 0.06 f) 0.08 g) 0.10 h) 0.20 i) 0.40 j) 0.50 k) 0.60 l) 0.80 m) 1.00 M [RPT] and 0.1M $NaNO_3$ at pH 10.0

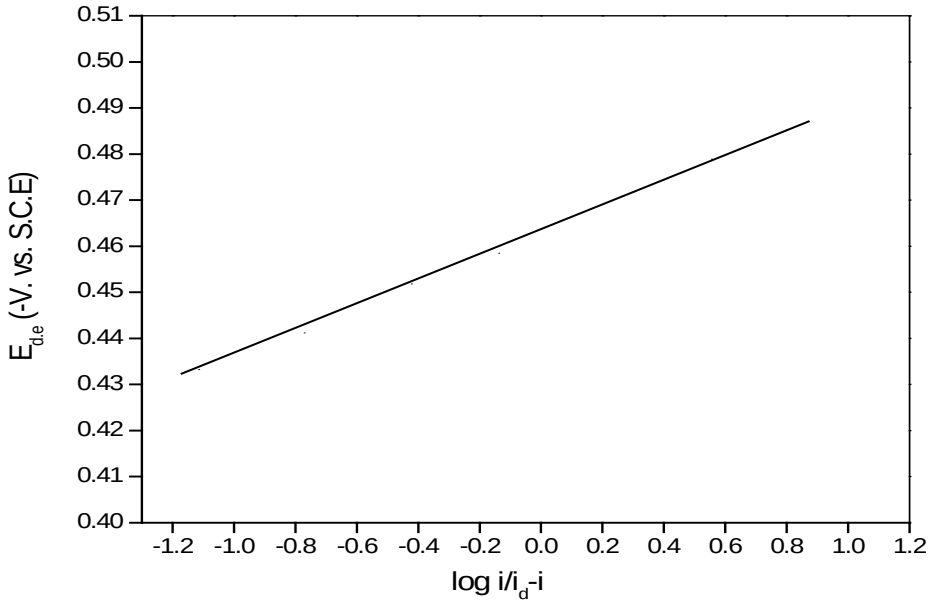


Fig. 2 : A typical log plot of 1.0 mM Copper in 0.1 M [RPT] and 0.1M $NaNO_3$ at pH 10.

TABLE – 6
Effect of Ligand– [RPT] concentration on Cadmium

$[Cd^{2+}]$ = 1.0 mM
$[NaNo_3]$ = 0.1M
pH = 10.0
Triton –x–100 = 0.002%

[RPT] (M)	**$E_{1/2}$** (–V.Vs S.C.E)	**i_d** (µA)	**Slope** (mV)
0.02	0.688	5.9702	30.50
0.03	0.695	5.9400	30.56
0.04	0.699	5.7868	30.60
0.05	0.703	5.7507	30.52
0.06	0.709	5.6986	30.60
0.08	0.717	5.6366	30.42
0.10	0.725	5.3889	30.35
0.20	0.742	4.7075	29.90
0.50	0.761	3.5306	29.60
0.60	0.766	3.3448	29.52
0.80	0.770	2.6015	29.50
1.00	0.772	2.0440	29.45

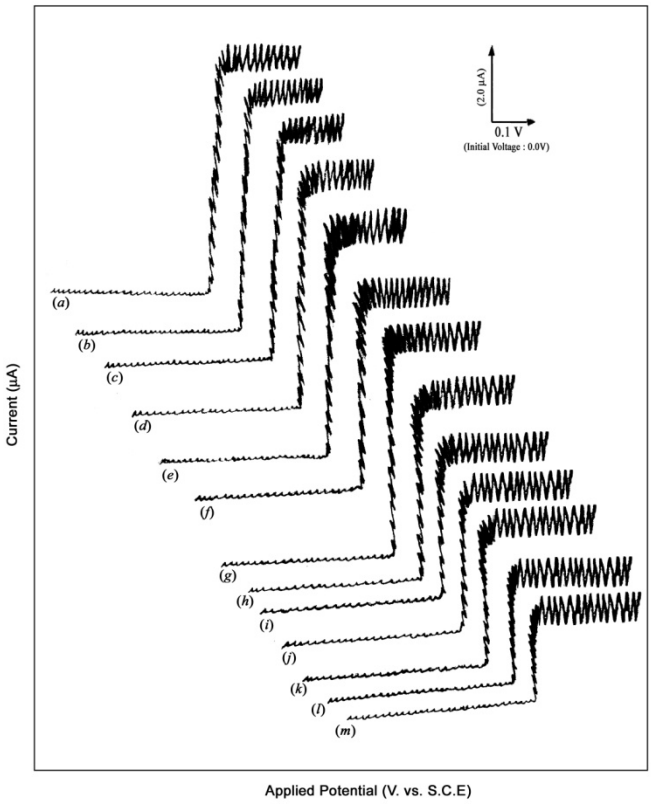


Fig. 3 : Polarograms of 0.2 mM Cadmium ion in a) 0.02 b) 0.03 c) 0.04 d) 0.05 e) 0.06 f) 0.08 g) 0.10 h) 0.20 i) 0.40 j) 0.50 k) 0.60 l) 0.80 m) 1.00 M [RPT] and 0.1M $NaNO_3$ at pH 10.0

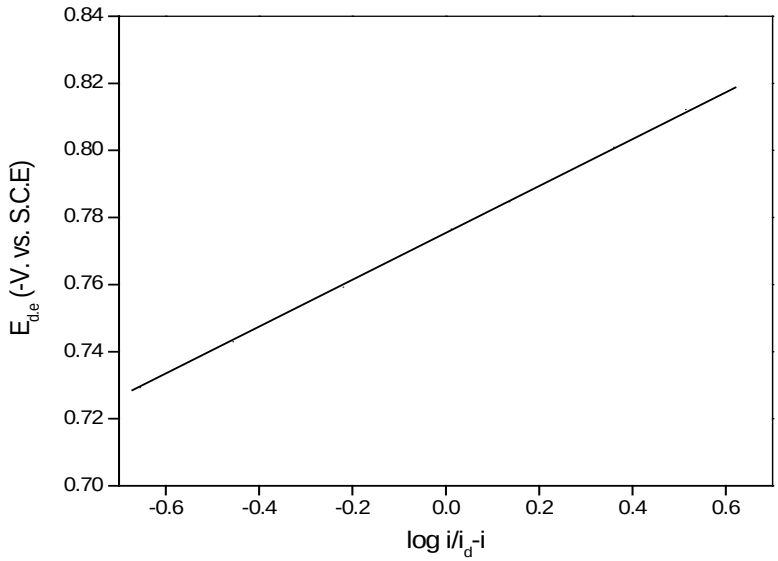


Fig. 4 : A typical log plot of 1.0 mM Cadmium in 0.1 M [RPT] and 0.1M $NaNO_3$ at pH 10.0

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, the author investigated in detail the influence of mercury height on diffusion current of metal ions such as copper(Il), cadmium(II)ions at 1.0 mM concentration in presence of fixed concentration of RPT ligand (0.1M), ionic concentration 0.1M $NaNO_3$ as supporting electrolyte and 0.002% of Triton-X-100 as maximum suppressor at pH 10.0. Results indicated that $i_d/\sqrt{h}$ values were constant with in the experimental error (Tables.7-8) suggesting the diffusion

controlled nature of both 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 – [RPT] system

$[Cu^{2+}]$ = 1.0 mM
[RPT] = 0.1M
$[NaNo_3]$ = 0.1M
pH = 10.0
Triton -x-100 = 0.002%

Height of Mercury Column h(cm)	i_d (µA)	$i_d/\sqrt{h}$
80	6.1909	0.6921
75	6.0280	0.6960
70	5.8445	0.6985
65	5.7022	0.6971
60	5.5392	0.7098

TABLE - 8
Effect of height of Mercury Column on Cadmium – [RPT] system

$[Cd^{2+}]$ = 1.0 mM
[RPT] = 0.1M
$[NaNo_3]$ = 0.1M
pH = 10.0
Triton -x-100 = 0.002%

Height of Mercury Column h(cm)	i_d (µA)	$i_d/\sqrt{h}$
80	5.6884	0.6359
75	5.5304	0.6310
70	5.3889	0.6421
65	5.2144	0.6467
60	5.0564	0.6425

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. In the present investigations, the carried out Polarographic studies (Fig 5 and 7) of copper and cadmium metal ions of biological and industrial importance. Metal ion concentration was varied from 0.4 mM to 1.2 mM in presence of complexing agent RPT (0.2M), 0.1M $NaNO_3$ as supporting electrolyte and 0.002% of Triton-X-100 at pH 10.0. Calibration graphs were drawn at different concentrations of metal ion under identical conditions as shown in Fig-6 and 8. 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 within the experimental error (Table-9-10). 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

[RPT] = 0.2M
[$NaNo_3$] = 0.1M
pH = 10.0
Triton -x-100 = 0.002%

[Cu^{2+}] (mM)	**i_d** (µA)	**i_d / c**
0.4	2.1375	5.3438
0.6	3.2063	5.3438
0.8	4.2751	5.3439
1.0	5.3440	5.3440
1.2	6.4190	5.3491

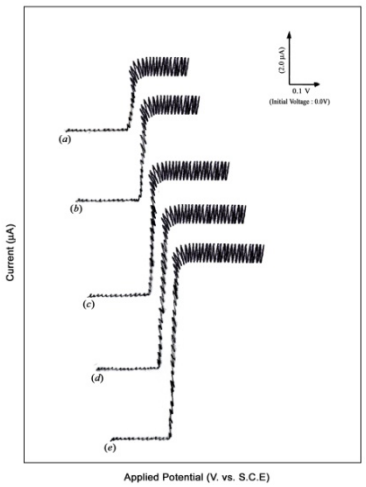


Fig. 5 : Polarograms of a) 0.4 b) 0.6 c) 0.8 d) 1.0 and e) 1.2 mM copper in 0.2 M [RPT] and 0.1M $NaNO_3$ at pH 10.0

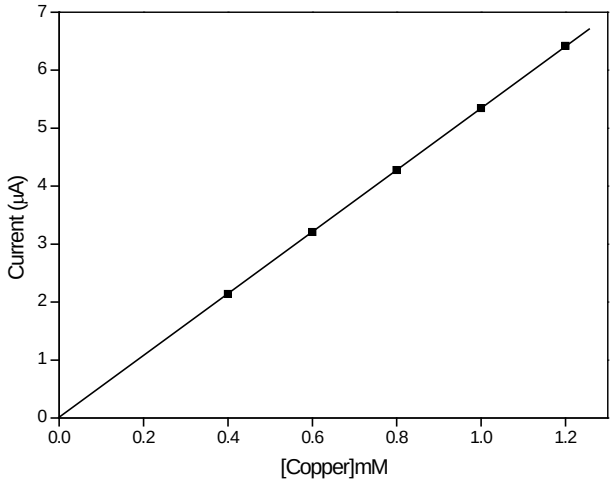


Fig. 6 : Calibration Plot of Copper ion in 0.2M ligand [RPT] and 0.1M $NaNO_3$ at pH 10.0

TABLE-10
Effect of Cadmium ion concentration on the Wave height

[RPT] = 0.2M
[$NaNo_3$] = 0.1M
pH = 10.0
Triton -x-100 = 0.002%

[Cd^{2+}] (mM)	**i_d** (µA)	**i_d / c**

0.4	1.8834	4.7085
0.6	2.8250	4.7082
0.8	3.7667	4.7084
1.0	4.7075	4.7075
1.2	5.6485	4.7072

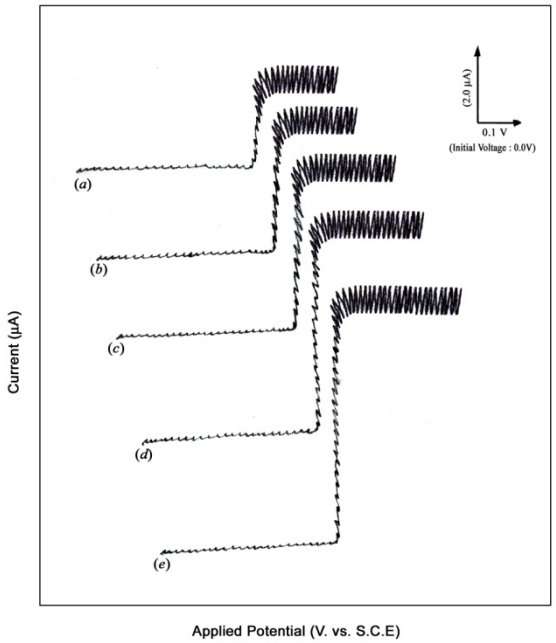


Fig. 7 : Polarograms of a) 0.4 b) 0.6 c) 0.8 d) 1.0 and e) 1.2 mM Cadmium in 0.2 M [RPT] and 0.1M $NaNO_3$ at pH 10.0

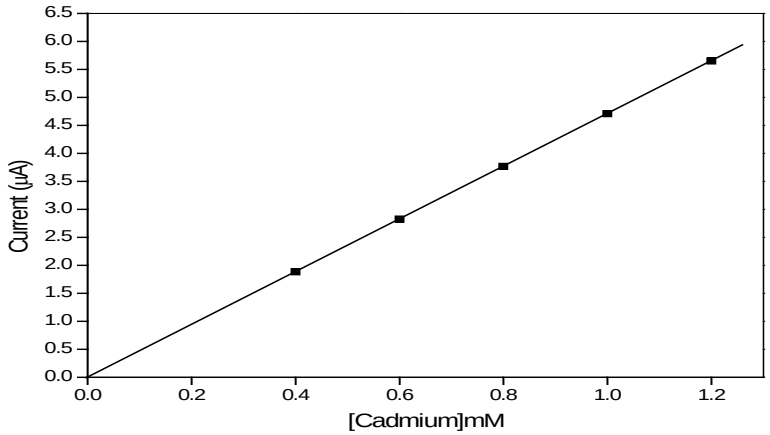


Fig. 8 : Calibration Plot of Cadmium ion in 0.2M ligand [RPT] and 0.1M $NaNO_3$ at pH 10.0

ii) Investigation of metal-to-ligand ratio and stability constants of cadmium – RPT reversible system

Earlier polarographic investigation on cadmium in presence of cornplexing agent RPT. 0.1M $NaNO_3$ as supporting electrolyte and 0.002% of Triton–X-l 00 as maximum suppressor at pH 10.0 revealed that cadmium undergone reversible electrode reaction at d.m.e. The graph plotted against $E_{½}$ and –log [RPT] 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 cadmium-RPT system. To start with various $F_0[X]$ functions were determined using the equation

$$F_0[X] = \text{Anti log}\left[\frac{0.4343nF}{RT}\Delta E_{1/2} + \log\frac{I_M}{I_C}\right]$$

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 calculated making use of the following equation

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

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 cadmium formed 1 : 2 complex with RPT and the step-wise formation constants were found to be $\beta_1 = 0.25\times10^6$ and $\beta_2 = 10.80\times 10^6$. Experimental results were tabulated in the Table-11

TABLE -11
Derived functions for Cadmium - [RPT] System

$[Cd^{+2}]$ = 1.0mM pH = 10.0
$[NaNO_3]$ = 0.1M Triton - x - 100 = 0.002%

[RPT] (M)	$\mathbf{i_d}$ (μA)	**Slope** (mV)	$\mathbf{E_{1/2}}$ (-V. vs S.C.E)	Δ $\mathbf{E_{1/2}}$ (-V.vs S.C.E)	**log I_M/I_C**	**$F_0[X] \times 10^4$**	**$F_1[X] \times 10^5$**	**$F_2[x] \times 10^6$**
0.00	6.1902	28.90	0.575	-	-	-	-	-
0.02	5.9702	30.50	0.688	0.113	0.0157	0.5856	2.9276	2.1350
0.03	5.9400	30.56	0.695	0.120	0.0179	1.0051	3.3502	2.8333
0.04	5.7868	30.60	0.699	0.124	0.0293	1.4010	3.5024	2.5050
0.05	5.7507	30.52	0.703	0.128	0.0320	1.9141	3.8280	2.6560
0.06	5.6986	30.60	0.709	0.134	0.0360	3.0562	5.0935	4.3216
0.08	5.6366	30.42	0.717	0.142	0.0407	5.6952	7.1188	5.7725
0.10	5.3889	30.34	0.725	0.150	0.0602	10.9808	10.9808	10.9808
0.20	4.7075	30.34	0.742	0.167	0.1190	46.1194	23.0596	10.2795
0.40	3.7165	29.70	0.757	0.182	0.2216	183.8771	45.9692	10.8655
0.50	3.5306	29.60	0.761	0.186	0.2440	262.8690	52.5737	10.0146
0.60	3.3448	29.52	0.766	0.191	0.2673	406.4937	67.7489	10.8746
0.80	2.6015	29.50	0.770	0.195	0.3765	709.6847	88.7105	10.7762
1.00	2.0440	29.50	0.772	0.197	0.4812	1052.3768	1052.3767	10.5237

$\beta_1 = 0.25 \times 10^6$; $\beta_2 = 10.80 \times 10^6$

VI. CONCLUSIONS

Determination of traces quantities of elements copper(II) and cadmium(II) using RPT Schiff base by polarographic method is not tedious and do not involve any heating , separation or extraction of the components. Determination of metal ions copper and cadmium using RPT 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, clinical analysis, analysis of drugs, pharmaceutical preparations and determination of pesticide or herbicide residues in the foods and other samples.

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