

## **Section – (i)**

### **Materials and Methods**

#### **Preparation of the solutions of the compounds investigated and other reagents-Significance of Voltammetric studies**

The chemicals employed in the studies are generally of analytical reagent grade. But whenever it is necessary, the chemicals are purified by the standard procedures reported in the literature. In case of solid substances, known amounts of compounds are weighed into standard flask and dissolved in distilled water. In the case of liquids, requisite volume of the liquid is placed with the help of a burette into the standard flask, dissolved in distilled water and the resulting solution is made up to the mark. The solutions thus prepared are standardized by standard procedures if necessary. The author in the present investigation mainly focused on the Voltammetric studies ( Both Polarography and Cyclic Voltammetric studies) of newly synthesized Schiff Bases derived from AMP and detailed aspects of electrochemical behaviour has been discussed

#### **Buffer solutions**

Britton-Robinson buffer solutions [1] are prepared from the stock solutions of boric acid, phosphoric acid, acetic acid and sodium hydroxide. The pH is checked with ELICO pH meter, model LI – 10, M/s. ELICO Private Limited, Hyderabad, India.

## **Mercury**

Analar mercury is further purified chemically according to the procedure described by Vogel<sup>2</sup> and is vacuum distilled.

## **Description of the instruments used**

### **1. pH meter**

The pH measurements are made with pH meter model LI – 10 manufactured by M/s. ELICO Private Limited, Hyderabad, India. The instrument operates on AC (220 volts) mains and is provided with two scales, one for 0.0 to 7.0 pH and the other for 7.0 to 14.0. Provision is made for temperature control in the instrument. Glass electrode EH – 60 (Beckman type) and a saturated calomel reference electrode are used as indicator electrode and reference electrode respectively. Buffer solution of pH 4.0, for acid range and pH 9.0 for alkaline range is used respectively to calibrate the instrument.

### **2. Recording Polarograph**

A CL – 25 Pen Recording Polarograph manufactured by M/s. ELICO Private Limited, Hyderabad, India is used to record current voltage curves. It consists of three units, (A) Dropping mercury electrode, (B) Mains operated Polarograph unit and (C) Mains operated self balancing strip chart recorder. The required span EMF can be adjusted with range selector switch. The electrolysis current is made to pass through a precision resistor placed in series with the cell, and millivolt drop (IR) is fed to a self balancing potentiometric strip chart recorder, and is recorded on the X-axis. The required current sensitivity is obtained with the help of current sensitivity and recorder sensitivity knob. The movement of chart paper is synchronised with a span drive motor and the span scanning voltage is represented on the Y – axis.

### 3. Polarographic cell

The polarographic cell used was a double walled beaker made up of corning glass fitted with a rubber cork. Dropping mercury electrode was inserted through one of the holes through which the mercury drops. Calomel electrode was used as the reference electrode and this was connected to the cell through a salt bridge.

Nitrogen gas from the cylinder was padded through alkaline pyrogalllic acid solution to remove any trace of oxygen present and through the supporting electrolyte solution and was allowed to bubble through the electrolyte solution present in the cell. This was done to remove the dissolved oxygen from the electrolytic solution which otherwise gives polarographic waves for the reduction of oxygen. The air was allowed to leave the cell through an outlet fitted with water, preventing air re-entering the cell again.

Water was allowed to circulate at constant temperature from a thermostat between the inner and outer walls of the double walled cell. The capillary having the characteristics  $1.80 \text{ mg}^{2/3} \text{ s}^{-1/2}$  at  $h = 80 \text{ cms}$  is employed in the studies.

### Cyclic Voltammetry

Cyclic voltammetry is yet another important voltammetric technique which provides the means to examine the nature or pathway of an electrochemical reaction in detail.

The current potential curves at stationary electrodes (like platinum electrode, hanging mercury drop electrode – HMDE, glassy carbon electrode) in unstirred solutions depend on the rate of change of applied potential. At a constant potential, the reduction or oxidation of an electroactive substance depletes a layer of solution

that extends further from the electrode surface into the bulk of the solution as time proceeds, resulting in a current decrease.

Consider the electrode reaction of the type,



At positive potentials the rate of reduction is negligible, the current due to the reaction will be very small. When the potential is scanned in the cathodic direction, the principal effect is the increase in current resulting from an increase in the ratio of the concentrations  $C^O_R/C^O_O$  as per the Nernst equation for a reversible reaction. If the reaction of the O – R couple is irreversible, the increase in current results from the increased rate of reduction of O.

As the applied potential moves to negative values, the ions or molecules of the oxidised species (O) are reduced as rapidly as they arrive at the electrode surface. This situation is encountered at potentials corresponding to the limiting region of the DC polarograms. At these potentials the two opposing effects discussed cause the current first to pass through a maximum value called the peak current,  $i_p$ , and then decrease again. The shape of peak polarogram for linear sweep voltammetry can be visualized at the superposition of an i-t decay curve on a steady state polarogram. The rate of reduction is faster compared to the rate of arrival of O at the electrode surface. However, it is similar to what is existing in the current decrease at higher negative potentials.

Voltammetry with linear potential sweep can be used as a single or multi-sweep technique. Voltammetry with stationary electrodes has several advantageous over conventional polarography such as

- (a) a wide range of potential sweep rates can be used
- (b) the experiment can be completed in a few seconds as against 5 to 10 minutes required in polarography and
- (c) The method is more sensitive than conventional polarography with DME.

However, there is a disadvantage in the analysis of mixtures, this technique is difficult because of the uncertainties in the base line of the second process [1].

**Fig:1.** represents a typical cyclic voltammogram for the reversible reduction reaction



Cyclic voltammetry is a multi-sweep technique in which the potential is varied in the form of an isosceles triangle. At  $t = 0$ , the potential sweep begins at zero volt. The potential is swept at a constant rate ( $dE/dt = V$ ) until the switching potential  $E_\lambda$  is reached. At this point the direction is reversed and the potential is swept back. The potential sweep may be continued for as many cycles as desired. **Figs. 1 and 2.** Illustrates the triangular wave shape for the potential variation. In the polarographic experiments, the changes in potentials are such that the rate of diffusion of oxidised and reduced forms to and from the electrode surface keep the system in equilibrium with the bulk solution at all times. In cyclic voltammetric experiments, the rate of variation of potential is too rapid for diffusional processes to maintain equilibrium with the bulk of the solution.

The relations in peak voltammetry for reversible, quasi-reversible and irreversible systems were considered by Matsuda and Ayabe [2] for linear diffusion

to a plane electrode area. At square centimeter, the peak current obtained for the forward polarisation is described by the Randles Sevcik

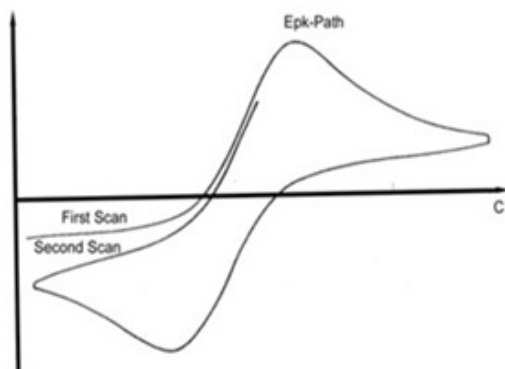


Fig:1: A Cyclic Voltammogram of a Reversible System



Fig:2: a) Type of Wave Used in Cyclic Voltammetry  
b) Type of iv curve obtained using Cyclic Voltammetry

$$i_p = 2.687 \times 10^5 n^{3/2} A D_O^{1/2} C_O V^{1/2} \quad (3)$$

Where

- $i_p$  = the peak current in micro amperes
- $C_O$  = the bulk concentration of oxidant in millimoles litre<sup>-1</sup>
- $V$  = the scan rate of volts S<sup>-1</sup>.
- $A$  = the area of the electrode in cm<sup>2</sup>, and
- $n$  = the number of electrons transferred

The numerical constant used in equation above was given by Nicholson and Shain [3].

The equations for reversible reactions were worked out by Shain and Nicholson [3-5]. The peak potential,  $E_p$  is given by the equation,

$$E_p = E_{1/2} - 0.029/n \quad \dots$$

(4)

Where  $E_{1/2}$  is the polarographic half-wave potential in volts. The potential of the anodic peak on a voltammogram of the reduced species is 0.029/n volts more positive than the  $E_{1/2}$ .

For the reversible reduction of O to R, the half-peak potential,  $E_{P/2}$  is given by

$$E_{P/2} = E_{1/2} + 0.028/n \quad \dots$$

(5)

Conversely, the anodic half-peak potential is 0.028/n volts more negative than the half-wave potential. The fundamental criterion of reversibility is therefore,

$$(E_{P/2})_c - (E_{P/2})_a = 0.056/n \text{ V} \quad \dots$$

(6)

The peak current  $i_p$ , for a total irreversible reduction of O to R is given by

$$i_p = 2.985 \times 10^5 \times n (\alpha_{na})^{1/2} A D_O V^{1/2} C_O V^{1/3} \quad \dots$$

(7)

The numerical constant is determined by Nicholson and Shain<sup>3</sup>.

The peak potential for an irreversible reaction is given by the expression,

$$E_p = E_O - 0.059/\alpha_{na} [0.4565] + \log \alpha_{na} D_O V^{1/2}/K_{s,h} \quad \dots$$

(8)

While half peak potential,  $E_{p/2}$  is described by

$$E_{p/2} = E_p + 0.048/\alpha n_a \quad \dots$$

(9)

In equation (7) and (8),  $\alpha$  is transfer coefficient,  $n_a$  is the number of electrons transferred in the slow step and  $K_{s,h}$  is the standard rate constant.

Since fast sweeps are employed, multi-electron transfer processes, fast enough to appear reversible in DC polarography may appear to be irreversible in cyclic voltammetry. As the sweep rate is increased, the slowness of the electron transfer step becomes more and more pronounced and deviations from Nicholson behaviour and become more marked. On the other hand, the fast electron-transfer step followed by a slow chemical transformation of the product into an electroactive species appear to be irreversible in ordinary polarography because the stable form of the product does not give an anodic wave having the same half wave potential as the cathodic wave of the starting material. If the sweep rate is high, such a process may appear to behave reversible because the inactivation can then occur only to limited extent and the deviations from reversible behaviour decrease as the sweep rate increases to a point where the finite speed of electron transfer becomes perceptible.

Nicholson [5] has used the separation in anodic and cathodic potentials for the evaluation of the rate constants of electron transfer. The cyclic voltammetry of a number of organic compounds with a view to study the intermediate stages of electrochemical reactions has been reported by Adams [6-8]. In cyclic voltammetric study the reaction responsible for the manifestation of the cathodic peaks may be charge transfer (reversible or irreversible) reaction or charge transfer reaction



coupled with a chemical reaction. This chemical reaction may proceed the charge transfer or succeed the charge transfer reaction. Further the reaction can be a irreversible.

### **Cyclic Voltammetry**

The cyclic voltammeter used consists of an X – Y recorder (**Model RE 0074**), a PAR 175 Potentiostat and an PAR 175 Universal Programmer. A single compartment cell model 303 SMDE supplied by PAR with silver wire as reference electrode and platinum wire as counter electrode is used in the studies. A stationary mercury drop electrode (SMDE 303) with a drop area  $0.0096 \text{ cm}^2$  is used as the working electrode.

In some studies BAS (Bioanalytical System) 100 A electrochemical analyser supplied by USA is used instead of the equipment described earlier. A single compartment Metrohm cell with calomel electrode and a platinum foil is used in the studies. A Silver electrode with a drop area of  $0.024 \text{ cm}^2$  is used as the working cathode.

The circuit diagram for cyclic voltammetric experiment is shown schematically in **Fig.3** which depicts

- (a) Function generator
- (b) Potentiostat
- (c) Recorder

#### **(a) Function generator**

This generates the desired triangular potential wave which is applied to the electrochemical cell through Potentiostat.

## **(b) Potentiostat**

The conventional three-electrode Potentiostat is connected to the working, reference, and auxiliary electrodes immersed in the test solution placed in the cell. It controls the potential of the WE with respect to the RE while simultaneously measuring the current flowing between the WE and the AE. The Potentiostat performs three functions:

- (a) It controls the applied potential, which is potential difference between the WE and RE (the applied potential controls what half reactions occur at the WE)
- (b) It allows to pass current between the WE and AE without passing current through the RE (which would change its potential if current did pass through it) and
- (c) It converts the cell current to a voltage for recording devices.

A Potentiostat must be able to bring the potential of the WE (with respect to the RE) to the desired level in a short enough time. The time taken by the Potentiostat for controlling the WE potential is called the rise time. The potentiostat's internal feedback circuits prevent all but a very small current from flowing between the WE and RE. Because the very basis of voltammetry is the control of electrode potential, a function generator is required to provide the potential sweep or pulse sequence to be applied to the WE. Most modern Potentiostat include a built-in sweep and / or pulse generator, and those which are interfaced to a computer usually rely on the computer to generate the desired waveform. The inputs to the potentiostat are the connections to the electrodes in

the cell. The outputs from the potentiostat are signal lines reflecting the current and potential of the WE(s).

### **(C) Recorder**

X – Y recorder is a plotter which simultaneously plots current versus voltage.

### **Technique of cyclic voltammetry**

This technique of cyclic voltammetry consists of applying voltage sweep to the working electrode to generate triangular wave with reference to the reference electrode of the cell, simultaneously monitoring the resulting current between the working electrode and the inert electrode. The current converted voltage when fed to X – Y recorder results in the observation of a cyclic voltammogram.

### **Potential scan**

Controlled potential electrolysis at mercury pool cathode was carried out at constant potential using Potentiostat PAR 173. The potential corresponding to limiting current of polarographic wave of the said compound is set on the potentiostat by setting the initial potential knob in clockwise direction, keeping the operating selector is turned to the position I, stand potential flows through the cell at the desired constant potential set earlier which can be read from the meter. As the electrolysis proceeds, the fall in the current is followed as a function of time.

### **5. Thermostat**

A circulating type thermostat, supply by M/s. Thoshniwal, Bombay, India, with water as the thermostatic bath liquid was employed to maintain a constant temperature with the range of  $\pm 0.01^{\circ}\text{C}$ .

## **6. Spectrophotometer**

A Synstronics visible spectrophotometer model 106 manufactured by M/s. Synstronics Instrument, Ahmedabad, India is used in the studies. The instrument is a single beam spectrophotometer having a grating of 600 lines/mm and the wavelength range is from 340 nm to 960 nm. The nominal spectral width is 20 nm, which is constant over the entire range. Full scale deflection is obtained over the wavelength range 340 – 600 nm. By adding a red filter and by interchanging the phototube the range is extended to 960 nm. The light source in the instrument is a 15 watt tungsten iodide filament lamp operated by an AC regulated power supply. High regulation in the power supply enables the lamp to function as a constant light intensity source. Matched glass cuvettes of 1 cm path length are used in the studies. The wavelength accuracy is  $\pm 5$  nm. The optical density values are correct upto the third decimal place,  $\pm 0.001$  are obtainable through the 4 digital display with the instrument.

## **7. Electrolysis Cell**

In its simplest form, the electrolysis cell is a single piece of glassware capable of holding an appropriate volume of a test solution containing one or more electroactive analytes. The cell is then maintained oxygen free by passing nitrogen over the solution through nitrogen inlet. The electrochemical cell consists of three electrodes which are immersed in this solution and are electrically connected to the potentiostat. The RE used is SCE, which is often isolated from the solution by a salt bridge to prevent contamination by leakage from the RE. The AE (platinum foil) and the glassy carbon Silver electrode, or carbonpaste are placed directly into the solution. Custom glassware designs include convenient fittings for mounting

electrodes, gas inlets and outlets for purging oxygen and temperature jackets. Since the limiting (peak) current in any type of voltammetry is temperature dependent, the cell is thermo stated for the required temperature.

## **8. Electrodes**

In the present work three electrode system is used i.e. WE / AE / REs. The RE used is SCE which is often isolated from the solution by a salt bridge to prevent contamination by leakage from the RE. The platinum foil as AE.Silver Electrode is used as working electrode in CVM studies. Hence Polarographic Half-wave potentials can not be compared with cathodic and anodic peak potentials of CVM studies because the working electrode in DC Polarography (SCE) and CVM studies (silver electrode) are different.

### **General Polarographic procedures**

#### **(A) Polarographic and cyclicvoltammetric procedures**

Polarographic behaviour of the title compounds at different

- (i) pH values
- (ii) Concentrations of the substrate,
- (iii) Heights of the mercury column, is studied adopting the following procedures.

#### **(i) Effect of pH**

8.0 ml of the buffer solution of desired pH (1.1 – 10.1), 2 ml of the stock solution of the substrate ( $1.0 \times 10^{-2}$  M) in dimethylformamide (DMF), 6 ml of dimethylformamide (DMF) and 4.0 ml of distilled water are mixed thoroughly in the polarographic cell and the polarograms are recorded after removing the dissolved

oxygen by passing pure and dry nitrogen gas through the solution for about fifteen minutes.

### (ii) Effect of concentration

8.0 ml of required buffer solution (pH 4.1) and a known aliquot of the substrate solution ( $1.0 \times 10^{-2}$  M) and the requisite volume of dimethylformamide are mixed in the polarographic cell to make the total volume 20 ml and the polarogram is recorded after deprecation.

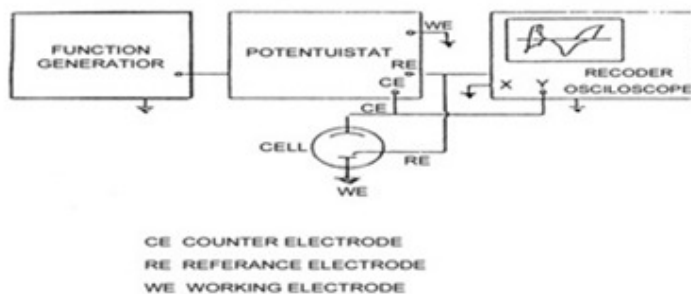


Fig : 3 Schematic cyclic voltammetric circuit

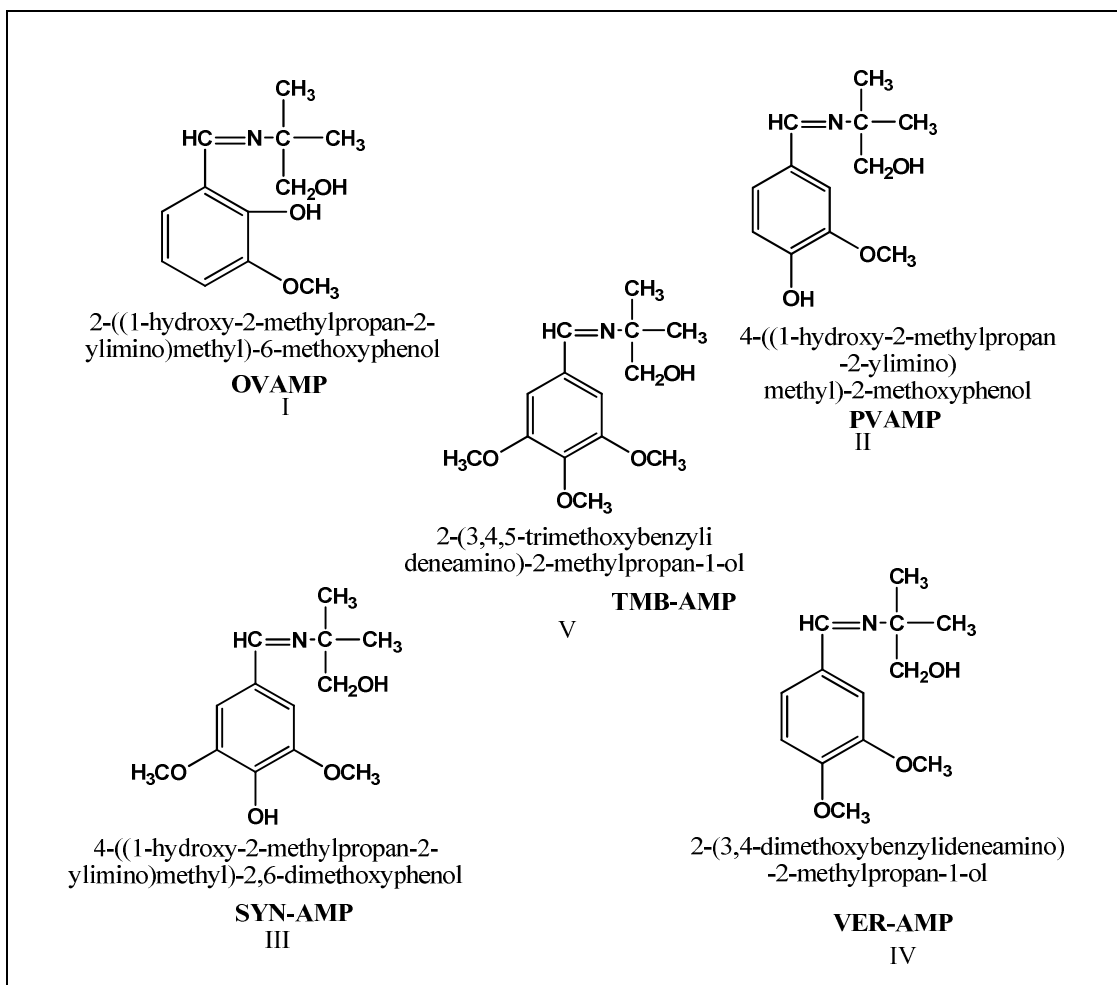
### iii) Effect of mercury column height

8.0 ml of the buffer solution (pH 4.1 and 8.1), 2.0 ml of the substrate ( $1.0 \times 10^{-3}$  M) stock solution, 6.0 ml dimethylformamide (DMF) and 4.0 ml of distilled water are mixed in the polarographic cell and the polarogram is recorded at different heights (80, 70, 60, 50 and 40 cms) of mercury column.

## **Section: (ii)**

### **Polarographic behaviour of Schiff Bases derived from AMP and Aromatic Substituted aldehyde:**

The synthesis and characterisation of Schiff Bases I-V were reported in the **Chapter III** of the thesis. The Schiff Bases I-V exhibit moderate antimicrobial activity and the results were incorporated in the **Chapter VII** of the thesis. In this Chapter, we have reported the redox behaviour of Schiff bases derived from AMP and aromatic substituted aldehyde (I to V) by using electrochemical techniques.



The electrochemical studies of Schiff bases were carried out

- In Britton-Robinson buffer solutions of pH 2.1 – 10.1
- Effect of Mercury column height was carried out at pH 4.10
- Kinetic parameters of redox behavior were carried out at pH 2.10-10.10
- Millicoulometric analysis was carried out for I to know the number of electrons involved in the redox behaviour of different functional groups present in I

The proposal redox mechanism of I-V was depicted in the **chart 1** the results and relevant graphs were presented in **Tables VI 1-5 and in Fig. 6-10**

Literature survey reveals [9-12] that not many Schiff bases were studied for their voltammetric behaviour. However, a few important reports on Schiff bases that appeared in the literature were briefly referred in the chapter at relevant places to support the results obtained in the present studies.



### General Polarographic behaviour:

The Schiff bases I-V in Britton-Robinson buffer solution exhibit one wave in the pH range 2.1-10.1. An inspection of the structure of I-V reveals that the sites susceptible for reduction at the dropping mercury electrode were the exocyclic  $>C=N-$  in Schiff bases.

The Polarographic reduction wave observed with I-V was attributed the reduction of Azo methyn group ( $>C=N-$ ). A polarographic wave generally exhibits one or other of the following characteristics.

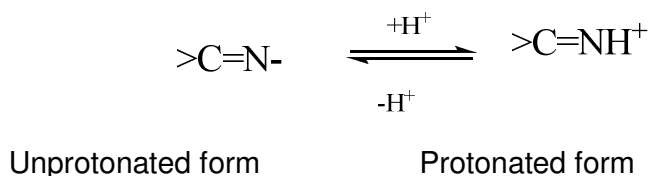
- (a) neither the half-wave potential nor the limiting current changes with pH,  
(or)
- (b) the half-wave potential shifts with pH, while the limiting current remains pH independent, (or)
- (c) both the half-wave potential and the limiting current change with pH.

The results presented in the Tables 1-5 suggest that in the present investigation both the half-wave potential and limiting current were pH dependent.

### Effect of pH on the half-wave potential

The results in the **Tables 1-5** show that the half-wave potential increases with increase in pH in the acid range but it remains unaltered in the alkaline pH range. The plot of the half-wave potential and the pH was a straight line up to pH 8.1 and the slope lies between 80-110 mV. The p (number of protons) values (**Tables 11-15**) were low and non-integers. This suggests that the proton transfer in the reduction process was a heterogenous process. The shift in the half-wave potentials with pH of the solution can therefore be ascribed to the following reasons.

- a) Both protonated form and unprotonated form of the depolariser were electro active. There exist an equilibrium between protonated form and unprotonated form [13]. The unprotonated form is reduced at more negative potentials than protonated form of the azomethine group.



- b) The pH dependence of the half-wave potential was caused not only by the antecedent chemical acid-base reaction but also by the consumption of protons in the reduction process.
- c) The pH of the solution in bulk was different from pH values at the electrode surface. In the presence of electric field the inequality was observed  $\Delta(\text{pHs}) < \Delta(\text{pHo})$  as the equilibrium shifted towards the unprotonated form, the  $E_{1/2}$  remains constant. It is seen from the **Figs. 6-10** that above pH 8.1, the shift in half-wave potential with pH was not so marked as in the acidic pH range.

$E_{1/2}$  – pH of Polarographic wave was  $\sqrt{\quad}$  shaped in the pH range of study. The  $E_{1/2}$  becomes practically constant in the alkaline pH range and this constancy in  $E_{1/2}$  may be due to the fact that both acidic and basic forms of the depolariser were electroactive. But in the pH range where the protonation rate decreases, the half-wave potentials of both the protonated form (acidic) and the unprotonated form (basic) were so close to each other that the waves merge [14] and a single wave was observed.  $E_{1/2}$  vs pH graph consists of two linear segments intercepting each

other and the point of interception of the two linear plots was approximately equal to  $pK_1$ .

#### **Effect of the height of the mercury column head (h) on the limiting current ( $i_l$ )**

The effect of mercury column height on the limiting current indicates the diffusion controlled nature of the polarographic wave. The  $i_l$  versus  $h^{1/2}$  plots are linear and passing through the origin. The values of  $i_l/h^{1/2}$  were constant as shown in the

**Tables 6-10.** The three Polarographic reduction waves were found to be diffusion controlled wave.

#### **Effect of concentration of the depolariser on the diffusion current**

The effect of concentration of the depolarizer on the diffusion current of Schiff bases on the diffusion current in concentration range of 0.20 – 2.0 M has been studied at typical pH values 4.10. The  $i_l$  versus concentration graphs were linear as shown in the Figs. 6-10, and are passing through the origin. The constancy of  $i_l/C$  values serves not only as a test for the diffusion controlled nature of the wave but also indicates the applicability of the polarographic method for the quantitative determination of I-V. From the results it was concluded that the two Polarographic reduction waves noticed in the acidic pH 4.1 were diffusion controlled waves.

#### **Nature of the electrode process**

The experimental results observed from the effect of concentration and mercury column height on the limiting current confirmed the diffusion-controlled nature of the limiting current. The electrode processes was found to be irreversible at low acidic pH values unlike the reversible electrode process observed for simple azo and azomethine compounds [15] under comparable conditions. The irreversible

nature of the process observed in the present investigations was also further confirmed by

- (a) The slopes of (0.08-0.15) of the semi-logarithmic plots ( $E_{de}$  Vs  $\log \frac{i}{i_{d-i}}$ ) do not confirm to the values expected for two or four electrons reversible reduction process respectively.
- (b)  $E_{1/2}$  shifts towards more negative potentials with increase in the depolariser concentration [16]
- (c) The heterogenous rate constant ( $k_{f,h}^0$ ) calculated from the Meites–Israel equation [17], the  $K_{f,h}^0$  values in the present investigations were less than  $10^{-4}$ .

$$E_{1/2} = 0.2412 + 0.05915/\alpha n_a \log 1.349 k_{f,h}^0 - 0.05915/\alpha n_a \log D_O^{1/2} \quad \dots (10)$$

- (d) The  $\Delta G^*$  values computed from the relation  $k_{f,h}^0 = KT/h \gamma_O \exp (\Delta G^*/RT)$  ..(4) Increases in pH range 1.1 – 7.1 and remains unaltered in alkaline pH range 8.1 – 10.1.

These observations suggest that the Polarographic reduction of azomethine (>C=N-) in I-V was found to be irreversible in nature. This may be due to the presence of bulky groups at the end of the >C=N- groups.

### Effect of pH on the limiting current

It is observed from the Table 1-5, the height of the wave decreases with increase of pH **Figs.6-10** and this suggests that both the protonated form (acidic) and the unprotonated form (basic) were transported to the electrode surface, and both of them may be electroactive. The limiting current depends on the nature of

electro active species, concentration of the species pH of the solution and nature of the solvent present in the solution, the following factors play an important role in deciding limiting current of the wave. The limiting current ( $i_l$ ) of the Polarographic reduction process may depend on one of these factors or some of these factors.

(i) Acid-base reaction or

(ii) A chemical reaction such as dehydration or ring opening hydrolysis or

(iii) The difference in the number of electrons involved in the reduction of acidic and basic forms or all of them.

(iv) All the mentioned factors

### Electrode reaction

The plots of  $-E_{dme}$  versus  $\log i/i_d - i$  shown in the Figs. 6-10 at typical pH 4.1 were linear but the slopes are not in agreement with the theoretical values (0.030 V and 0.015 V for 2-electron and 4-electron reduction, respectively) expected for the reversible waves. This indicates that the electrode reaction is irreversible. The slopes further indicate that the tendency of the irreversibility increases with increase in the pH. Tome's criteria [18] was also employed to determine the irreversible nature of the polarographic wave. It gives the relationship between  $E_{1/4}$  and  $E_{3/4}$  as follows.

$$E_{1/4} - E_{3/4} = 0.0564/\alpha n_a \text{ V for reversible} \quad \dots(11)$$

$$E_{1/4} - E_{3/4} = 0.05172/\alpha n_a \text{ V for irreversible} \quad \dots(12)$$

It follows from the equation (13) that the difference between potentials  $E_{1/4}$  and  $E_{3/4}$  depends only on the number of electrons ( $n_a$ ) exchanged in the elementary process. The  $\alpha n_a$  values obtained from the above equation are almost equal to the

values obtained from conventional logarithmic plots. The  $\alpha n_a$  values obtained from conventional log plots are shown in the Tables 10-15.

The half-wave potential increases with pH and this suggests that the protons are involved in the reduction process. The number of protons involved in the reduction process is calculated from the equation (14). The half-wave potential remain constant in alkaline pH range 8.1 – 10.1

$$\Delta E_{1/2}/\Delta pH = 0.05915/\alpha n_a p \quad \dots(13)$$

### **Millicoulometric method**

There is much interest in knowing the number of electrons (n), involved per molecule during the reaction at the dropping mercury electrode. The use of Ilkovic equation  $i_d = 607 n D^{1/2} m^{2/3} t^{1/6} C$  to determine 'n' from the average diffusion current ( $i_d$ ) and other quantities, requires a knowledge of the diffusion coefficient of the depolariser undergoing electrochemical reduction. This obviously has a limitation. Another method was based on a fundamental equation for the polarographic wave is even more restricted because it applies only to electrochemically reversible reaction and to the rate limiting steps. It is possible to determine the value of 'n' (number of Faradays per mole of electrode reaction) by the method developed by DeVris and Kroon [19] and this method was shown to give results within  $\pm 2\%$  for several organic compounds.

$$E_{dmc} = \frac{E_{1/2} - 0.05912/\log i/(i_d - i)}{\alpha n} \quad \dots (14)$$

A mercury pool cathode was used for determining the number of electrons (n) in the millicoulometer described by DeVris and Kroon [19]. The value of 'n' was determined using the formula

$$n_2 = n_1 (\Delta i_{d \text{ cad}}/i_{d \text{ cad}}) (i_{d \text{ sub}}/\Delta i_{d \text{ sub}}) C_1 V_1 / C_2 V_2 \quad \dots (15)$$

Where

$i_d$  = diffusion current ( $\mu\text{A}$ )

$\Delta i_d$  = change in the diffusion current ( $\mu\text{A}$ ) of polarograms obtained,

when the experimental solution is subjected to the electro-reduction.

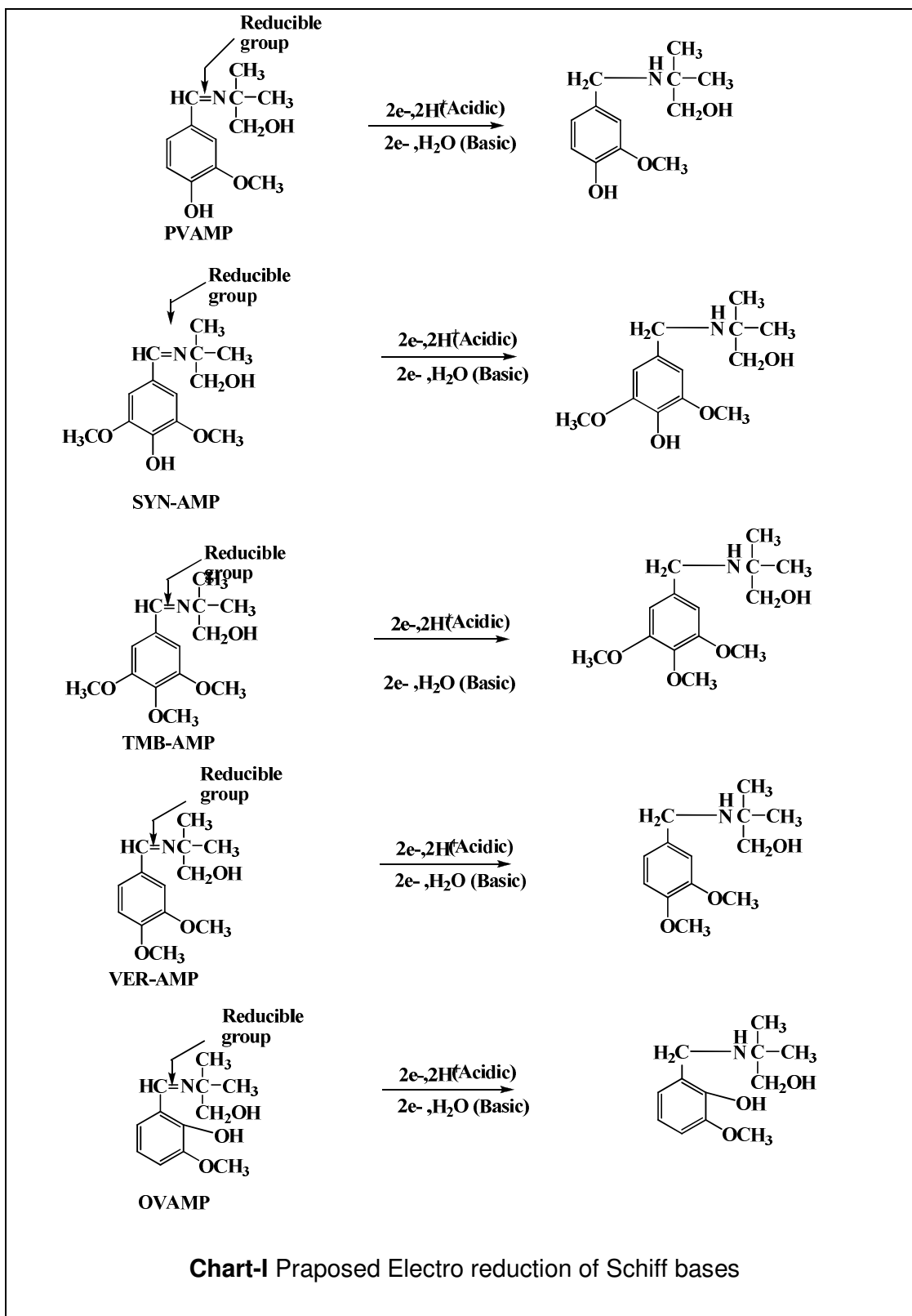
$n_1$  = number of electrons involved in the reduction of cadmium ions

$n_2$  = number of electrons involved in the reduction of substrate, (4a).

The Millicoulometric experiment was performed on I in Britton-Robinson buffer solution of pH 4.1 containing 40% (V/V) aqueous dimethyl formamide. The Millicoulometric data was shown in the **Table 16**. The I in the experimental conditions exhibit one Polarographic reduction wave. The Polarographic reduction wave was ascribed to the electron reduction (I) of azomethine  $>\text{C}=\text{N}-$  group to amine stage. The Millicoulometric experiment was performed by with  $\text{CdSO}_4$  as reference standard.

### **Reduction mechanism in Buffer solutions of pH 2.10 – 10.10**

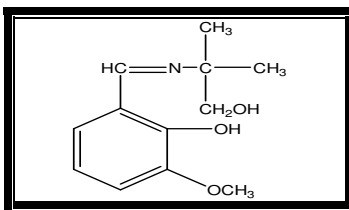
The Schiff bases 1-5 contain one electro-reducible group, namely exocyclic azomethine group ( $>\text{C}=\text{N}-$ ). The proposed electro-reduction of Schiff bases has been depicted in **Chart-I**.





**Table: 1. Polarographic results of O-VAMP in Britton Robinson buffer solutions**

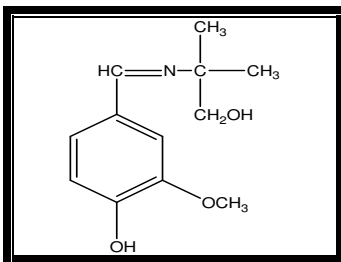
**( $1 \times 10^{-3}$  mM) Medium: Aqueous DMF (40% v/v)**



pH	$E_{1/2}$ vs SCE	Limiting Current $i_l$ ( $\mu$ A)
2.1	0.72	3.8
3.1	0.78	3.8
4.1	0.84	3.8
5.1	0.90	3.7
6.1	0.96	3.6
7.1	1.02	3.5
8.1	1.08	3.4
9.1	1.08	3.4
10.1	1.08	3.4

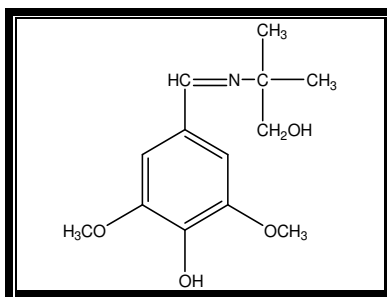
**Table: 2 Polarographic results of P-VAMP Briton Robinson buffer solutions**

**( $1 \times 10^{-3}$  mM) Medium : Aqueous DMF (40% v/v)**



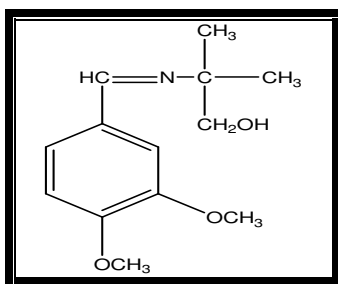
pH	$E_{1/2}$ vs SCE	Limiting Current $i_l$ ( $\mu$ A)
2.1	0.57	4.0
3.1	0.66	4.0
4.1	0.75	4.0
5.1	0.84	3.9
6.1	0.93	3.8
7.1	1.05	3.7
8.1	1.14	3.6
9.1	1.14	3.6
10.1	1.14	3.6

**Table: 3 Polarographic results of SYN-AMP Briton Robinson buffer solutions  
( $1 \times 10^{-3}$  mM) Medium: Aqueous DMF (40% v/v)**



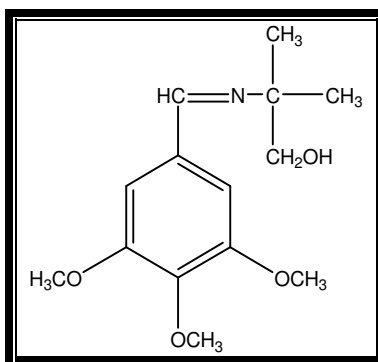
pH	$E_{1/2}$ vs SCE	Limiting Current $i_l$ ( $\mu$ A)
2.1	0.45	3.5
3.1	0.54	3.5
4.1	0.63	3.5
5.1	0.72	3.4
6.1	0.81	3.3
7.1	0.90	3.2
8.1	0.99	3.1
9.1	0.99	3.1
10.1	0.99	3.1

**Table: 4 Polarographic results of VER-AMP Briton Robinson buffer solutions  
( $1 \times 10^{-3}$  mM) Medium : Aqueous DMF (40% v/v)**



pH	$E_{1/2}$ vs SCE	Limiting Current $i_l$ ( $\mu$ A)
2.1	0.51	3.6
3.1	0.60	3.6
4.1	0.69	3.6
5.1	0.78	3.5
6.1	0.87	3.4
7.1	0.96	3.3
8.1	1.05	3.0
9.1	1.05	3.0
10.1	1.05	3.0

**Table:5 Polarographic results of TMB-AMP Britton Robinson buffer solutions ( $1 \times 10^{-3}$  mM) Medium : Aqueous DMF (40% v/v)**



pH	$E_{1/2}$ vs SCE	Limiting Current $i_l$ ( $\mu\text{A}$ )
2.1	0.48	3.4
3.1	0.57	3.4
4.1	0.66	3.4
5.1	0.75	3.5
6.1	0.84	3.3
7.1	0.93	3.2
8.1	1.02	3.0
9.1	1.02	3.0
10.1	1.02	3.0

**Table: 6 Effect of Mercury Column height (h) on the limiting current ( $i_l$ ) of TMB-AMP ( $1 \times 10^{-3}$  M) Medium: aqueous dimethyl foramamide (40%v/v)**

Mercury column height (h)(cm)	pH = 4.1		pH = 8.1	
	First wave		First wave	
	$i_l$ ( $\mu$ A)	$i_l/\sqrt{h}$	$i_l$ ( $\mu$ A)	$i_l/\sqrt{h}$
80	3.8	0.420	3.4	0.38
70	3.5	0.42	3.1	0.38
60	3.0	0.40	2.80	0.36
50	2.8	0.40	2.50	0.36

**Table : 7 Effect of Mercury Column height (h) on the limiting current ( $i_l$ ) of SYN-AMP ( $1 \times 10^{-3}$  M) Medium: aqueous dimethyl foramamide (40%v/v)**

Mercury column height (h)(cm)	pH=4.1		pH=8.1	
	First wave		First wave	
	$i_l$ ( $\mu$ A)	$i_l/\sqrt{h}$	$i_l$ ( $\mu$ A)	$i_l/\sqrt{h}$
80	4.0	0.440	3.6	0.40
70	3.70	0.440	3.30	0.40
60	3.20	0.42	2.91	0.38
50	3.00	0.42	2.78	0.38

**Table : 8 Effect of Mercury Column height (h) on the limiting current ( $i_l$ ) of VER-AMP ( $1 \times 10^{-3}$  M) Medium: aqueous dimethyl foramamide (40%v/v)**

Mercury column height (h)(cm)	pH=4.1		pH=8.1	
	First wave		First wave	
	$i_l$ ( $\mu$ A)	$i_l/\sqrt{h}$	$i_l$ ( $\mu$ A)	$i_l/\sqrt{h}$
80	3.5	0.38	3.1	0.34
70	3.2	0.38	2.81	0.34
60	2.90	0.36	2.50	0.32
50	2.61	0.36	2.30	0.32

**Table: 9 Effect of Mercury Column height (h) on the limiting current ( $i_l$ ) of O-VAMP  
( $1 \times 10^{-3}$  M) Medium: aqueous dimethyl foramamide (40%v/v)**

Mercury column height (h)(cm)	pH=4.1		pH=8.1	
	First wave		First wave	
	$i_l$ ( $\mu\text{A}$ )	$i_l/\sqrt{h}$	$i_l$ ( $\mu\text{A}$ )	$i_l/\sqrt{h}$
80	3.6	0.40	3.0	0.34
70	3.30	0.40	2.80	0.34
60	3.00	0.38	2.40	0.30
50	2.70	0.38	2.20	0.30

**Table: 10 Effect of Mercury Column height (h) on the limiting current ( $i_l$ ) of P-VAMP  
( $1 \times 10^{-3}$  M) Medium: aqueous dimethyl foramamide (40%v/v)**

Mercury column height (h)(cm)	pH=4.1		pH=8.1	
	First wave		First wave	
	$i_l$ ( $\mu\text{A}$ )	$i_l/\sqrt{h}$	$i_l$ ( $\mu\text{A}$ )	$i_l/\sqrt{h}$
80	3.4	0.38	3.0	0.32
70	3.10	0.38	2.68	0.32
60	2.8	0.36	2.40	0.30
50	2.5	0.36	2.20	0.30

**Table: 11. Polarographic characteristics and kinetic parameters of TMB-AMP ( $1 \times 10^{-3}$  mM) Medium : Aqueous dimethyl formamide (40% v/v)**

pH	$-E_{1/2}/\text{pH}$ (Mv)	$\alpha_{na}$	No. of protons p	$D \times 10^{-6}$ $\text{cmsec}^{-1}$	$I^* \times 10^3$	$K^0_{fh} \text{ cm sec}^{-1}$	$\Delta G^* \text{ k cal mole}^{-1}$
2.1	0.086	0.41	0.51	2.85	4.04	$4.25 \times 10^{-4}$	9.20
4.1	0.086	0.46	0.58	1.92	3.34	$2.30 \times 10^{-4}$	9.77
6.1	0.086	0.51	0.64	1.11	2.54	$1.09 \times 10^{-4}$	10.49
8.1	0.086	0.58	0.69	0.55	1.84	$4.43 \times 10^{-5}$	11.04
10.1	0.086	0.58	0.69	0.55	1.84	$4.25 \times 10^{-5}$	11.04

**Table:12. Polarographic characteristics and kinetic parameters of SYN-AMP ( $1 \times 10^{-3}$  mM) Medium : Aqueous dimethyl formamide (40% v/v)**

pH	$-E_{1/2}/\text{pH}$ (Mv)	$\alpha_{na}$	No. of protons p	$D \times 10^{-6}$ $\text{cmsec}^{-1}$	$I^* \times 10^3$	$K^0_{fh} \text{ cm sec}^{-1}$	$\Delta G^* \text{ k cal mole}^{-1}$
2.1	0.087	0.47	0.69	3.02	4.2	$5.18 \times 10^{-4}$	10.20
4.1	0.087	0.52	0.76	2.01	3.4	$2.76 \times 10^{-4}$	10.78
6.1	0.087	0.65	0.96	1.01	2.4	$9.97 \times 10^{-5}$	11.34
8.1	0.087	0.74	1.10	0.53	1.7	$10.4 \times 10^{-5}$	12.01
10.1	0.087	0.74	1.10	0.53	1.7	$10.4 \times 10^{-5}$	12.01

**Table: 13. Polarographic characteristics and kinetic parameters of VER-AMP (1x 10<sup>-3</sup> mM) Medium : Aqueous dimethyl farmamide (40% v/v)**

pH	-E <sub>1/2</sub> /pH (Mv)	α <sub>na</sub>	No. of protons p	D X 10 <sup>-6</sup> cmsec <sup>-1</sup>	I* X 10 <sup>3</sup>	K <sup>0</sup> fh cm sec <sup>-1</sup>	ΔG* k cal mole <sup>-1</sup>
2.1	0.086	0.43	0.54	3.02	4.1	4.19x10 <sup>-4</sup>	9.07
4.1	0.086	0.45	0.62	2.40	3.4	3.01x10 <sup>-4</sup>	10.01
6.1	0.086	0.51	0.76	1.50	2.8	1.52x10 <sup>-4</sup>	10.89
8.1	0.086	0.63	0.91	0.43	1.2	5.10x10 <sup>-5</sup>	11.45
10.1	0.086	0.63	0.91	0.43	1.2	5.10x10 <sup>-5</sup>	11.45

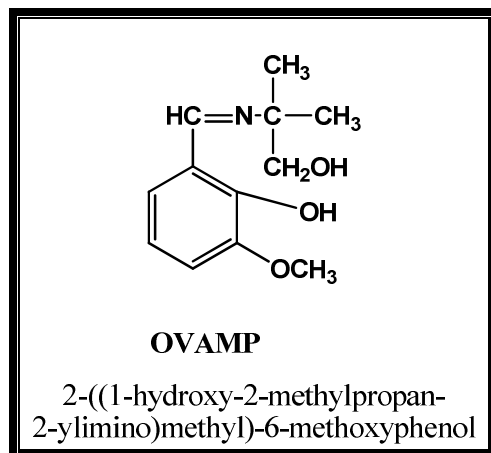
**Table: 14. Polarographic characteristics and kinetic parameters of O-VAMP (1x 10<sup>-3</sup> mM) Medium : Aqueous dimethyl farmamide (40% v/v)**

pH	-E <sub>1/2</sub> /pH (Mv)	α <sub>na</sub>	No. of protons p	D X 10 <sup>-6</sup> cmsec <sup>-1</sup>	I* X 10 <sup>3</sup>	K <sup>0</sup> fh cm sec <sup>-1</sup>	ΔG* k cal mole <sup>-1</sup>
2.1	0.084	0.42	0.62	2.87	4.0	5.33x10 <sup>-4</sup>	11.58
4.1	0.084	0.52	0.76	1.99	3.1	3.62x10 <sup>-4</sup>	12.01
6.1	0.084	0.59	1.06	1.22	2.0	1.31x10 <sup>-4</sup>	12.43
8.1	0.084	0.65	1.19	0.59	1.2	6.70x10 <sup>-5</sup>	12.89
10.1	0.084	0.65	1.19	0.59	1.2	6.70x10 <sup>-5</sup>	12.89

**Table:15. Polarographic characteristics and kinetic parameters of P-VAMP (1x 10<sup>-3</sup> mM) Medium :Aqueous dimethyl farmamide (40% v/v)**

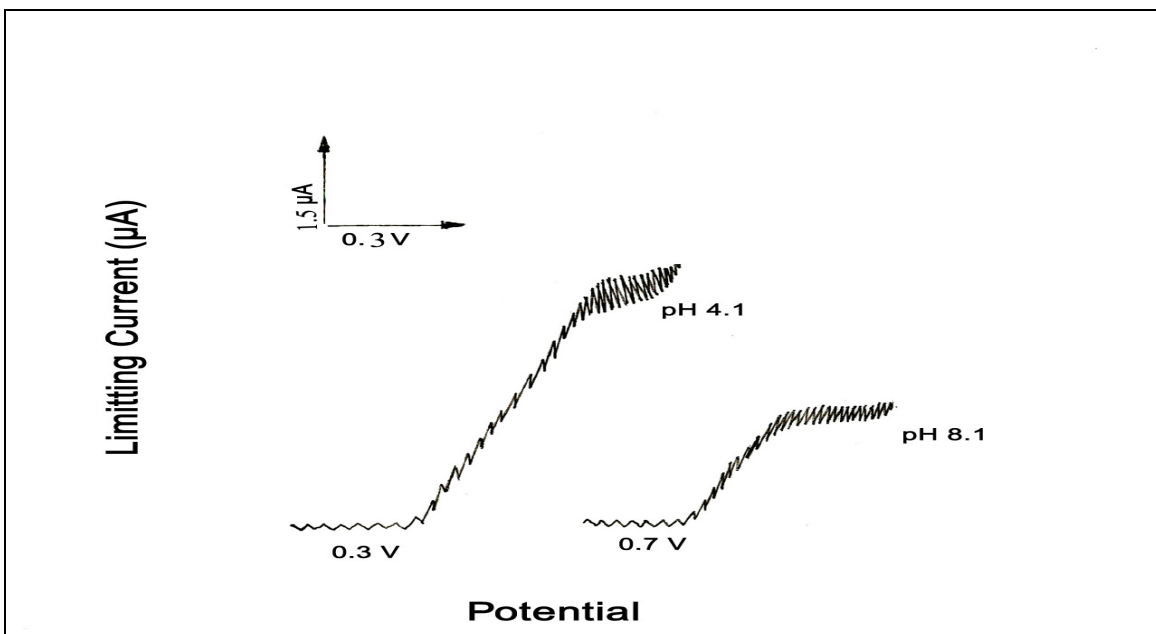
pH	-E <sub>1/2</sub> /pH (Mv)	α <sub>na</sub>	No. of protons p	D X 10 <sup>-6</sup> cmsec <sup>-1</sup>	I* X 10 <sup>3</sup>	K <sup>0</sup> fh cm sec <sup>-1</sup>	ΔG* k cal mole <sup>-1</sup>
2.1	0.090	0.42	0.72	3.43	4.5	3.31x10 <sup>-4</sup>	11.87
4.1	0.090	0.50	0.87	2.47	3.8	1.40x10 <sup>-4</sup>	12.40
6.1	0.090	0.59	1.10	1.58	2.8	6.40x10 <sup>-5</sup>	12.98
8.1	0.090	0.68	0.97	0.57	1.8	3.84x10 <sup>-5</sup>	13.40
10.1	0.090	0.68	0.97	0.57	1.8	3.84x10 <sup>-5</sup>	13.40

**Table – 16 Millicoloumetric of OVAMP Concentration =0.8 mM at pH 4.1 and 8.1  
Medium :Aqueous DMF 40% (v/v), Volume=0.5 ml**

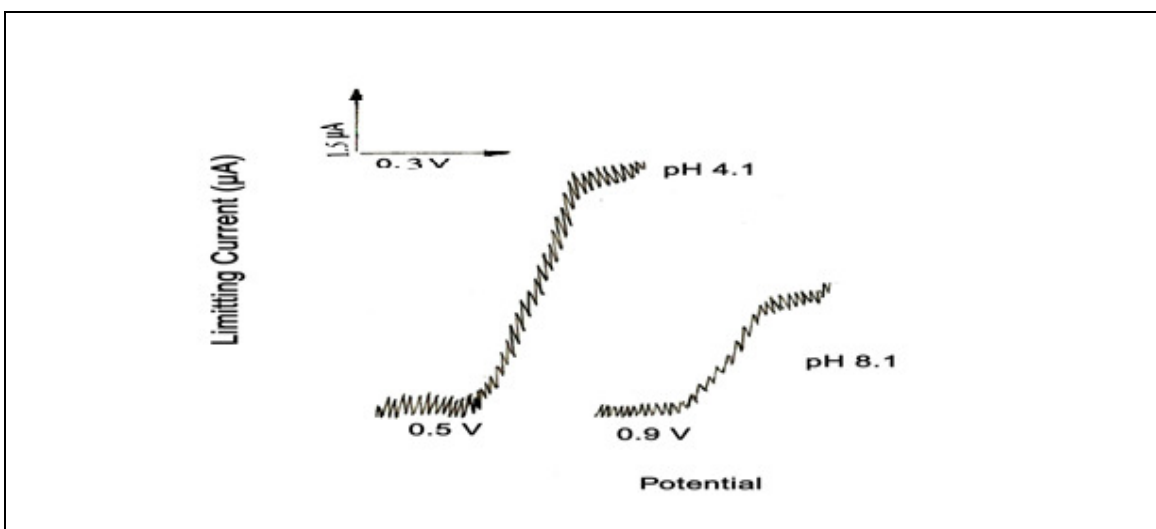


pH	Current (μA)	ηvalue
4.10	4.0	-
	3.6	1.9
	3.3	1.8
8.10	3.6	0
	3.3	1.9
	3.1	1.8





**Fig:4. Polarogram of O-VAMP ( $1 \times 10^{-3} \text{ M}$ ) at pH 4.1 and 8.1**



**Fig:5 Polarogram of ( $1 \times 10^{-3} \text{ M}$ ) P-VAMP at pH 4.1 and 8.1**

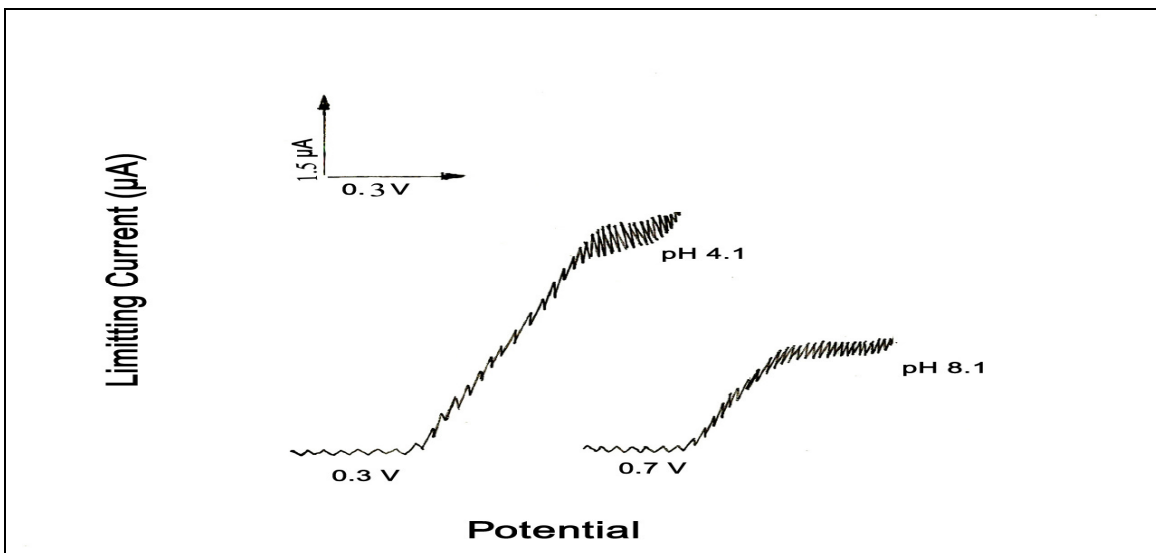


Fig:6. Polarogram of SYN-AMP ( $1 \times 10^{-3}$  M) at pH 4.1 and 8.1

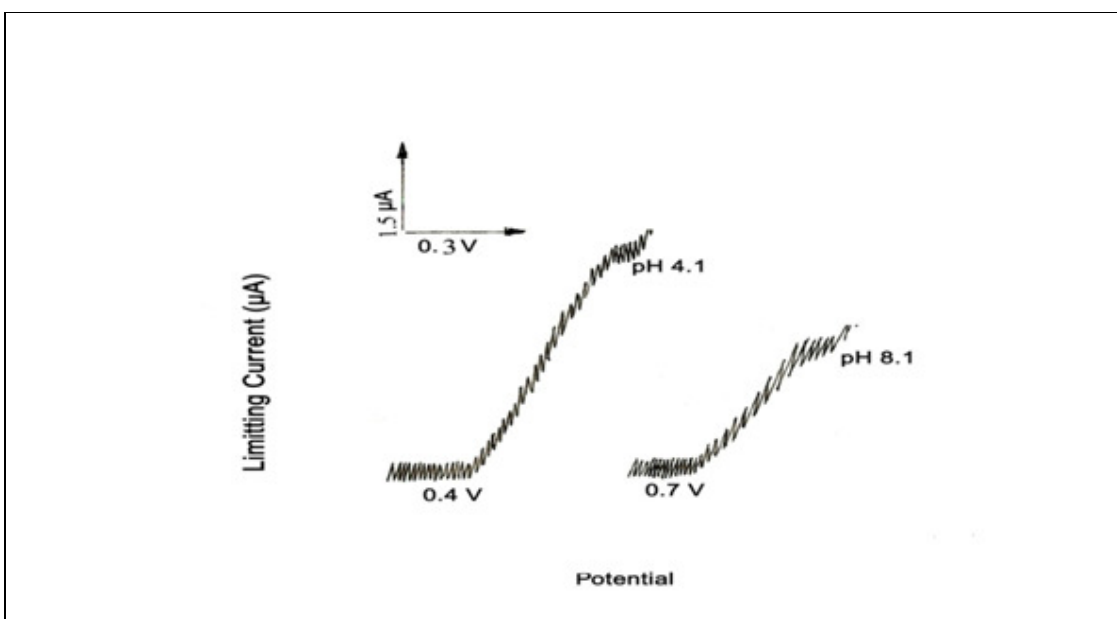


Fig:7. Polarogram of VER-AMP ( $1 \times 10^{-3}$  M) at pH 4.1 and 8.1

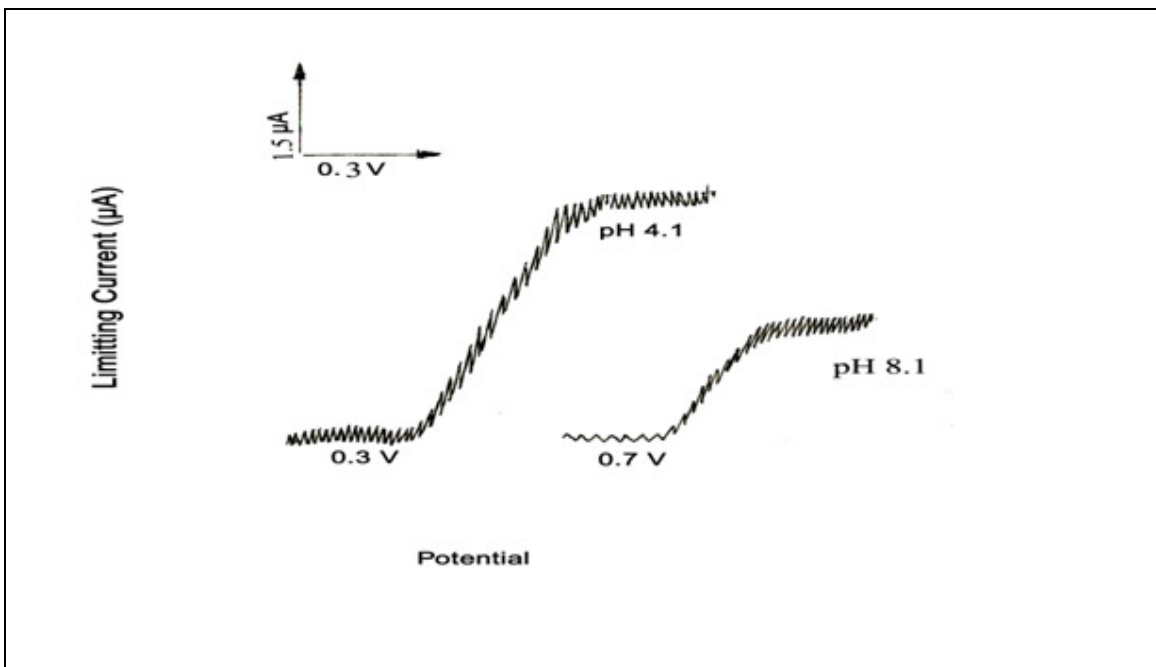
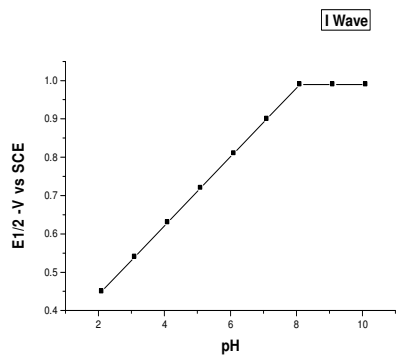
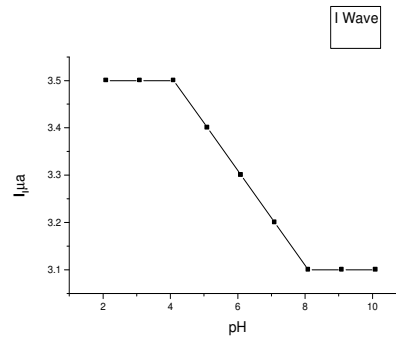


Fig:8. Polarogram of TMB-AMP ( $1 \times 10^{-3} \text{ M}$ ) at pH 4.1 and 8.1

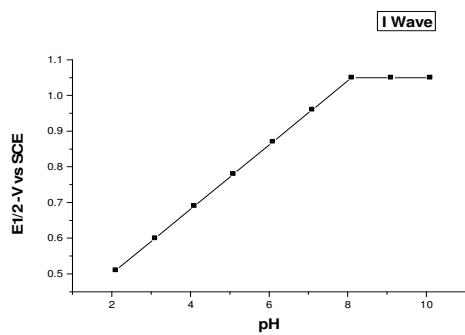


(a) Plot of  $-E_{1/2}$  vs pH

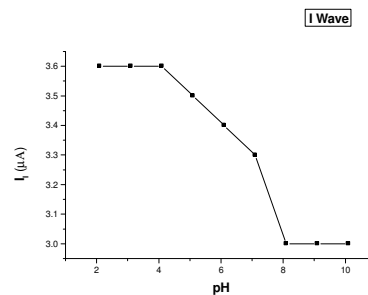


(b) Plot of limiting Current ( $I_l$ ) vs

**Fig:9** .Polarographic characteristics of **VER-AMP** ( $1 \times 10^{-3} M$ ) :Medium aqueous dimethyl formamide at given pH

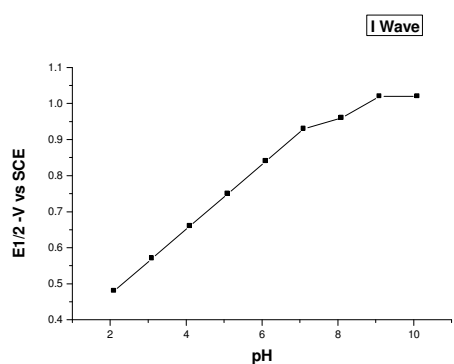


(a) Plot of  $-E_{1/2}$  vs pH

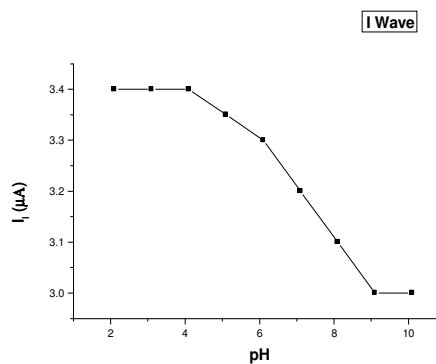


(b) Plot of limiting Current ( $I_l$ ) vs

**Fig: 10.** Polarographic characteristics of **O-VAMP** ( $1 \times 10^{-3} M$ ) :Medium aqueous dimethyl formamide at given pH

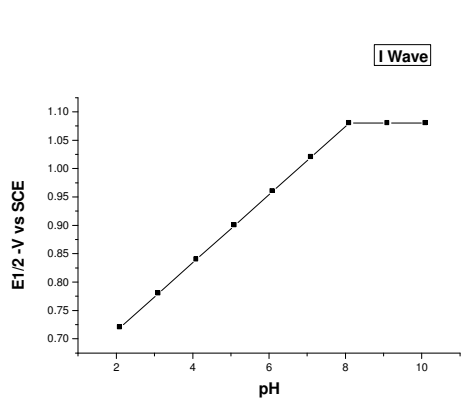


(a) Plot of  $-E_{1/2}$  vs pH

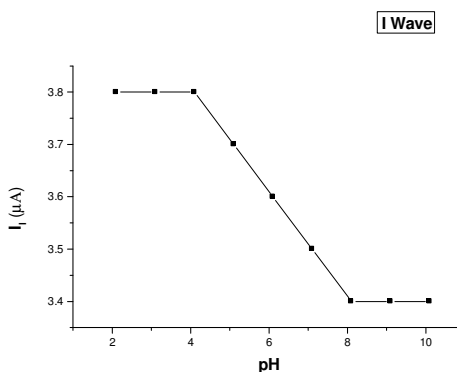


(b) Plot of limiting Current ( $I_l$ ) vs

**Fig: 11.** Polarographic characteristics of **P-VAMP** ( $1 \times 10^{-3} M$ ) :Medium aqueous dimethyl formamide at given pH

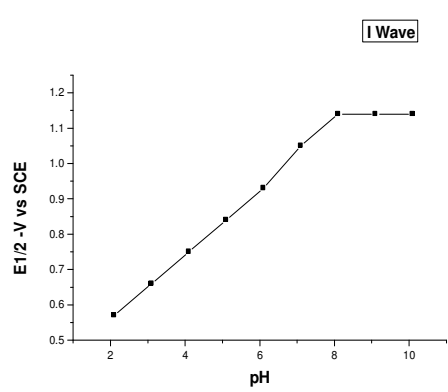


(a) Plot of  $-E_{1/2}$  vs pH

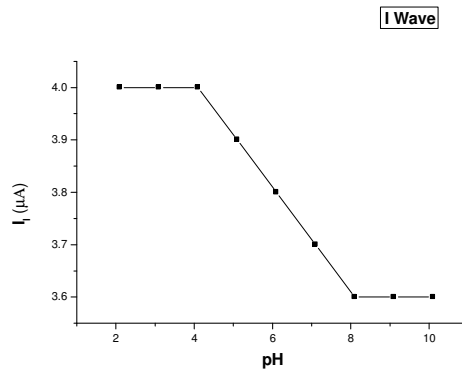


(b) Plot of limiting Current ( $I_l$ ) vs

**Fig:12.** Polarographic characteristics of **TMB-AMP** ( $1 \times 10^{-3} M$ ) :Medium aqueous dimethyl formamide at given pH



(a) Plot of  $-E_{1/2}$  vs pH

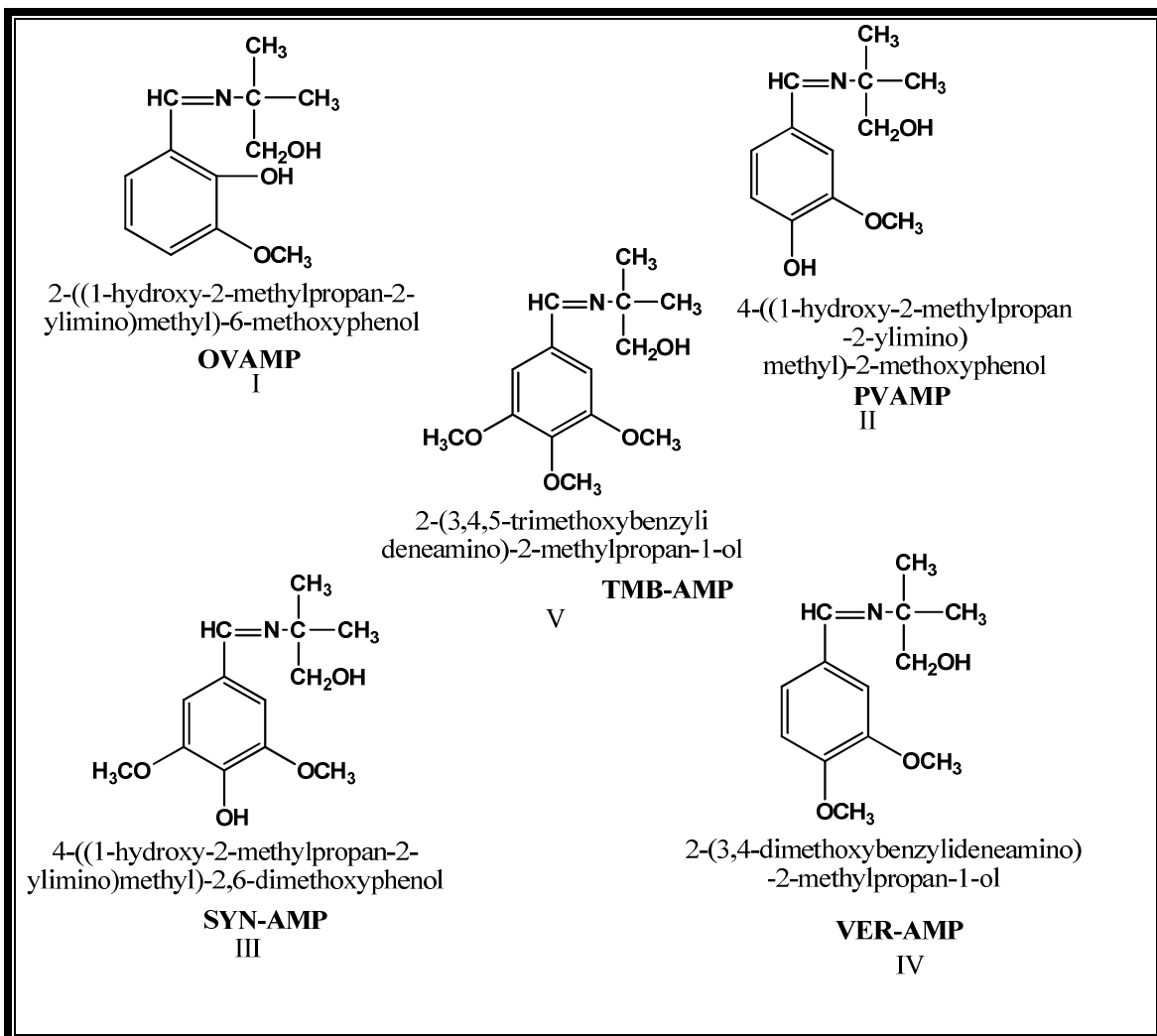


(b) Plot of limiting Current ( $I_i$ ) vs pH

**Fig: 13.** Polarographic characteristics of **SYN-AMP** ( $1 \times 10^{-3} \text{M}$ ) :Medium aqueous dimethyl formamide at given pH

## Section – (iii)

### Cyclic voltammetric studies of Schiff bases from AMP at Silver Electrode



#### General Observations:

The cyclic voltammetric experiments Schiff bases (I-V) were conducted at the Silver electrode in Britton - Robinson buffer solutions of  $P^H$  values 4.1, and, 8.1 at different scan rates viz.  $10\text{ mvs}^{-1}$ ,  $20\text{ mvs}^{-1}$ ,  $50\text{ mv S}^{-1}$ ,  $100\text{ mv S}^{-1}$ ,  $200\text{ mVS}^{-1}$ , and  $500\text{ m VS}^{-1}$ . It was noticed from the Table VI.1 to VI.5 cathodic peak was noticed in all sweep rates in the solutions of pH 4.1 – 8.1.

Peak potentials and peak currents change with change in the scan rates. The voltammograms of Schiff bases derived from AMP and Substituted benzaldehydes observed at typical pH values 4.1 and 8.1 at  $100 \text{ mVS}^{-1}$  scan rate were shown in the **Figs.11-12**.

#### **Dependence of peak potential and peak current on scan rates**

The cathodic peak potentials become more negative and the cathodic peak currents increase with the increase in the scan rate as shown in the **Tables 22 - 30**.

#### **Effect of pH on peak potentials and peak current**

The cathodic peak potentials shifted to more negative values and the peak currents decreased with the increase in the pH. The peak potential and the peak currents observed at different scan rates and at different pH values are given in the **Tables 22 - 30**.

#### **Discussion**

In Britton-Robinson buffer solutions of pH 4.1 and 8.1 Schiff bases (I-V), exhibit two cathodic peak in all sweep rates.

For a reversible charge transfer,  $O + ne \rightarrow R$ , the peak potential is independent of scan rate [20] and the separation of anodic peak and cathodic peak potentials ( $E_{pa} - E_{pc} = \Delta E_p$ ) is  $60/n \text{ mV}$  at  $25^\circ\text{C}$  and the ratio of anodic peak current to cathodic peak current must be unity. On the other hand, a plot of  $i_{pc} / \nu^{1/2}$  versus sweep rate is a straight line parallel to sweep rate axis and it is contrary to the behaviour of a reversible system, the irreversible nature of the electrode process is characterized by

- dependence of peak potential on sweep rate,
- the absence of anodic peak in the reverse scan, in acidic pH solutions



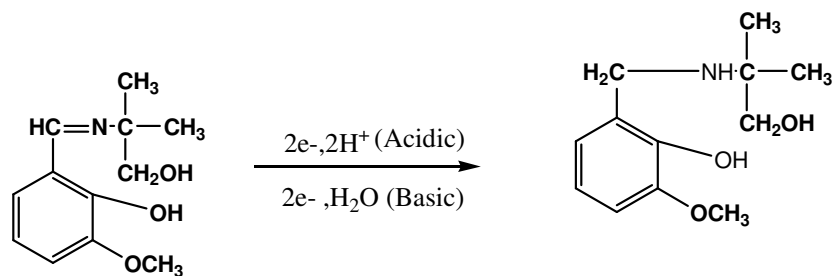
- The anodic peak and cathodic peak potentials ( $E_{pa} - E_{pc} = \Delta E_p > 60/n \text{ mV}$ ) at 25°C

The above mentioned facts clearly rule out the possibility of a fast electron transfer which is characteristic of a reversible behaviour. The linear plot of  $i_{pc}$  versus  $\nu^{1/2}$  suggests the diffusion-nature of the electrode process. The Schiff bases (I-V) exhibit one anodic peak in all sweep rates

The number of polarographic reduction waves in DC polarography and number of cathodic peaks in CVM studies are one and the same. However an additional anodic peak was noticed in Schiff bases (I-V) under experimental conditions. Based on experimental results in DC polarography and CVM studies the following mechanism has been proposed for Schiff bases **(I-V)**.

- a) The cathodic peak was ascribed to two electron reduction of azomethine group to amine stage.
- b) The anodic peak was attributed to 2e oxidation of primary alcohol to aldehyde functional group. The oxidation of  $\text{-CH}_2\text{OH}$  to  $\text{-CHO}$  peak either one step or in two steps.

### Reduction Mechanism at pH 4.1 and 8.1



#### OVAMP

2-((1-hydroxy-2-methylpropan-2-ylidene)methyl)-6-methoxyphenol

### Oxidation mechanism at pH 4.1 and 8.1

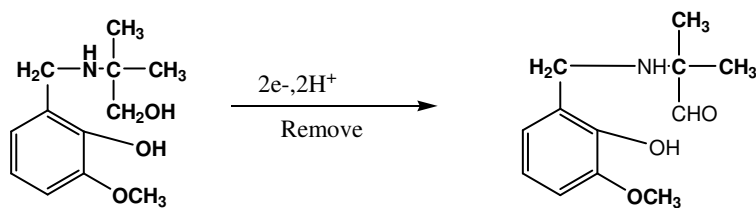


Chart: 2 Proposed Redox mechanism of Schiff bases

## RESULTS

**Table - 22 Cyclic voltammetric results of Schiff bases ( $1 \times 10^{-3} \text{M}$ ) Medium: aqueous dimethyl foramamide (40%v/v): at pH=4.1**

Schiff Base	Sweep rate (mv/sec)	Cathodic peak potentials (Epc)	Cathodic peak currents (ipc)	Anodic peak potentials (Epa)	Anodic peak currents (ipa)
		I	I	I	I
TMB-AMP	0.010	0.66	0.782	0.41	0.337
	0.020	0.72	1.105	0.47	0.476
	0.050	0.78	1.743	0.53	0.75
	0.100	0.84	2.47	0.59	1.064
	0.200	0.90	3.5	0.65	1.5
	0.500	0.99	5.52	0.74	2.38

**Table - 23 Cyclic voltammetric results of Schiff bases ( $1 \times 10^{-3} \text{M}$ ) Medium: aqueous dimethyl foramamide (40%v/v): at pH = 4.1**

Schiff Base	Sweep rate (mv/sec)	Cathodic peak potentials (Epc)	Cathodic peak currents (ipc)	Anodic peak potentials (Epa)	Anodic peak currents (ipa)
		I	I	I	I
S YN-AMP	0.010	0.71	0.80	0.46	0.35
	0.020	0.77	1.13	0.52	0.5
	0.050	0.83	1.8	0.58	0.8
	0.100	0.89	2.5	0.64	1.1
	0.200	0.95	3.6	0.7	1.5
	0.500	1.04	5.7	0.8	2.5

**Table - 24 Cyclic voltammetric results of Schiff bases ( $1 \times 10^{-3} \text{M}$ ) Medium: aqueous dimethyl foramamide (40%v/v): at pH=4.1**

Schiff Base	Sweep rate (mv/sec)	Cathodic peak potentials (Epc)	Cathodic peak currents (ipc)	Anodic peak potentials (Epa)	Anodic peak currents (ipa)
		I	I	I	I
VER-AMP	0.010	0.6	0.33	0.38	0.4
	0.020	0.69	0.48	0.4	0.56
	0.050	0.75	0.75	0.5	0.9
	0.100	0.81	1.0	0.55	1.28
	0.200	0.87	1.5	0.66	1.79
	0.500	0.96	2.4	0.7	2.84

**Table-25 Cyclic voltammetric results of Schiff bases ( $1 \times 10^{-3} \text{M}$ ) Medium: aqueous dimethyl foramamide (40%v/v): at pH=4.1**

Schiff Base	Sweep rate (mv/sec)	Cathodic peak potentials (Epc)	Cathodic peak currents (ipc)	Anodic peak potentials (Epa)	Anodic peak currents (ipa)
		I	I	I	I
O-VAMP	0.010	0.66	0.78	0.46	0.33
	0.020	0.72	1.1	0.52	0.47
	0.050	0.78	1.74	0.58	0.75
	0.100	0.84	2.47	0.64	1.0
	0.200	0.90	3.49	0.7	1.5
	0.500	0.99	5.52	0.79	2.3

**Table-26 Cyclic voltammetric results of Schiff bases ( $1 \times 10^{-3} \text{M}$ ) Medium: aqueous dimethyl foramamide (40%v/v): at pH=4.1**

Schiff Base	Sweep rate (mv/sec)	Cathodic peak potentials (Epc)	Cathodic peak currents (ipc)	Anodic peak potentials (Epa)	Anodic peak currents (ipa)
		I	I	I	I
P-VAMP	0.010	0.68	0.671	0.36	0.4
	0.020	0.74	0.948	0.42	0.5
	0.050	0.8	1.49	0.48	0.8
	0.100	0.86	2.12	0.54	1.3
	0.200	0.92	3.0	0.60	1.8
	0.500	1.01	4.7	0.7	2.8

**Table-27 Cyclic voltammetric results of Schiff bases ( $1 \times 10^{-3} \text{M}$ ) Medium: aqueous dimethyl foramamide (40%v/v): at pH=8.1**

Schiff Base	Sweep rate (mv/sec)	Cathodic peak potentials (Epc)	Cathodic peak currents (ipc)	Anodic peak potentials (Epa)	Anodic peak currents (ipa)
		I	I	I	I
TMB-AMP	0.010	0.9	0.6	0.7	0.2
	0.020	1.02	1.0	0.77	0.3
	0.050	1.08	1.5	0.83	0.4
	0.100	1.10	2.1	0.89	0.7
	0.200	1.2	3.0	0.95	0.99
	0.500	1.3	4.8	1.04	1.5

**Table-28 Cyclic voltammetric results of Schiff bases ( $1 \times 10^{-3} \text{M}$ ) Medium: aqueous dimethyl foramamide (40%v/v): at pH=8.1**

Schiff Base	Sweep rate (mv/sec)	Cathodic peak potentials (Epc)	Cathodic peak currents (ipc)	Anodic peak potentials (Epa)	Anodic peak currents (ipa)
		I	I	I	I
S YN-AMP	0.010	1.01	1.1	0.76	0.2
	0.020	1.07	1.6	0.82	0.3
	0.050	1.13	2.5	0.88	0.4
	0.100	1.19	3.6	0.94	0.7
	0.200	1.25	5.1	1.0	0.9
	0.500	1.34	8.2	1.09	1.5

**Table-29 Cyclic voltammetric results of Schiff bases ( $1 \times 10^{-3} \text{M}$ ) Medium: aqueous dimethyl foramamide (40%v/v): at pH=8.1**

Schiff Base	Sweep rate (mv/sec)	Cathodic peak potentials (Epc)	Cathodic peak currents (ipc)	Anodic peak potentials (Epa)	Anodic peak currents (ipa)
		I	I	I	I
VER-AMP	0.010	0.86	0.22	0.72	0.13
	0.020	0.92	0.31	0.78	0.41
	0.050	0.98	0.49	0.84	0.45
	0.100	1.04	0.70	0.9	0.9
	0.200	1.1	0.99	0.96	1.29
	0.500	1.19	1.57	1.05	2.0

**Table-30 Cyclic voltammetric results of Schiff bases ( $1 \times 10^{-3} \text{M}$ ) Medium: aqueous dimethyl foramamide (40%v/v): at pH=8.1**

Schiff Base	Sweep rate (mv/sec)	Cathodic peak potentials (Epc)	Cathodic peak currents (ipc)	Anodic peak potentials (Epa)	Anodic peak currents (ipa)
		I	I	I	I
O-VAMP	0.010	0.96	0.6	0.76	0.2
	0.020	1.02	1.0	0.82	0.3
	0.050	1.08	1.5	0.88	0.4
	0.100	1.14	2.1	0.94	0.7
	0.200	1.20	3.0	1.0	0.9
	0.500	1.29	4.8	1.09	1.5

**Table-31 Cyclic voltammetric results of Schiff bases ( $1 \times 10^{-3} \text{M}$ ) Medium: aqueous dimethyl foramamide (40%v/v): at pH=8.1**

Schiff Base	Sweep rate (mv/sec)	Cathodic peak potentials (Epc)	Cathodic peak currents (ipc)	Anodic peak potentials (Epa)	Anodic peak currents (ipa)
		I	I	I	I
P-VAMP	0.010	0.98	0.5	0.66	0.5
	0.020	1.04	1.3	0.7	0.7
	0.050	1.1	1.4	0.78	1.1
	0.100	1.16	1.7	0.84	1.6
	0.200	1.22	2.4	0.9	2.2
	0.500	1.31	3.9	0.99	3.6

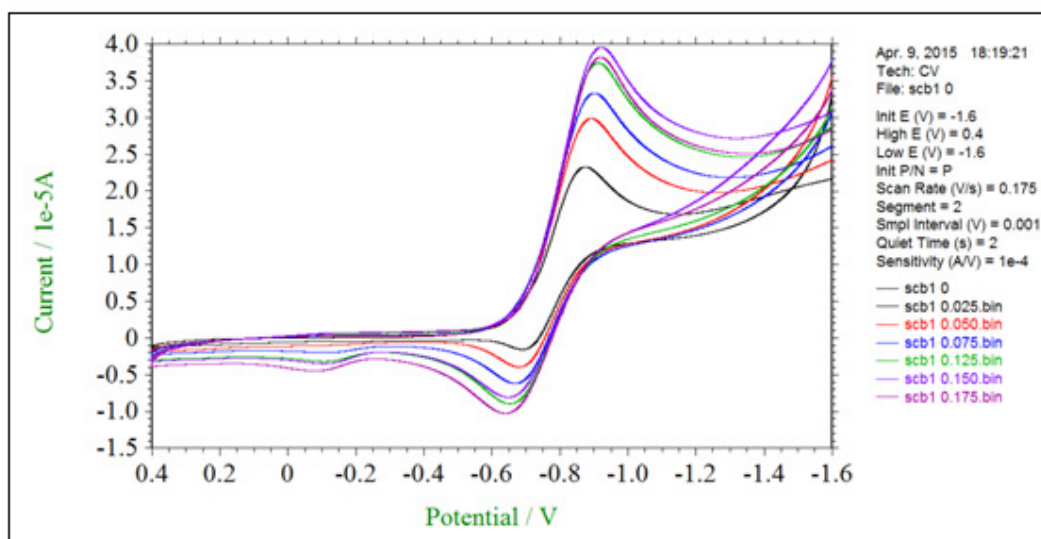
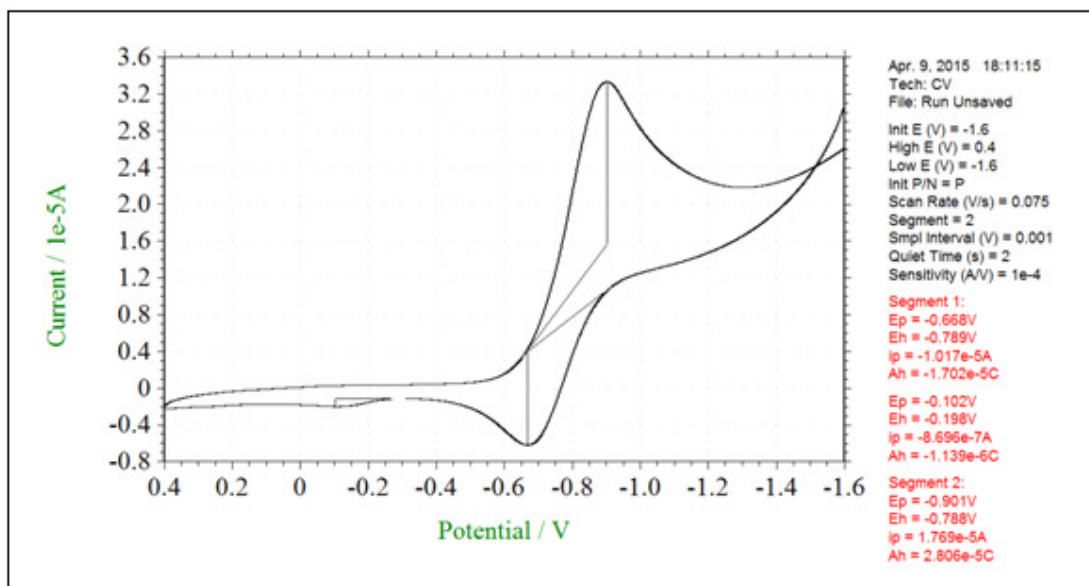


Fig :14. Cyclic Voltammograms of single and Overlay plot of O-VAMP



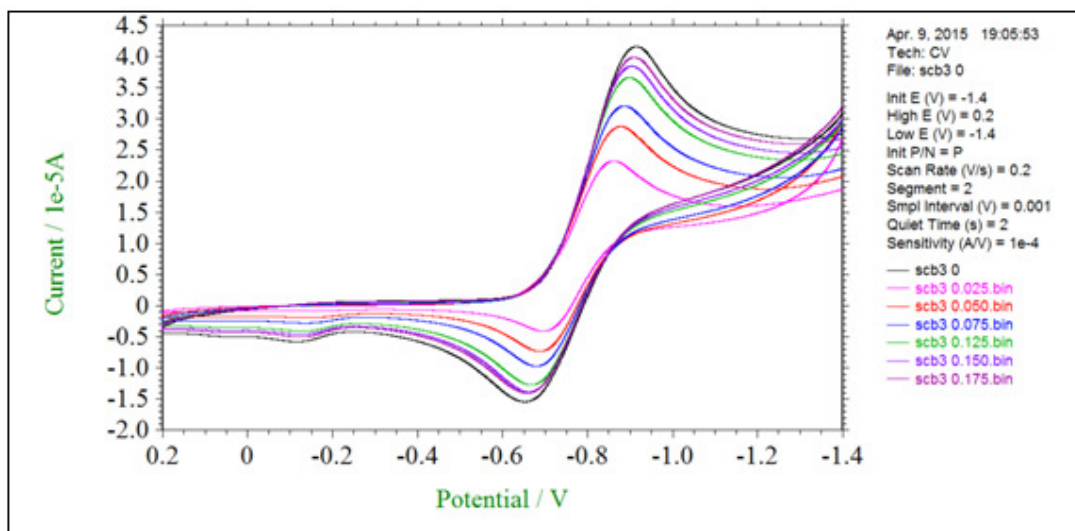
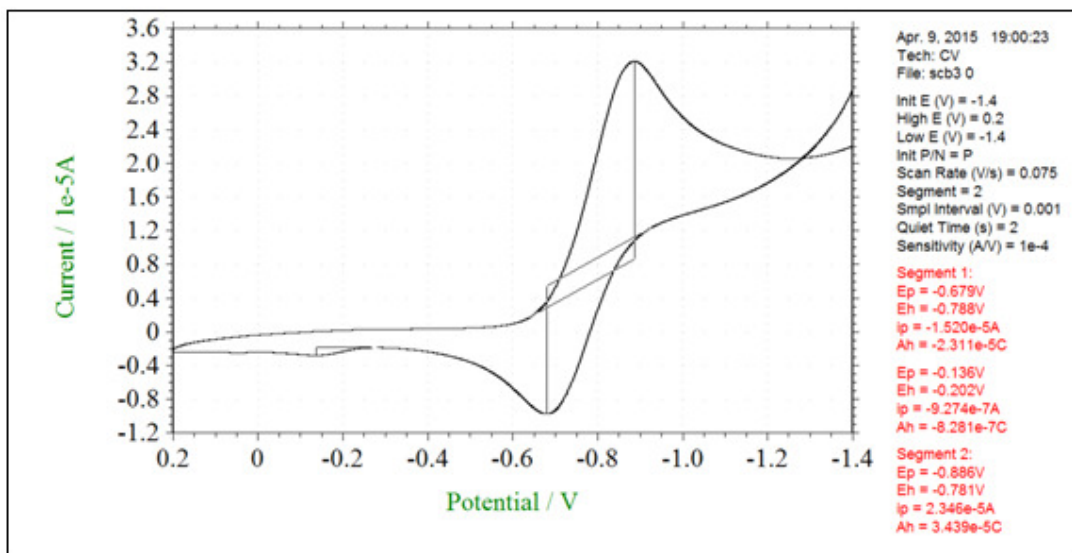


Fig :15. Cyclic Voltammograms of single and Overlay plots of SYN-AMP

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