Electrochemical study of Mn^{2+} Redox system on 4-hydroxybenzylidene-Carbamide -CTAB modified Glassy Carbon Electrode

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Abstract

The 4-hydroxybenzylidenecarbamide-cetyltrimethylammoniumbromide modified glassy carbon electrode (ligand-CTAB/GCE) is prepared by drop coating technique. The complexation effect of Mn^{2+} with the ligand is studied through scan rate effect, concentration effect in cyclic voltammetry technique. Transfer coefficient number (αn) of Mn^{2+} ion on ligand-CTAB/GCE is found to be 0.204. The surface concentration of electroactive species (Γ) on ligand-CTAB/GCE was found to be 0.9436 x 10^{-8} molcm^{-2}. The rate constant for manganese ion redox system is first order and found to be 1.857s^{-1}. The optimum pH for manganese redox system on ligand-CTAB/GCE is found to be 6. The interference of Cu^{2+}, Cd^{2+} and Hg^{2+} ions on manganese redox system is investigated through the interference study. Cyclic voltammetry, chronoamperometry and chronocoulometry study shows that manganese redox system has diffusion controlled process. The stability of the film on GCE is investigated through the multisweep cycle experiment and is found to be stable.

Keywords: Cyclic voltammetry, chronoamperometry, chronocoulometry, interference study, pH effect.

Introduction

Compound containing an azomethane group (-CH=N-) are known as Schiff bases. Schiff bases are generally bi- or tri-dentate ligands capable of forming very stable complexes with transition metals. Schiff base metal complexes with different drugs are relatively less studied. The stable and versatile complex was formed between metal element and Schiff base. The chelate formation was observed from the construction of the molecular model., Metal complexes have higher pharmacological activity of antibiotics as compared to the free ligands. In many cases the pharmacological activity of antibiotics after complexation with metals is enhanced as compared to that of the free ligands[1-4].

Manganese is an essential element, which plays an important role in the activation of many enzymes involved in metabolic process of man, animals and plants. In the natural environment manganese can occur in several oxidation states (+II, +III, and +IV), in soluble and insoluble forms; its concentration in natural waters ranges from 0.001 to 1.0µgml^{-1}. The maximum allowed content in water varies according to its proposed use: for domestic water it is 0.05µgml^{-1} and for irrigation water is 2.0µgml^{-1}. Because manganese is important, highly sensitive methods are required for its detection. Various techniques have been used for the detection of manganese in biochemical and environmental samples, such as spectrophotometry and atomic absorption spectrometry. Usually such techniques need enrichment steps and furthermore, as regards selectivity and sensitivity, often favour only one of these two aspects. For these reasons, electroanalytical techniques are the most used in metal detection in complex samples.

Surfactant is a linear molecule with a hydrophilic (attracted to water) head and a hydrophobic (repelled by water) end. Due to its unique molecular structure, surfactants have been extensively used in the fields of electrochemistry and electroanalytical chemistry for various purposes. Surfactants, containing hydrophobic and hydrophilic groups, can change the properties of the electrode/solution interface and subsequently influence the electrochemical process of other substances[5]. Adsorption of surfactant aggregates on the electron transfer, gently enhance the peak current, change the redox potential or charge transfer coefficients or diffusion coefficients as well as alter the stability of electrogenerated intermediates or electrochemical products[6,7].

In this work, we will investigate the preparation of 4-hydroxybenzylidenecarbamide-CTAB modified glassy carbon electrode and its use in study of complexation of Mn^{2+} with 4-hydroxybenzylidenecarbamide through electrochemistry.   .

Reagents: CTAB (HIMEDIA), manganous sulphate (Rankem) p-hydroxybenzaldehyde (HIMEDIA), urea (Rankem), alcohol, chloroform (Fisher Scientific).

Material and Methods

Electrochemical workstations of CHI. USA: Model 600D with potentiostate driven by electroanalytical measuring softwares was connected to PC computer to perform cyclic voltammetry (CV), chronocoloumetry (CC), and chronoamperometry (CA). An Ag/AgCl (3M KCl) and platinum wire are used as a reference and counter electrode respectively. The working electrode used in this study was ligand-CTAB/GCE obtained by evaporated ligand and CTAB on GCE using chloroform as a solvent.

Polishing of Glassy Carbon Electrode: The glassy carbon electrode is polished with fine alumina powder (0.3micron) on a wet polishing cloth. To do so a part of the cloth is mode wet with deionized water and alumina powder is sprinkled on it. The glassy carbon electrode is then polished on this surface by pressing softly the electrode against the polishing surface in the end for 3-5 minutes. The electrode is then thoroughly washed with deionized water. At this point the electrode surface would look like a shiny black mirror.

Experimental procedure: First of all, the cell and the Teflon top (with the counter electrode) are cleaned with deionized water; any excess water is wiped off with a tissue paper. A small magnetic stir-bar is put in the cell. The cell is filled with desired volume of the analyte solution and the Teflon cap is placed on the cell. The reference electrode and the purging tube are inserted through the holes. The purging tube should be halfway inside the solution. A range of metal ion concentration (1mM to 5mM) is used.

Results and Discussion

Synthesis of Schiff base: The Schiff base is prepared by mixing an ethanolic solution (30ml of 1.22g 0.01mol) of p-hydroxybenzaldehyde (0.60g, 0.01mol) of urea in the same volume of ethanol. Few drops of dil HCl were added to adjust pH 4 and the obtained mixture then refluxes with stirring for 2h. The precipitate is collected by filtration through Buchner funnel, recrystallized from ethyl alcohol and derived at ambient temperature. The synthetic scheme 1.

Chracterization of ligand: IR spectral data (KBr disc, γ/cm^{-1}): Usual broad band in the region around 3826 due to the NH_2 stretching frequency of the amide group of the ligand. The band at 1597 due to the U(C=N) stretching frequency. The band at 1667 due to the presence of carbonyl group. (C=O). The band at 3167 due to the phenolic OH group.

^{1}H NMR data (δ ppm in $CDCl_3$): A singlet at 3.5 equivalent to 1H indicates Ar-OH, A multiplet centered at 6.9 and 7.7 equivalent to 4H is due to aromatic protons. A singlet at 9.7 is due to amide NH resonances. A broad peak at 10.5 is due to -CH=N-.

Mass spectrum data: m/z, 164.25. Molecular formula: $C_8H_8N_2O_2$

Preparation of ligand-CTAB/GCE modified glassy carbon electrode: The surfactant is added to control and keep the size of the particles small so that the surface area is higher and diffusion of counter ions is more facile. CTAB is a commonly used surfactant for obtaining small and uniform sized ligand particles. Hence in the present study we have used this surfactant and soft template as it possesses long chains. The soft CTAB is easily removed by washing with water.

A solution evaporation technique was employed[8,9]. It is done by evaporating a certain quantity of ligand and CTAB solution onto the clean GCE surface. The solution of 1mM CTAB is prepared by dissolving CTAB in chloroform to form a colourless solution. The solution of 0.1% of ligand is prepared by dissolving ligand in chloroform to form a colourless solution. A 10μL solution of CTAB is then deposited onto GCE by successive fast drying of the CTAB droplets to produce thin film of CTAB. A 10μL solution of ligand is then deposited onto CTAB/GCE by successive fast drying of the ligand droplets to produce ligand-CTAB film on GCE.

Electrochemical study of Mn^{2+} ion on ligand-CTAB modified glassy carbon electrode: Scan rate effect: Figure 1A shows the cyclic voltammogram of Mn^{2+} at the ligand-CTAB/GCE when the scan rate (v) varies from 10 to 160mV/s and its parameters are tabulated in table 1. As shown in Fig.1B (Ipc Vs $v^{1/2}$) peak currents of Mn^{2+} are proportional to the scan rate, which indicates that the electrode process is diffusion controlled. From figure 1C, the slope of the linear plot of Ipc vs V and the surface concentration of the electroactive species (Γ) can be estimated to be about 0.9436×10^{-8} mol cm^{-2} according to equation 1[10].

$$Ip = n^2F^2v A\Gamma 4RT \qquad (1)$$

As shown, with increasing scan rate, the peak potential is shifted to a more negative potential. Becaues of the irreversible electrode process of the reduction reaction of Mn^{2+}, the Laviron's equation[11] was used to estimate αn and ks values by using the equation 2.

$$Ep = E^0 + RT/\alpha nF[In(RTks/anF)-Inv] \qquad (2)$$

Where α is the electron transfer coefficient, ks is the standard rate constant of the surface reaction, v is the scan rate, n is the electron transfer number and E^0 is the formal potential. ks and αn values can be calculated from the intercept and slope of the linear plot of Ep with respect to Ln v, if the value of E^0 is known.

The E^0 value at ligand-CTAB film modified GCE can be deduced from the intercept of Ep vs v plot on the ordinate by extrapolating the line to $v = 0$ (figure 1D). Knowing E^0 and from the graphical representations of Ep vs Ln v for Mn^{2+} in the presence of Mn^{2+} (figure 1E), the values of $\alpha n = 0.204$ and $ks = 1.857$ s^{-1} are obtained from the slope and intercept, respectively.

Concentration effect: Figure (2A) shows the calibration curve of Mn^{2+} ion in different concentration (1mM-5Mm) in 0.1M NH_4F and its parameters are tabulated in table 2. The calibration plot (figure 2B) is performed at the ligand-CTAB/GCE with a good linearity of cathodic current versus Mn^{2+} as described by $Y = 1.562 X + 0.685$, $R^2 = 0.997$. A sharp reduction peak at -0.4V shows that the formation of complex between Mn^{2+} ion and ligand. The following type of reduction would be possible.
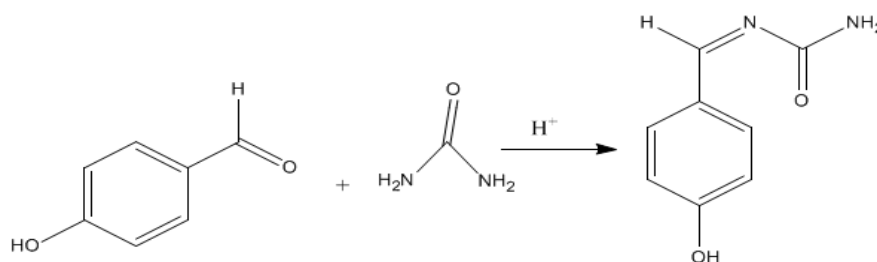
Sheme-1
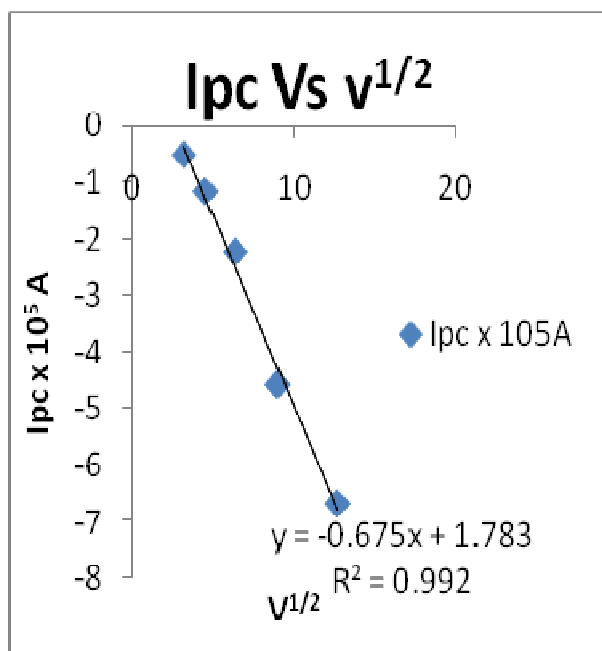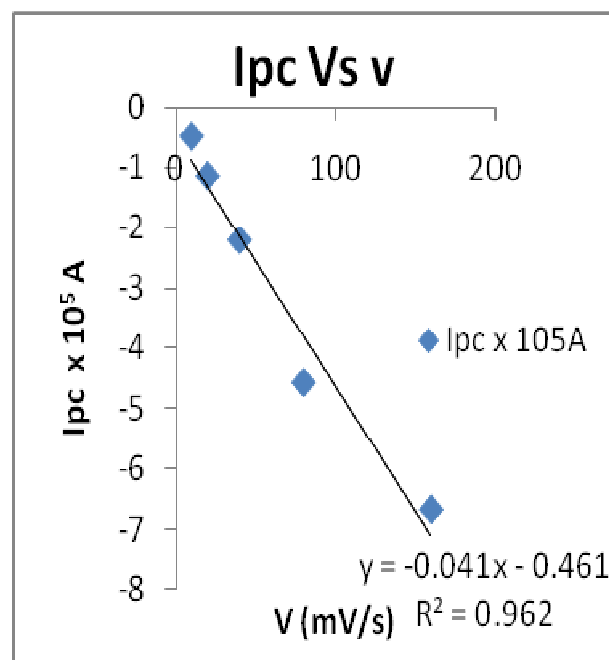**Synthesis of 4-hydroxybenzylidenecarbamide**
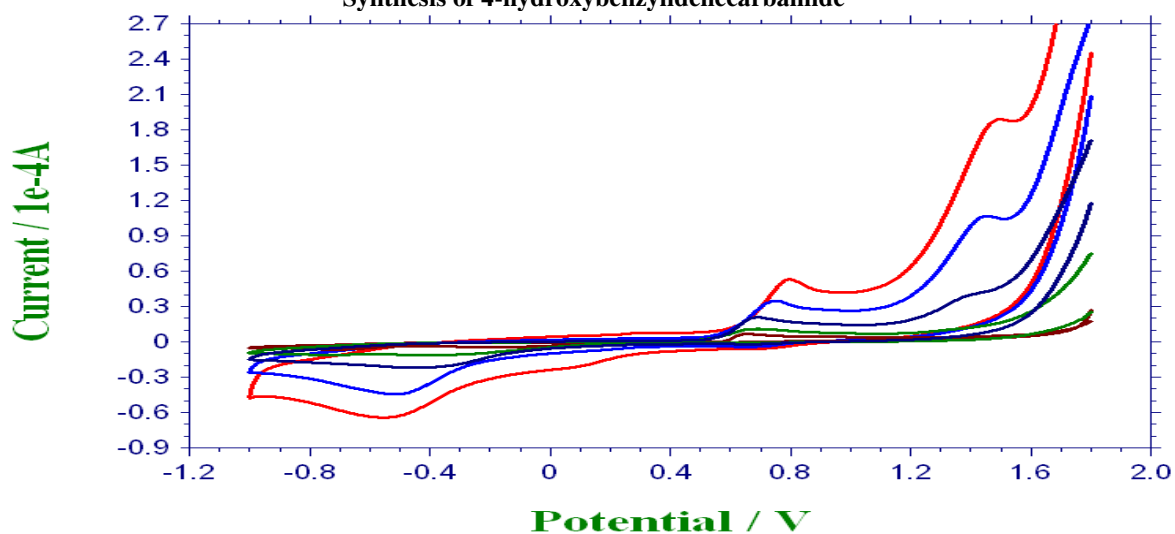
Figure-1A
CV for 1mM Mn^{2+} ion on ligand-CTAB/GCE in 0.1M NH$_4$F solution at different sweep rates

$$y = -0.675x + 1.783$$
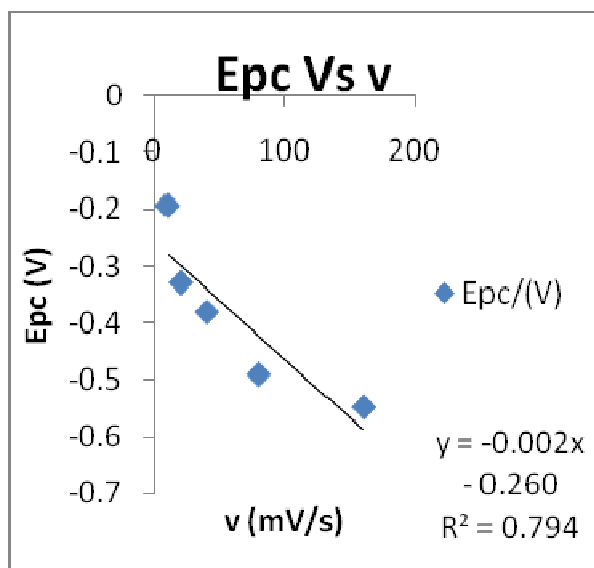$$R^2 = 0.992$$

Figure-1B

$$y = -0.041x - 0.461$$
$$R^2 = 0.962$$
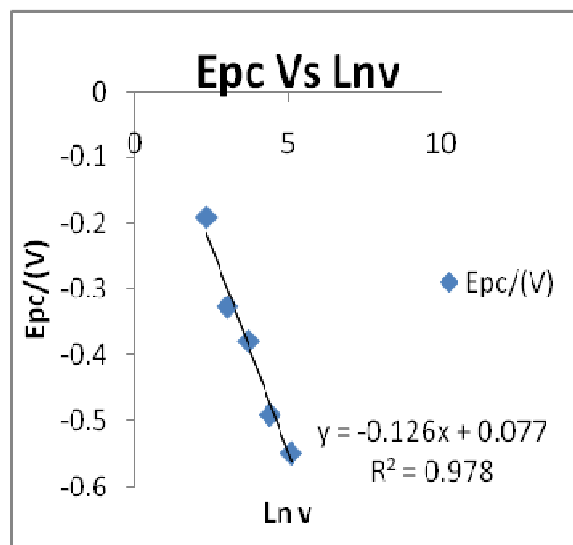
Figure-1C

Figure-1D

Figure-1E

Figure-1B) A plot of Ipc Vs $v^{1/2}$; **C)** A plot of Ipc Vs v; **D)** A plot of Epc Vs v; **E)** A plot of Epc Vs Lnv

Table-1
Cyclic Voltammetric parameters for 1mM Mn^{2+} ion on ligand-CTAB/GCE in 0.1M NH_4F solution at different sweep rates

Sweep rate (mV/s)	Ipc x 10^5 (A)	Epc (V)	Ipa x 10^5 (A)	Epa (V)
10	-0.4949	-0.1918	0.6974	0.6551
20	-1.145	-0.3279	1.125	0.6970
40	-2.214	-0.3799	2.186	0.6867
80	-4.574	-0.4900	3.523	0.7494
160	-6.678	-0.5476	5.583	0.7964

i) $H_2O \longrightarrow OH_{ads} + H^+ + e^-$

ii) $Mn^{2+} + 2OH_{ads} \longrightarrow MnO_2 + 2H^+$

iii) $MnO_2 + H^+ + e^- \longrightarrow MnOOH$

iv) $MnOOH + 3H^+ + e^- \longrightarrow Mn^{2+} + 2H_2O$

v) $Mn^{2+} + Ligand \longrightarrow Mn\text{-}Ligand \ complex$

In oxidation steps three peaks at 0.2V, 0.7V and 1.4V are appeared. It may follow the ECE mechanism.

i) $Mn^{2+}\text{- Ligand complex} \longrightarrow Mn^{3+}\text{-ligand complex} + e^-$

ii) $Mn^{3+} + 2H_2O \longrightarrow MnOOH + 3H^+$

iii) $MnOOH$

$\longrightarrow MnO_2 + H^+ + e^-$

(or)

Disproportionation mechanism

i) $Mn^{2+}\text{-ligand complex} \longrightarrow Mn^{3+}\text{-ligand complex} + e^-$

ii) $2Mn^{3+} \longrightarrow Mn^{2+} + Mn^{4+}$

iii) $Mn^{4+} + 2H_2O \longrightarrow MnO_2 + 4H^+$

The peak current values are increased with increasing concentration which suggests that diffusion controlled process.

pH effect: The Cyclic Voltammogram for 1mM Mn^{2+} ion on ligand-CTAB/GCE at different pH's is shown in figure 3A and its parameters are tabulated in table.3. The pH solution is varied from 2 to 10 to determine its effect on the formation of complex between Mn^{2+} and ligand on ligand-CTAB/GCE surface. At pH 2 and 4 Mn^{2+} form electroinactive complex which is confirmed from absence of characteristic peaks of manganese ion. It is observed that the oxidation current of Mn^{2+} gradually and linearly decreases with increasing of pH from 6 to 10 accompanied by a linear shift in oxidation potential which satisfies the linear equation of $Ipa(\mu A) = 1.691pH + 0.242$ with correlation coefficient of $R^2 = 0.570$ (figure 3B) and $E(V) = -0.108pH + 1.299$ with correlation coefficient of $R^2 = 0.975$ (figure 3C).

Outside this range of pH lower oxidation and reduction peak heights are observed. At low pH (< 4), there is a tendency for incomplete precipitation of the insoluble dioxide, which leads to a lower peak height. However, at higher pH (>10), the decrease in the peak height can be attributed to the increasingly competitive production of $Mn(OH)_2$, which can react with

dissolved oxygen to precipitate $Mn(OH)_4$ in solution. The literature shows that the electrode reaction depends on the solubility product of $Mn(OH)_2$ [12]. Consequently, the use of an electrolyte in neutral or slightly acid solution is suggested. Thus pH 6 is chosen because a very well defined reduction peak is obtained.
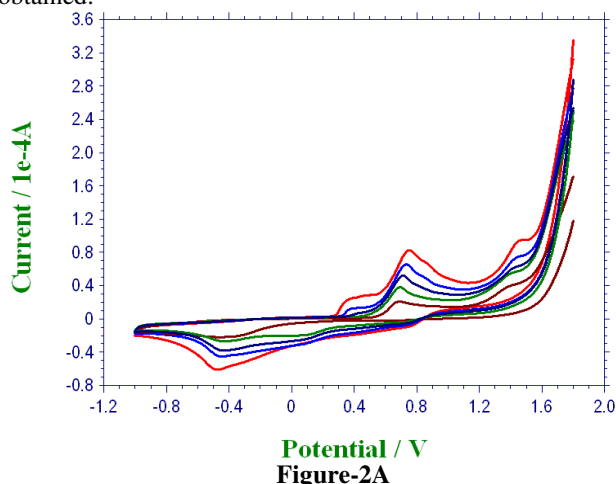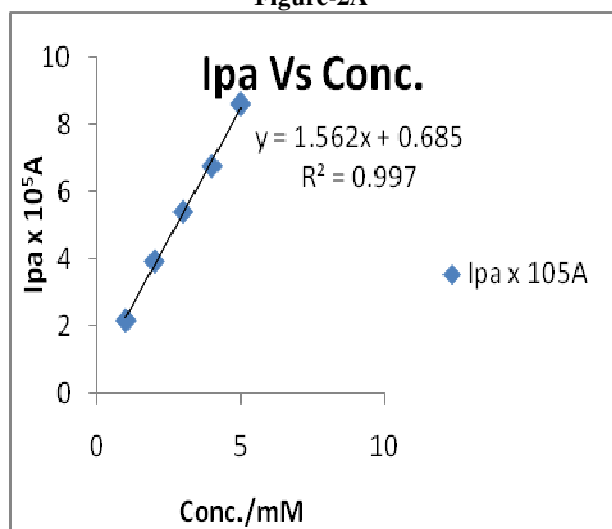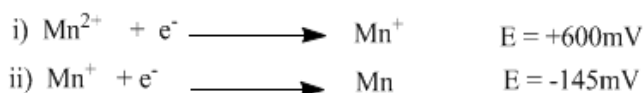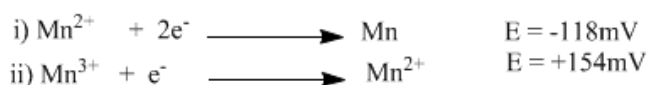

Figure-2A

Figure-2B
(A) Cyclic Voltammogram for different concentrations of Mn^{2+} ion on ligand-CTAB/GCE at 40mV/s. B) A plot of Ipa Vs Conc

The mechanism of the reduction steps is explained as follow:

$$i) \quad Mn^{2+} + e^- \longrightarrow Mn^+ \qquad E = +600mV$$
$$ii) \quad Mn^+ + e^- \longrightarrow Mn \qquad E = -145mV$$

On the other hand, the potential of the reduction peak of Mn^{2+} to $Mn(0)$ value is explained as follow [13].

$$i) \quad Mn^{2+} + 2e^- \longrightarrow Mn \qquad E = -118mV$$
$$ii) \quad Mn^{3+} + e^- \longrightarrow Mn^{2+} \qquad E = +154mV$$

The characteristic peak for the above reduction process is not observed. The new peaks at -0.6V, +0.4V and +0.6V confirms the formation of complex between ligand and Mn^{2+}.

Table-2
Cyclic Voltammetric parameters for different concentrations of Mn^{2+} ion on ligand-CTAB/GCE at 40mV/s

Conc. (mM)	Ipc x 10^5 (A)	Epc (V)	Ipa x 10^5 (A)	Epa (V)
1	-2.214	-0.4009	2.186	0.6867
2	-2.688	-0.4166	3.936	0.6918
3	-3.898	-0.4375	5.400	0.7179
4	-4.651	-0.4482	6.749	0.7337
5	-6.258	-0.4849	8.591	0.7494

The potentials of the anodic peak and of the cathodic peak shift towards more negative values with increasing pH. The shape and position of the anodic peaks suggests that the oxidation reaction is diffusion controlled.

From figure (3D), the half-wave potential, $E_{1/2}$ of manganese redox system is pH-dependent. One linear segment is found with slope values of -47mV/pH. The total number of protons that also participates in the redox process of Mn may vary in accordance with the pH range. Depending on the number of protons taking part in the redox process with two electron transfer, the $E_{1/2}$ will shift by -59.2mV/pH ($2H^+$), -29.6mV/pH (H^+) and 0.0mV/pH (without H^+) [14]. So there are two protons transferred in the redox reaction in the pH range of 2-10. Thus the thermodyanamic driving force for the catalysis will vary with pH, making the peak currents and the shapes of the cyclic voltammetry change at different pH values. The results obtained show that the pH 6.0 is optimum for electrochemical behavior of manganese ion on ligand-CTAB/GCE.
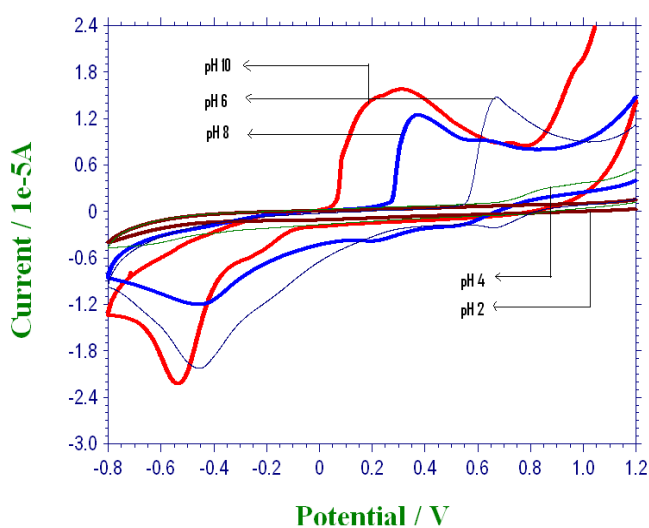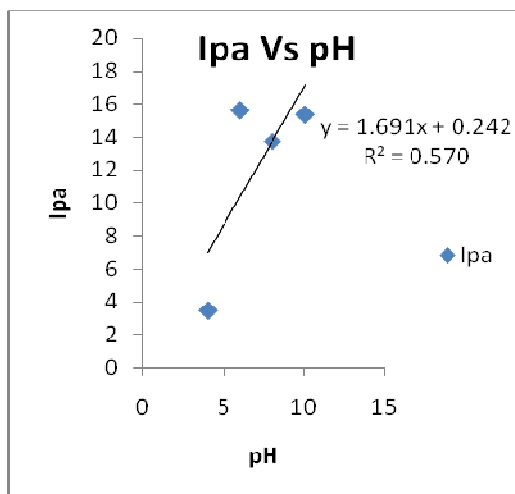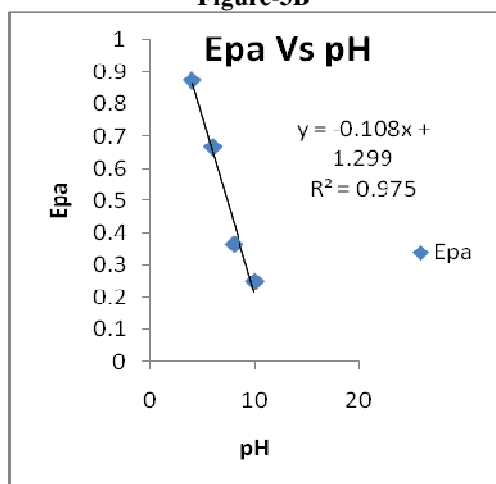

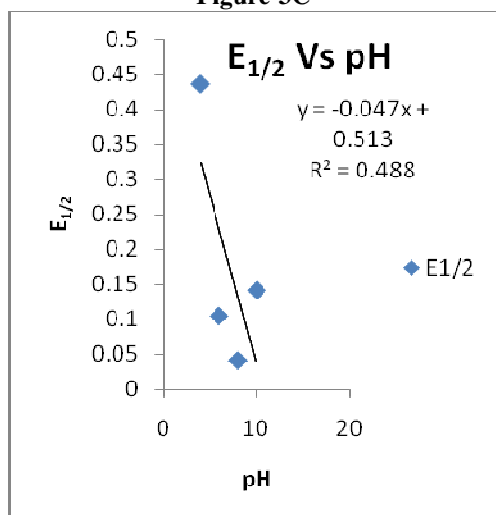**Figure-3A**

Figure-3B

Figure-3C

Figure-3D
A) Cyclic voltammogram for 1mM Mn²⁺ ion on ligand-CTAB/GCE at different pH's. B) A plot of Ipa Vs pH; C) A plot of Epa Vs pH; D) A plot of E₁/₂ Vs pH.

Table-3
Cyclic voltametric parameters for 1mM Mn^{2+} ion on ligand-CTAB/GCE at different pH's

pH	Ipc x 10^5 (A)	Epc (V)	Ipa x 10^5 (A)	Epa (V)	$E_{1/2}$ (V)
2	-	-	-	-	-
4	-	-	0.3500	0.8737	0.4368
6	-2.099	-0.4577	1.566	0.6676	0.1049
8	-1.291	-0.4487	1.376	0.3659	0.0414
10	-2.229	-0.5338	1.541	0.2505	0.1416

Chronoamperometry and Chronocoulometry study: The Cottrell and Anson plots of different concentrations of Mn^{2+} ion in ammonium fluoride medium on ligand-CTAB/GCE is shown in figure (4 and 5) respectively. The diffusion co-efficient values are tabulated in table-4. According to the Cottrell and Anson equations, the diffusion co-efficient values are decreased with increasing concentration. This suggests that manganese redox system has diffusion controlled process on ligand-CTAB/GCE.
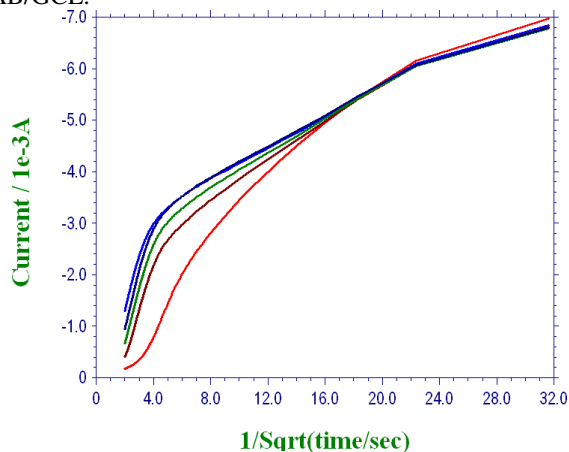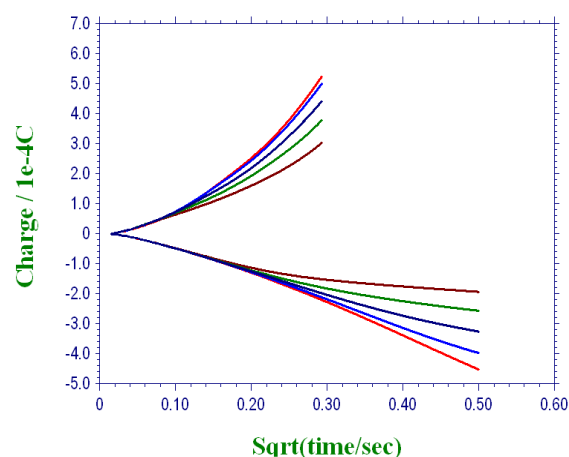

Figure-4

Figure-5
Figure- 4 and 5
Cottrell and Anson plots for different concentrations of Mn^{2+} ion on ligand-CTAB/GCE in 0.1M NH₄F solution

Table-4
Diffusion co-efficient values for different concentrations of Mn^{2+} ion on ligand-CTAB/GCE in 0.1M NH$_4$F solution

Conc. (mM)	Chronoamperometry method		Chronocoulometry method	
	Slope value x 10^4	D x 10^5 (cm^2/s)	Slope value x 10^3	D x 10^6 (cm^2/s)
1	-3.017	2.210	-0.2235	3.031
2	-9.045	4.966	-0.4093	2.542
3	-9.593	2.482	-0.6561	2.903
4	-9.700	1.427	-0.9195	3.207
5	-8.356	0.6781	-1.109	2.986

Interference Study: The Cyclic Voltammogram for the mixture of 1mM Mn^{2+}, 1mM Cu^{2+}, 1mM Cd^{2+} and 1mM Hg^{2+} in 0.1M NH$_4$F medium on a) bare GCE; b) CTAB/GCE; c) ligand/GCE; d) ligand-CTAB/GCE is shown in figure 6. Possible interference of some metals in the voltammetric detection of 1mM Mn^{2+} is studied by addition of the interfering ion to a solution containing 1mM of Cu^{2+}, Cd^{2+} and Hg^{2+} using the optimized conditions at pH 6. Except CTAB/GCE, in all the electrodes, manganese ion does not exihibit reduction peak. On CTAB/GCE, two characteristic peaks at -0.4V and -0.7V are appeared which is due to formation of amalgam between Mn & Hg. On ligand-CTAB/GCE the reduction peaks for Cu, Hg and Mn could not be appeared which is may be due to the formation of the complex between the ions. The oxidation peaks for Cu and Hg are appeared on ligand-CTAB/GCE. But in case of ligand/GCE and ligand-CTAB/GCE, all the ions exihibit well defined oxidation and reduction peaks. This is confirmed that

CTAB has crucial role in formation of complex between ligand and metal ions.

Multi sweep cycle experiment: Typical cyclic voltammograms (CVs) obtained in NH$_4$F solution with 5mM MnSO$_4$ is presented in figure 7. It can be seen that both the oxidation peak current and the reduction peak current are greatly enhanced with the potential scanning cycle number. As shown in figure 7, the oxidation peak is sharper than its corresponding reduction peak, i.e. the oxidation peak and its reduction are not symmetrical. For example, in the first cycle, the reduction peak current is about -9.128 x 10^{-5}A and its peak potential is located at around -0.553V vs SCE, while its oxidation peak current and peak potential values are 6.624 x 10^{-5}A, 1.125 x 10^{-5}A, 1.238 x 10^{-4}A and 0.5348V, 0.7755V, 1.4761V respectively. The broaden peak about 0.4V is due to formation of Mn-ligand complex. The closed peaks around 0.8 and 1.4 are due to formation of MnO$_2$ layer on the electrode surface.

Based on the previous report, the Mn(II) oxidation to MnO$_2$ proceeds either through ECE or disproportination mechanism[15].

Thus we can attribute the broad reduction peak and the attenuated reduction peak current are due to the disproportination of Mn^{3+}, that is to say Mn^{3+} is consumed by the following chemical reactions, leading to the formation of either Mn-ligand complex or manganesedioxides on the surface of the glassy carbon electrode. The following type of Mn-ligand complex is possible.
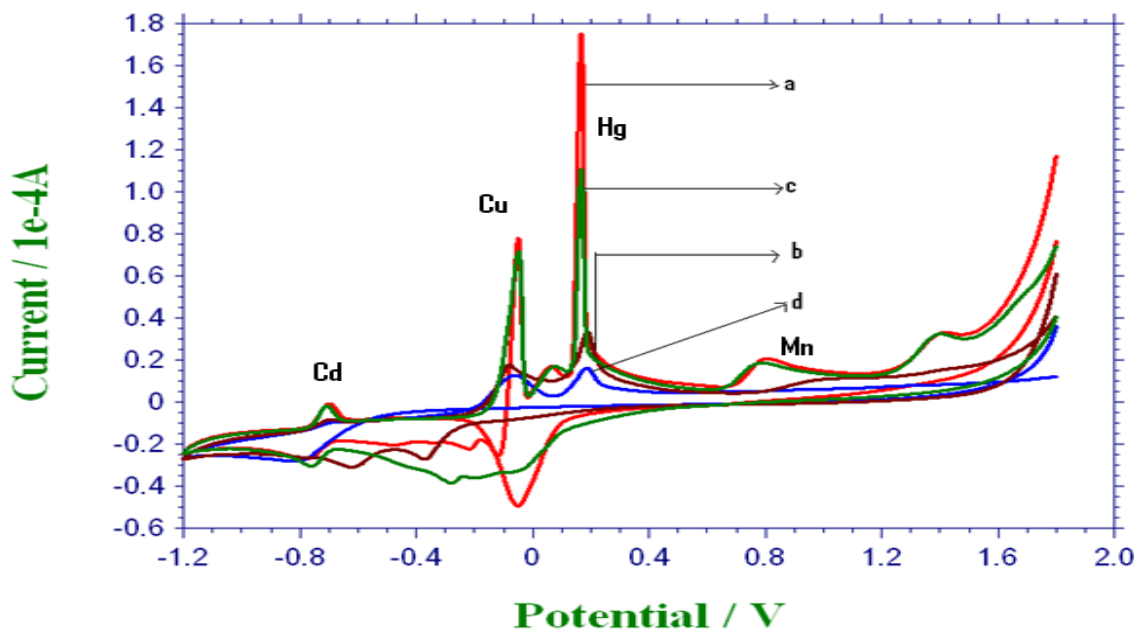
Figure-6
Cyclic Voltammogram for 1mM Mn^{2+}; 1mM Cu^{2+}; 1mM Hg^{2+}; 1mM Cd^{2+} ion on a)bare GCE; b) CTAB/GCE; c)ligand/GCE; d) ligand-CTAB/GCE in 0.1M NH$_4$F solution
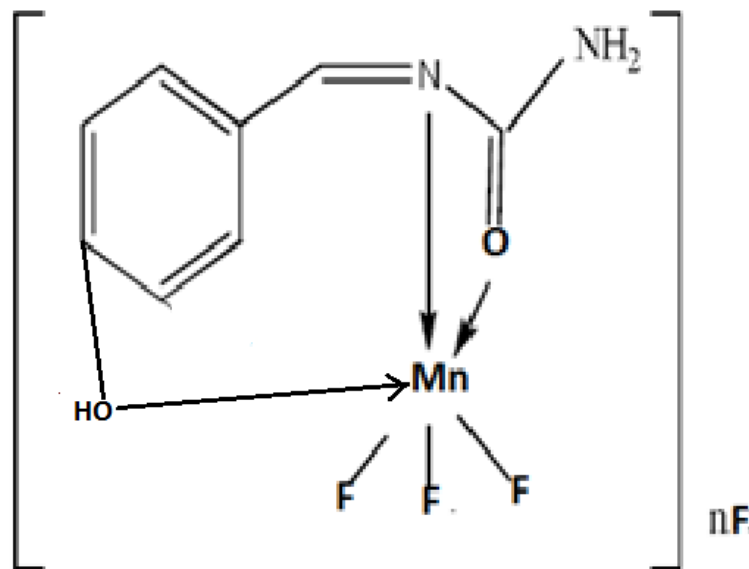
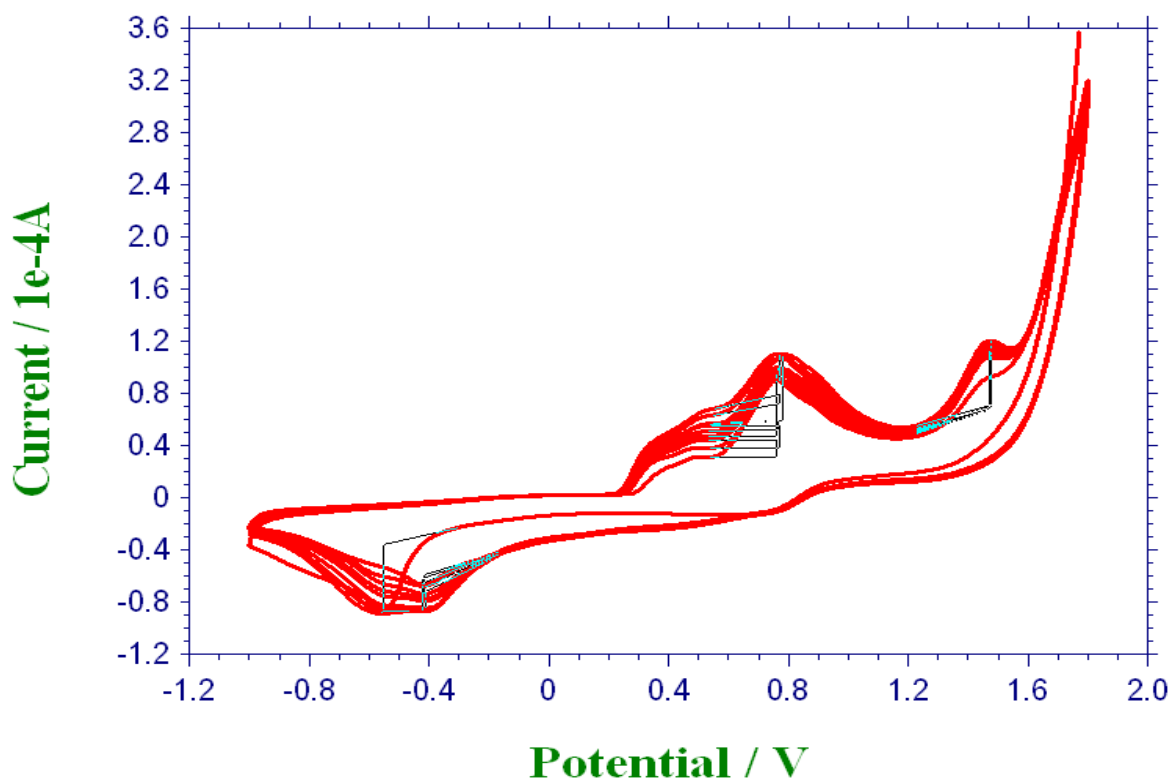**Structure of [trisfluoro4-hydroxybenzylidenecarbamidomanganese (II)] complex**

Figure-7
Cyclic Voltammogram for 5mM Mn^{2+} ion on ligand-CTAB/GCE at 10cycles in 0.1M NH$_4$F solution.

Stability study: Cyclic voltammogram for 1mM Mn^{2+} ion on ligand-CTAB/GCE at various time intervals (1, 2, 3, 4 and 8 days) in 0.1M NH$_4$F medium is presented in figure 8. The anodic and cathodic peaks show moreover same response in all the days. The anodic peak current is slightly decreased which is due to the complexation effect. Thus ligand-CTAB film has stable adsorption on the GCE at various time intervals.
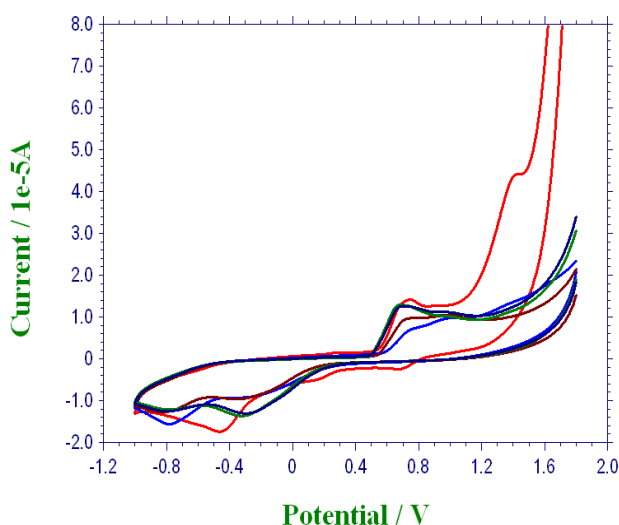
Figure-8
Cyclic Voltammogram for 1mM Mn^{2+} ion on ligand-CTAB/GCE at various time intervals (1, 2, 3, 4, 8 days) in 0.1M NH$_4$F medium

Conclusion

The complexation effect of Mn^{2+} ion with the ligand is observed from the shift of anodic peak into positive side and cathodic peak into negative side. From chronoamperometry and chronocoloumetry study, diffusion co-efficient values are decreased with increasing concentration of Mn^{2+} ion. In concentration effect peak current values are increased with increasing concentration of Mn^{2+} ion. These results suggest that Mn^{2+} has diffusion controlled process on ligand-CTAB/GCE. There are two protons involved in the manganese redox system which is observed from the E$_{1/2}$ shift with pH values. The interference study explains formation of complex between various metal ions with ligand. Multi sweep cycle experiment and stability study shows that Mn^{2+} redox system has stable response on ligand-CTAB/GCE. Thus 4-hydroxybenzylidenecarbamide-CTAB/GCE is used for removal of excess of Mn^{2+} ions in real samples.

Acknowledgements

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