Voltammetric studies of 2-acetyl-5-methylthiophenesemicarbazone and its Cobalt(II) complex

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Abstract- Cyclic Voltammetric approach was used to investigate the electrochemical properties and various parameters on semicarbazone 2-acetyl-5-methylthiophene (AcMeSC) and its Co(II) complex in buffers (Britton-Robinson and Phosphate buffer) with pH values ranging from 5 to 8. The characterization of ligand is mainly based on elemental analysis, IR spectra. Numerous physico-chemical effects on the ligand have been reported, including the effects of sweep potential, pH, buffer and solvent (methanol, DMF).

Keywords- **2-acetyl-5-methylthiophene semicarbazone, Cyclic Voltammetry, Kinetic parameters, Electrochemical studies, Cobalt complex.**

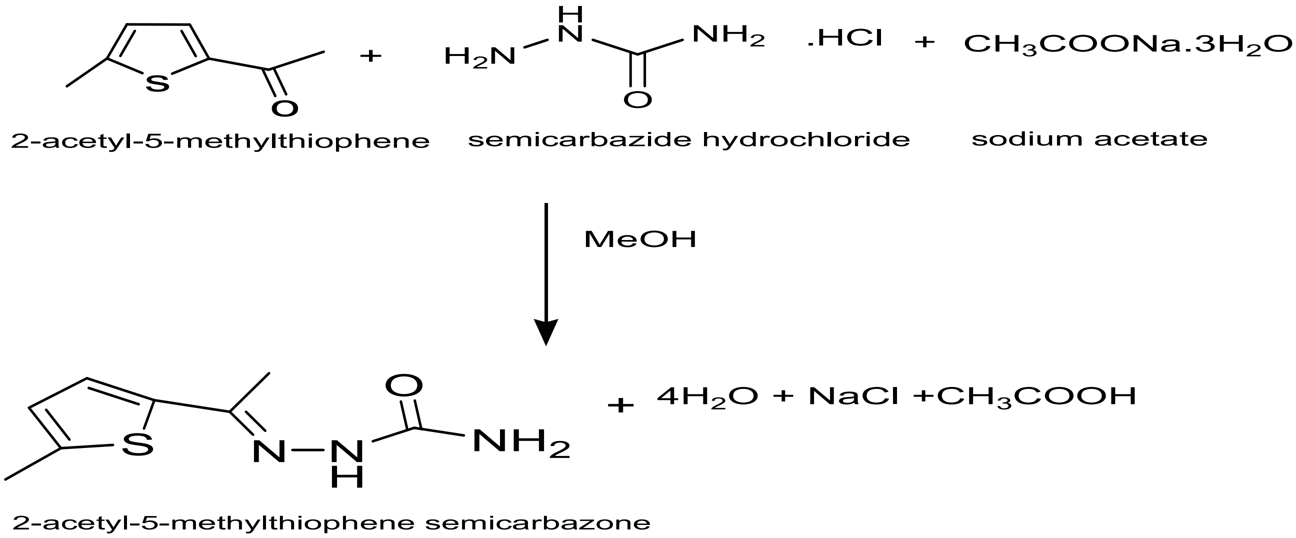
I. INTRODUCTION

Due to their ease in forming stable complexes with the majority of transition metal ions, Schiff bases play a significant role in inorganic chemistry. Since it is now known that many of these complexes may serve as models for physiologically significant entities, the discipline of bioinorganic chemistry has seen an increase in interest in Schiff base complexes [1–5]. Multiple metals can be coordinated by Schiff base ligands [6–10].

Many things can be accomplished with Schiff bases, including treating cancer, acting as antibacterial agents, antiviral agents, antifungal agents, and for numerous other biological qualities. Complexes of several transition and inner transition metals with bi-, tri-, and tetradentate Schiff bases are useful. They serve as compelling models for metalloenzymes, effective catalysts for the reduction of dinitrogen and dioxygen [11]. Cyclic voltammetry plays a vital role in assessing electronic reduction and oxidation in Schiff bases and metal complexes. It results in a plot between applied voltage and current referred as Cyclic Voltammogram. [12–14] In this paper we are discussing about cyclic voltammetric studies and other extensive studies of 2-acetyl-5-methylthiophene semicarbazone and its cobalt complex.

II. LIGAND SYNTHESIS

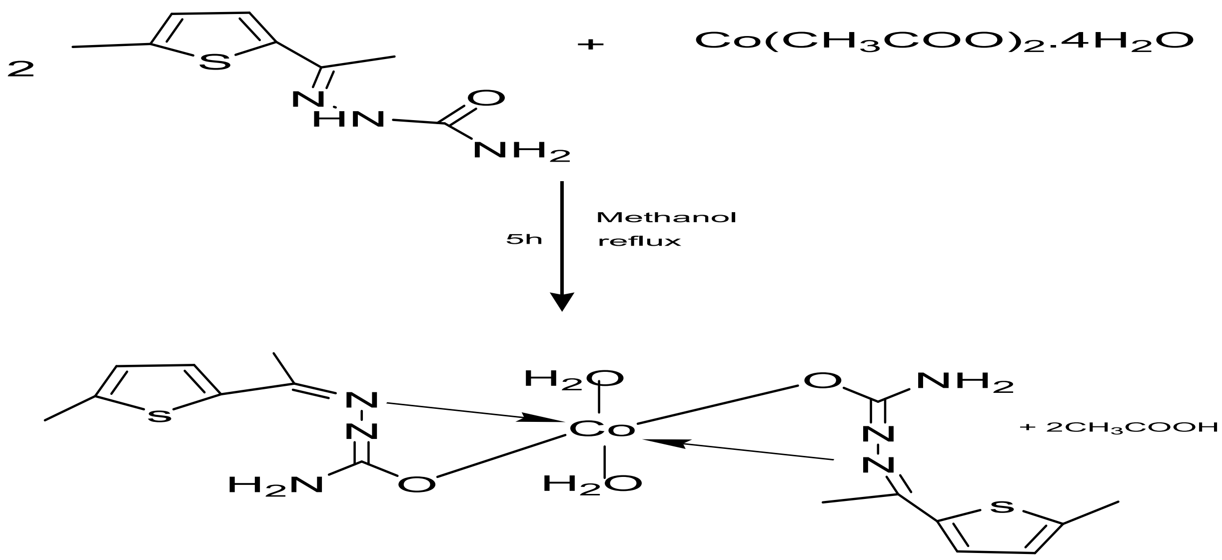
Semicarbazone was synthesized by mixing 2-acetyl-5-methylthiophene, semicarbazide hydrochloride and sodium acetate trihydrate (equimolar ratio) in methanol (Scheme I). AcMeSC was synthesized by the standard procedure, as available in the literature. [15-16]



Scheme I: Synthesis of 2-acetyl-5-methylthiophene semicarbazone

III. COMPLEX SYNTHESIS

The 2-AcMeSC cobalt complex was synthesized in a methanolic solution of ligand, by mixing it with a solution of Co(II) acetate (in methanol) in 2:1 molar ratio respectively, refluxing the mixture for 5 hours, and drying it in vacuum over fused $CaCl_2$ (Scheme II).



Scheme II : Synthesis of 2-AcMeSC Co(II) complex

IV. CHARACTERIZATION

Infrared study

The absence of a υ(C=O) band (1745 cm^{-1}) of ketone, and the presence of a υ(C=N) band occurred [17] at 1622-1632 cm^{-1} in the ligand spectra, indicated condensation between the ketonic group and the amino group of semicarbazide. In comparison with the semicarbazone spectra, the Co(II) complex exhibited the ν(C=N) band in the

1590–1603 cm^{-1} region, showing the band shift to lower wave numbers, and indicating that the nitrogen was coordinated to the metal ion. The υ(C=O) band disappearance at 1700 ± 100 cm^{-1} (initially present in the semicarbazone spectra), in the Co(II) complex spectra, indicated that the participation of ketonic oxygen resulted in a bond formation. The appearance of new bands in the 579–560 and 386-322 cm^{-1} regions assignable to υM-O and υM-N, respectively, reflected the bonding of the metal ions to oxygen and nitrogen atoms [18-21].

Elemental analysis-
On the C, H, N, O and S elemental analyzers, elemental analysis was performed using a microanalytical approach.

Sr.No.	Specification	Colour & state	Yield (%)	Elemental analysis				
				C	H	N	S	Co
1.	2-Acetyl-5-methylthiophene semicarbazone ($C_8H_{11}N_3OS$)	Yellow Solid	78	48.71 (48.69)	5.62 (5.61)	21.30 (21.28)	16.26 (16.25)	-
2.	Cobalt(II) complex	Dark yellow solid	**75**	39.42 (39.38)	4.96 (4.95)	17.24 (17.22)	13.16 (13.14)	12.09 (12.07)

V. CYCLIC VOLTAMMETRIC STUDIES

- For voltammetric analysis, stock solutions of ligand was prepared by mixing compound solution, with solvents viz., DMF, acetone, methanol and buffer solutions like Britton-Robinson(BR) and Phosphate buffers making the net volume 10 mL.
- Experimental solution of metal complex was prepared by mixing 1mL of 0.01Mcomplex solution, 8mL solvent.
- The three electrodes system (glassy carbon electrode-working electrode, Ag/AgCl-reference electrode and a Pt wire-auxillary electrode) was used for analysis. The kinetic parameters were calculated by following equations [22-24]:

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

$$I_p = 3.01\times10^5\, n\left(\alpha_n\right)^{1/2} A\, C\, D_0^{1/2}\, v^{1/2}$$

$$E_P = -\frac{RT}{\alpha_n F}\left[0.78 + \ln\left(\frac{D_0^{1/2}}{k^{\circ}_{f,h}}\right) + \ln\left(\frac{\alpha_n F v}{RT}\right)^{1/2}\right]$$

Most of the cyclic voltammograms were recorded with an initial potential (Ei) value of +800mV and a switching potential value (Es) of -1600 mV for semicarbazone and Ei +800mV and Es -1000mV for metal complex. The recorded voltammograms and their tabulated data are shown below:-

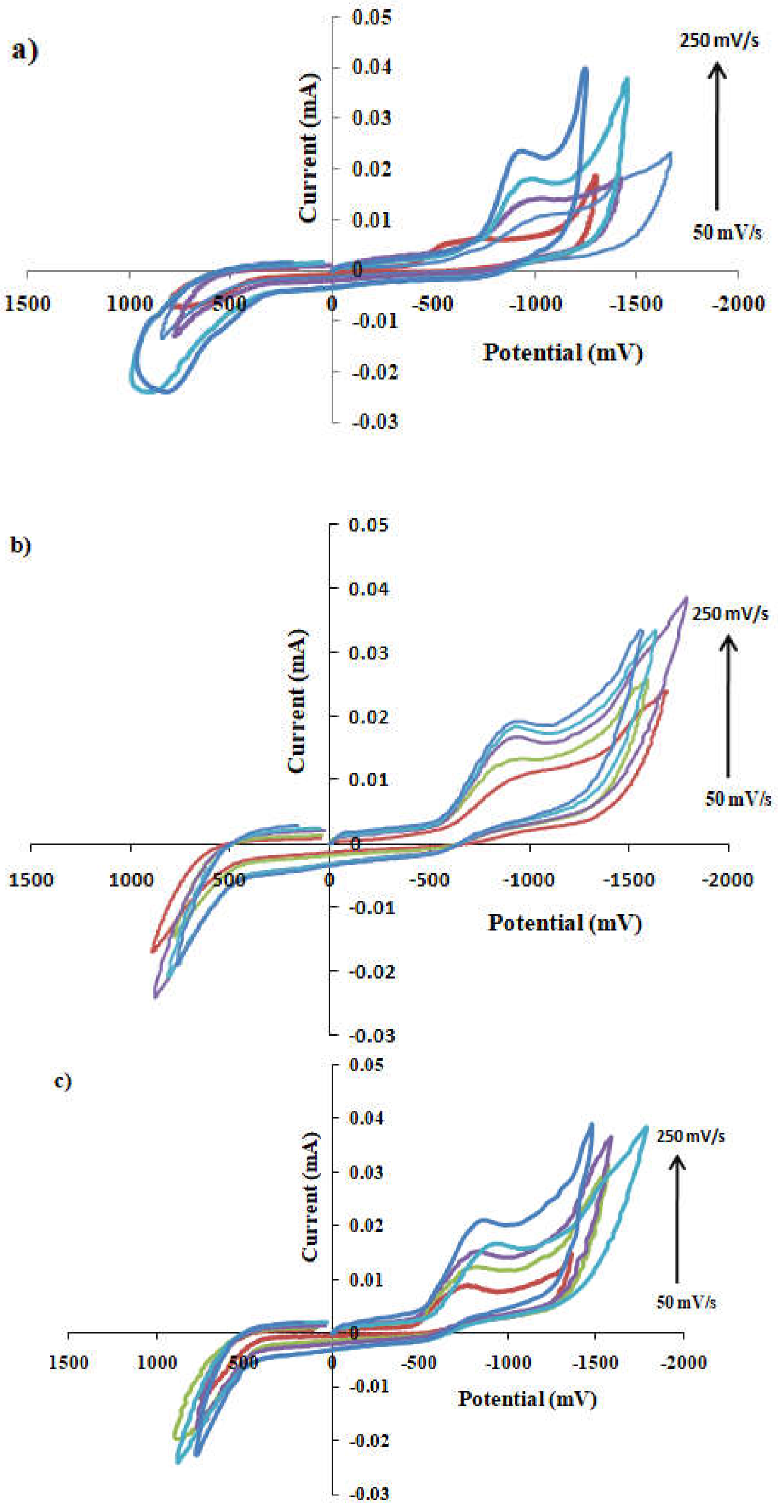


Figure: 1 Cyclic voltammograms of AcMeSC in acetone-BR buffer at a)pH 5 b)pH 7 c)pH 8

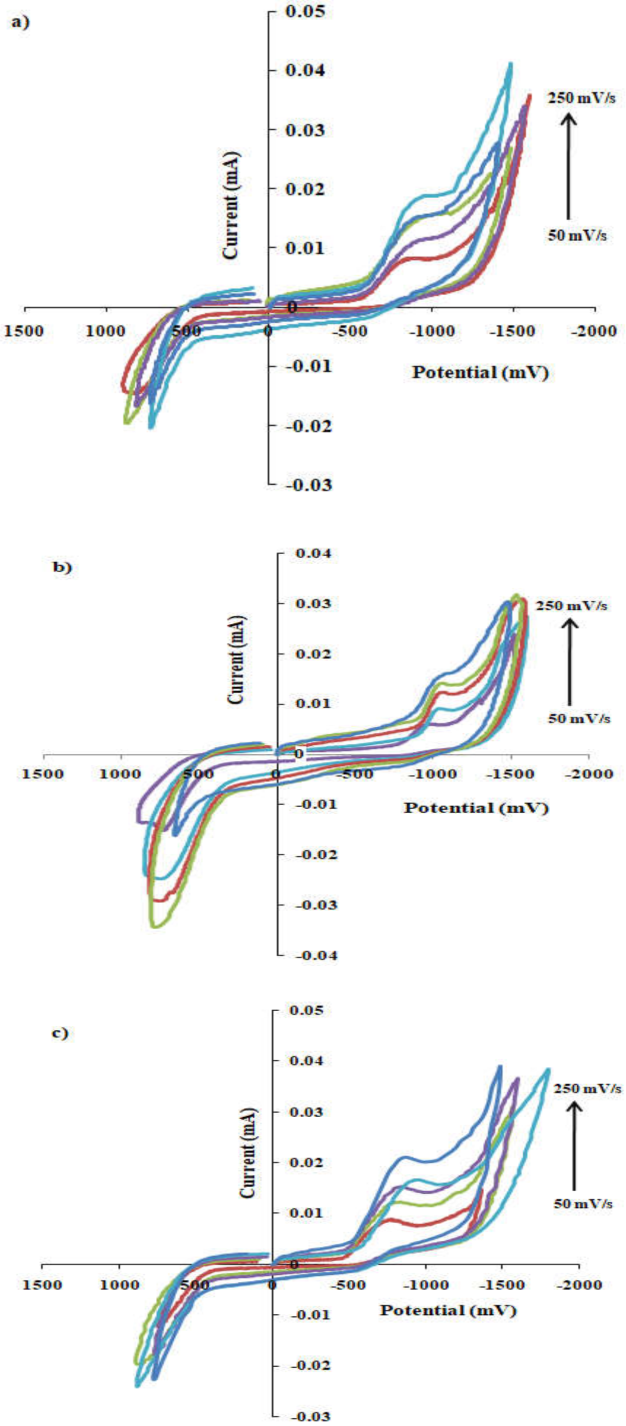


Figure: 2 Cyclic Voltammograms of AcMeSC in methanol-BR buffer at a)pH 5 b)pH 7 c) pH 8

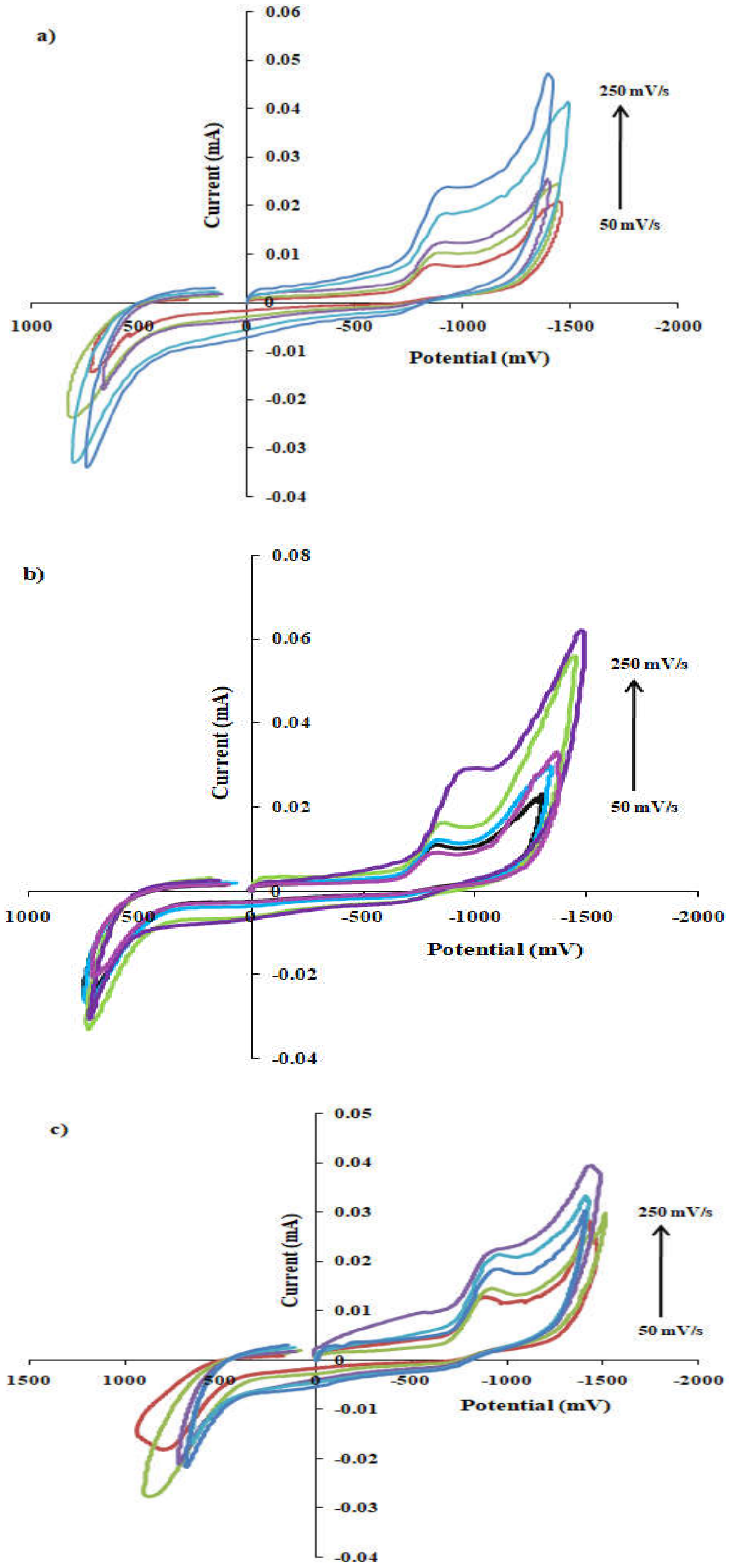


Figure: 3 Cyclic Voltammograms of AcMeSC in methanol-phosphate buffer at a)pH 5 b)pH 7 c)pH 8

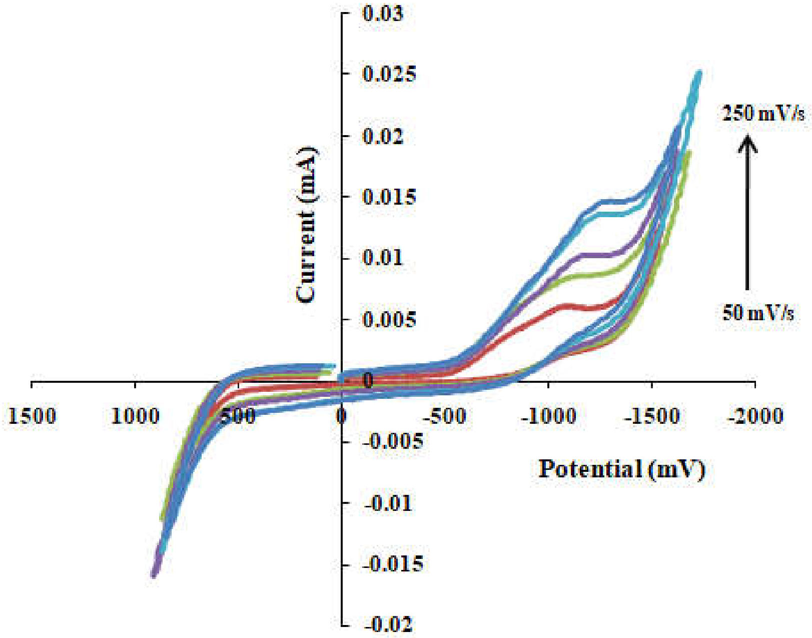


Figure: 4 Cyclic Voltammogram of AcMeSC in DMF-BR buffer at pH 8

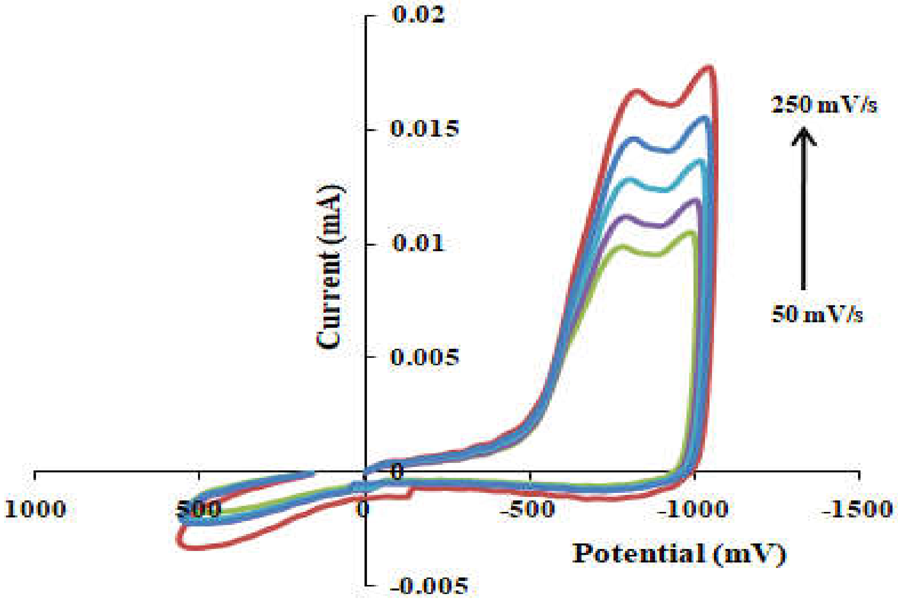


Figure: 5 Cyclic voltammograms of 1mM Co(II) complex of AcMeSC in DMF.

Table I
Voltammetric parameters of 1mM 2-acetyl-5-methylthiophenesemicarbazide in methanol- BR buffer at different pH levels

pH	v mVs^{-1}	E_{pc} mV	I_{pc} µA	$E_{p/2}$ mV	$I_{pc}/v^{1/2}$	α_n	$D_0^{1/2}$x10^3 cm^{2}s^{-1}	$k°_{f,h}$ cm.s^{-1}
5	50	-800	5.5	-620	0.77	0.265	4.7555	1.91E-06
	100	-860	8.3	-680	0.83	0.266	5.0650	1.06E-06
	150	-960	8.8	-710	0.72	0.190	5.1888	5.56E-06
	200	-975	9.7	-720	0.68	0.187	4.9920	5.41E-06
	250	-990	11.6	-730	0.73	0.183	5.3977	6.06E-06
7	50	-805	6.7	-661	0.95	0.331	5.1834	2.82E-07
	100	-880	10.8	-690	1.08	0.251	6.7847	1.90E-06
	150	-975	11.2	-720	0.91	0.187	6.6557	7.22E-06
	200	-990	12.1	-760	0.85	0.207	5.9144	2.77E-06
	250	-1000	12.8	-780	0.80	0.217	5.4721	1.67E-06
8	50	-930	6.9	-840	0.97	0.530	4.2186	4.29E-11
	100	-985	10.9	-925	1.09	0.795	3.8476	5.92E-16
	150	-1010	11.4	-950	0.93	0.795	3.2835	2.24E-16
	200	-1040	14.1	-960	0.99	0.596	4.0646	3.1E-13
	250	-1060	15.8	-980	1.01	0.595	4.0773	2.05E-13

Table II
Voltammetric parameters of 1mM 2-acetyl-5-methylthiophenesemicarbazide in acetone- BR buffer at various pH levels.

pH	v mVs^{-1}	E_{pc} mV	I_{pc} µA	$E_{p/2}$ mV	$I_{pc}/v^{1/2}$	α_n	$D_0^{1/2}$x10^3 cm^{2}s^{-1}	$k°_{f,h}$ cm.s^{-1}
5	50	-570	5.5	-450	0.77	0.3972	3.8848	1.1E-06
	100	-820	7.0	-720	0.70	0.4770	3.1899	1.62E-09
	150	-910	13.0	-740	1.06	0.2801	6.3123	4.96E-07
	200	-940	17.7	-785	1.25	0.3070	7.1094	1.58E-07
	250	-950	23.1	-810	1.46	0.3407	7.8770	4.69E-08
7	50	-860	8.6	-530	1.21	0.1444	10.0734	9.35E-05
	100	-970	10.9	-730	1.09	0.1987	7.6961	5.73E-06
	150	-1000	13.8	-820	1.12	0.2510	7.0785	5.36E-07
	200	-1020	17.9	-890	1.26	0.3407	6.8249	1.40E-08
	250	-1030	24.3	-920	1.53	0.3669	7.9856	4.48E-09
8	50	-920	8.8	-560	1.24	0.1445	10.3041	7.96E-05
	100	-990	11.7	-760	1.17	0.2073	8.0878	3.78E-06
	150	-1005	14.7	-880	1.20	0.3289	6.5869	2.28E-08
	200	-1025	18.2	-920	1.28	0.3669	6.6869	3.75E-09
	250	-1040	24.6	-970	1.55	0.3975	7.7668	6.99E-10

Table III
Voltammetric parameters of 1mM 2-acetyl-5-methylthiophenesemicarbazide in methanol- phosphate buffer at different pH levels.

pH	ν mVs^{-1}	E_{pc} mV	I_{pc} µA	$E_{p/2}$ mV	$I_{pc}/\nu^{1/2}$	α_n	$D_0^{1/2}$x10^3 cm^{2}s^{-1}	$k°_{f,h}$ cm.s^{-1}
5	50	-820	7.1	-700	1.00	0.3975	5.0124	2.95E-08
	100	-880	10.3	-725	1.03	0.3077	5.8441	2.95E-07
	150	-890	12.4	-740	1.01	0.3180	5.6507	1.58E-07
	200	-895	18.1	-780	1.28	0.4147	6.2552	6.46E-09
	250	-920	23.9	-800	1.51	0.3975	7.5458	9.43E-09
7	50	-822	10.5	-710	1.48	0.4258	7.1622	1.71E-08
	100	-885	11.5	-750	1.15	0.3533	6.0893	5.65E-08
	150	-900	13.2	-790	1.07	0.4336	5.1514	2.59E-09
	200	-922	18.4	-810	1.30	0.4258	6.2754	2.85E-09
	250	-935	24.1	-830	1.52	0.4542	7.1182	9.57E-10
8	50	-832.3	11.5	-715	1.62	0.4076	8.0175	2.84E-08
	100	-888	13.6	-760	1.36	0.3726	7.0123	3.30E-08
	150	-905	19.9	-795	1.62	0.4336	7.7662	3.58E-09
	200	-930	20.4	-822	1.44	0.4416	6.8319	1.56E-09
	250	-940	24.2	-840	1.53	0.4770	6.9892	3.82E-10

Table IV-
Voltammetric parameters of 1mM 2-acetyl-5-methylthiophenesemicarbazide in BR-buffer in numerous solvents at pH 8.

Solvents	ν mVs^{-1}	E_{pc} mV	I_{pc} µA	$E_{p/2}$ mV	$I_{pc}/\nu^{1/2}$	α_n	$D_0^{1/2}$x10^3 cm^{2}s^{-1}	$k°_{f,h}$ cm.s^{-1}
Acetone	50	-920	8.8	-560	1.24	0.1445	10.3041	7.96E-05
	100	-990	11.7	-760	1.17	0.2073	8.0878	3.78E-06
	150	-1005	14.7	-880	1.20	0.3289	6.5869	2.28E-08
	200	-1025	18.2	-920	1.28	0.3669	6.6869	3.75E-09
	250	-1040	24.6	-970	1.55	0.3975	7.7668	6.99E-10
Methanol	50	-930	6.9	-840	0.97	0.530	4.2186	4.29E-11
	100	-985	10.9	-925	1.09	0.795	3.8476	5.92E-16
	150	-1010	11.4	-950	0.93	0.795	3.2835	2.24E-16
	200	-1040	14.1	-960	0.99	0.596	4.0646	3.1E-13
	250	-1060	15.8	-980	1.01	0.595	4.0773	2.05E-13
DMF	50	-1055	5.9	-845	0.83	0.2271	5.5106	7.08E-07
	100	-1100	8.4	-860	0.84	0.1987	5.9309	1.62E-06
	150	-1120	9.4	-890	0.76	0.2073	5.3055	8.68E07
	200	-1240	13.3	-915	0.94	0.1467	7.7280	7.54E-06
	250	-1285	14.5	-960	0.91	0.1466	7.5383	5.71E-06

Table V: Voltammetric parameters of Co(II) complex of 2-AcMeSC in DMF-$NaClO_4$.

Complex Conc.	**v (mVs^{-1})**	**E_{pc} (mV)**	**$E_{p1/2}$ (mV)**	**I_{pc} (µA)**	**$Ipc/v^{1/2}$**
1mM	50	-739.05	-610	09.49	1.3422
	100	-766.15	-660	11.09	1.1090
	150	-776.95	-675	12.65	1.0334
	200	-787.91	-690	14.44	1.0212
	250	-799.02	-703	16.48	1.0423

VI. CONCLUSIONS

Effect of scan rate: In the voltammetric experiments , a single peak was observed in cathodic side indicating an irreversible nature .The peak potential value shifted towards more negative direction as the scan rate increases. As shown in Table I at pH 5, potential (Epc) increases as -800, -860, -960, -975, -990mV at scan rate 50, 100, 150, 200, 250 mV/s respectively indicating that the electrochemical process was irreversible. Similar trends were observed at various pH levels in the considered solvent media as depicted in Figures 1-3.

Effect of pH: The pH effect upon 2-AcMeSC reduction was investigated as concluded in Tables 1 to 3. It can be seen as in Table II at a constant scan rate of 50mV/s, the peak potential (Epc) value changes from -570, -860, -920mV at pH 5, 7, 8 respectively. Therefore it can be concluded that with the increase in pH, peak potential shifted to more negative values. A rapidly reducible protonated intermediate formation might be the reason for the obtained results. A graphical representation in figure 6 illustrates the pH effect on peak potential values. At other sweep rates viz., 100mV/s to 250mV/s similar trends were observed.

Effect of solvent: For a comparative study, peak potential values were calculated in three solvents viz, acetone, methanol and DMF at a constant pH and same buffer(BR buffer). As evident from Table IV it can be seen that peak potential shifted to more cathodic side in DMF solvent due to difficulty in reduction. This result can be inferred by the dielectric constant values of DMF, methanol and acetone – 36.71, 32.7 and 20.7 respectively which suggests their decreasing polarity and hence difficulty in reduction in DMF > Methanol > Acetone.

Effect of Buffer: Two different buffer media, Phosphate and BR buffers were used for cyclic voltammetric studies. At At a constant pH of 5 and scan rate 50mV/s, the peak potential in BR and Phosphate buffer are respectively -930mV and -832.3mV which can be overseen from Table I and III. Therefore, peak potential is more negative in BR buffer in comparison with Phosphate buffer. This can be inferred due to easy reduction in more polar phosphate buffer as concluded in figure7. In the above studies we concluded that at other pH situations like 7 or 8, similar trends were observed as in table I and III.

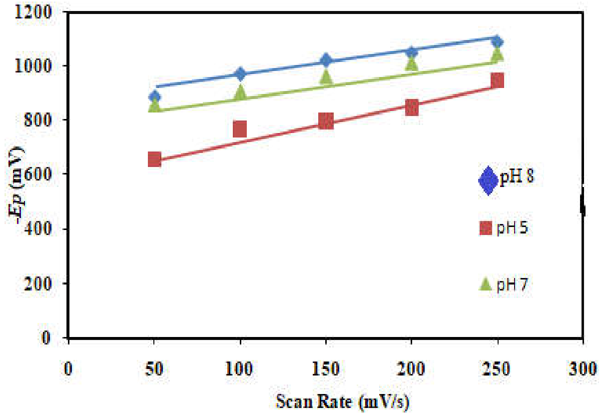


Figure 6. Potential vs. scan rate in acetone with BR buffer (pH 5, 7 and 8).

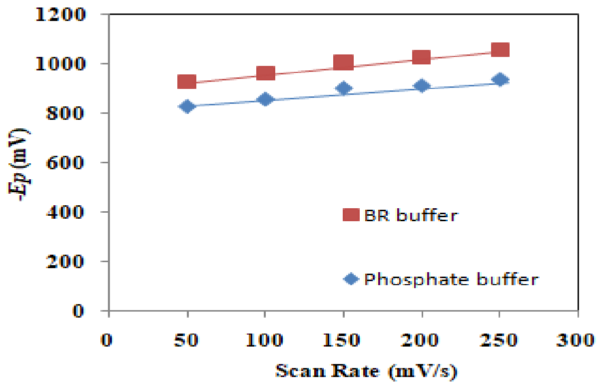


Figure 7: Potential vs. scan rate in methanol at pH 8 for different buffers.

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