

PREPARATION AND CHARACTERIZATION OF IRON(III) COMPLEX OF SACCHARIN

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ABSTRACT

Complex of iron(III) with saccharin, $[\text{Fe}(\text{C}_7\text{H}_4\text{O}_3\text{SN})_2\text{Cl}]$ has been prepared in aqueous medium. The IR and electronic spectral analysis suggest that two saccharin molecules are attached to the metal ion through N atom and there is no chemically coordinated or crystalline water in the complex molecule. The magnetic moment value indicates the paramagnetic character of the complex. The cyclic voltammetric study indicates a quasi-reversible electron transfer process due to the presence of iron in the compound.

Key words: Characterization, Iron(III) complex, Saccharin

INTRODUCTION

Metal and metal ions are important for all living system. Among them iron is essential to all organisms. Iron is vital for almost all living organisms which participate in a wide variety of metabolic processes, including oxygen transport, DNA synthesis, and electron transport (Lieu *et al.* 2001). As a functional component of heme, iron participates in oxygen transport by hemoglobin (Ponka 1999) and drug detoxification by cytochrome P450 in liver (Danielson 2002). Iron present as Fe(III) in protoporphyrin is used as oxygen carrier and maintains the circulation of oxygen in the body by redox reaction.

Saccharin is a ligand, which can act as a mono dentate, bi dentate and tetra dentate ligand. So it may form coordination bond with the transition metal ion. However, saccharin is used as pharmaceutical excipients in the formulation of different medicinal products like syrup, suspension as a sweetening agent (Kibbe 2000). In biological system, especially in human body the actual mechanism of electrochemical interaction between the essential trace element like Fe and saccharin of the drug excipients need to be investigated. Very few investigations have been reported about these pharmacological phenomena (Negro 1994). Moreover, iron is the main constituent of blood. Therefore a basic knowledge about its redox behaviour in the presence of different ligands and at different pH values is very important. Various electrochemical techniques are useful for studying the redox behavior of electro active species. Cyclic voltammetry has been

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chosen for this present study because of its effectiveness in investigation of the redox behaviour of electro active species. Many papers about metal-saccharin complexes have been published from our laboratory (Romman *et al.* 1993, Malik *et al.* 1999, Romman *et al.* 1999, Ahmed *et al.* 1981, Haider *et al.* 1992). In the present paper we report the preparation of iron saccharin complex and its speciation by different chemical, physico-chemical and spectroscopic analysis. In addition, the redox behavior of the complex was studied on GCE, Au and Pt electrode using cyclic voltammetric technique.

MATERIALS AND METHODS

All the chemicals, solvents and ligand used in the synthesis and analytical work were Analar grade obtained from E. Merck of Germany. Iron content of the complex was determined by titrimetric method. The iron(III) in the complex was reduced to iron(II) then titrated with $K_2Cr_2O_7$ (Bassett *et al.* 1989). The percentage of C, H, S, N and Cl were determined by an elemental analyzer at Tohoku University, Japan. Infrared spectra of saccharin and the complex were recorded on a calibrated Fourier Transform IR Spectrophotometer (FTIR, 8300, Shimadzu, Japan) in the range of 400 - 4600/ cm^{-1} using KBr pallets. The UV-visible spectrum of the complex was recorded using UV-visible Spectrophotometer, Model UV-160A, Shimadzu (Japan), in the wavelength range, 200-1100 nm using paraffin oil as dispersion medium. Magnetic moment of the complex was determined using Sherwood Scientific Magnetic Susceptibility Balance, Cambridge, England, and Model: Magway MSB Mk1. The MSB works on the basis of a stationary sample and moving magnets.

Cyclic voltammetric (CV) studies were conducted with a PC controlled potentiostat, Epsilon Electrochemical Analyzer; developed by Bioanalytical System, Inc. U.S.A. A three-electrode electrochemical cell made of borosilicate glass and Teflon cap was used in this study: Glassy carbon (GC), Au and Pt were used as working electrode, Ag/AgCl (standard KCl) was used as reference electrode and Pt wire as counter electrode. 99.997% nitrogen (Bangladesh Oxygen Ltd.) was used for purging purpose and deionized water was used for cyclic voltammetric study. The working electrode was cleaned by polishing on cloth using alumina powder. Solutions of iron-saccharin complex were prepared in deionized water.

Method of preparation: The aqueous solutions of the ligand (1.025 g in 20 mL water) and $FeCl_3$ (0.815 g in 20 mL water) were prepared separately and then mixed at room temperature. The reaction mixture was heated to about 50 to 60°C on a waterbath for about half an hour and kept at room temperature for crystallization. Red crystals were separated by filtration, washed with deionized water and dried over silica gel in a

Electronic spectral analysis: The electronic spectrum of the Fe-saccharin complex is shown in Fig. 1. The assignments have been done on the basis of some standard references (Lang 1961, Gillam and Strem 1957, Jatte and Orchin 1962). The absorption bands between 200 – 350 nm are observed for the ligand part of the complex and that at higher wave length is due to the metal ion. The $n \rightarrow \sigma^*$ absorption bands appeared at ~ 295 nm and the $n \rightarrow \pi^*$ transition band appeared at $\sim 307 - 350$ nm. The broad bands centering around 412 may be assigned for the d-d electronic transition and CT transition of the metal. The d \rightarrow d transition supports the colored appearance of the complex.

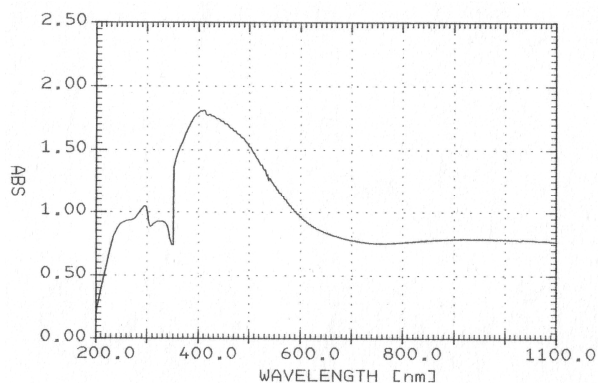


Fig. 1. UV-visible spectrum of $[\text{Fe}(\text{C}_7\text{H}_4\text{O}_3\text{SN})_2\text{Cl}]$.

Magnetic properties: This study revealed that the Fe-Sac complex has μ_{eff} , 2.0414 BM corresponding to the presence of one unpaired electron in the 3d orbital (Mamun *et al.* 2011). This means in this complex iron is in the trivalent oxidation state, Fe^{3+} with d^5 electronic configuration. Since magnetic properties is directly related to the d-electron arrangements of the transition metal ions, the Fe^{3+} ion is paramagnetic having the electronic arrangement in 3d level as $t_{2g}^5 e_g^0$. However, the μ_{eff} value reveals the low spin paramagnetic nature of the complex.

Quasi-static thermogravimetric (QSTG) analysis: The QSTG curve (Fig. 2) shows that the first step weight-loss is about 0.07%. This is due to the loss of adhering surface water of the sample. The second weight loss during the decomposition of the compound is ($\sim 11\%$) below 235°C , this weight loss correspond to loss of two molecules of CO due to the decomposition of two carbonyl groups present in the complex molecule. The next weight loss up to 700°C may be due to loss of 2 molecules of NH_3 and SO_2 . The lost step weight loss before attaining the constant weight at higher temperature may be due to the removal of most of the organic part of the complex as H_2 , CH_4 etc. The remaining constant weight, 15% which corresponds to the weight of FeO.

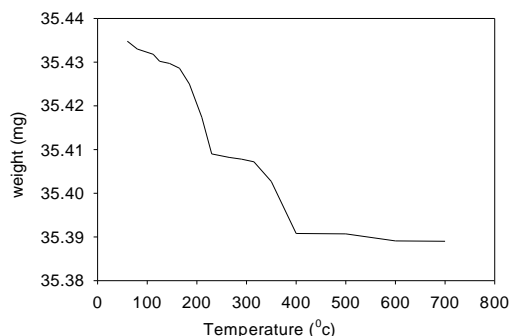


Fig. 2. QSTG curve of $[\text{Fe}(\text{C}_7\text{H}_4\text{O}_3\text{SN})_2\text{Cl}]$.

The QSTG analysis may be summarized as follow:

Sample ID	Weight of the sample (mg)	Decomposition pattern		Probable finding
		Decomposition temperature °C	% weight loss	
$[\text{Fe}(\text{C}_7\text{H}_4\text{O}_3\text{SN})_2\text{Cl}]$	35.4348	50-235	0.07	May be due to loss of moisture two molecules CO may be lost One molecule each of SO_2 and NH_3 may be lost, followed by total decomposition of organic part as H_2 , CH_4 etc. Residue about 15.12% (FeO)
			11.45	
		335-700	75.98	

Cyclic voltammetric studies: The redox behavior of Fe(III) in $[\text{Fe}(\text{C}_7\text{H}_4\text{O}_3\text{SN})_2\text{Cl}]$ in aqueous medium was observed using CV technique on GC, Au and Pt electrode at the scan rate 100 mV s^{-1} within the potential window 1.2 to -1.0 V at room temperature. The CV of Fe(III) in the complex and that of the free ligand, at Au electrode are shown in Fig. 3.

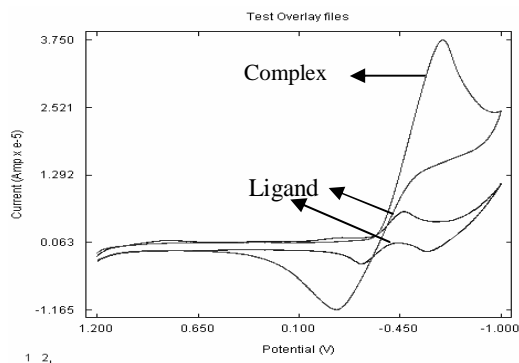
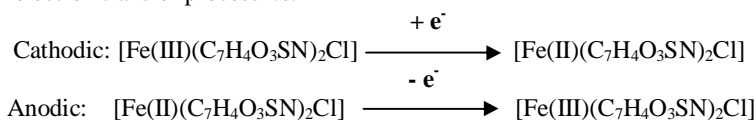


Fig. 3. Cyclic voltammograms of Fe(III) complex and free saccharin at Au electrode vs. Ag/AgCl.

The CV of Fe(III)-complex shows a cathodic peak at the potential - 0.6757 V and an anodic peak at - 0.07801 V on Au electrode. The cyclic voltammogram indicate that there is a one -electron transfer process i.e.



Variation of scan rate: The cyclic voltammograms of Fe(III) complex in aqueous medium at Au electrode vs Ag/AgCl at different scan rate are displayed in Fig. 4(a) and the current-potential data, peak separation, peak current ratio of the voltammograms are recorded in Table 1. The plot of peak current vs SQRT of scan rate is shown in Fig. 4 (b).

The voltammograms of the complex at different scan rate express that with the increase of scan rate the peak current of both the anodic and cathodic peaks increase. However, the cathodic peaks are shifted towards right and the anodic peaks are shifted to the left direction. In a slow voltage scan the diffusion layer grows much further from the electrode in comparison to a fast scan. Consequently, the flux to the electrode surface is considerably smaller at slow scan rates than it is at faster rates. As the current is proportional to the flux towards the electrode, the magnitude of the current becomes lower at slow scan rates and higher at high scan rates. The general conclusion is that the redox system is diffusion controlled (David and Gosser 1993).

Table 1. Current-potential data, peak separation, peak current ratio of the voltammograms of Fe-Sac at different scan rates on Au electrode.

Scan rate (v) Vs ⁻¹	Anodic peak potential, E _{pa} V (-)	Cath ^c peak potential, E _{pc} V (-)	Anodic peak current, i _{pa} μA (-)	Cath ^c peak current, i _{pc} μA	Peak separation, ΔE = (E _{pa} - E _{pc}) V	Peak current ratio, i _{pa} /i _{pc}
0.050	0.2327	0.5627	1.7024	2.8005	0.3315	0.6078
0.100	0.2275	0.5967	1.4376	3.7265	0.3692	0.3857
0.150	0.2158	0.6332	1.1872	4.2092	0.6950	0.2820
0.200	0.2086	0.6512	0.9067	4.5471	0.7038	0.1994

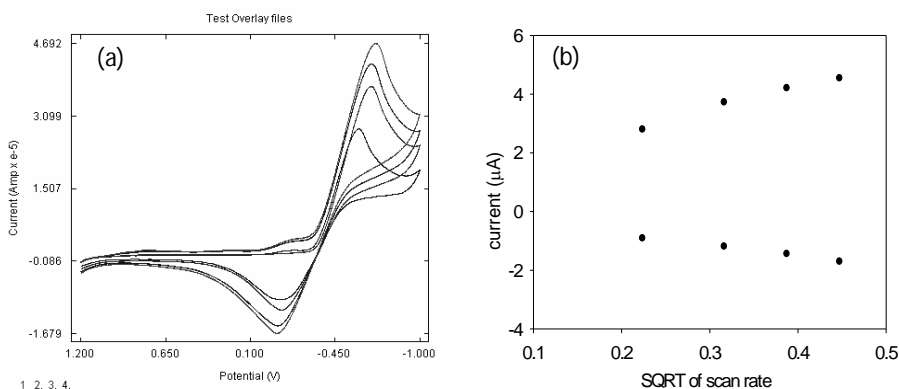


Fig. 4. Cyclic voltammograms of Fe-Sac complex in aqueous medium on Au electrode vs Ag/AgCl at (a) different scan rate and (b) the variation of peak current with sq. root of scan rate.

Fig. 4b indicates that the linear plot for anodic process passes through origin whereas that for cathodic process does not, which may be due to the fact that the electrode process on the cathode is to some extent adsorptive controlled (Bard and Faulkner 1980).

The variation of peak potential separation with scan rate for the complex at Au electrode vs Ag/AgCl at different scan rate are displayed in Fig. 5. It is found that with the increase of scan rate the peak separation increases. The ratio of the anodic and cathodic peak current for the electroactive species is quite smaller than unity and decreases with scan rate. These observations suggest that the system is not reversible but it may be called as quasi reversible process (Mamun *et al.* 2011).

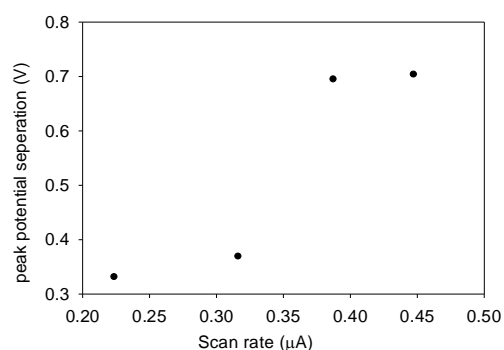


Fig. 5. Variation of peak potential separation with scan rate for Fe-Sac complex on Au electrode vs Ag/AgCl at different scan rate.

Effect of electrode material: The redox behavior of Fe(III) in the complex at different electrodes are shown in Fig. 6. Pair of cathodic and anodic peaks is found on Au electrode. However, two pairs of cathodic and anodic peaks appeared on Pt electrode. On GC electrode no significant response was found.

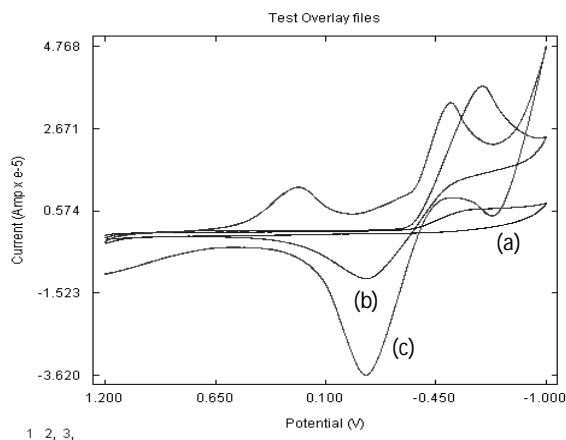


Fig. 6. Cyclic voltammetric response of the Fe(III) in the complex at (a) GCE, (b) Au and (c) Pt electrode vs. Ag/AgCl.

With the variation of electrode material the redox behavior of Fe(III) in the complex changes significantly regarding the number, position and current of both the cathodic and anodic peaks. It is difficult to explain this behaviour exactly, but one thing may be said that the mechanism of the electrode processes on different surfaces is quite different (Bard and Faulkner 1980). At gold electrode the voltammogram shows usual pattern for Fe(II)–Fe(III) system. The voltammogram of Fe(II)–Fe(III) system of the complex at Pt electrode is very much unusual, it contains two pair of cathodic and anodic peaks which needs further investigation for proper explanation.

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