



Cyclic Voltammetric Reduction of 2, 4-Dihydroxy Acetophenone Semicarbazone and Thiosemicarbazone at Glassy Carbon Electrode

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ABSTRACT

Electrochemical reduction behavior of 2,4-dihydroxy acetophenone semicarbazone and thiosemicarbazone is studied on glassy carbon electrode in CH₃OH-Britton Robinson buffer at pH 3,5, 7, 9 and phosphate buffer (pH 5.8,8) using cyclic voltammetric technique. Single irreversible reduction wave is observed due to the reduction of semicarbazone and thiosemicarbazone moiety. The effect of change in pH, buffer, ligand and sweep rate is evaluated. The electrode process is found to be irreversible and diffusion controlled. Kinetic parameters are calculated from cyclic voltammetric measurements.

Keywords: 2,4-Dihydroxy acetophenone, Semicarbazone, Thiosemicarbazone, GC electrode, B-R buffer, Phosphate buffer and Cyclic voltammetry.

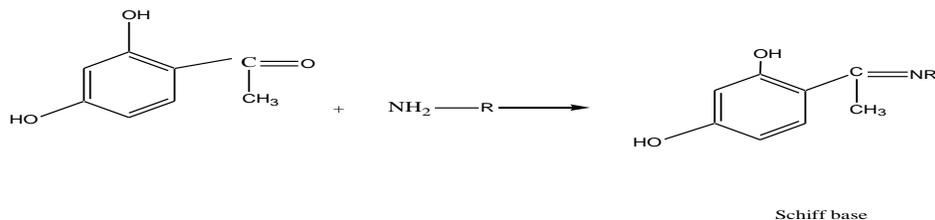
INTRODUCTION

Semicarbazones and thiosemicarbazones are amongst the most widely studied nitrogen and oxygen/sulphur donor ligands. They have been a subject of interest in recent decades due to their biological activity, good complexing properties and analytical applications [1-4]. Systematic perusal of earlier literature reveals that inspite of the variegated importance associated with semicarbazone and thiosemicarbazone compounds, relatively few reports exist on their electrochemical behavior [5-6]. Electrochemical behavior of Co (II) and Ni (II) with amino acids have also been reported in our laboratory [7]. Hence, efforts have been laid down to undertake cyclic voltammetric studies on semicarbazone(SC) and thiosemicarbazone(TSC) of 2,4-dihydroxy acetophenone .The kinetic parameters such as charge-transfer coefficient (α_n), diffusion coefficient ($D_0^{1/2}$) and rate constant ($K_{f,h}^{\circ}$) have been calculated.

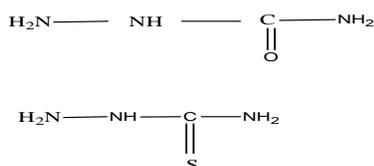
MATERIALS AND METHODS

All chemicals employed were of analytical grade. Methanol was freshly distilled prior to use. The ligands semicarbazone and thiosemicarbazone were synthesized by the condensation of 2, 4-dihydroxy acetophenone with semicarbazide hydrochloride and thiosemicarbazide in 1:1 molar ratio using absolute alcohol as the reaction medium and the crystals that separated out were recrystallized from the same solvent. The cyclic voltammetric data were recorded with a fully computer controlled Basic Electrochemistry System. A three electrode combination system was used. This consisted of a glassy

carbon (GC) working electrode, an Ag/AgCl reference electrode and a Pt wire auxiliary electrode. An Elico digital pH meter was employed for pH measurements and all measurements were carried out at laboratory temperature.



Where $\text{NH}_2\text{---R}$ is



Glassy carbon electrode was cleaned prior to the investigation with 0.1 μm alumina on a polishing cloth using double distilled water as the lubricant. The activity of electrode was tested using solution of ferricyanide/ferrocyanide in 0.1M KCl. The stock solutions of 2, 4-diHyAcSC and 2,4-diHyAcTsc (5mM) was prepared in methanol. Britton-Robinson buffer, Phosphate buffer were prepared in doubly distilled water. In the typical cyclic voltammetric experiment, reaction mixture consisted of compound solution, methanol (the minimum volume necessary to keep the compound in the solution) and buffer solution (keeping the overall volume constant 10 mL). Before recording the current voltage curve, the solution was deoxygenated by purging a stream of nitrogen gas for 15 min prior to the experiments in order to remove dissolved oxygen from the media. The three electrodes were connected to the electrochemical cell. Required scan rates, current sensitivity, initial potential and final potential were applied and resulting current was measured as a function of applied potential.

RESULTS AND DISCUSSION

The electrochemical reduction behavior of the synthesized semicarbazone and thiosemicarbazone compounds were studied at glassy carbon electrode in CH_3OH media using B-R buffer and phosphate buffer respectively, at various sweep rates, pH values. All the compounds exhibit one irreversible reduction peak.

Thus, the kinetic parameters such as charge-transfer coefficient (α_n), diffusion coefficient ($D_0^{1/2}$) and rate constant ($k_{f,h}^\circ$) have been calculated for irreversible and diffusion controlled reduction by using following equations [8-11] and reported in tables (1-4).

$$|E_p - E_{p/2}| = \frac{1.857RT}{\alpha_n F} = \left(\frac{47.7}{\alpha_n}\right) mV \quad (1)$$

$$I_p = 3.01 \times 10^5 n (\alpha_n)^{1/2} A C D_0^{1/2} \nu^{1/2} \quad (2)$$

$$E_p = -\frac{RT}{\alpha_n F} \left[0.78 + \ln\left(\frac{D_0^{1/2}}{k_{f,h}^\circ}\right) + \ln\left(\frac{\alpha_n F \nu}{RT}\right)^{1/2} \right] \quad (3)$$

Effect of scan rate on cyclic voltammetric behaviour of thiosemicarbazone at pH 3,5,7,9 of BR buffer: This is shown in figures 1-4 and reported in table 1

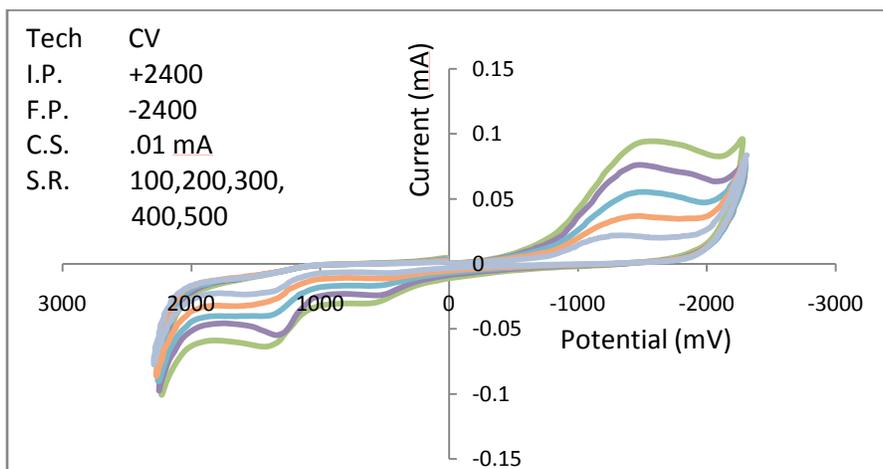


Fig. 1 Cyclic Voltammograms of 2, 4-diHyAcTSC in CH₃OH-BR buffer at pH 3

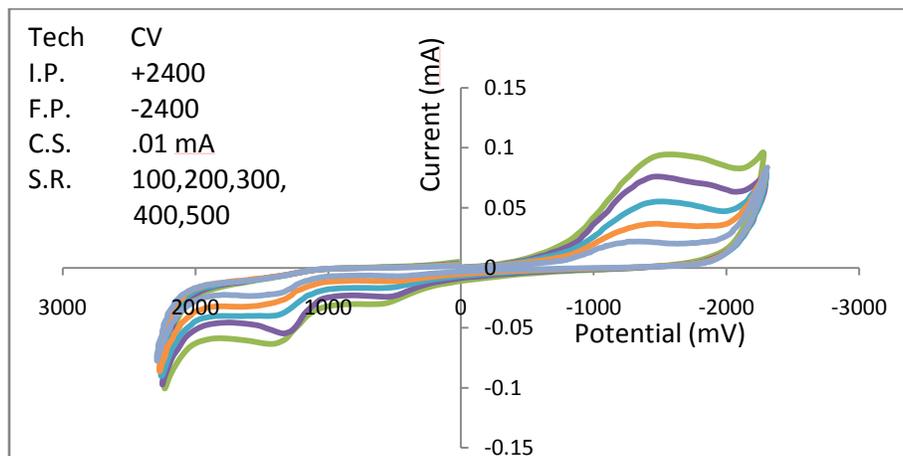


Fig. 2 Cyclic Voltammograms of 2, 4-diHyAcTSC in CH₃OH-BR buffer at pH 5

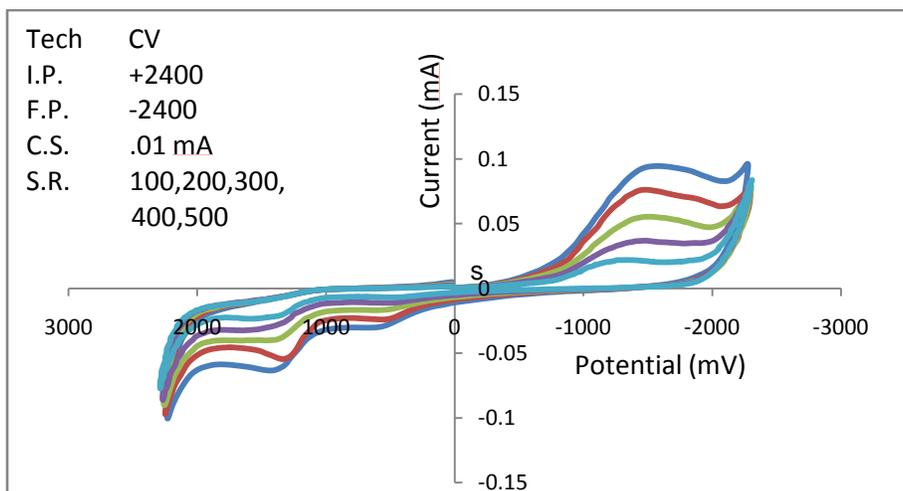


Fig. 3 Cyclic Voltammograms of 2,4-diHyAcTSC in CH₃OH-BR buffer at pH 7

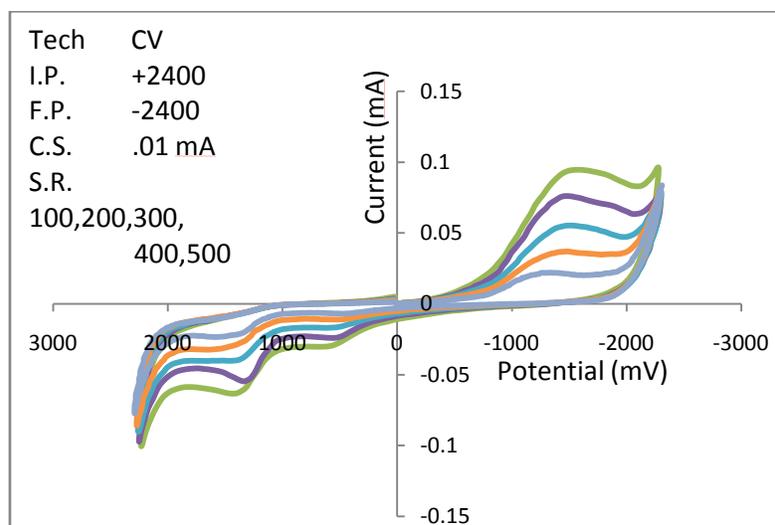


Fig. 4 Cyclic Voltammograms of 2,4-diHyAcTSC in CH₃OH-BR buffer at pH 9

Table.1. Effect of scan rate on cyclic voltammetric behaviour of 2,4-diHyAcTsc in CH₃OH-BR buffer at pH 3,5,7,9 (fig. 1-4)

pH	ν mVs ⁻¹	E_{pc} mV	I_{pc} mA	$E_{p/2}$ mV	$I_{pc}/\nu^{1/2}$	α_n	$D_0^{1/2}$ cm ² s ⁻¹	$k_{f,h}^*$ cm.s ⁻¹
3	100	-1120	0.0136	-870	0.221	0.1908	0.019599	8.95x10 ⁻⁰⁶
	200	-1290	0.0320	-950	0.3182	0.14029	0.038028	7.53x10 ⁻⁰⁵
	300	-1350	0.0529	-1000	0.2638	0.13629	0.052076	11.10x10 ⁻⁰⁵
	400	-1380	0.0723	-1040	0.273	0.14029	0.060754	10.40x10 ⁻⁰⁵
	500	-1420	0.0921	-1110	0.2701	0.15387	0.066096	5.03x10 ⁻⁰⁵
5	100	-1150	0.0152	-890	0.344	0.18346	0.022338	1.11x10 ⁻⁰⁵
	200	-1310	0.0336	-970	0.3359	0.14029	0.039929	7.09x10 ⁻⁰⁵
	300	-1370	0.0558	-1030	0.3463	0.14029	0.054142	8.48x10 ⁻⁰⁵
	400	-1410	0.0744	-1090	0.3685	0.14906	0.060651	5.61x10 ⁻⁰⁵
	500	-1440	0.0933	-1140	0.3483	0.159	0.065868	3.39x10 ⁻⁰⁵
7	100	-1180	0.0168	-970	0.330	0.22714	0.022189	1.33x10 ⁻⁰⁶
	200	-1330	0.0356	-990	0.3642	0.14029	0.042306	6.73x10 ⁻⁰⁵
	300	-1390	0.0568	-1070	0.3596	0.14906	0.053467	4.81x10 ⁻⁰⁵
	400	-1420	0.0767	-1130	0.3525	0.16448	0.059523	2.33x10 ⁻⁰⁵
	500	-1490	0.0947	-1190	0.3497	0.159	0.038617	1.46x10 ⁻⁰⁵
9	100	-1200	0.0171	-1010	0.3437	0.25105	0.021483	3.71x10 ⁻⁰⁷
	200	-1360	0.0369	-1050	0.3663	0.15387	0.041871	2.88x10 ⁻⁰⁵
	300	-1470	0.0575	-1110	0.3585	0.1325	0.057409	7.9x10 ⁻⁰⁵
	400	-1500	0.0777	-1150	0.3645	0.13629	0.066242	7.33x10 ⁻⁰⁵
	500	-1530	0.0989	-1210	0.3782	0.14906	0.072112	3.72x10 ⁻⁰⁵

Effect of scan rate on cyclic voltammetric behaviour of thiosemicarbazone at pH 5.8 and 8 of Phosphate buffer: The results are shown in figures 5, 6 and results reported in table 2.

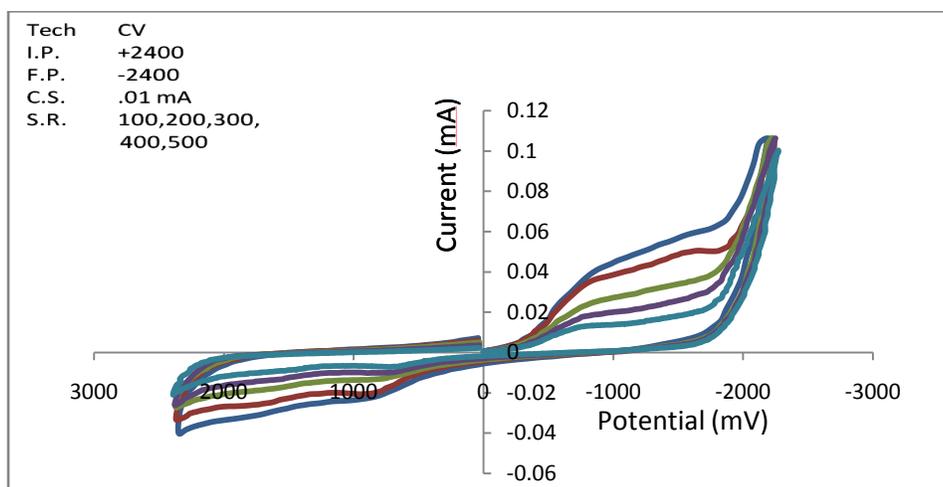


Fig. 5 Cyclic Voltammograms of 2,4-diHyAcTSC in CH₃OH-Phosphate buffer at pH 5.8

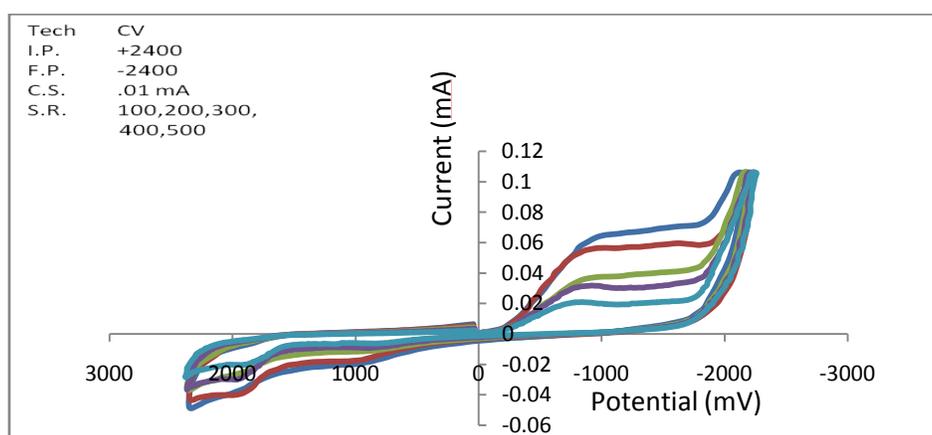


Fig. 6 cyclic voltammograms of 2,4-diHyAcTSC in CH₃OH-Phosphate buffer at pH 8

Table:2. Effect of scan rate on cyclic voltammetric behaviour of 2,4-diHyAcTSC in CH₃OH-Phosphate buffer at pH 5.8-8 (fig. 5-6)

pH	ν mVs ⁻¹	E_{pc} mV	I_{pc} mA	$E_{p/2}$ mV	$I_{pc}/\nu^{1/2}$	α_n	$D_0^{1/2}$ cm ² s ⁻¹	$k_{f,h}^*$ cm.s ⁻¹
5.8	100	-820	0.0052	-330	0.016444	0.09735	0.010491	0.014297
	200	-870	0.0078	-390	0.017441	0.09938	0.011013	0.021458
	300	-960	0.0098	-420	0.017892	0.08833	0.011984	0.026876
	400	-1020	0.0147	-550	0.023243	0.10149	0.014523	0.040466
	500	-1110	0.0197	-690	0.02786	0.11357	0.016456	0.054443
8	100	-870	0.0054	-350	0.017076	0.09173	0.011223	0.014822

	200	-920	0.0089	-400	0.019901	0.09173	0.01308	0.02443
	300	-990	0.0107	-470	0.019535	0.09173	0.012839	0.029369
	400	-1080	0.0156	-590	0.024666	0.09735	0.015736	0.042889
	500	-1150	0.0217	-700	0.030688	0.106	0.018763	0.05982

Effect of scan rate on cyclic voltammetric behaviour of semicarbazone at pH 3,5,7,9 of BR buffer: The results are depicted in figures 7-10 and presented in table 3.

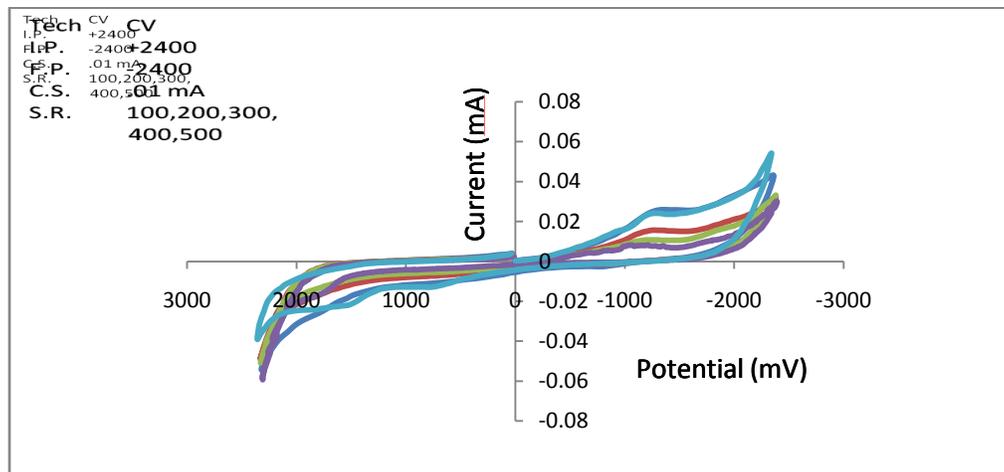


Fig. 7 Cyclic Voltammograms of 2,4-diHyAcSC in CH₃OH-BR buffer at pH 3

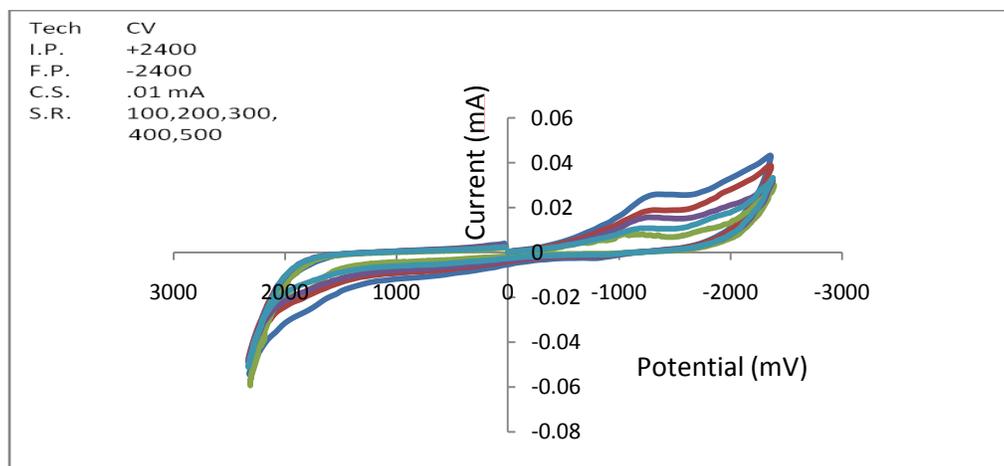


Fig. 8 Cyclic Voltammograms of 2,4-diHyAcSC in CH₃OH-BR buffer at pH 5

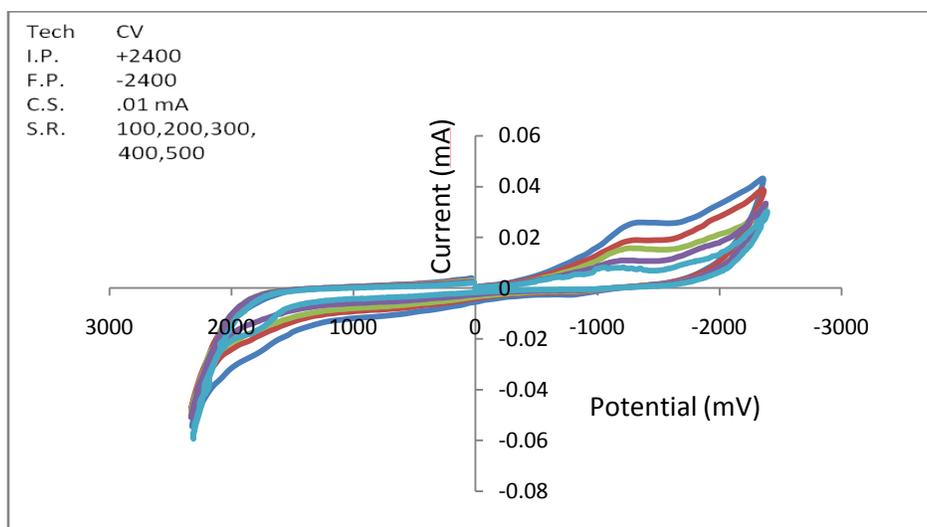


Fig. 9 Cyclic Voltammograms of 2,4-diHyAcSC in CH₃OH-BR buffer at pH 7

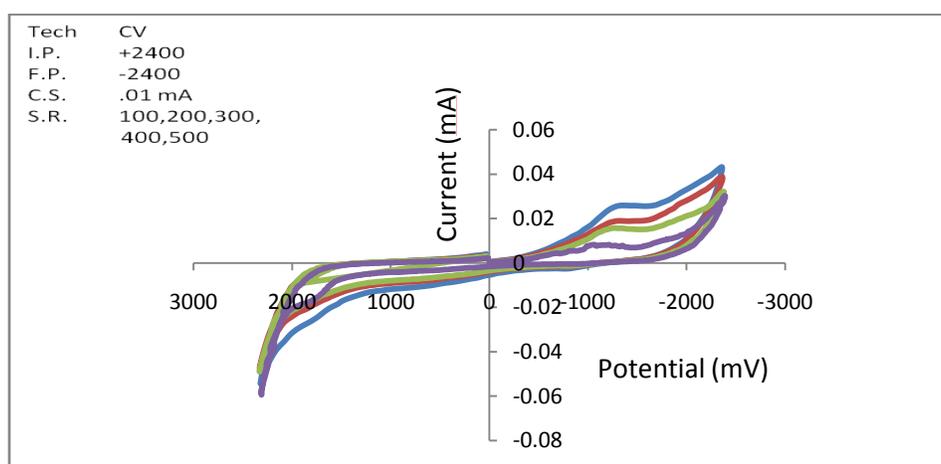


Fig. 10 Cyclic Voltammograms of 2,4-diHyAcSC in CH₃OH-BR buffer at pH 9

Table:3. Effect of scan rate on cyclic voltammetric behaviour of 2,4-diHyAcSC in CH₃OH-BR buffer at pH 3,5,7,9 (fig. 7-10)

pH	v mVs^{-1}	E_{pc} mV	I_{pc} mA	$E_{p/2}$ mV	$I_{pc}/v^{1/2}$	α_n	$D_0^{1/2}$ cm^2s^{-1}	$k_{f,h}$ cm.s^{-1}
3	100	-900	0.0056	-380	0.017709	0.09173	0.011639	0.000305
	200	-1030	0.0092	-440	0.020572	0.08085	0.014402	0.000486
	300	-1070	0.0122	-500	0.022274	0.08368	0.015327	0.000505
	400	-1130	0.0199	-610	0.031465	0.09173	0.02068	0.000476
	500	-1190	0.0230	-730	0.032527	0.1037	0.020106	0.000255
5	100	-910	0.0075	-570	0.023717	0.13629	0.012788	8.11×10^{-05}
	200	-990	0.0122	-630	0.02728	0.1325	0.014918	9.99×10^{-05}
	300	-1130	0.0142	-740	0.025926	0.12231	0.014756	8.84×10^{-05}
	400	-1160	0.0167	-820	0.026405	0.14029	0.014033	4×10^{-05}
	500	-1210	0.0207	-960	0.029274	0.1908	0.013341	3.49×10^{-06}
7	100	-920	0.0058	-390	0.018341	0.09	0.01217	0.000312
	200	-1070	0.0101	-470	0.022584	0.0795	0.015944	0.000498
	300	-1110	0.0145	-530	0.026473	0.08224	0.018376	0.000561
	400	-1180	0.0201	-640	0.031781	0.08833	0.021286	0.00047

	500	-1210	0.0239	-750	0.0338	0.1037	0.020893	0.000244
9	100	-950	0.0090	-620	0.02846	0.14455	0.014901	5.8×10^{-05}
	200	-1070	0.0135	-690	0.030187	0.12553	0.01696	9.78×10^{-05}
	300	-1150	0.0148	-780	0.027021	0.12892	0.01498	6.23×10^{-05}
	400	-1190	0.0205	-850	0.032413	0.14029	0.017226	4.17×10^{-05}
	500	-1230	0.0239	-980	0.0338	0.1908	0.015403	3.47×10^{-06}

Effect of scan rate on cyclic voltammetric behaviour of semicarbazone at pH 5.8 and 8 of Phosphate buffer: The results are presented in table 4 and shown in figures 11,12

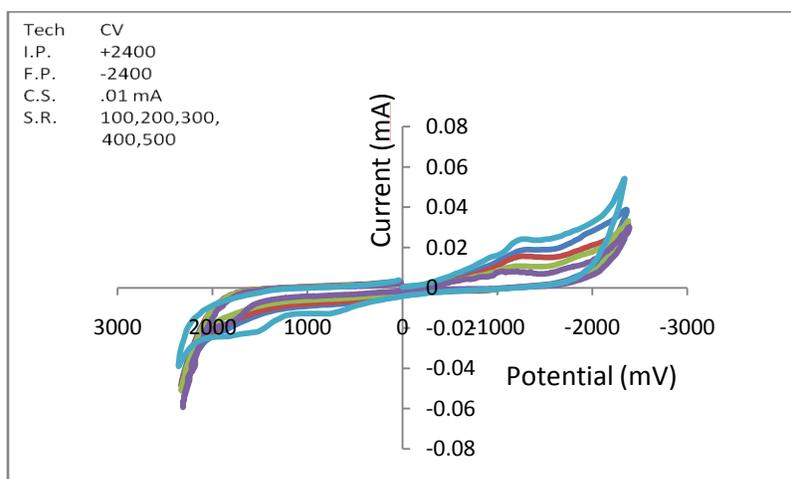


Fig. 11 Cyclic Voltammograms of 2, 4-diHyAcSC in CH₃OH-Phosphate buffer at pH 5.8

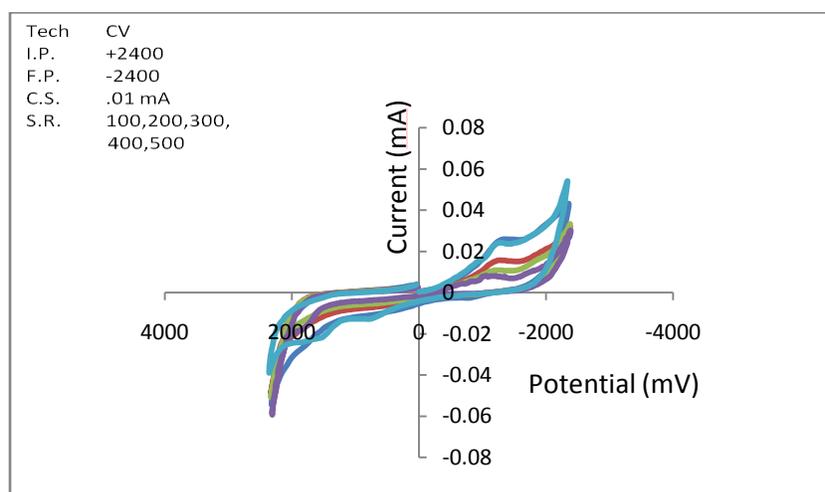


Fig. 12 Cyclic Voltammograms of 2,4-diHyAcSC in CH₃OH-Phosphate buffer at pH 8

Table 4. Effect of scan rate on cyclic voltammetric behaviour of 2,4-diHyAcSC in CH₃OH-Phosphate buffer at pH 5.8-8 (fig. 11-12)

pH	ν mVs ⁻¹	E_{pc} mV	I_{pc} mA	$E_{p/2}$ mV	$I_{pc}/\nu^{1/2}$	α_n	$D_0^{1/2}$ cm ² s ⁻¹	$k_{f,h}^*$ cm.s ⁻¹
5.8	100	-740	0.0107	-420	0.033836	0.2168	0.014465	1.3×10^{-04}

	200	-790	0.0163	-490	0.036448	0.2385	0.014856	7.27×10^{-05}
	300	-820	0.0212	-570	0.038706	0.3180	0.013663	7.7×10^{-06}
	400	-870	0.0332	-630	0.052494	0.3407	0.017902	3.28×10^{-06}
	500	-950	0.0400	-650	0.056569	0.2385	0.023057	4.03×10^{-05}
8	100	-760	0.0174	-430	0.055024	0.2073	0.024051	2.28×10^{-04}
	200	-830	0.0283	-510	0.063281	0.2168	0.027052	1.61×10^{-04}
	300	-870	0.0329	-620	0.060067	0.3180	0.021203	6.43×10^{-06}
	400	-930	0.0459	-640	0.072574	0.2510	0.028832	3.72×10^{-05}
	500	-970	0.0547	-670	0.077357	0.2385	0.031531	4.58×10^{-05}

The current function ($I_{pc}/v_{1/2}$) has been found to be fairly constant with respect to sweep rate indicating that the reduction of Schiff base is diffusion controlled. The results described above indicate that this system involves charge transfer followed by irreversible chemical reaction. This clearly indicates that the Schiff base reduction is irreversible.

Effect of scan rate: The cyclic voltammograms were recorded by varying the scan rate (100-500 mV/s), keeping the pH and the concentration of solution constant. The data show one irreversible reduction peak at all scan rates. The peak potential value shifted in the more negative potential with an increase in the scan rate. The peak potential shift was higher when the scan rate increased. This means that under these conditions the electrochemical process is more irreversible. Peak current also increases as the scan rate increased for all the compounds.

Effect of pH: The effect of pH upon the reduction of semicarbazones and thiosemicarbazones was investigated. Peak potential values of the compounds are found to be changed with the pH value of the solution (Fig.13, 14) this dependence of the peak potential on pH indicating that proton transfer also takes place in the electrode reaction [12-13]. The peak potential shifts in more negative values depending upon the pH of the solution. This means that the reduction is easier in acidic media and difficult in media where the proton concentration is low. The ease of reduction is found to be more in acidic pH than in alkaline pH which may be because of the formation of easily reducible protonated intermediate.

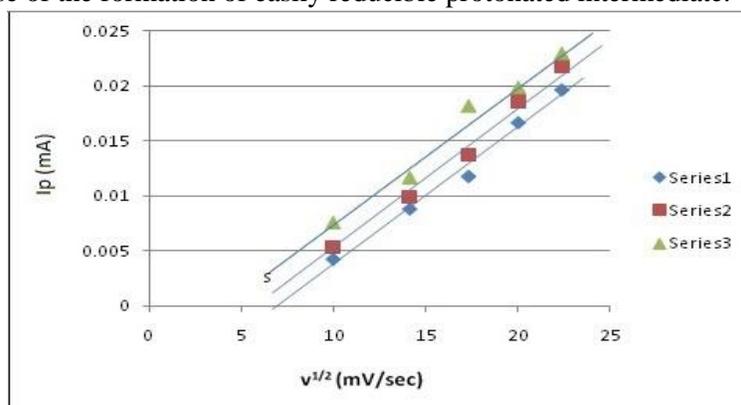


Fig.13 Effect of pH on I_p vs $v^{1/2}$ for 2,4-diHyAcSc in CH_3OH -BR buffer [Here Serise1 at 5pH,Serise2 at 7pH,Serise3 at 9pH]

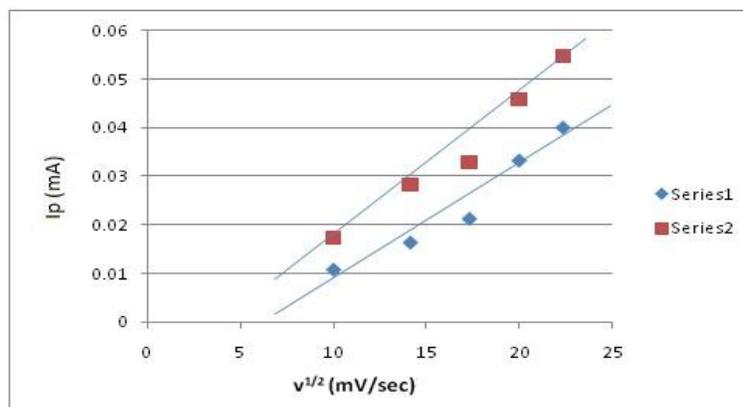
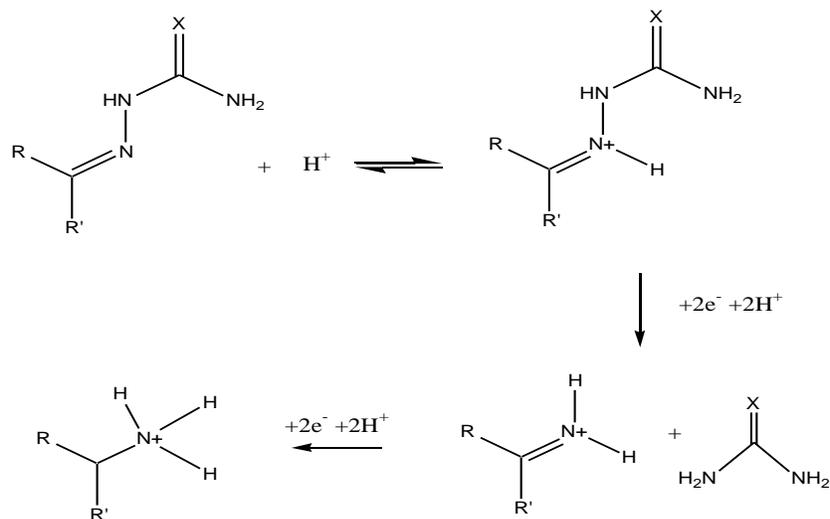


Fig.14 Effect of pH on I_p vs $v^{1/2}$ for 2,4-diHyAcSc in CH_3OH -Phosphate buffer [Here Serise1 at 5.8pH,Serise2 at 8pH]

Effect of buffer solution: The effect of buffer solutions (BR buffer and Phosphate buffer) upon the reduction of semicarbazones and thiosemicarbazones was investigated. Peak potential values of the compounds are found to be changed with the buffer solution. Phosphate buffer is more polar than BR buffer because of more ionization of component of phosphate buffer. Phosphate buffer consists of strong acid and strong base solution and BR buffer consists of comparatively weak acid (i.e. Acetic acid) so Phosphate buffer is more polar than BR buffer. This dependence of the peak potential on buffer solution indicating that ionization of buffer also takes place in the electrode reaction. The peak potential shifts in less negative values depending upon the polarity of the buffer solution. This means that the reduction is easier in more polar buffer solution (phosphate buffer) and difficult in less polar buffer solution (BR buffer) where the ionization is low.

Effect of O-atom and S-atom of ligand: The effect of O-atom and S-atom of ligand upon the reduction of semicarbazone and thiosemicarbazone was investigated. The peak potential value shifted in the more negative potential in reduction of thiosemicarbazone comparison to semicarbazone because in thiosemicarbazone S-atom is present which is less electronegative than O-atom present in semicarbazone so O-atom decreases electron density on nearest N-atom. That is why reduction is easy at protonation site in semicarbazone and reduction is comparatively difficult in thiosemicarbazone.

Proposed reduction mechanism for semicarbazone/thiosemicarbazone



CONCLUSIONS

The results obtained in the present study show that 2,4-diHyAcSC & 2,4-diHyAcTsc presently investigated undergoes easily reduction. Keeping in view of feasibility of the site of reduction and on the basis of cyclic voltammetric results, the reduction mechanism may be suggested for electro reduction of above studied semicarbazones and thiosemicarbazones, similar that reported in the literature [14]. The mechanism finds supports by the fact that electrochemical reduction found to be pH dependent. The E_{pc} shifts towards negative potential with pH, as protons are consumed in the reduction and the reaction occurs through easily reducible protonated intermediate.

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