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CYCLIC VOLTAMMETRIC REDUCTION OF 7-HYDROXY AND ACETOXY FLAVONES AT GLASSY CARBON ELECTRODE

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Electrochemical reduction behavior of 7-acetoxyflavone was compared with 7-hydroxyflavone on glassy carbon electrode with DMF and 60% DMF/Britton Robinson buffer at pH 3.8 & 10.1 using cyclic voltammetry. Single irreversible reduction waves were observed due to the reduction of keto moiety. The effects of change in medium, pH and sweep rate were evaluated. The electrode process was found to be diffusion controlled and enhanced substituent effect was noticed due to extended conjugation. Kinetic parameters were calculated from cyclic voltammetric measurements using R.S.Nicholson and I.Shain's equation.

Keywords: 7-hydroxy flavone, GC electrode, B.R.Buffer and Cyclic voltammetry.

INTRODUCTION

7-hydroxy flavone and its derivatives have been found useful as therapeutic agents, as general and local anti-inflammatory agents and administered orally or parenterally in the treatment of vascular diseases [1-2]. A thorough literature survey reveals that there is no report on the cyclic voltammetric study of 7-hydroxy and acetoxy flavones. The present work is a continuation of our research work on the reduction behaviour of flavonoids by Normal Pulse Polarographic (NPP) and Cyclic Voltammetric (CV) methods [3-5].

EXPERIMENTAL

The CV data were recorded with BAS 100 Electrochemical Analyzer with Glassy carbon (GC) cathode and Pt wire anode in dimethyl formamide (DMF) and aqueous DMF media with Tetrabutyl ammonium bromide (TBAB) as supporting electrolyte at different sweep rates (20, 50, 100 and 200 mVs^{-1}). IR spectra of the compounds were recorded on Perkin Elmer 1430 ratio recording spectrophotometer using KBr pellets. UV spectra were recorded on Jasco UVIDEC-430B (double beam) Jasco RC-150M Desk Top spectrophotometer.

A saturated calomel electrode was used as the reference electrode in aqueous medium and a gel type Ag/AgCl electrode (BSA. MF2020) was used in non aqueous Medium. The GC electrode used in the present work was fabricated from 2.5 mm diameter rod (A 0.048 cm) supplied by Tokai, Japan. The GC rods were cut into pieces of 5 mm length and sealed into a pyrex glass tube fitted with a suitable ground joint for easy mounting in the cell. For the purpose of achieving good reproducible surface, the solid electrodes were subjected to rigorous pre treatment schedules. The GC electrode was polished to mirror finish using different grades of emery from 1/0 to 4/0 in a progressive manner and then thoroughly rinsed with conductivity water.

The solutions were deoxygenated by purging with nitrogen gas for 15 minutes prior to measurements and during the measurement a stream of nitrogen gas was passed over the solution. The controlled potential electrolysis was carried out in a 250 ml beaker and a ceramic diaphragm (14.5 cm x 4.5 cm) was used to separate the anolyte from the catholyte. 7-acetoxy flavone (7A) was prepared by dissolving 60 mg of 7-hydroxy flavone(7) in 1.5 ml of pyridine and adding 1.5 ml of acetic anhydride to it in drop wise. The reaction mixture was left overnight in a stoppered flask at room temperature and then poured into 90 ml ice cold water with constant stirring and left undisturbed for one hour. The insoluble product was isolated by filtration and recrystallised from methanol [6]. 7-hydroxy flavone was purchased from Research organics, Madras and recrystallised from methanol. The Britton Robinson buffer was prepared from 0.04 *M* acetic acid, phosphoric acid and boric acid and the *p*H was adjusted with 0.2 N NaOH.

RESULTS AND DISCUSSION

The typical cyclic voltammogram recorded for the compounds are represented in the Figs. 1-2 and the cyclic voltammetric data of the compounds are given in Tables I and II.

Effect of sweep rate

The peak potential (E_p) value shifts towards more negative side as the sweep rate (v) increases. The cathodic peak current (i_p) increases with increasing sweep rate. The current function ($i_p/v^{1/2}$) has been found to be fairly constant with respect to sweep rates indicating that the electrode process is diffusion controlled. The diffusion coefficient and heterogeneous rate constant for electrode reaction decreases with increasing scan rate as expected for an irreversible electron transfer step [6].

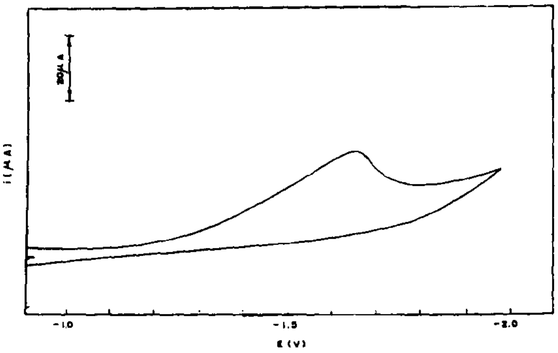


Fig. 1: Typical cyclic voltammogram of compound 7 medium - DMF; sweep rate -20 mVs^{-1}

Effect of medium and *p*H

The peak potential values of the compounds in DMF medium have been found to be more negative than in aqueous medium. The ease of reduction is found to be more in acidic *p*H than in alkaline *p*H which may be because of the formation of more easily reducible protonated radical intermediates. No linear relationship is found for $I_p/v^{1/2}$ with v and $I_p/v^{1/2}$ decreases with increasing v. Hence there must be a chemical reaction coupled with the electrochemical process. The coupling chemical reaction should probably be a protonation.The heterogeneous rate constant values for the electrode reactions have been found to be higher in acidic medium than in alkaline medium (Table III).

Effect of Nature of Substituent

From the observed E_p values, it is evident that the ease of electro reduction of acetylated derivative is higher than that of its hydroxy derivative in both media. It has been proved that when these groups are present in positions conjugated to the carbonyl group the hydroxyl group decreases while the acetoxyl group increases the ease of reduction process. The correlation of the E_p obtained in DMF medium and $c = o$ with σ indicate that the same factors which are operating in altering the IR stretching frequency of the carbonyl group are responsible for the ease of reduction of this group.

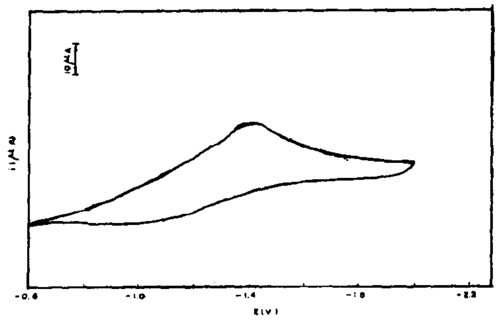


Fig. 2: Typical cyclic voltammogram of compound 7A medium - DMF; sweep rate 100 mVs^{-1}

TABLE I: Cyclic voltammetric data of 7-hydroxyflavone

Medium	S rate (V/s)	$-E_{pc}$ (V)	i_{pc} (μA)	D x 10^6 (cm^2/s)	αn_a
DMF	0.20	1.774	19.781	10.106	0.2361
	0.10	1.748	10.634	6.991	0.2359
	0.05	1.655	8.609	7.639	0.2362
	0.02	1.648	5.446	7.645	0.2363
60% DMF BR buffer *p*H = 3.8	0.20	1.257	17.790	6.512	0.2960
	0.10	1.208	12.460	6.508	0.2910
	0.05	1.192	9.214	7.144	0.2890
	0.02	1.140	6.126	7.809	0.2930
*p*H = 10.1	0.20	1.375	15.612	5.385	0.2760
	0.10	1.341	11.998	6.459	0.2710
	0.05	1.281	8.131	5.909	0.2730
	0.02	1.259	5.419	6.515	0.2750

TABLE II: Cyclic voltammetric data of 7-acetoxyflavone

Medium	S rate (V/s)	$-E_{pc}$ (V)	i_{pc} (μA)	D x 10^6 (cm^2/s)	αn_a
DMF	0.20	1.447	14.169	5.247	0.2330
	0.10	1.381	10.429	5.705	0.2321
	0.05	1.372	7.409	5.753	0.2324
	0.02	1.312	5.198	7.059	0.2331
60% DMF BR buffer *p*H = 10.1	0.20	1.227	16.131	6.767	0.2342
	0.10	1.192	11.450	6.825	0.2340
	0.05	1.144	8.219	7.036	0.2339
	0.02	1.090	5.695	8.441	0.2341
*p*H = 3.8	0.20	1.093	15.205	6.064	0.2321
	0.10	1.053	11.352	6.745	0.2327
	0.05	1.020	8.868	8.236	0.2326
	0.02	0.967	5.733	8.612	0.2324

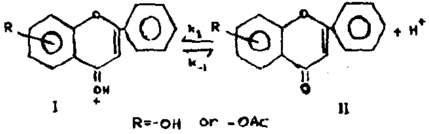
Mechanism

A single cyclic voltammetric 2 electron reduction wave is observed. EPR in situ spectrum confirmed the free radical intermediate formed during the electrochemical reduction of 7-hydroxy and acetoxy flavones. The light yellow coloured reactant solution is decolourised in acidic *p*H which may be accounted by the protonation. In alkaline *p*H the yellow colour deepens which is due to the ionization of the free hydroxyl group. The electrode process in neutral or alkaline medium could therefore be considered to be a mono anion radical (III) formation by the addition of one electron followed by protonation of the ion- radical.The uptake of the second electron occurs with no further requirement of activation energy, so that only a single cyclic voltammetric 2 electron wave is observed and further protonation of (iv) leads to the product (Fig. 3).

TABLE III

	$K_{s,h}$ $cm.s^{-1}$ x 10^{-7}		
Compound	DMF	60% DMF in BR buffer *p*H 3.8	60% DMF in BR buffer *p*H 10.1
7	6.4937	7.6125	3.3095
7A	8.6520	9.8532	5.4129

Scheme 1



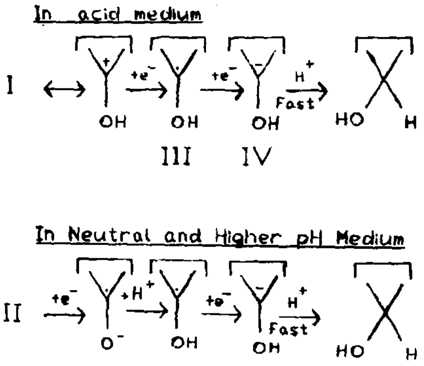


Fig. 3

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