Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2015, 4 (3): 975-979

(International Peer Reviewed Journal)

Electrochemical Behaviour of for Cd(II)-VAMP and Cu(II)-VAMP Complex systems

K.Ramanjaneyulu[1], K.Hari Nagamaddaiah[1], J.Latha[2] and K.Sudhakar Babu[*1]

1. Department of Chemistry, Sri Krishnadevaraya University, Anantapuramu, A.P, **INDIA**
2. Department of Environmental Sciences, S.K.U. College of Engineering and Technology, Sri Krishnadevaraya University Anantapuramu-515003 A.P, **INDIA**

Email: kramansku@gmail.com

Accepted on 12th April 2015

ABSTRACT

Electrochemical Behaviour of *for Cd(II) and Cu(II)-VAMP complex systems have been evaluated polarographically. The new Schiff Base derived from 2-Amino-2-Methyl-1-propanol having good complex ability towards Cd (II) and Cu(II) ions. In presence of new Schiff Base, detailed Polarographic investigation has been carried out. The obtained results indicate that the electrode reactions in both the systems were diffusion controlled* undergoing reversible and irreversible. *The Kinetic parameters like activity transfer co-efficient and forward rate constants (α_n, $k^0_{f,h}$) have been evaluated in present research study.*

Keywords: Schiff base, Vanillin, AMP, Polarography, Kinetic parameters.

INTRODUCTION

A perusal of literature revealed that complexation of Cd(II) and Cu(II) with Schiff bases derived from 2-amino- 2-methyl-1-Propanol(Shortly known as AMP)are very scare. Vyas et al [1,2] reported indium complexes with salicylaldehyde tris schiff base Potentiometrically and determined stability constant in aqueous medium while Rao et al., [3] reported Polarographic studies for the determination of the metal in presence of copper in standard alloys and also K.Sudhakar Babu [5] reported Polarographic study of Kinetic parameters for In(III)-OVT and Pd (II)-OVT complexes. In the present communication a detailed Polarographic investigation on electro reactions of Cd(II) and Cu(II) with a new Schiff base vanillin-AMP have been reported. In view of the irreversible nature of the reduction wave, the kinetic parameters like α_n and $k^0_{f,h}$ for Cu(II)-VAMP System have been calculated by employing Koutckey's theoritical treatment as extended by Meities and Israel [4]. The Stability Constant for Cd(II)-VAMP also determined.

MATERIALS AND METHODS

Metal ion solutions were prepared from BDH AR Samples. Ligand solution was prepared in 30% (v/v) methanol aqueous medium from the recrystalized sample for studying metal ion. Double distilled mercury was used for d.m.e. All the solutions were prepared in air free conducting water. Potassium nitrate solution

(0.1 M) for both cadmium and copper was used to maintain constant ionic strength. Triton-X-100 (0.002%) was used as maximum suppressor. Purified hydrogen gas was employed for deoxygenation of all experimental solutions prior to recording .The pH of the solution was adjusted to 8.0 for both cadmium and copper systems.

Polarograms were recorded using ELICO DC polarograph (CL-25). ELICO glass capillary had the characteristics m=1.7434 mg sec^{-1} and t=4 sec in open circuit. ELICO Digital pH meter was employed to measure pH of the solutions. Lingane and latimer H-type cell was used. The toshniwal thermostat-15 was used to keep the temperature at 26 +0.1^{0}C.

Synthesis and Characterization of VAMP: 4-Hydroxy-3-methoxy-benzaldehyde (0.05 mol) was added to 50 mL of methanol and 2-amino 2-methyl-1-propanol (5 mL, 0.05 mol) was dissolved in 50 mL of distilled water. These two solutions were mixed in a clean 250 mL round bottom flask and stirred well with a magnetic stirrer then it was refluxed for 1 h. A light yellow colored product was formed, it was separated by filtration and washed several times with hot water and methanol and dried in vacuum. This compound was recrystalized from methanol. The percentage of yield was 80% and melting point of the compound was 194-197^0 C.

The new Schiff base VAMP was characterized on the basis of elemental and spectral analysis .The IR Spectra of VAMP Showed peak at 1590 cm^{-1} indicates the presence of >C=N group. The elemental analysis of VAMP{C % =64.44(64.49),H %=7.58(7.61),N % =6.23(6.27)} Confirms the molecular formula of the ligand.

RESULTS AND DISCUSSION

Cadmium – VAMP complex System: A single and well defined Polarograms were obtained for Cd (II) in presence of V–AMP in concentration 0.05M in 30% (V/v) methanol–water medium at pH 8.0. The halfwave potential shifted towards more negative potential with increasing concentration of the Schiff base indicating complex formation.

The plots of log $\left(\frac{i}{id-i}\right)$ –0.546 log t were linear with slope values (29 + 5 mv) much higher than expected for two electron reversible electrode reduction which suggested that the reduction was irreversible (Table 1). The direct proportionality of the diffusion current to the square root of the mercury column indicated that the reduction was entirely diffusion controlled.

Table 1: Effect of Ligand concentration on the Polarograms of Cd(II) ion

$[Cd^{2+}]$	:	0.4 Mm
$[KNO_3]$	:	0.1M
pH	:	8.0
Triton -X-100	:	0.002%

[VAMP] M	El/2 (–VvsSCE)	I_d 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

Cu (II) – VAMP complex System: A single well defined diffusion controlled were mere obtained in presence of varying concentrations (0.005 – 0.05M) of VAMP in 0.1 M potassium nitrate as supporting electrolyte. The shift in the half wave potential of copper towards more cathodic value revealed the complex formation with the ligand. The log plots of the Polarograms with linear slope values much higher (60 + 5 mv) than that of the theoretical values expected for two electron reduction (Table 2). The constancy of $\frac{i_d}{\sqrt{h}}$ values indicated that the reduction was diffusion controlled.

Table 2: Effect of Ligand Concentration on the Polarogram of Cu(II) ion

$[Cu^{2+}]$: 0.4 Mm
$[KNO_3]$: 0.1M
pH : 8.0
Triton -X-100 : 0.002%

[VAMP] M	El/2 (–VvsSCE)	I_d 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

The reduction being irreversible for Cu(II)-VAMP systems systems the kinetic parameters like forward rate constant ($k^{\circ}_{f,h}$) and transfer coefficient (α_n) were evaluated using Koutecky's theoretical treatment as extended by Meites and Israel which involves the following equations

$$E_{d,e} = E' - \frac{0.0542}{\alpha n}\left[\log\frac{i}{i_d - i} - 0.546\log t\right]$$

$$E' = -0.2412 + \frac{0.05915}{\alpha n}\log\frac{1.349k^{o}_{f,h}}{D^{1/2}}$$

In the above equation both $E_{d,e}$ and E' are with respect to Calomel Electrode. Mximum currents at the end of the mercury drop were taken in to account for calculation instead of average currents. The value of 't' was measured at different potentials on the rising portion of the wave, between 10 and 90 percent of i_d . the values of αn are obtained by equating the slope of the straight lines from plots of $E_{d,e}$ Vs $\log\left(\frac{i}{i_d - i}\right)$ – 0.546 log t with $\frac{0.0542}{\alpha n}V$. The intercept of the plot gave the value of the parameter E' at different concentrations of the ligand. The values of diffusion coefficient (D) were determined using the Ilkovic Equation. The values of E', D and αn were utilized to evaluate $k^{\circ}_{f,h}$ (Tables 3,4).

Table 3: Determination of Stability Constants for Cd(II)-VAMP System

$[Cd^{2+}]$: 0.4 Mm
$[KN0_3]$: 0.1M
pH : 8.0
Triton -X-1 00 : 0.002%

[VAMP]	Log [VAMP]	$E_{1/2}$	$\Delta E_{1/2}$	Slope
0.0	-	0.580	-	-
0.005	-2.3010	0.6375	0.0575	31.58
0.008	-2.0969	0.6450	0.0650	31.82
0.010	-2.0000	0.6525	0.0725	31.25
0.020	-1.6989	0.6600	0.0800	30.77
0.030	-1.5228	0.6675	0.0875	30.43
0.040	-1.3979	0.6750	0.0950	29.63
0.050	-1.3010	0.6828	0.1028	29.41

$ß_{MXj} = 1.2 \times 10^6$

Table 4: Kinetic parameters of Cu (ll)-VAMP Complex System

$[Cu^2+]$: 0.4mM
$[KNO_3]$: 0.1M
pH : 8.0
Tritan X-100 : 0.002%

[VAMP] M	El/2 (–VvsSCE)	E' (-V vs SCE)	αn	$D^{½} \times 10\text{-}^3$ $cm^2 sec^{-1}$	k^0_{fh} cm sec^{-1}
0.005	0.1705	0.2082	0.9225	1.9457	6.6404×10^{-2}
0.008	0.1775	0.2174	0.9225	1.9034	6.4960×10^{-2}
0.01	0.185	0.2266	0.9225	1.8611	6.3517×10^{-2}
0.02	0.1925	0.2350	0.9225	1.7765	6.063×10^{-2}
0.03	0.200	0.2450	0.9198	1.6919	5.7742×10^{-2}
0.04	0.215	0.2450	0.9198	1.5650	5.3411×10^{-2}
0.05	0.2225	0.2360	0.9198	1.4804	50523×10^{-2}

APPLICATIONS

The obtained results indicate that the electrode reactions in Cu(II)-VAMP Complex System was diffusion controlled and irreversible. The Kinetic parameters like activity transfer co-efficient and forward rate constants (α_n, $k^0_{f,h}$) and also Stability Constants have been evaluated in present research study.

CONCLUSIONS

From the obtained $k^0_{f,h}$ values it has been observed that the reduction of Cu(II)-VAMP complexes become more and more irreversible with increasing concentration of the complexing agent VAMP.

ACKNOWLEDGMENTS

The authors are thankful to Sri Krishnadevaraya University Authorities for providing such an environment for carrying out research work.

REFERENCES

[1] M.S. Patel, T. Trivedi, D.N Vyas, *J. Electrochem. Soc. India*, **1978,** 26, 67.
[2] M.S.Patel, T. Trivedi, D.N. Vyas, *J. Indian. chem. Soc*, **1979,** 56, 126**.**

[3] V.S.Raghavendra Rao, K. Hussain Reddy, R. Sreenivasulu, *J. Electrochem. Soc. India,* **1985,** 34, 209**.**
[4] L. Meites, Y. Israel, *J. Am. Cem. Soc,* **1961,** 83, 4903**.**
[5] K.Sudhakar Babu, J.Sreeramulu, R. Sreenivasulu, B.Hariharnath, K.Shantha, *J. Electrochem Soc.India,* **2004,** 53, 10-12**.**

AUTHORS' ADDRESSES

1. **Prof.K.Sudhakar Babu**
Professor of Chemistry,
S.K.University,
Anantapuramu - 515 003
Mobil No: +91-9849362240

2. **Dr.J.Latha**
Dept. of Environmental Sciences
S.K.U.College of Engineering & Technology
Anantapuramu - 515 003
Mobil No; +91-9704561461

3. **K.Ramanjeneyulu**
Research Scholar, Dept. of Chemistry
S.K.University
Anantapuramu - 515 003
Mobil No: +91-7799853862

4. **K.Hari Nagamaddaiah**
Research Scholar, Dept. of Chemistry
S.K.University
Anantapuramu - 515 003
Mobil No: +91-9985340181