



**Polarographic Study Of Cd(II) And Cu(II) Ions  
In Presence Of New Schiff Base**

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Accepted on 15<sup>th</sup> January 2015

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**ABSTRACT**

*The use of organic reagents in inorganic analysis is a major field of interest. A perusal of literature revealed that the number of Schiff bases were synthesized from (trishydroxymethyl) methyl-amine, 2-amino-2-methyl-1,3-propane-di-ol, 2-amino-2-ethyl-1,3-propane-di-ol with various carbonyl compounds and possess many important applications in the fields of greater interest like Medicine, Pharmacy, Agriculture etc., in the present investigations synthesis and characterisation of Vaniline with 2-amino 2-methyl 1-Propanol (AMP) are described for the first time. In order to establish the complexing ability of the ligand cadmium and copper ions were selected for carrying - Polarographic investigation.*

**Keywords:** Schiff base, Polarography, AMP, Vanillin.

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**INTRODUCTION**

2-amino-2-methyl-1-propanol (briefly known as AMP) is an alkanolamine. AMP and its derivative have innumerable applications in the fields of significant interest like medicine, pharmacy and agriculture [11-16]. AMP and its derivatives possess bactericidal and fungicidal activity. Besides its applications in various fields AMP also forms complexes with metal ions because of the presence of basic site namely – NH<sub>2</sub> group. The basic nature of the compound and its pK<sub>b</sub> also support the formation of metal complex. Perusal of literature revealed that number of references were cited employing various techniques about the behaviour of cadmium and copper towards Schiff bases, derived from alkanolamine and carbonyl compounds. Vyas et al [2] were the first to report complexes of cadmium with Schiff bases namely salicylaldehyde Tris (ST) and benzaldehyde Tris (BT) in 60% (v/v) methanol-water medium using potentiometry. They also presented the polarographic evidence for cadmium Schiff base complexes with ST, BT and also with vanillin Tris (VT) [3]. The same authors while studying the complexation of cadmium ion with ST, established a new method for the determination of ligand-proton stability constant by polarographic method [1]. The stability constants and molar absorptivities of complexes of copper(II) with 2-amino-2-methyl-1-propanol (AMP) in aqueous medium were determined employing spectrophotometric method [8] even though the available few references on metal complexes of AMP not fully established the coordinating ability of AMP towards metals, but only emphasized the applications

those complexes in biological fields. Synthesis, structural, magnetic and spectral properties of alkanolamine complexes of Pt, W, Ni, Ag, Au and Zn have been reported [4, 5, 6, 7, 9, 10]. In addition to Tris, AMP is one of the important compounds of unique series of alkanolamines. Literature survey reveals that significant alkanolamine such as Tris has been employed extensively as complexing agent in polarographic analysis.

Keeping the above facts in view, the author in the present investigation, prepared new Schiff base (VAMP) derived from alkanolamine and studied its complexing ability towards Cadmium and Copper metal ions in 40% V/V methanol water medium employing Polarographic technique. The detailed electrochemical investigation includes studies like effect of hydrogen ion concentration, effect of ligand concentration, effect of height of mercury column and effect of metal ion concentration complex systems on the Cd(II) and Cu(II)-VAMP.

## MATERIALS AND METHODS

All chemicals used were of Analytical grade metal ion solutions of Cadmium and Copper were prepared from Metal ion solutions of AR sample and analyzed by standard methods. Recrystallised Schiff base (VAMP) was used as complexing agent. As the ligand was not freely soluble in water, 40% V/V methanol-water medium was maintained uniformly throughout the experiment to establish the complexation towards and Cadmium and Copper. The ionic strength was kept constant at 0.1M by using potassium nitrate for all metal studies. 0.002% Triton-X-100 was used as maximum suppressor. Double distilled mercury was employed for dropping mercury was employed for dropping mercury electrode. Purified nitrogen was employed for deoxygenation of all test solution prior to recording. All the solutions were prepared in double distilled water.

An ELICO DC recording Polarograph Model CL-357 (Digital) was used for recording the polarograms. Saturated calomel electrode was used as reference electrode. An ELICO glass capillary having the following characteristics  $m=2.686\text{gm/sec}$   $t=4\text{ sec}$  in open circuit at constant height of mercury head (75.0 cm) was used. The pH measurements of the solutions were recorded with an Elico digital pH meter model L1 127 pH adjustments were made using 0.1 M  $\text{HNO}_3$  (or) 0.1M NaOH as the case may be. Solutions were taken in the polarographic cell consisting of counter electrode, reference electrode (SCE) and working electrode (D.M.E) [three electrode system] clamped to a stand with a clip. Nitrogen gas is passed through the inlet tube and a Provision is given to the gas after bubbling through the solution. Toshniwal Thermostat type GL-15 was used to keep the temperature at  $30\pm 1^\circ\text{C}$ .

## RESULTS AND DISCUSSION

**Effect of pH on Cadmium and Copper metal ions in presence of new Schiff Base:** The hydrogen ion concentration has marked influence on the half-wave potential of the metal ion. At any particular concentration of the ligand if the pH was increased the half-wave potential of the metal ion gradually shifted towards more negative value. The main aim of the study of effect of pH on metal ions is to ascertain the appropriate pH value at which well-defined polarograms can be obtained so as to enabling to estimations of metal ions and also to know the number carry out quantitative of protons participating in the electrode reaction.

The influence of overall hydrogen ion concentration on the polarographic characteristics of Cd(II) and Cu(II) in presence of the new Schiff Base (VAMP) were carried out in detail. From the results it was observed that pH has considerable effect on diffusion current and half-wave potential. With increasing pH, the half-wave potential of the complex shifted towards more cathodic value tables.1,2

The stock solution (0.1M) of new Schiff base VAMP) showed a pH value in between 8.0 and 8.5. Hence for uniformity sake pH 8.0 was fixed in all the cases to carryout other polarographic studies such as ligand concentration, effect of height of mercury column and effect of metal ion concentration.

**Table – 1**

Effect of pH on Cadmium – VAMP complex

[Cd <sup>2+</sup> ]	:	0.4 mM
[KNO <sub>3</sub> ]	:	0.1 M
[VAMP]	:	0.03 M
Triton-X-100	:	0.002%

pH	E <sub>1/2</sub> (-V vs SCE)	E <sub>3/4</sub> – E <sub>1/4</sub> mV
6.0	0.6574	30.77
7.0	0.6641	31.25
8.0	0.6675	30.00
9.0	0.7043	30.00
10.0	0.7433	29.63

**Table – 2**

Effect of pH on Copper – VAMP complex

[Cu <sup>2+</sup> ]	:	0.4 mM
[KNO <sub>3</sub> ]	:	0.04 M
[VAMP]	:	0.1 M
Triton-X-100	:	0.002%

pH	E <sub>1/2</sub> (-V vs SCE)	E <sub>3/4</sub> – E <sub>1/4</sub> mV
7.0	0.1802	76.2
8.0	0.2150	77.6
9.0	0.2589	75.1
10.0	0.2786	78.3

**Effect of VAMP concentration on Cd and Cu metal ions:** The effect of different concentrations of ligand on the polarographic characteristics of Cadmium and Copper was carried out in detail. The main purpose of the study is to find out a suitable range of ligand concentration wherein the waves are well defined and useful for analytical work. Polarograms were recorded for varying concentrations of ligand [VAMP] using 0.4 mM metal ion concentration for Cd(II) and Cu(II). Ligand range selected to study the effect of wave height on metal ions was varied from 0.005 to 0.05M. From the polarograms, it was observed that the half-wave potentials shifted towards more cathodic values where as diffusion current decreased with increase in concentration of VAMP indicating complex formation. The slope value obtained from log (i/i<sub>d-i</sub>) vs E<sub>d-e</sub> plots and E<sub>s/4</sub>-E<sub>i/4</sub> values deduced from current voltage curves revealed that Cadmium-VAMP undergo reversible electrode reaction with two electron Reduction at d.m.e. Further the slope values obtained from the graphs for Cu-VAMP complex system revealed that the electrode reaction was undergone irreversible. The results were incorporated in tables - 3, 4. Keeping in view the influence of ligand concentration on wave heights, appropriate concentration of ligand was fixed for studies like effect of pH, effect of height of mercury column and effect of metal ion concentration.

Table – 3

Effect of ligand VAMP concentration on cadmium

[Cd <sup>2+</sup> ]	:	0.4 mM
[KNO <sub>3</sub> ]	:	0.04 M
pH	:	8.0
Triton-X-100	:	0.002%

[VAMP]	E <sub>1/2</sub> (-V vs SCE)	i <sub>d</sub> μA	Slope mV
0.005	0.6375	2.60	31.58
0.008	0.6450	2.55	31.82
0.010	0.6525	2.50	31.25
0.020	0.6600	2.45	30.77
0.030	0.6675	2.39	30.43
0.040	0.6750	2.30	29.63
0.050	0.6825	2.25	29.41

Table – 4

Effect of ligand VAMP concentration on copper

[Cu <sup>2+</sup> ]	:	0.4 mM
[KNO <sub>3</sub> ]	:	0.04 M
pH	:	8.0
Triton-X-100	:	0.002%

[VAMP]	E <sub>1/2</sub> (-V vs SCE)	i <sub>d</sub> μA	Slope mV
0.005	0.1705	2.30	60.5
0.008	0.1775	2.25	60.9
0.010	0.1850	2.20	63.7
0.020	0.1925	2.10	60.5
0.030	0.2020	2.05	64.5
0.040	0.2150	1.85	63.7
0.050	0.2225	1.75	61.0

**Effect of height of mercury column:** For ascertaining the validity of Ilkovic equation and also the diffusion controlled nature of the polarographic waves it is necessary to investigate the relationship between wave height and square root of the height of mercury column. According to the theory of current-voltage curves a linear relationship between diffusion current and the square root of the height of mercury column is essential in order to draw a thermodynamic conclusion about the electrochemical process occurring at the dropping mercury electrode. Specifically in quantitative polarography, this study is of great importance. In addition to that it also helps in ascertaining whether the wave is controlled by kinetic (or) catalytic (or) adsorption factors.

Influence of height of mercury column on the polarograms of Cd(II) and Cu(II) metal ions in presence of VAMP as complexing agent and in appropriate supporting electrolyte was studied at different heights of mercury column. The results showed that with the change of height of mercury column. The results showed that with the change of height of mercury column the wave heights also changed.  $i_d/\sqrt{h}$  values for all the systems remained constant within the experimental error tables 5,6 suggesting that all the metal ions under consideration were diffusion controlled. Mercury height of 75.0 cm was selected for recording all the experiments.

**Table 5:**

Effect of height of mercury column

[Cd <sup>2+</sup> ]	:	0.4 mM
[KNO <sub>3</sub> ]	:	0.04 M
pH	:	8.0
Triton-X-100	:	0.002%

Height of the mercury column h (cm)	$i_d$ $\mu$ A	$i_d/\sqrt{h}$
75.0	2.39	0.2771
65.0	2.23	0.2766
55.0	2.05	0.2764
45.0	1.85	0.2757
35.0	1.64	0.2772

**Table 6:**

Effect of height of mercury column

[Cu <sup>2+</sup> ]	:	0.4 mM
[KNO <sub>3</sub> ]	:	0.04 M
pH	:	8.0
Triton-X-100	:	0.002%

Height of the mercury column h (cm)	$i_d$ $\mu$ A	$i_d/\sqrt{h}$
75.0	1.85	0.2136
65.0	1.72	0.2133
55.0	1.58	0.2130
45.0	1.43	0.2131
35.0	1.26	0.2129

**Effect of metal ion concentration:** The influence of metal ion concentration on the polarograms usually be carried out to ascertain the validity of Ilkovic equation. Furthermore, quantitative estimations of metal ions can also be determined through the effect of metal ion concentration on diffusion current. This can be achieved only when diffusion current is linearly proportional to the concentration of metal ion. The general method is to construct a calibration plot between metal ion concentration and wave height which should pass through the origin. The unknown concentration of the metal ion can be computed from the plot drawn. The effect of metal ion concentration on polarographic wave heights for Cd(II) and Cu(II) was carried out. In all systems, single well-defined waves were obtained over the concentration range studied.

Calibration plots drawn for all the metal ions under consideration gave straight lines passing through the origin suggesting the diffusion controlled nature of the electrode reaction,  $i_d/C$  values remained same with in the experimental error **tables - 7, 8**. The range of the metal 0.2 to 1.0 mM. Higher concentrations of metal Ion concentration varied from Ion have not been take into consideration for recording polarograms because of the formation of heavy precipitation.

**Table 7:**

Effect of cadmium ion concentration on the wave height

[VAMP]	:	0.03 M
[KNO <sub>3</sub> ]	:	0.1M
pH	:	8.0
Triton-X-100	:	0.002%

[Cd <sup>2+</sup> ] mM	$i_d$ $\mu$ A	$i_d/C$
0.2	1.19	5.950
0.4	2.39	5.975
0.6	3.58	5.966
0.8	4.75	5.937
1.0	5.95	5.950

**Table 8:**

Effect of copper ion concentration on the wave height

[VAMP]	:	0.04 M
[KNO <sub>3</sub> ]	:	0.1M
pH	:	8.0
Triton-X-100	:	0.002%

[Cu <sup>2+</sup> ] mM	$i_d$ $\mu$ A	$i_d/C$
0.2	0.92	4.600
0.4	1.85	4.625
0.6	2.78	4.633
0.8	3.7	4.625
1.0	4.62	4.620

## CONCLUSIONS

The results of this study have shown that the preparation of new Schiff base will be a new addition to the already well existing Schiff base chemistry. The present electro chemical investigation may add new dimensions to the existing literature on the polarographic studies of Metal – Schiff base complexes. It may, therefore, will be claimed as a novel attempt as far as polarography of Metal – Schiff base complex is concerned. The detailed electro chemical investigation of Cd (II) and Cu (II)-VAMP complex systems may add new dimensions to coordination chemistry of metal complexes.

**ACKNOWLEDGEMENT**

- I am very thankful to S.K. University authorities for providing such an environment for doing better research very much.
- It's my pleasure to express my thanks to Department of Chemistry for giving an opportunity to do research.

**REFERENCES**

- [1] M.S. Patel, T. Trivedi, D.N. Vyas, *J. Electro. Chem, Soc. India*, **1977**, 26, 21.
- [2] T. Trivedi, M.S. Patel, D.N. Vyas, *J. and Indian Chem. Soc.*, **1978**, 55, 980.
- [3] M.S. Patel, T. Trivedi, D.N. Vyas, *Indian J. Chem.*, **1978**, 16A, 724.
- [4] Rao G.N.Murthy, C.S.R, Prakash A, *Indian J. Chem., Sec.A*, **1982**, 21A (2), 203+5(Eng).
- [5] F.D.Rochon, P.C. Kong, R. Melanson, *Can. J.Chem*, **1984**, 62(12), 2657-2660, (Eng).
- [6] Nagel, Yvonne; Beck, Wolfgang *Z. Anorg. Allg. Chem*, **1985**, 529, 57-60.
- [7] Kokunvr, yu vi Bochicareva, V.A; Sakharov S.G.Buslae, yu 1A Koard. *Khim*, **1985** 11 (11), 36- 40.
- [8] Brown Herbert C; Prasad, J.V.N.rana., *J. org. chem.* **1986**, (24), 4526-39 (Eng).
- [9] Canepari, silvia, Carunchino, Vincenzo, Castellano, Paola; Messina, *Talanta*, **1997**, 44, 2059-2067.
- [10] Canepari, silvia, Carunchino, Vincenzo, Castellano, Paola; Messina, *Talanta Ann. Chime (Rome)* **1999**, 89 (1-2), 37-43.
- [11] Hirakawa, Kazujaki, Sugiura, Masakazu, Yamamotom Eizo. *JP* 75, 58, 227, 21, May **1997**.
- [12] Zagorevskii. V.A.Khimm-Farm. *Zh.* 14(12), 35-39 (Russ), **1980**.
- [13] Stradi, Riccardo, *Ger.Offen.*3.035.53.10.09 Apr. **1981**.
- [14] Szentivanyi, A.Szentivanyi.*J.Adv. Immunopharmacol.*2; *Proc.Int.Conf.* 2<sup>nd</sup>, 269-276 (eng), **1982**.
- [15] Heffernan, James Gerard; Hydes, Paul Cedric, Picker Donald Harold, *Eur.Pat.Appl.EP* 167, 057, **1986**.
- [16] Terajima, Atsuro, *JP.* 01, 102, 084, 19, Apr.**1989**.