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ORIGINAL ARTICLE

Investigations on the redox behaviour of manganese in manganese(II)–saccharin and manganese(II)–saccharin–1,10-phenanthroline complexes

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Abstract The redox behaviour of manganese system in Mn–Sac and Mn–Sac–Phen complexes were studied using cyclic voltammetry technique at glassy carbon electrode (GCE) in 0.1 M KCl electrolyte. The CV of Mn–Sac solution is more or less similar to that of uncoordinated Mn (in $MnCl_2$) accept slight difference in peak position and peak current. The presence of secondary ligand phenanthroline (in Mn–Sac–Phen complex) changes the CV of Mn system largely compared to those of uncoordinated Mn and Mn–Sac. The redox system is irreversible in Mn–Sac and quasi-reversible in Mn–Sac–Phen complex. The effect of concentration and pH on the redox behaviour of Mn system have been studied for both the complexes.

1. Introduction

Metal ions are essential components of different organs of animals such as blood, bones, teeth, nerves and for some proteins and enzymes. Manganese is an essential microelement for many biological systems. Traces of manganese are found in many plants and a healthy adult human contain about 10–20 mg of manganese (Greenwood and Earnshaw, 2005). Lack of manganese in the diet of animals causes testicular atrophy, though the cause of this is not known. Manganese is necessary in the body to active arginase, which is the principle enzyme for the formation of urea (Guyton, 1981).

However, saccharin is used as pharmaceutical excipients in the formulation of different medicinal products like syrup, suspension as a sweetening agent. Investigation of mechanism of electrochemical interaction between the essential trace element like Mn and saccharin in biological system is necessary. Among all the voltammetric techniques, the cyclic voltammetry is extremely popular in electrochemical research, because it can provide useful information about redox reactions. Earlier we studied the interaction of Mn(II) with aspartic acid and redox behaviour of Mn(II)/(IV) system in our laboratory (Rahman et al., 2007). Here in this communication we have studied and compared the redox behaviour of Mn system in two different Mn-complexes.

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2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents like manganese chloride (BDH Chemicals Ltd., Poole, England) saccharin (Aldrich Chemical Co. Ltd., Gillingham, Dorset, England), 1,10-phenanthroline (BDH Chemicals Ltd., Poole, England) were of reagent grade. The buffers were prepared using sodium acetate (MERCK, Germany) and acetic acid (Sigma–Aldrich Laborchemikaline, GmbH) (Robinson and Stokes, 1968). For cleaning and all other purposes deionized water was used. 99.997% (BOC, Bangladesh) nitrogen was used for purging purpose.

2.2. Equipments

This study was carried out using an Epsilon Electroanalyser developed by Bioanalytical System, Inc., USA. A glassy carbon electrode was used as working electrode, which was cleaned by polishing on cloth using alumina powder. Ag/AgCl electrode and Pt wire were used as reference and counter electrodes, respectively. An AGE (VELP SCIENTIFICA) magnetic stirrer with a teflon coated magnetic bar and a pH meter (METTLER, TOLEDO) was employed for stirring and measuring of the pH of the solutions, respectively. All glasswares used in the preparation of solutions were made of pyrex glass.

2.3. Preparation and characterization of the complexes

The manganese–saccharin and manganese–saccharin–1,10-phenanthroline complexes were prepared and characterized according to the published procedure (Romman et al., 1999; Haider et al., 1981).

3. Results and discussion

3.1. Cyclic voltammogram (CV) of manganese–saccharin (Mn–Sac) complex

The redox behaviour of 2 mM solution of manganese–saccharin complex was studied in 0.1 M KCl as supporting electrolyte at room temperature using cyclic voltammetric technique within the potential window from 1600 mV to −900 mV at glassy carbon electrode. The CVs of 3 mM MnCl and 3 mM Mn–Sac complex solutions in 0.1 M KC and 0.1 M KCl are shown in Fig. 1.

The CVs of Mn(IV)/Mn(II) system for uncoordinated and coordinated manganese are more or less same except a little difference in peak position and peak intensity. From Fig. 1 we can see that in uncoordinated Mn ($MnCl_2$), there are two catholic peaks at potential c_1 (0.8847 V) and c_2 (0.1243 V) and two anodic peaks at potential a_1 (1.0607) and a_2 (0.3254). For coordinated Mn (Mn–Sac) also, we found that there are two catholic peaks at potentials c_1 (0.8555 V) and c_2 (0.1246 V) and two anodic peaks at potential a_1 (1.0740 V) and a_2 (0.3432 V).

The cathodic peaks are correspond to the following reactions:

$$\mathrm{Mn(IV)} \xrightarrow{+e^-} \mathrm{Mn(III)} \xrightarrow{+e^-} \mathrm{Mn(II)}$$

and the anodic peaks are correspond to the following reactions:

$$\mathrm{Mn(II)} \xrightarrow{-e^-} \mathrm{Mn(III)} \xrightarrow{-e^-} \mathrm{Mn(IV)}$$

A series of cyclic voltammograms of the 3 mM Mn–Sac complex in KCl electrolyte at different scan rates are shown in Fig. 2 and the parameters from the CVs are listed in Table 1.

From Table 1, we can see that for both the cathodic peaks, the peak potentials are gradually decreased as the scan rate increased and for both the anodic peaks, the peak potentials are gradually increased as the scan rate increased. The increasing and decreasing rates of potential are very small. The plot of peak potential separation vs scan rate in Fig. 3 demonstrate that the potential separation increases with the increase of scan rate which is a limitation due to charge transfer kinetics or ohmic potential (iR) drop (Zhang, 1972). From Fig. 4 we can see that the peak current of both cathodic and anodic peaks increase as the scan rate increases.

Table 1 shows that as the scan rate increases the peak current ratio (i_{pa_1}/i_{pc_1}) decreases and the values of peak current ratios are far from the unity, which demonstrate that the system is irreversible.

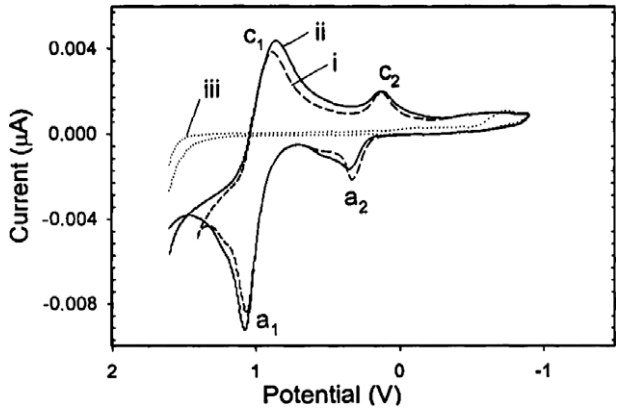

Figure 1 The CVs of (i) 3 mM $MnCl_2$, (ii) 3 mM Mn–Sac in 0.1 M KCl and (iii) electrolyte 0.1 M KCl at scan rate 100 mV s^{-1}.

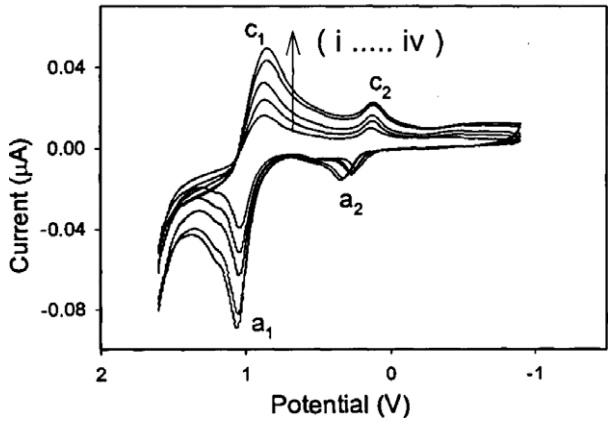

Figure 2 The CV of 2 mM Mn–Sac in 0.1 M KCl at the scan rates (i) 30, (ii) 60, (iii) 90, (iv) 160 and (v) 200 mV s^{-1}.

Table 1 Current–potential data, for Mn–Sac complex (2 mM solution in 0.1 M KCl) at different scan rates.

Scan rate, ν ($V\,s^{-1}$)	Anodic peak potential for 1st peak, E_{pa_1} (V)	Anodic peak potential for 2nd peak, E_{pa_2} (V)	Cathodic peak potential for 1st peak, E_{pc_1} (V)	Cathodic peak potential for 2nd peak, E_{pc_2} (V)	Anodic peak current for 1st peak, I_{pa_1} (μA)	Anodic peak current for 2nd peak, I_{pa_2} (μA)	Cathodic peak current for 1st peak, I_{pc_1} (μA)	Cathodic peak current for 2nd peak, I_{pc_2} (μA)	Peak potential separation, $\Delta E_1 = E_{pa_1} - E_{pc_1}$ (V)	Peak current ratio, i_{pa_1}/i_{pc_1}
0.030	1.0399	0.2339	0.8760	0.1314	39.15	10.37	16.263	10.248	0.1639	2.4073
0.060	1.0467	0.2680	0.8691	0.1255	51.81	11.66	23.995	13.253	0.1776	2.1592
0.090	1.0536	0.2680	0.8621	0.1210	62.78	13.37	32.158	16.263	0.1915	1.9522
0.160	1.0604	0.3158	0.8555	0.1178	82.11	14.66	43.757	21.418	0.2049	1.8765
0.200	1.0672	0.3432	0.8486	0.1109	89.41	15.52	49.342	22.277	0.2186	1.8120

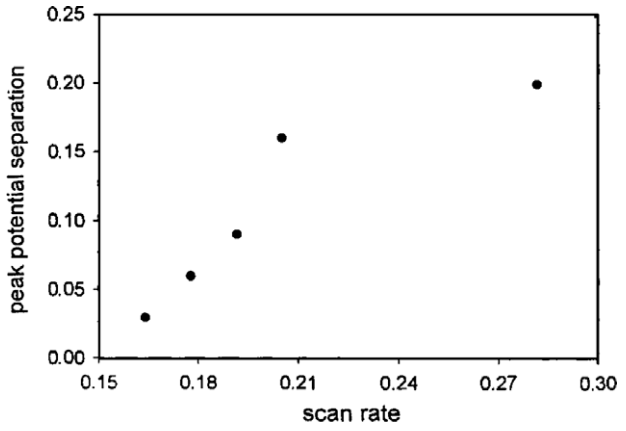

Figure 3 Variation of peak potential separation against scan rate for Mn–Sac complex.

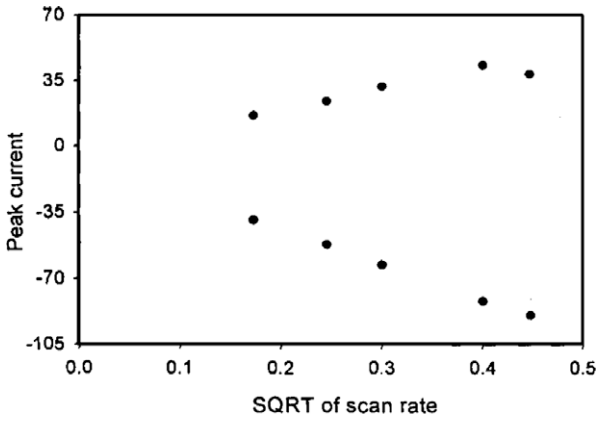

Figure 4 Variation of peak current against SART of scan rate.

3.2. pH effect on the CV of Mn–Sac complex

In the acetate buffer the redox behaviour of Mn(IV)/Mn(II) system in Mn–Sac complex is quite different. Both the cathodic peaks and the anodic peaks move to the right with respect to that in KCl solution. Another important feature is that one

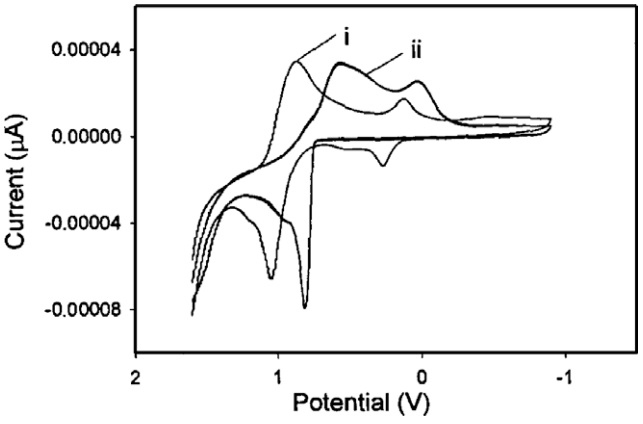

Figure 5 The CV of (i) 2 mM Mn–Sac complex in KCl and (ii) in acetate buffer.

of the anodic peaks is disappeared. The comparison of the CV of the complex in 0.1 M KCl solution and in buffer medium of pH 5.4 is shown in Fig. 5.

The CV of the Mn–Sac complex was also studied at different pH values (4.1, 4.5, 4.9, 5.2 and 5.4). From that study we observed CVs are basically similar but the peak position and current intensity are changed though these changes are not regular for cathodic peaks but nearly regular for anodic peaks. The effect of pH values on peak potential for anodic peak are shown in Fig. 6.

3.3. Concentration effect

The CV of Mn–Sac complex at various concentrations (1 mM, 2 mM and 3 mM) are shown in Fig. 7. The plot of anodic peak current against concentration is shown in Fig. 8.

From Figs. 7 and 8 it is observed that with the increase in concentration there is a gradual linear increase in peak current, which may be due to the presence of a large amount of electroactive species at higher concentration. The increase peak current with concentration, also gives the idea that the system may be both diffusion controlled (Bard and Faulkner, 1980a). Since the line is not passing through origin we can predict that adsorption may take place at the electrode surface (Bard and Faulkner, 1980b).

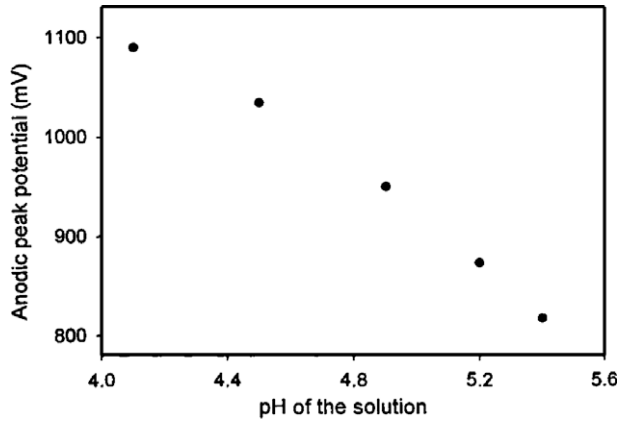

Figure 6 Variation of peak potential against the pH of solution.

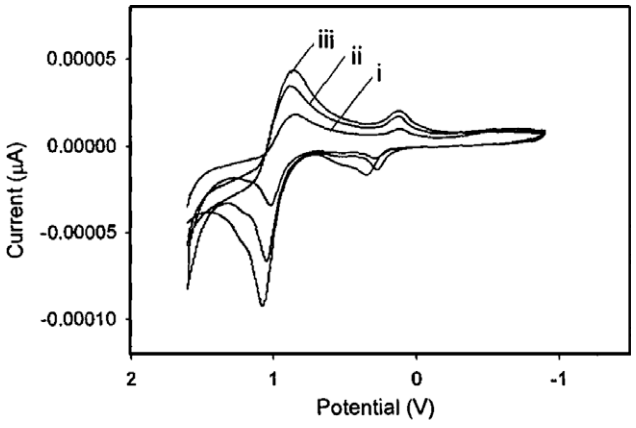

Figure 7 CV of Mn–Sac of concentration (i) 1 mM; (ii) 2 mM and (iii) 3 mM in 0.1 M KCl at 100 mV s^{-1} scan rate.

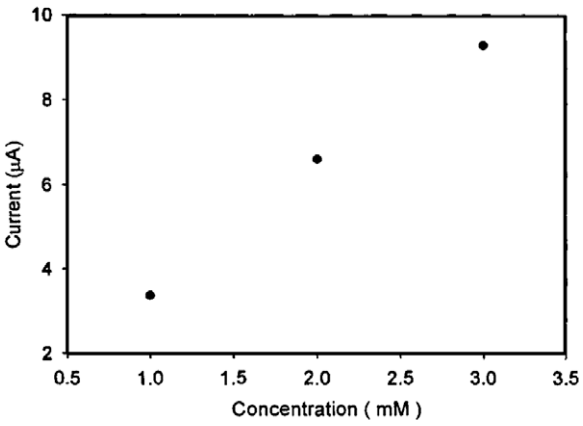

Figure 8 Variation of anodic peak current against con.

3.4. Redox behaviour of manganese–saccharin–1,10-phenanthroline complex

The redox behaviour of Mn–Sac–Phen complex in KCl and in aqueous medium was analyzed at room temperature using the

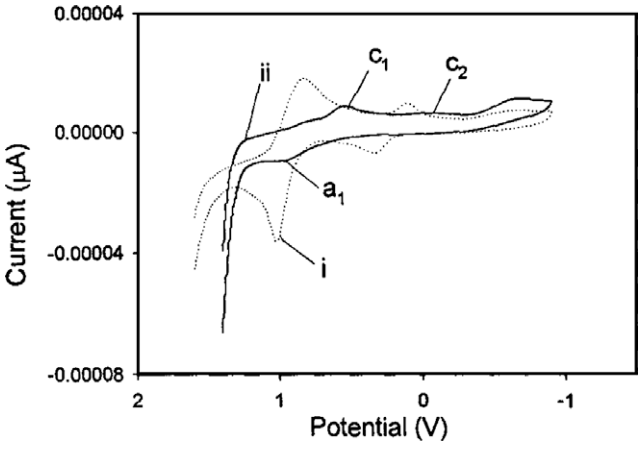

Figure 9 CV of (i) Mn–Sac and (ii) Mn–Sac–Phen of 1 mM in 0.1 M KCl solution at scan rate 120 mV s^{-1}.

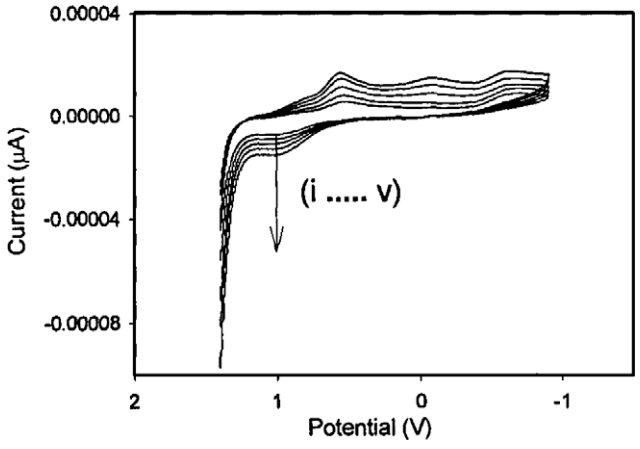

Figure 10 CVs of Mn–Sac–Phen complex of 1 mM solution in KCl electrolyte at scan rates (i) 75, (ii) 100, (iii) 140, (iv) 180 and (v) 225 mV s^{-1}.

Table 2 Current–potential data, for Mn–Sac–Phen complex at different scan rates.

Scan rate, v (V s^{-1})	SQRT of scan rate, $v^{1/2}$	Anodic peak potential, E_{pa} (V)	Cathodic peak potential for 1st peak, E_{pc_1} (V)	Cathodic peak potential for 2nd peak, E_{pc_2} (V)	Anodic peak current, i_{pa} (μA)	Cathodic peak current for 1st peak, i_{pc_1} (μA)	Cathodic peak current for 2nd peak, i_{pc_2} (μA)	Peak potential separation, $\Delta E = (E_{pa} - E_{pc_1})$ (V)	Peak current ratio, i_{pa}/i_{pc_1}
0.075	0.27386	1.0544	0.5265		7.03	5.747	0.3296	0.5279	1.1189
0.100	0.31623	1.0607	0.5391	0.032	8.81	8.233	0.5285	0.5216	1.0701
0.140	0.37417	1.0544	0.5516	0.051	10.59	11.429	0.8943	0.5028	0.9266
0.180	0.42426	1.0544	0.5642	0.076	12.72	14.981	1.2140	0.4798	0.8491
0.225	0.47434	1.0292	0.5705	0.089	15.20	17.112	1.4981	0.4587	0.8883

same technique and same potential window and the same set of electrode, as in case of Mn–Sac complex. The comparison of the CVs of the complexes Mn–Sac and Mn–Sac–Phen (1 mM solution) in 0.1 M KCl are shown in Fig. 9.

Due to the presence of secondary ligand phenanthroline the redox behaviour of Mn(IV)/Mn(II) system has been changed considerably. Here two cathodic peaks c_1 (0.5516 V) and c_2 (−0.064) and one anodic peak a_1 (1.0732) are observed. The cathodic peaks move towards right and the intensity of both cathodic and anodic peaks have been reduced considerably. A series CVs of Mn–Sac–Phen complex of 1 mM in KCl electrolyte at different scan rates are given in Fig. 10. The parameters are listed in Table 2.

Fig. 11 shows the peak potential separation increases with the increases of scan rate, which is same as of Mn–Sac complex. From Fig. 12 we observed that the peak current increases in both cathodic and anodic cases as the scan rate increases.

So from the above observation, we can say that the Mn–Sac–Phen system is not reversible but quasi-reversible. The system is both diffusion and kinetic controlled and adsorption take places at the electrode surface as like as Mn–Sac system (Bard and Faulkner, 1980b).

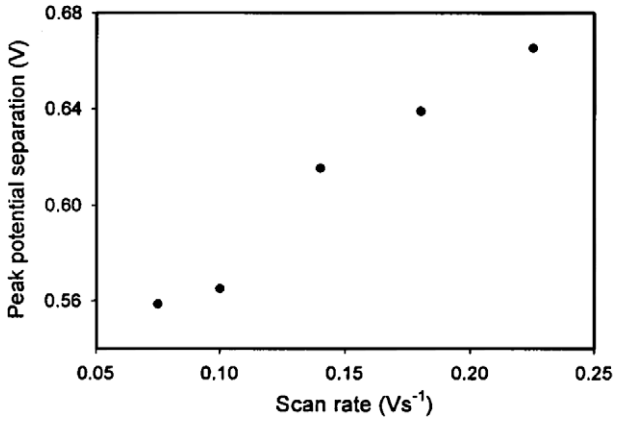

Figure 11 Variation of peak potential separation against scan rate for Mn–Sac–Phen complex.

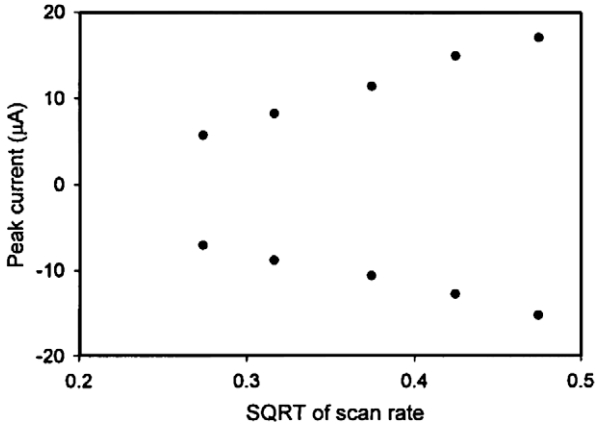

Figure 12 Variation of peak current against SQRT of scan rate of Mn–Sac–Phen complex.

From Table 2, we see the sequence of change of the peak potentials are different from that of Mn–Sac complex. Here we see, the catholic peak potentials E_{pc_1} and E_{pc_2} increase with the increase of scan rate. But for the anodic peak, the peak potential is almost steady and the peak current ratio is closer to unity.

3.5. Effect of pH

The CV of 1 mM Mn–Sac–Phen complex in acetate buffer of pH 5.4 at the scan rate 100 mV s^{-1} within the potential window 1400 mV to −1200 mV is compared with that in 0.1 M KCl in Fig. 13 and the CVs in various pH (4.1, 4.5, 4.9, 5.2 and 5.4) at the same concentration and same scan rate are shown in Fig. 14.

The CV of the complex in acetate buffer shows Mg amerences with respect to that in KCl solution. Two sharp peaks (one cathodic, c_2 and one anodic, a_2) have been developed. The redox behaviour of Mn(IV)/Mn(II) system has been modified sharply in the acetate buffer medium. Studying the CV of the Mn–Sac–Phen complex in different pH values we get very small gradual change. The CVs are more or less identical

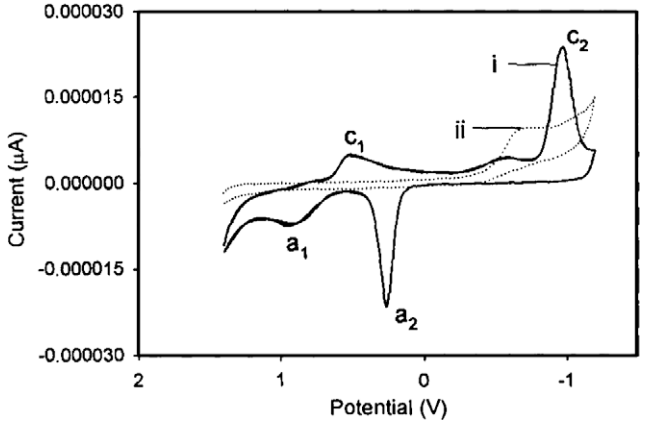

Figure 13 CV of (i) Mn–Sac–Phen in buffer solution of pH 5.4 and (ii) blank buffer solution at scan rate 100 mV s^{-1}.

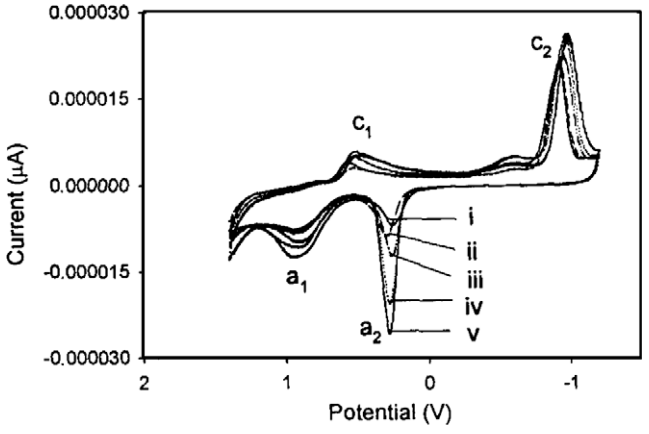

Figure 14 CVs of 1 mM Mn–Sac–Phen complex in acetate buffer of pH (i) 4.1, (ii) 4.5, (iii) 4.9, (iv) 5.2 and (v) 5.4 at scan rate 120 mV s^{-1}.

Table 3 Current–potential data, for Mn–Sac–Phen complex in buffer at different scan rates.

pH value	Anodic peak potential for 1st peak, E_{pa_1} (V)	Anodic peak potential for 2nd peak, E_{pa_2} (V)	Cathodic peak potential for 1st peak, E_{pc_1} (V)	Cathodic peak potential for 2nd peak, E_{pc_2} (V)	Anodic peak current for 1st peak, i_{pa_1} (A e^{-5})	Anodic peak current for 2nd peak, i_{pa_2} (A e^{-5})	Cathodic peak current for 1st peak, i_{pc_1} (A e^{-5})	Cathodic peak current for 2nd peak, i_{pc_2} (A e^{-5})
4.1	0.9525	0.2563	0.5760	0.915	1.244	0.679	0.3995	2.0540
4.5	0.9169	0.2989	0.5191	0.915	1.060	0.880	0.3258	2.1634
4.9	0.9098	0.2634	0.5333	0.951	0.984	1.212	0.5006	2.2676
5.2	0.9311	0.2776	0.5120	0.958	0.831	2.057	0.6011	2.6249
5.4	0.9240	0.2874	0.4978	0.979	0.791	2.573	0.5364	2.6416

Table 4 Current–potential data, Tafel slope b, diffusion coefficient D and the charge transfer rate constant, h_f calculated from the voltammograms of free Mn and Mn–Sac, Mn–Sac–Phen complexes on GCE at room temperature.

Sample ID	Scan rate, v (V s^{-1})	Concentration, C (mM)	Cathodic peak potential, E_{pc} (V)	Cathodic peak current, i_{pc} (μA)	Tafel slope $b = 2.303RT/\varpi naF$	Diff^n coefficient $D \times 10^{11}$ (cm^{-2} s^{-1})	$-\log k_f$ (cm s^{-1})	Charge transfer rate constant $k_f \times 10^6$ (cm s^{-1})
Free Mn	0.060	3.0	0.8847	27.988	0.0394	0.1082	5.5662	2.72
	0.140	3.0	0.8784	47.251				
Mn–Sac	0.090	2.0	0.8621	32.158	0.0897	0.4873	5.4178	3.82
	0.200	2.0	0.8486	49.342				
Mn–Sac–Phe	0.100	1.0	0.5391	8.233	0.2265	0.2904	5.7314	1.86
	0.180	1.0	0.5642	14.981				

$T = 298$ K, $n =$ no. of electron transferred $= 2$, $R = 8.314$ J K^{-1} mol^{-1}, $F = 96{,}500$C, $A =$ surface area of the electrode $= 0.05$ cm^2.

except small difference in peak position and peak current. The parameters from Fig. 14 are shown in Table 3.

From Table 3 we see that the peak current of both the cathodic peak current increases with pH value (decreasing acidity). In case of anodic peaks, the peak current i_{pa_1} decreases and the peak current i_{pa_2} increases as the pH increases.

3.6. Charge transfer rate constant

The heterogeneous charge transfer rate constant, k_f, has been calculated using the current–potential data obtained from the cyclic voltammograms of free Mn(II) and its complexes in 0.1 M KCl. The current–potential data, Tafel slope, diffusion coefficient and charge transfer rate constants at room temperature for these voltammograms are listed in Table 4.

4. Conclusion

From our experiment we observed that the redox processes of both Mn–Sac and Mn–Sac–Phen complexes are diffusion controlled as well as kinetic controlled. Considering the peak potential separation and peak current ratio data we can say that the redox process for Mn–Sac is irreversible and Mn–Sac–Phen is quasi-reversible. The charge transfer rate constant k_f for Mn–Sac system is greater than Mn–Sac–Phen system.

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