

## Electrochemical Studies of Interaction of Ammonium metavanadate with Geimsa Stain and Pyrazole derivative cyclic voltammetrically

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**Abstract:** The redox behavior of ammonium metavanadate  $\text{NH}_4\text{VO}_3$  alone and on the interaction with Geimsa Stain and Pyrazole derivative via cyclic voltammetry (CV) has been studied. 0.1M  $\text{H}_3\text{PO}_4$  was used as supporting electrolyte and  $\text{NH}_4\text{VO}_3$  as source for +5 vanadium ions. The cyclic voltammograms gave a quasi-reversible redox couple pattern for +5 to +4 vanadium ions in phosphoric acid medium. The redox behavior of ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) was studied by the interaction of Geimsa stain and pyrazole as ligand forming complexes in 0.1 M phosphoric acid. The study indicated that vanadium (+5) is converted to vanadium (+3) via two steps on using potential window range from 1.5V to -1.5 V (vs./AgCl/KCl(s)). The thermodynamic parameters, stability constant ( $k_s$ ) and Gibbs free energies of complexation ( $\Delta G_c$ ) resulted from the interaction of  $\text{NH}_4\text{VO}_3$  with both Geimsa stain and Pyrazole derivative ligands gave better results for the interaction of Geimsa Stain than that in case of pyrazole derivative.

**keywords:** CV- $\text{NH}_4\text{VO}_3$  (AMV) - quasireversibility- Complex-Geimsa.

### 1.Introduction

The electrochemistry of element vanadium has been studied for many years by different authors and with the aid of different techniques.[1-3]

For many reasons, it still remains a great deal for vanadium and hydrolysis reactions[3]. The hydrolysis reactions and the extensive association under some conditions play role in the vanadium redox processes. The electrochemical behavior of V(V)/V(IV) redox couple was studied by many authors in acidic solutions using different electrodes[4]. It was found that the redox reaction was irreversible with gold electrode of uncertainty, because of many oxidation states

was irreversible with gold electrode. Ishii examined by chronopotentiometry of V (V) in phosphoric acid solutions the presence of two redox couples: V (V)/V (IV) and V (IV)/V (III), the first is reversible and the second is irreversible [5]. A number of authors studied the electrochemical behavior of V (V) in potassium hydroxide solutions and observed a large cathodic peak happened at that of hydrogen evolution at mercury electrode [6]. The aim of this work is to study the cyclic voltammetry

(CV) of vanadium (V) in form of  $\text{NH}_4\text{VO}_3$  and study the effect of both Geimsa Stain and Pyrazole derivative ligands on its voltammograms. Geimsa Stain has many applications in biology and is regarded as the world's standard diagnostic technique for malaria's plasmodium. Also Pyrazole derivative has it and is considered anticancer, anti-inflammatory, and antimicrobial agent because it has cyclic ring which plays important role in chelating.

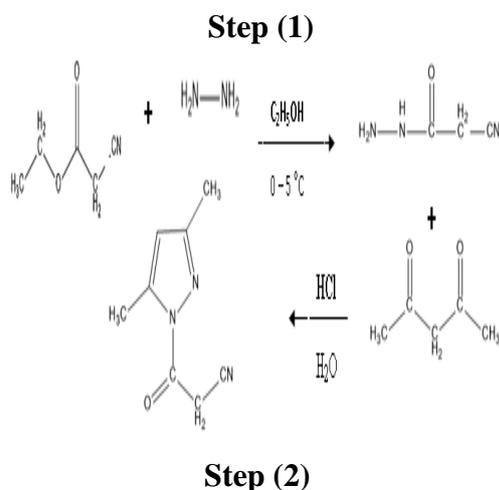
### 2. Experimental

#### Materials

The materials used are Ammonium Metavanadate ( $\text{NH}_4\text{VO}_3$ ) provided from BDH Company. Phosphoric acid provided from El-Gomheria Company. Geimsa Stain used is from Ranken Co (R F C L). All the above chemicals are used without purification avoiding their damage and Pyrazole derivative is prepared by two steps as follows:

Step (1): Formation of hydrazide by the reaction between ethyl cyano acetate and hydrazine in presence of ethyl alcohol by stirring in ice bath at 0-5 °C.

Step (2): Formation of Pyrazole derivatives by the reaction between hydrazide and acetyl acetone in presence of conc HCl and water.



### Instrumentation

The study was carried out using DY2000 Multichannel potentiostat made in USA for

Voltammetric measurements applying cell contains 30 ml of the supporting electrolyte 0.1 M  $H_3PO_4$  jointed with three electrodes.

The three electrodes used were Pt wire used as counter electrode, Silver/Silver Chloride, reference electrode and solid glassy carbon

electrode (GC) as working electrode. The cell used is:  $Ag/AgCl_{(s)}$ ,  $KCl_{(s),(aq)}$  |  $H_3PO_4$  |  $V(V)$  | GC

It is necessary to clean the working electrode on fine emery paper. The GC afterwards was washed several times, with absolute ethanol and double distilled water after washing with water to remove any adhering materials.

### 2. Results and Discussion

Ammonium metavanadate ( $NH_4VO_3$ ) redox reduction peak which assigned to one behavior, in the presence and absence of Geimsa Stain and Pyrazole derivative has been determined in 0.1M Phosphoric acid.

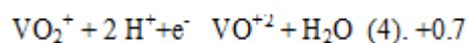
#### V (V) electrochemical behavior in 0.1 M Phosphoric acid.

Cyclic voltammetry of ammonium metavanadate, V (V) (1mM) scan between 1500 to -1500 mV is given in fig (1). The addition of ammonium metavanadate ions to the basic

electrolyte shows noticeable addition of the redox peak currents. Cathodic scan shows three reduction peaks, where as the anodic scan shows one oxidation peak. correspond to vanadium oxidation. From Fig (1) we noticed different reduction peaks which are, peak I at  $\sim +0.3$  V is the first reduction peak which assigned to one electron reduction of +5 to +4. Peak II corresponds to vanadium oxidation couple V (IV) / V (V) which appears at

+ 0.6 V (vs. Ag/AgCl). The redox behavior of peak I and peak II is quasireversible since there is large potential difference between the anodic and cathodic peaks. A small reduction peak, Peak III at  $\sim -0.3$  V is likely to further reduction of vanadium ions from vanadium (IV) to vanadium (III) since pentavalent vanadium compounds can be reduced to lower valency states by electrochemical methods [7] using a number of metals like mercury, platinum, gold or pyrolytic graphite [8]. couple V(IV)/V(V) which appears at reversible since there is large potential

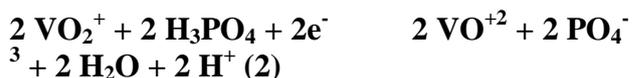
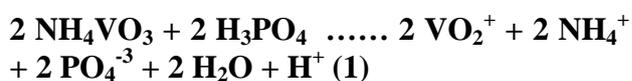
In strongly acidic media, the half reaction of V (IV)/ V (V) corresponds to:



(vs Ag/AgCl). The redox

is at 1.012 V in  $H_2SO_4$  behaviors of peak I and Peak II is quasi-

The reaction between  $NH_4VO_3$  and  $H_3PO_4$  forming  $VO_2^+$  which reduced to  $VO^{+2}$  using one electron and finally  $VO^{+2}$  is reduced to  $V^{+3}$ . Therefore the suggested mechanism for redox  $NH_4VO_3$  in 0.1 M  $H_3PO_4$  is as follows in equations (1,2,3) [9].



#### Effect of $NH_4VO_3$ concentration

Changing of ammonium metavanadate ( $NH_4VO_3$ )

concentration has noticeable effect on the voltammograms obtained in 0.1 M  $H_3PO_4$  at

18°C and scan rate 0.02 V/sec using 2 mM, 2.5 mM and 3 mM salt (Fig 2). It was observed that there is increase in the  $I_{pa}$  and  $I_{pc}$  for the waves obtained by increasing  $NH_4VO_3$  concentration. Table (2) In Table (2) there is a decrease in the anodic peak potential  $E_{p,a}$ , Cathodic peak potential  $E_{p,c}$  and the peak potential difference indicating rate determining reaction. difference between the anodic and the

We noticed from Table (2) increase in anodic peak current  $I_{pa}$ , Cathodic peak current  $I_{pc}$ , anodic diffusion coefficient ( $D_a$ ), Cathodic diffusion coefficient ( $D_c$ ), heterogeneous rate constant for electron transfer ( $k_s$ ), Cathodic surface coverage  $\Gamma_c$  and Cathodic quantity of electricity by increase  $NH_4VO_3$  concentration in this section. III at  $\sim -0.4$  is likely to further reduction

From Fig (3) we noticed that by drawing the relation between peak potential and  $NH_4VO_3$  concentration that the anodic peak potential is shifted towards more positive potentials but the cathodic one is shifted towards more negative potentials with increasing of ammonium metavanadate concentration. The reason of that may be due to the decrease in reversibility of AMV in  $H_3PO_4$ .

Also the increase in anodic and cathodic current at the glassy carbon electrode (GCE) is due to the increase in effective surface area of the GCE caused by the specific interaction between the glassy carbon electrode (GCE) and AMV. methods[7].using a number of metals

## 2.2 .Effect of scan rate on redox behavior of $NH_4VO_3$

The effect of scan rate on the redox behavior of

### Effect of addition of Geimsa Stain (GS)

$NH_4VO_3$  alone in 0.1M  $H_3PO_4$  was studied. Different scan rates ranging from 100-10 mV/s and shown in Fig (4) Different additions of Geimsa Stain (GS)

The peak potential separation, current potential data, heterogeneous electron transfer rate constant ( $k_s$ ), cathodic surface coverage  $\Gamma_c$ , anodic surface coverage ( $\Gamma_a$ ) and anodic quantity of electricity  $Q_a$  is recorded in Table (3) and we noticed that by decreasing scan rate from (0.1-0.01) that anodic peak potential decreases and cathodic peak potential increases and so the peak potential separation decreases

and the unbalanced behavior of the thermodynamic parameter values is due to the quasireversibility of the reaction. At scan rate equal to  $0.05 V.S^{-1}$ , the peak potential spacing ( $\Delta E_p$ ) is equal to 0.2V which is greater than  $0.059/2 V$  and increased with increasing scan rate indicating irreversible or quasireversible reaction. A fast, reversible one electron transfer would ideally have a  $\Delta E_p=0.059 V$  at 298K. were done on AMV till 1:1 stoichiometric

We noticed from Fig (4) that the reaction is quasireversible because by decreasing scan rate the peak potential is shifted to more negative potential. The reaction is slow because the voltage applied will not result in the generation of complex is formed(see fig ).concentration at electrode surface as predicted by Nernst equation:

$$E = E^0 + RT/nF \ln ([M^{n+1}]/[M^n])$$

It is indicated as given in fig ( ) that the This is because the kinetics of reaction is slow, therefore the equilibria are not established rapidly compared to the voltage scan rate.

Therefore Randles-Sevcik equation for quasireversible system. [10, 11].

$$I_p = (2.99 \times 10^5) n (\alpha n_a)^{1/2} A C D^{1/2} v^{1/2}$$

cathodic peak potential at nearly + 0.3 V and Where  $\alpha$  is the transfer coefficient,  $n_a$  is the number of electrons involved in redox reactions, A is the area of the electrode, C concentration of  $NH_4VO_3$ , D is the diffusion coefficient,  $I_p$  is the peak current and  $v$  is the scan rate used which is mainly 0.1 V/S. The total current of the system is:

$$I = i_{faradic} + I_{charging} \quad (4)$$

When scan rate increases, the charging current will increase and more current flows. Following equations:

$$v = dV/dt \quad (5)$$

$$i = I_{faradic} + dQ/dt \quad (6)$$

$$i = i_{faradic} + dQ/dV \cdot v \quad (7)$$

$$I = i_{faradic} + C \cdot v \quad (8)$$

Where C is the capacitance the anodic peak potential at + 0.5 V. It was concluded that an complex is formed from

As seen in Table (3) and by applying

equation (7) we observe increase in current intensity for  $\text{NH}_4\text{VO}_3$  by increase of the scan rate favouring diffusion controlled reactions.

### 2.3. Effect of addition of ligands:

#### Effect of addition of Geimsa Stain (GS):

Different additions of Geimsa Stain (GS) were done on AMV till 1:1 stoichiometric complex is formed (see Fig 5, Table 4).

It is indicated as given in Fig (5) that the cathodic peak potential at nearly + 0.3 V disappeared and the anodic peak potential at + 0.5 V. It was concluded that an complex is formed from the interaction of ammonium metavanadate with Geimsa Stain (GS).

#### 2.4. Effect of addition of Pyrazole on AMV

We have studied the effect of different additions of pyrazole stepwise to 3 mM AMV and also examined at various scan rates 0.01, 0.02 & 0.1 V/S as shown in Fig (6) It is observed from Fig (6) and Table (5) that peak potential decreases by decreasing concentration of Pyrazole and the peak currents. Also the diffusion coefficients ( $D_a$  &  $D_c$ ) decrease. Heterogeneous rate constant ( $k_s$ ) of electron transfer also decreases.

#### 2.5. Effect of scan rate on 1:1 complex (AMV with GS)

As shown in Fig(5) for 1:1 stoichiometric complex formed by the interaction of AMV with GS, The effect of scan rate has been studied at ( 100 mV, 200 mV and 10 mV) and using window range from 1.75 to -1.75V.

By changing the scan rate, the peak potential and peak current change. This indicates that the reaction is quasireversible process and shift in the peak potential occurs. The relation between peak current and square root of scan rate as given in Fig (7) is not linear indicating quasireversibility of the discussed reaction.

From the relation between peak separation potential  $\Delta E_p$  and scan rate ( $v$ ) as given in Fig (8) not linear result is obtained supporting also the quasireversibility of the waves.

#### 2.8. Effect of scan rate on 1:1 Pyrazole derivative complex with AMV:

We studied the effect of scan rate for the interaction of AMV with Pyrazole derivative in stoichiometric of 1:1 in 0.1 M  $\text{H}_3\text{PO}_4$  not clear straight line was obtained indicating the

quasireversibility reaction of Pyrazole derivative with AMV.

### 2.6. Stability constants and Gibbs free energies for complexation

Analysis was done on AMV+ Geimsa Stain and AMV + Pyrazole derivative on the formed 1:1 complex to estimate the stability constants and Gibbs free energies of complexation following equation (9).

$$\Delta G \text{ (KJ/mol)} = -2.303 RT \log \beta_c \text{ (9) [19-28].}$$

Where  $\Delta G$  is the free energy, R is the general constant of gases  $8.314 \text{ J.mole}^{-1}.\text{K}^{-1}$ , T temperature in Kelvin and  $\beta_c$  stability constant of complexes.

By the comparison between the two Tables 6&7 for Geimsa Stain (GS) and Pyrazole derivative complexes, we noticed that the stability constants

for Geimsa Stain complexes have greater  $\log \beta_j$  (  $\log$  stability constant ) than Pyrazole derivative complexes indicating greater interaction of the first ligand than that of the second.

The scan rate effect for Geimsa Stain+ AMV, Pyrazole derivative + AMV as indicated in Figs 9& 10, that the decrease in scan rate is followed by decrease in stability and Gibbs free energies of complexation.

### 3. Conclusions

The solvation reaction done between AMV and both of Geimsa Stain and Pyrazole derivative is quasi-reversible reaction. [12-18].

The quasi-reversibility was supported also from the relation between ratio of peak currents and scan rate and the relation between peak currents and square root of scan rate.

The cyclic voltammetry data for pure AMV, like  $\Gamma_a$  (anodic surface coverage), cathodic surface coverage,  $Q_a$  (anodic quantity of electricity),  $Q_c$

(cathodic quantity of electricity) decrease in presence of Geimsa Stain (GS) and Pyrazole derivative ligands, indicating more complexation.

Geimsa Stain exhibits good complexation parameters with AMV compared to Pyrazole derivative giving more stability constant and Gibbs free energies of complexation.

**Table (1)** Some electric and kinetic parameters of the cyclic voltammogram of 1.5 mM AMV ( 0.05 M) in 30 ml H<sub>3</sub>PO<sub>4</sub>(0.1 M) at GCE , scan rate 0.1 V/sec and 18oC.

(M)mM	(-)I <sub>pa</sub> (A)	I <sub>pc</sub> (A)	D <sub>c</sub>	Γ <sub>c</sub> Mol/cm <sup>2</sup>	K <sub>s</sub> cm.s <sup>-1</sup>
1	1.9*10 <sup>-5</sup>	4.8*10 <sup>-5</sup>	9.72*10 <sup>-14</sup>	6.4*10 <sup>-10</sup>	1.4*10 <sup>-4</sup>
1.5	1.97*10 <sup>-5</sup>	5.4*10 <sup>-5</sup>	5.54*10 <sup>-14</sup>	7.1*10 <sup>-10</sup>	1.2*10 <sup>-4</sup>

**Table (2)** Analysis data of different concentration of AMV in 30 ml H<sub>3</sub>PO<sub>4</sub> (0.1 M) at GCE, 18oC and scan rate 0.02.

ml of M	E <sub>pa</sub> (V)	E <sub>pc</sub> (V)	ΔE <sub>p</sub> (mV)	i <sub>pa</sub> (A)	I <sub>pc</sub> (A)	D <sub>a</sub> cm <sup>2</sup> .s <sup>-1</sup>	D <sub>c</sub> cm <sup>2</sup> .s <sup>-1</sup>	K <sub>s</sub> 10 <sup>2</sup> cm.s <sup>-1</sup>	Γ <sub>c</sub> 10 <sup>7</sup> Mol.Cm <sup>-2</sup>	(+) Q <sub>c</sub> 10 <sup>5</sup> C(couloum)	α <sub>na</sub>
2	0.69	0.299	391	7.56x10 <sup>-6</sup>	9.07x10 <sup>-6</sup>	2.5x10 <sup>-10</sup>	3.5x10 <sup>-10</sup>	6.94	1.7	2.3	0.6
2.5	0.68	0.292	388	10.4x10 <sup>-6</sup>	15.7x10 <sup>-6</sup>	3.1x10 <sup>-10</sup>	7x10 <sup>-10</sup>	9.7	2.9	3.9	0.7
3	0.66	0.28	380	16.8x10 <sup>-6</sup>	26.1x10 <sup>-6</sup>	5.7x10 <sup>-10</sup>	13.8x10 <sup>-10</sup>	8.9	4.8	6.6	0.4

**Table (3)** Different scan rates of (1.5 mM AMV) and their effect on some of thermodynamic and electric parameters at GCE and 18oC.

v(volt/sec)	v <sup>1/2</sup>	E <sub>pa</sub>	E <sub>pc</sub>	ΔE <sub>p</sub> (mV)	(-)I <sub>pa</sub> *10 <sup>6</sup> (A)	I <sub>pc</sub> *10 <sup>5</sup> (A)	D <sub>a</sub> cm <sup>2</sup> .s <sup>-1</sup>	D <sub>c</sub> *10 <sup>14</sup> cm <sup>2</sup> .s <sup>-1</sup>	K <sub>s</sub> C*10 <sup>5</sup> cm.s <sup>-1</sup>	Γ <sub>c</sub> *10 <sup>10</sup>	(+)Q <sub>c</sub> *10 <sup>5</sup> (C)	Γ <sub>a</sub> *10 <sup>10</sup> Mol/cm <sup>2</sup>	(-)Q <sub>a</sub> *10 <sup>5</sup> (C)
0.1	0.32	0.48	0.22	260	19.7	5.36	9.03x10 <sup>-15</sup>	6.6	12.8	7.1	2.7	2.6	0.99
0.05	0.224	0.43	2.20E-01	210	14.6	3.69	9.9x10 <sup>-15</sup>	6.3	2.9	9.8	3.7	3.9	1.5
0.02	0.14	0.37	0.29	80	8.35	1.61	8.1x10 <sup>-15</sup>	2.99	0.1	10.6	4.03	5.5	2.1
0.01	0.1	0.35	0.33	20	6.21	0.256	8.9x10 <sup>-15</sup>	0.15	0.01	3.4	1.3	8.2	3.1

**Table (4)** Different additions of Geimsa Stain at 1.5mM ammonium metavanadate with GCE , scan rate 0.1V/Sec and their effect on ( anodic peak current I<sub>pa</sub> , Cathodic peak current I<sub>pc</sub> , surface coverage Γ and heterogeneous transfer rate constant k<sub>s</sub> etc

MI of L	E <sub>pa</sub> (V)	E <sub>pc</sub> (V)	ΔE <sub>p</sub> (V)	I <sub>pa</sub> (A)*10 <sup>5</sup>	I <sub>pc</sub> (A) *10 <sup>5</sup>	I <sub>pa</sub> /I <sub>pc</sub>	K <sub>s</sub> C*10 <sup>4</sup> cm.s <sup>-1</sup>	Γ <sub>c</sub> *10 <sup>9</sup> Mol/cm <sup>2</sup>	(+)Q <sub>c</sub> 10 <sup>5</sup> (C)	α <sub>na</sub>
0.2	0.52	0.25	0.27	1.44	8.28	0.17	2.2	1.1	4.2	0.4
0.5	0.51	0.24	0.27	1.39	9.86	0.14	1.3	1.3	4.9	0.1
1	0.52	0.15	0.37	1.47	11.4	0.13	20.8	1.5	5.7	0.3
2	0.49	0.19	0.3	0.84	10.2	0.08	5.4	1.4	5.14	0.4
3	0.496	0.16	0.339	1.46	5.73	0.25	9.7	0.75	2.9	0.9

**Table (5)** Gradual addition of pyrazole derivative (0.1M) to 3 mM Ammonium metavanadate(0.1 M) in 30 ml H<sub>3</sub>PO<sub>4</sub> supporting electrolyte at GCE , 18oC and scan rate 0.02V/sec and its effect on the thermodynamic parameters.

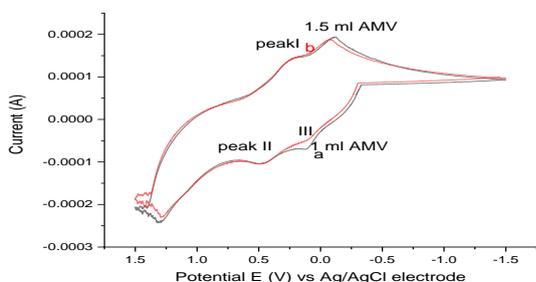
MI of L	E <sub>pa</sub> (V)	E <sub>pc</sub> (V)	ΔE <sub>p</sub> (V)	(-)I <sub>pa</sub> *10 <sup>5</sup> (A)	I <sub>pc</sub> *10 <sup>5</sup> (A)	D <sub>a</sub> *10 <sup>10</sup>	D <sub>c</sub> *10 <sup>9</sup>	k <sub>s</sub> *10 <sup>2</sup> cm.s <sup>-1</sup>	Γ <sub>c</sub> *10 <sup>7</sup> Mol/cm <sup>2</sup>	(+)Q <sub>c</sub> *10 <sup>5</sup>
1	0.67	0.285	0.4	2.22	4.12	10.6	3.7	0.12	7.5	10.3
2	0.665	0.28	0.385	2.13	3.6	10.4	2.97	0.1	6.6	9.1
3	0.662	0.28	0.382	1.99	3.3	9.6	2.6	9.1	6.04	8.3
4.5	0.65	0.265	0.385	1.64	2.7	7.1	1.9	8.1	4.9	6.7
6	0.64	0.25	0.39	1.42	2.1	5.7	1.28	7.3	3.9	5.3
9	0.62	0.22	0.4	0.92	2.01	2.7	1.3	9.1	3.7	5.04

**Table (6)** Effect of different scan rates on stability constant β<sub>j</sub> and Free energy of complex ΔG for 1:1 stoichiometric GS complexes:

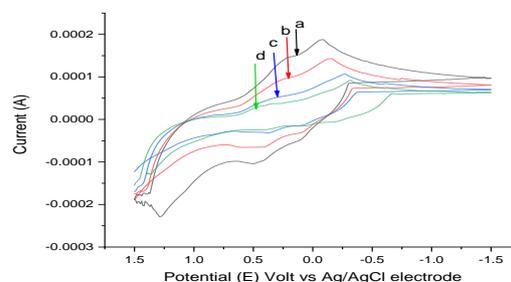
v(Volt/sec)	[L]Mol/cm <sup>3</sup>	(E°)M(V)	(E°)C(V)	ΔE mv	Log β <sub>j</sub>	B <sub>j</sub>	ΔG (KJ/mol)
0.1	2.17*10 <sup>-3</sup>	0.35	0.3265	0.024	3.5	2995.7	-19.4
0.05	2.17*10 <sup>-3</sup>	0.325	0.253	0.072	5.2	143195.6	-28.7
0.02	2.17*10 <sup>-3</sup>	0.33	0.229	0.101	6.2	1445852.6	-34.3
0.01	2.17*10 <sup>-3</sup>	0.34	0.2085	0.132	7.2	16453535.01	-40.2

**Table( 7)** Effect of different scan rates on stability constant  $\beta_j$  and Free energy of complex  $\Delta G$  for 1:1 stoichiometric pyrazole derivative complex.

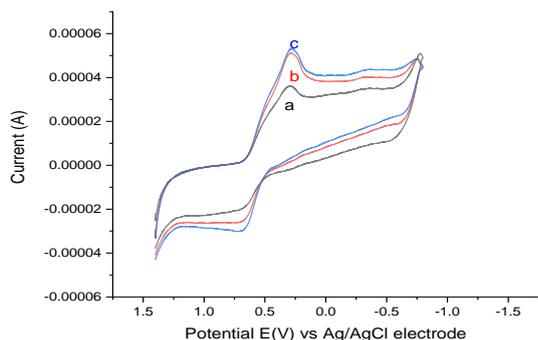
v(Volt/sec)	[M]*10 <sup>-3</sup> Mol/l	[L]*10 <sup>-3</sup> Mol/l	(E°)M(V)	(E°)C(V)	$\Delta E_{mv}$	Log $\beta_j$	$\beta_j$	$\Delta G$ (KJ/mol)
0.1	8.33	8.33	0.455	0.455	0	2.1	120	11.6
0.01	8.33	8.33	0.478	0.47	0.008	2.4	227	13.1
0.005	8.33	8.33	0.486	0.45	0.036	3.3	2115.14	18.5



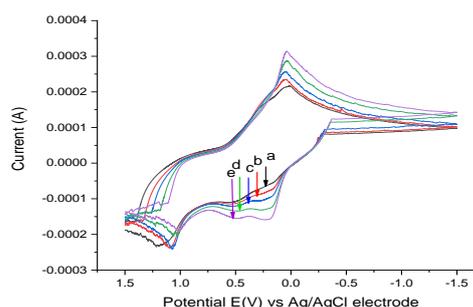
**Fig 1:** cyclic voltammograms of 1mM ammonium metavanadate (0.05M) and 1.5 mM in 30 ml H<sub>3</sub>PO<sub>4</sub> 0.1M supporting electrolyte at (GCE, 18oC and scan rate 0.1V/sec).



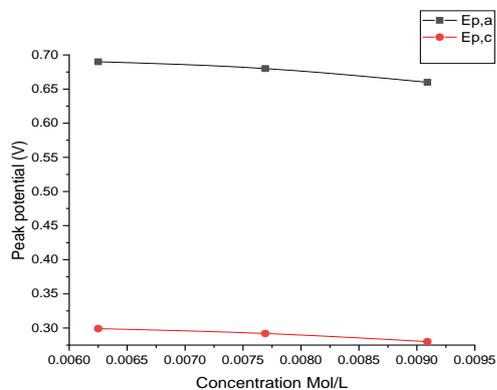
**Fig (4)** Effect of scan rate on 1.5 mM AMV (0.05 M) with GCE, at 18 °C black wave (scan rate 0.1 V/sec), red wave (scan rate 0.05), blue wave (scan rate 0.02) and green wave (scan rate 0.01).



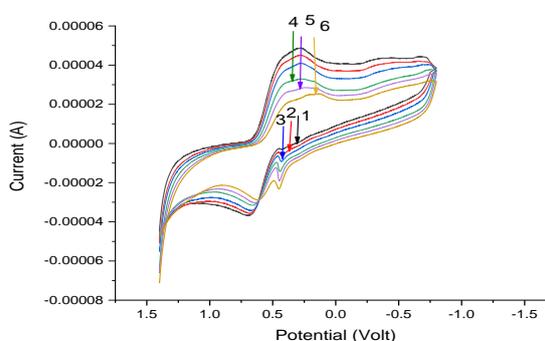
**Fig (2)** CVs of different concentration of AMV(0.1 M): a; 2mM, b; 2.5mM and c 3mM in 0.1 M H<sub>3</sub>PO<sub>4</sub> as supporting electrolyte at glassy carbon electrode (GCE), 18oC and scan rate 0.02.V/sec



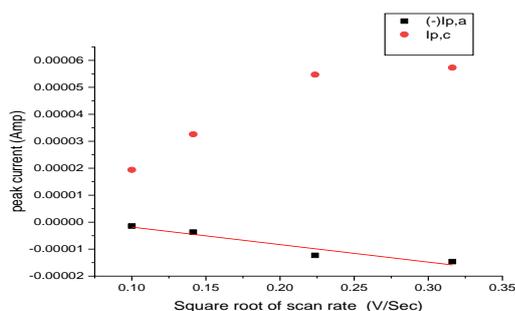
**Fig (5)** Cyclic voltammograms for addition of a) 0.2 ml, b) 0.5 ml, c) 1 ml, d) 2ml, e) 3ml gimsa stain on 1.5 ml AMV at 18°C in the range of (-1.75 to +1.75) at scan rate 0.1 (V/sec) with GCE



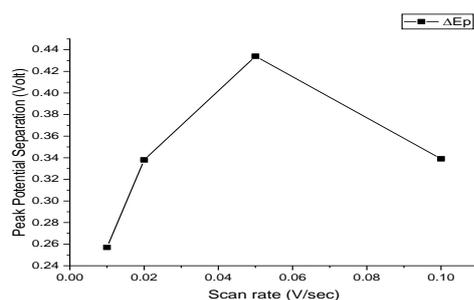
**Fig(3)** The relationship between peak potential (V) and concentration of AMV (3 mM) in 30 ml H<sub>3</sub>PO<sub>4</sub>(0.1 M) with GCE, at 18oC and scan rate 0.02 V/sec.



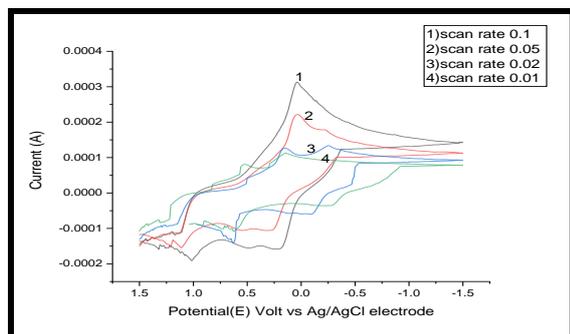
**Fig (6)** Cyclic voltammograms of pyrazole derivative(0.1 M) addition: (1) 1 ml ligand 2) 2 ml 3) 3 ml, 4) 4.5 ml, 5) 6 ml and 6) 9 ml ligand on 3mM AMV at scan rate 0.02 V/sec and 18oC in the range of (1.75to -1.75 V).



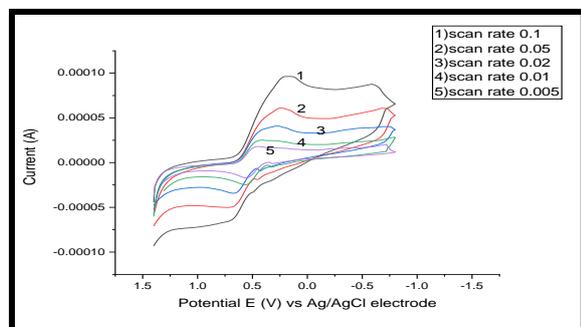
**Fig (7)** The relationship between Peak current (A) on the Y axis and the square root of scan rate (Volt/sec) on the X axis for Geimsa complex at GCE and 18°C



**Fig (8)** The relationship between peak separation (V) on the Y-axis and scan rate (V) on the X axis for Geimsa complex



**Fig (9)** Effect of different scan rates ranging from (10-100) mV /sec on ( 1.5 mM AMV + GS) 1:1 complex in 30 ml H<sub>3</sub>PO<sub>4</sub> 0.1 M supporting electrolyte with GCE at 18oC



**Fig (10)** Effect of different scan rates (10, 5, 2, 1, 0.50) mV/sec to pyrazole derivative(0.1 M) addition at 3mM AMV (0.1) (1:1complex) at GCE and 18oC

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