Electrochemical Studies of Indium (III) and Nickel (II) Ions in the presence of New Schiff Base

M. V. N. V. Prasad Gupta[1], Meer Althaf Ahamed[2], S. Ramanaiah[3], K. Sreenivasulu[4*]

[1]Department of Chemistry, S. B. S. Y. M. Degree College, Kurnool, Andhra Pradesh, India, [2]Department of Chemistry, Osmania UG and PG College, Kurnool, Andhra Pradesh, India, [3]Department of Chemistry, Rayalaseema University, Kurnool, Andhra Pradesh, India, [4]Department of Chemistry, Sri Krishnadevaraya University, Anantapur, Andhra Pradesh, India

ABSTRACT

Schiff bases, resacetophenone imines (renal proximal tubule [RPT]) ligand was synthesized using Tris (hydroxymethyl) methylamine (Tris) and resacetophenone and has not been used so far for the determination of lead and tellurium in trace quantities. Effect of pH on wave height for In-(RPT) and Ni-(RPT) systems has been studied at pH 6.5–11.0 in 0.1 M NaNO₃, 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 indium and nickel on wave height at pH 10.0 have been studied. The author also investigates the metal-ligand ratio and stability constants of tellurium-RPT by the reversible system.

Key words: Polarographic, Schiff base, Indium, Nickel and Deford and Hume method.

1. INTRODUCTION

Many numbers of Schiff bases were synthesized from Tris (hydroxymethyl) methylamine with different aldehydes and were tested as pharmaceutical intermediates [1,2]. Schiff bases prepared by Inoyatov [3] act as an effective polymers. Spectrophotometric work [4] on the azomethine of pyridoxal-5[1]-phosphate-Tris was carried out and determined the formation constant (*pKa*) values. Patel [5] reported the polarographic determination of ligand-proton stability constants for Salicylaldehyde-Tris (ST) Schiff base in 50% dimethylformamide (DMF). Effect of pH, amine concentration and solution composition of pyridoxal-5'-phosphate-Tris were reported by Sevilla *et al.* [6] employing the polarographic technique, Sreenivasulu and Sreeramulu [7] 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 [8-12] and determines metal-ligand ratio and stability constants of complexes of Tellurium(II) and Lead(II) in the presence of Schiff bases derived from Tris and various ketones in KNO₃ as supporting electrolyte at pH 10.5 in 50% DMF-water medium.

Recently, we have developed polorograpic methods for the determination of In(III) and Ni (II) using RPT as a complexing agent in NaNO-, as the supporting electrolyte at pH 10.0 in methanol-water medium (40:60). The studies include the 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 l-[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.

2. EXPERIMENTAL

2.1. Preparation and Characterization of Resacetophenone Imines (Renal Proximal Tubule [RPT]) Ligand

2.1.1. Preparation of the ligand

Equimolar concentrations of Tris (hydroxymethyl) methylamine TR1SJ and 1-[2,4-dihydroxy phenyl] cthanonc were dissolved separately in mcthanol and refluxed for 1 h in methanol and ethanol solvent mixture in the presence of few drops of acid catalyst, namely SOC1₂. 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
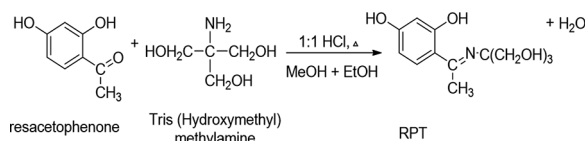
2.1.2. Characterization of the ligand

The characterization of the Schiff base was made by elemental analysis, Chemical reactions, and infrared (IR) studies. Elemental analysis for Carbon, Hydrogen, Oxygen, and Nitrogen present in the Schiff base

was obtained from CDR1, Lucknow, India. Chemical analysis for the functional groups, i.e., carbonyl (>C=0) and amine (-NH.) groups were earned out by standard procedure and found to be absent indicating the formation of azomethine.

An IR spectrum for the derived Schiff base was recorded by KBr pallet method employing Perkin Elmer IR spectroscopy. The IR spectrum of the compound (RPT) formed between Tris (hydroxymethyl) methylamine and resacetophenone showed a 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, and OH-stretching), 3190–3180 cm^{-1} (broad, medium, and phenolic OH), 1600, 1580, 1500, 1480 cm^{-1} (aromatic >C=C< vibrations), and 1220 cm^{-1} (small, medium, and >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 Table 1.

2.2. Nuclear Magnetic Resonance (NMR) Spectra

In the present investigation, ^{1}H NMR spectrum was obtained for the ligand RPT using Gemini – 200 MHz ^{1}H NMR spectrometer from IICT, Hyderabad, in DMSO-D3 solvent at room temperature. Important chemical shift values for various protons such as methyl proton attached to azomethine group, methyl protons of hydroxymethyl group, hydroxyl protons of hydroxymethyl group, hydroxyl protons of the aromatic hydroxy group, and aromatic protons present in the compound were summarized in Table 2.

Table 1: Analytical and IR spectral data of (RPT) ligand`.

Molecular formula	$C_{12}H_{17}NO_5$	
Color	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}	

>C═N─

RPT: Renal proximal tubule

Table 2: ^{1}H NMR spectral data for (RPT) ligand in DMSO–D^6.

Different protons in the ligand	δ Chemical shift in ppm
H$_3$C–C=N (methyl protons attached to azomethine group)	3.38
–CH$_2$OH (methyl protons of hydroxymethyl group)	3.80
–CH$_2$OH (hydroxyl protons of hydroxymethyl group)	4.57
Ar–OH (hydroxyl Protons of Aromatic hydroxy group)	5.91
Aromatic protons	6.52–7.61

RPT: Renal proximal tubule

3. RESULTS AND DISCUSSION

3.1 Polarographic Behavior of Individual Metal Ions (In^{3+}, Ni^{2+}) in Presence of RPT

3.1.1 Effect of pH on the wave height

The main purpose of studying the effect of hydrogen ion concentration on the 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 to present in mixture solutions. In the present study, the effect of pH on various metal ions in the presence of 0.1M NaNO$_3$ as the supporting electrolyte at 0.1M ligand concentration at mercury height of 70.0 cm in 40:60 methanol-water medium. The pH range studied for indium and nickel was between 6.5 and 11.0. From $E_{3/4}$ to $E_{1/4}$ value computed from the polarograms of pH studies indicated that indium and nickel reduced reversibly as shown in Tables 3 and 4, respectively.

Table 3: Effect of pH on Indium - (RPT) system.

pH	$E_{1/2}$	$E_{3/4} - E_{1/4}$
	(–V vs. S.C.E)	(mV)
10.0	0.811	76.78
10.5	0.814	76.78
11.0	0.822	78.50
11.5	0.934	75.82
12.0	1.039	75.10

[In^{3+}]=0.2 mM, [RPT] =0.1M, [NaNo$_3$]=0.1M, Triton –x–100=0.002%, RPT: Renal proximal tubule

Table 4: Effect of pH on Nickel - (RPT) system.

pH	$E_{1/2}$	$E_{3/4} - E_{1/4}$
	(–V vs. S.C.E)	(mV)
6.5	0.829	79.22
8.0	0.868	79.68
9.0	0.911	79.48
10.0	1.069	79.02
11.0	1.152	79.02

[Ni^{2+}]=1.0 mM, [RPT]=0.1M, [NaNO$_3$]=0.1M, Triton –X–100=0.002%, RPT: Renal proximal tubule

Table 5: Effect of ligand – (RPT) concentration on indium.

[RPT]	$E_{1/2}$	i_d	Slope
(M)	(–V vs. S.C.E)	(μA)	(mV)
0.04	0.775	1.7558	82.35
0.06	0.790	1.7382	82.34
0.08	0.798	1.7250	81.86
0.10	0.811	1.5524	80.65
0.20	0.826	1.4109	80.46
0.40	0.843	1.1983	80.00
0.60	0.847	0.9916	80.04
0.80	0.851	0.7712	80.02

[In^{3+}]=0.2 mM, [NaNO$_3$]=0.1M, pH=10.0, Triton–x–100=0.002%, RPT: Renal proximal tubule

3.1.2. Effect of ligand concentration

Effect of ligand concentration on the 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 carry out the 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 the ligand with various metal ions. In view of the above advantages, the author in the present investigations studied the effect of varying concentrations of the RPT ligand on indium (III) and nickel (IV) 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 indium and nickel ions under consideration by the fact that diffusion current (id) decreased whereas half-wave potential (E½) shifted toward more negative values with increasing concentration of the ligand as shown in Figures 1-4 and Tables 5 and 6. Further, the studies also suggested that indium and nickel reduced reversibly at d.m.e.
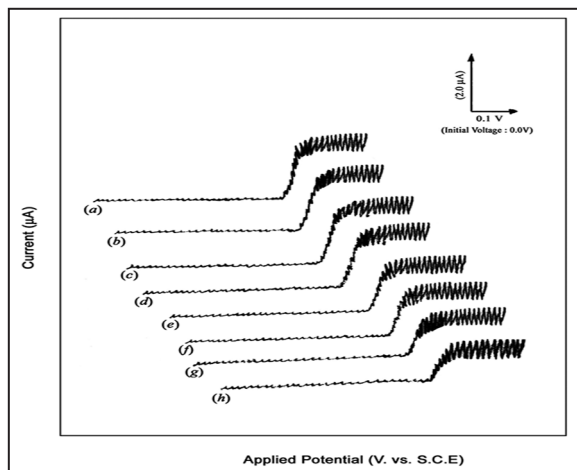
3.1.3. Effect of height of the mercury column

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 $\frac{i_d}{\sqrt{h}}$ values. In the present studies, the author investigated in detail the influence of mercury height on diffusion current of metal ions such as indium(III), nickel(II) ions at 1.0 mM concentration in the 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 $\frac{i_d}{\sqrt{h}}$ values were constant within the experimental error (Tables 7 and 8) which indicates that the diffusion controlled nature of both the metal ions under consideration at d.m.e. Mercury height of 70.0 cm was fixed to carry out other studies such as effect of pH effect of ligand concentration and effect of metal ion concentration.

3.1.4. Effect of metal ion concentration

The studies of the 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 carry out the quantitative determination of metal ions by constructing
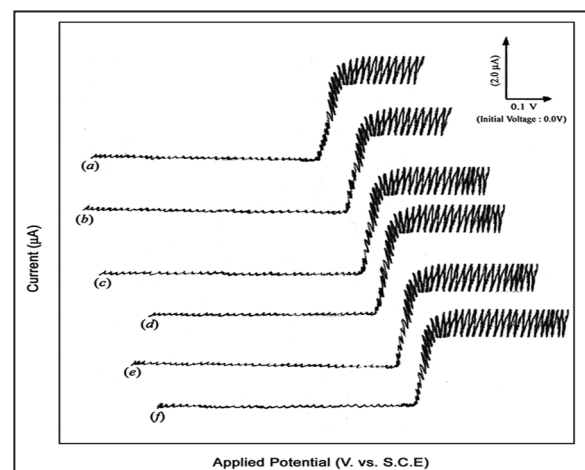

Figure 1: Polarograms of 0.2 mM indium ion in (a) 0.04, (b) 0.06, (c) 0.08, (d) 0.10, (e) 0.20, (f) 0.40, (g) 0.60, (h) 0.80 renal proximal tubule and 0.1M NaNO$_3$ at pH 10.0.

Figure 3: Polarograms of 1.0 mM nickel ion in (a) 0.04, (b) 0.06, (c) 0.08, (d) 0.10, (e) 0.20, (f) 0.30 renal proximal tubule and 0.1M NaNO$_3$ at pH 10.0.
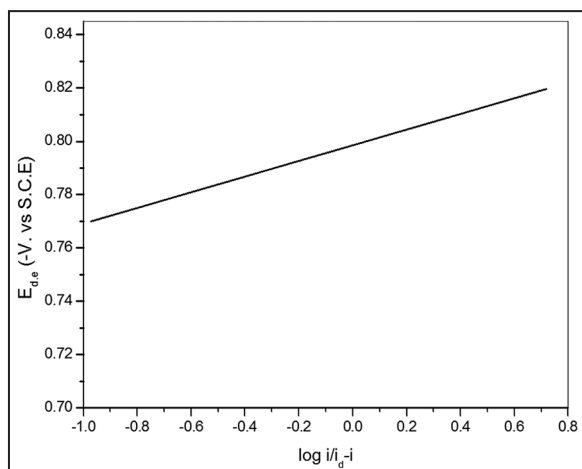

Figure 2: A typical log plot of 1.0 mM Indium in 0.1 M renal proximal tubule and 0.1M NaNO$_3$ at pH 10.0.
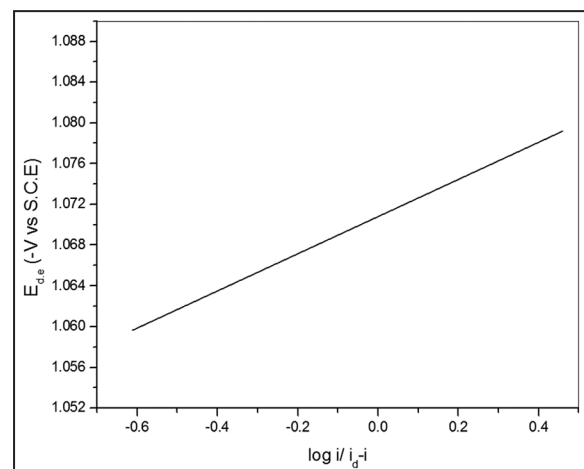

Figure 4: A typical log plot of 1.0 mM nickel in 0.1 M renal proximal tubule and 0.1M NaNO$_3$ at pH 10.0.

Table 6: Effect of ligand– (RPT) concentration on nickel.

[RPT]	$E_{1/2}$	i_d	Slope
(M)	(–V vs. S.C.E)	(µA)	(mV)
0.04	1.061	2.8849	84.56
0.06	1.063	2.8632	84.58
0.08	1.066	2.8137	84.28
0.10	1.069	2.7860	82.80
0.20	1.073	2.5902	82.64
0.30	1.078	2.5056	81.58

$[Ni^{2+}]$=1.0 mM, $[NaNO_3]$=0.1M, pH=10.0, Triton–x–100=0.002%, RPT: Renal proximal tubule

Table 7: Effect of height of mercury column on indium – (RPT) system.

Height of mercury column	i_d	$i_d/\sqrt{h}$
h (cm)	(µA)	
80	1.6601	0.1856
75	1.6047	0.1853
70	1.5524	0.1855
65	1.4931	0.1852
60	1.4369	0.1855

$[In^{3+}]$=0.2 mM, [RPT] =0.1M, $[NaNO_3]$=0.1M, pH=10.0, Triton–x–100=0.002%, RPT: Renal proximal tubule

Table 8: Effect of height of mercury column on nickel – (RPT) system.

Height of mercury column	i_d	$i_d/\sqrt{h}$
h (cm)	(µA)	
80	2.9782	0.3329
75	2.8847	0.3331
70	2.7860	0.3330
65	2.6850	0.3330
60	2.5807	0.3332

$[Ni^{2+}]$=1.0 mM, [RPT]=0.1M, $[NaNO_3]$=0.1M, pH=10.0, Triton–x–100=0.002%, RPT: Renal proximal tubule

Table 9: Effect of indium ion concentration on the wave height.

$[In^{3+}]$	i_d	$i_d/\sqrt{h}$
(mM)	(µA)	
0.1	0.7005	7.0056
0.2	1.4109	7.0545
0.3	2.1179	7.0566
0.4	2.8184	7.0472
0.5	3.5272	7.0544

[RPT]=0.2M, $[NaNO_3]$=0.1M, pH=10.0, Triton–X–100=0.002%

Figure 5: Polarograms of (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4, and (e) 0.5 mM indium in 0.2 M renal proximal tubule and 0.1M $NaNO_3$ at pH 10.0.

Figure 6: Polarograms of (a) 0.4, (b) 0.6, (c) 0.8, (d) 1.0, and (e) 1.2 mM nickel in 0.2 M renal proximal tubule and 0.1M $NaNO_3$ at pH 10.0.

Figure 7: Calibration plot of indium ion in 0.2M ligand renal proximal tubule and 0.1M $NaNO_3$ at pH 10.0.

calibration plots at different concentrations of the depolarizer. In the present investigations, the carried out polarographic studies

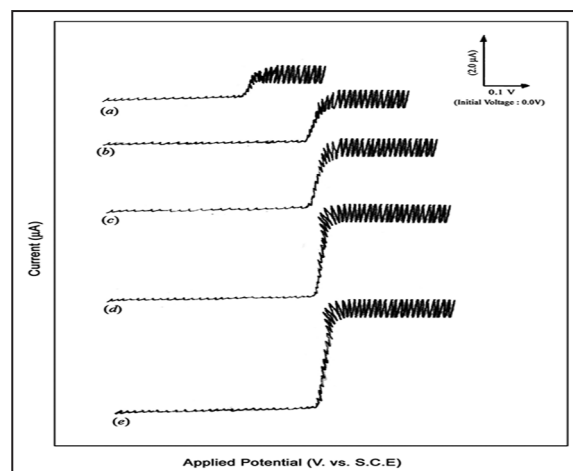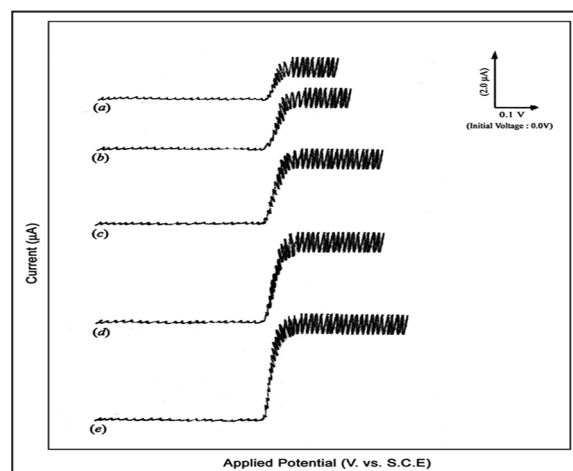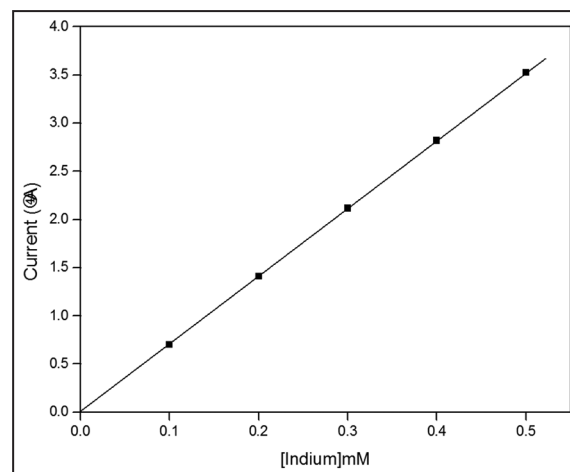(Figures 5 and 6) of indium and nickel metal ions of biological and industrial importance. Metal ion concentration was varied from

0.4 mM to 1.2 mM in the 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 Figures 7 and 8. In all the instances, straight line plots were obtained passing through
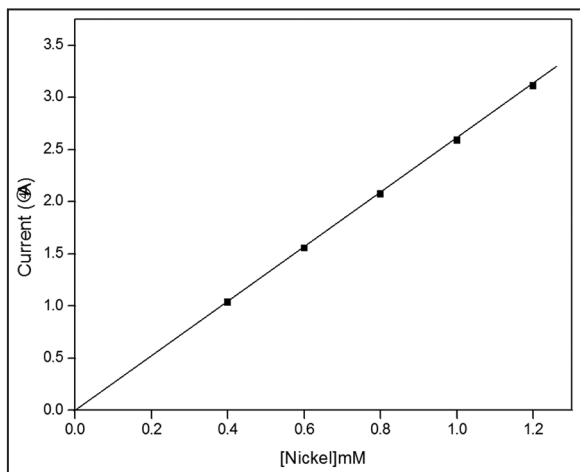

Figure 8: Calibration plot of nickel ion in 0.2M ligand renal proximal tubule and 0.1M NaNO$_3$ at pH 10.0.

Table 10: Effect of nickel ion concentration on the wave height.

[Ni^{2+}] (mM)	id (μA)	$i_d/\sqrt{h}$
0.4	1.0362	2.5905
0.6	1.5540	2.5903
0.8	2.0723	2.5905
1.0	2.5902	2.5902
1.2	3.1085	2.5904

[RPT]=0.2M, [NaNO$_3$]=0.1M, pH=10.0, Triton–X–100=0.002%

the origin indicating the validity of Ilkovic equation. Values computed for i_d/c were constant within the experimental error was shown in Tables 9 and 10. The metal ions whose half-wave potential difference was >0.2 V wer`Ze selected to carry out quantitative analysis present in binary mixtures constituting different important ores and alloys.

3.2. Determination of ligand number and stepwise formation constants of Copper RPT system

Earlier polarographic investigation on nickel in the presence of complexing agent RPT. 0.1M NaNO$_3$ as supporting electrolyte and 0.002% of Triton–X–100 as maximum suppressor at pH 10.0 revealed that nickel undergone reversible electrode reaction at d.m.e. The graph plotted against E$_{1/2}$ and -log (RPT) gave a smooth curve showing the existence of various stepwise complex equilibria in solution. The author, therefore, prepared the solution in 40:60 methanol:water medium. Lingane method was, therefore, adopted for the determination of metal-to-ligand ratio and stability constant of indium - RPT complex using the following equation:

$$\Delta E_{1/2} = \frac{0.0591}{n}\log\beta_{mxJ} + J\frac{0.059}{n}\log[X]$$

Where the symbols represent their usual significance. The coordination number (J) $\frac{0.059}{n}$ was determined by equating the slope A the plot to J where "n" representing a number of participating in the electrode reaction. The ligand number obtained from the slop "A" the graph was found to be two. Further, the stability constant of indium - RPT system calculated at 1.0 M concentration to the ligand RPT was equal to $\beta_{mxJ} = 8.2943 \times 10^7$. Experimental results were tabulated in Table 11.

4. CONCLUSIONS

Determination of traces quantities of elements indium(III) and nickel(IV) using RPT Schiff base by the polarographic method is not tedious and does not involve any heating, separation, or extraction of the components. Determination of metal ions indium and nickel using RPT ligand is simple and selective and rapid, can be applicable in determinations in metallurgy, environmental analysis (air, water, and seawater contaminants), food analysis, toxicology, clinical analysis,

Table 11: Derived functions for copper - (RPT) system.

[RPT] (M)	i_d (μA)	Slope (mV)	E$_{1/2}$ (-V. vs. S.C.E)	Δ E$_{1/2}$ (-V vs. S.C.E)	log I$_M$/I$_C$	F$_0$[X]×10^5	F$_1$[X]×10^6	F$_2$[x]×10^7
0.00	7.7378	57.44	0.205	-	-	-	-	-
0.02	7.5150	59.76	0.355	0.150	0.0127	0.9843	4.9215	-
0.03	7.3480	58.62	0.359	0.154	0.0224	1.3666	4.5553	-
0.04	7.0975	57.54	0.361	0.156	0.0375	1.6487	4.1218	-
0.05	7.0143	57.74	0.364	0.159	0.0426	2.0982	4.1965	-
0.06	6.6800	57.54	0.367	0.162	0.0638	2.7712	4.6186	-
0.08	6.2626	57.52	0.386	0.181	0.0918	12.6335	15.7919	8.4887
0.10	5.8445	57.44	0.390	0.185	0.1219	18.3838	18.3838	9.3830
0.20	5.3440	57.48	0.404	0.199	0.1607	58.6242	29.3121	10.1560
0.40	5.0100	57.52	0.419	0.214	0.1887	196.8432	49.2108	10.0525
0.50	4.5925	57.48	0.424	0.219	0.2265	314.7277	62.9455	10.7891
0.60	4.1750	57.44	0.427	0.222	0.2680	435.5557	72.5926	10.5987
0.80	3.7575	57.42	0.433	0.228	0.3138	765.7045	95.7130	10.8391
1.00	3.3401	57.42	0.437	0.232	0.3648	1169.1569	116.9156	10.7915

β_1=0.90×10^7, β_2=10.80×10^7, [In^{+3}]=1.0mM, [NaNO$_3$]=0.1M, pH=10.0, Triton–x–100=0.002%

analysis of drugs, pharmaceutical preparations, and determination of pesticide or herbicide residues in the foods and other samples.

5. ACKNOWLEDGMENT

REFERENCES

1. N. Robert, C. Michel, V. Patrice, M. Jose, (1985) Reactivite du tris(hydroxymethyl)aminomethane avec des nitro-aldehydes aromatiques. Synthese de nouveaux composes antimicrobiens, *Tetrahedron Letter*, **26**: 5523-5524.

2. K. Sreenivasulu, P. S. Khan, R. Sreenivasulu (2017) Polarographic methods for the determination of copper (II) and cadmium (II) using Schiff base as chromogenic reagent, *International Journal of Scientific and Research Publications*, **7**: 278-288.

3. S. M. Lee, K. S. Sim, K. M. Lo. (2015) Synthesis, characterization and biological studies of diorganotin(IV) complexes with tris[(hydroxymethyl)aminomethane] Schiff bases, *Inorganica Chimica Acta*, **429**: 195-208.

4. K. M. Patel, K. N. Patel, N. H. Patel, M. N. Patel, S. Chandrasekhar, R. F. Cunico (2000) Synthesis, characterization and antimicrobial activities of some transition metal complexes with the schiff base of 5-bromosalicylaldehyde and o-aminophenol and 2,2′-bipyridylamine, *Inorganic and Nano-Metal Chemistry*, **30**: 1965-1973.

5. R. Sreenivasulu, J. Sreeramulu, (2004) Synthesis and characterisation of new schiff bases, *Journal of Acta Ciencia Indica*, **30**: 181-184.

6. R. V. Savalia, A. P. Patel, P. T. Trivedi, H. R. Gohel, D. B. Khetani, (2013) Rapid and economic synthesis of Schiff base of salicylaldehyde by microwave irradiation, *Research Journal of Chemical Sciences*, **3**: 97-99.

7. X. Zhou, X. Liu, X. Yang, D. Shang, J. Xin, X. Feng, (2008) Highly enantioselective hydrophosphonylation of aldehydes catalyzed by tridentate Schiff base aluminum(III) complexes, *Angewandte Chemie International Edition*, **47**: 392-394.

8. K. C. Gupta, A. K. Sutar, (2008) Catalytic activities of Schiff base transition metal complexes, *Coordination Chemistry Reviews,* **252**: 1420-1450.

9. R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S. I. Noro, S. Kitagawa, (2004) Immobilization of a metallo Schiff base into a microporous coordination polymer, *Angewandte Chemie International Edition*, **43**: 2684-2687.

10. P. G. Lacroix, (2001) Second-order optical nonlinearities in coordination chemistry: The case of bis(salicylaldiminato) metal Schiff base complexes, *European Journal of Inorganic Chemistry*, **2001**: 339-348.

11. K. Ramanjaneyulu, K. H. Nagamaddaiah, J. Latha, K. S. Babu, (2015) Electrochemical behaviour of for Cd(II)-VAMP and Cu(II)-VAMP complex systems, *Journal of Applicable Chemistry*, **4(1)**: 284-296.

12. A. K. Goswami, K. K. Kodli, N. Choubisa, A. Panwar, R. Dashora, R. S. Chauhan, (2015) Polarographic studies of 3-hydroxy-3-phenyl-1-(dichloro phenyl) triazene with Ni (II) complex, *Rasayan Journal of Chemistry*, **8(2)**: 172-175.