

# VOLTAMMETRIC STUDIES OF THE REDUCTION OF FURFURAL ON GLASSY CARBON ELECTRODE IN AQUEOUS SOLUTIONS.

M GANESAN, M KOTTAISAMY\*, S THANGAVELU\* AND P MANISANKAR†

Department of Chemistry, Vivekananda College, Tiruvedagam, India

\*Central Electrochemical Research Institute, Karaikudi-623 006, India

†Chemistry Department, Alagappa University, karaikudi-623 003, India

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The electrochemical reduction of furfural is studied on glassy carbon electrode in aqueous buffer solutions using voltammetric technique. Tafel slope obtained from steady state voltammetry is pH dependent. Cyclic voltammetric data have shown that a single wave is formed in acidic and alkaline pH and two waves are formed at neutral pH particularly at higher concentration and the overall reduction process is a kinetically controlled irreversible process.

**Key words:** Voltammetry, glassy carbon, furfural.

## INTRODUCTION

Furfural is chemically reduced [1] to furfuryl alcohol by vapour phase hydrogenation. Electrochemical reduction of furfural has been studied earlier [2] on dropping mercury electrode (DME) under different pH conditions. Two waves are observed on DME below pH 5.0 and a single wave is observed above pH 5.0. Among the two waves observed, the first wave is reported to be reversible and corresponds to the addition of an electron to the protonated furfural molecule and the second wave to the addition of an electron to the free radical and is irreversible. Above pH 5.0, the observed two waves merged into a single two electron wave and the height of the wave decreased at alkaline pHs. These polarographic data have not however, explained extensively the influence of pH.

It has also been reported [3] that furfural undergoes reduction on zinc-cadmium electrodes to give a dimerized product. The reduction of furfural is also studied in ethanol water mixture of 1N H<sub>2</sub>SO<sub>4</sub> on copper, copper amalgam and electrodeposited cadmium electrode [4]. However, the effect of pH on the reduction behaviour of furfural is not considered.

In the present investigation reduction behaviour of furfural has been studied in the pH range of 4.75 to 12.7 on glassy carbon electrode.

## EXPERIMENTAL

A H-type glass cell with three electrode assembly was used for these experiments. This cell was divided into two compartments by a fine porous glass frit. The glassy carbon disc of dia 5 mm (working electrode) was connected to the saturated calomel electrode (SCE) (reference electrode) by a capillary containing agaragar-potassium chloride bridge. Platinum sheet electrode was used as the counter electrode. All other details of the cell and instrumentation are same as reported earlier [5 and 6].

Double distilled water was used for the preparation of solutions. Analytical grade sodium hydroxide, potassium dihydrogen phosphate were used for the preparation of the solvent-supporting electrolyte. LR grade furfural was distilled twice and then used.

### Electrochemical measurements

Electrolytic hydrogen purified by passing through alkaline

pyrogallol, concentrated sulphuric acid and double distilled water was passed through the electrolyte for 20 minutes for deaeration as well as for maintaining an inert atmosphere within the cell. The glassy carbon electrode tightly inserted into a glass tube, finished and polished mechanically was used for the voltammetric studies. The above electrode was degreased with trichloroethylene, washed with double distilled water and was positioned into the cell containing solvent supporting electrolyte. Both catholyte and anolyte were the same. All the experiments were done at a constant temperature of 295 K.

Potentials were applied from a potential scan generator through a potentiostat and the current out put was recorded using a fast response X-Y recorder. The electrode surface was electrochemically pretreated by cycling the potential of the electrode between the potential -0.6 V and -1.8 V vs SCE for a few minutes before actual recording of the current.

## RESULTS AND DISCUSSION

### Steady State Voltammetry

Figures 1 and 2 show the potential vs log current density plots derived from the steady state voltammograms recorded for the reduction of furfural on glassy carbon electrode in phosphate buffer of different pH conditions. Tafel slope analysis of the plots show that the Tafel slope value is pH dependent. In slightly acidic pH, the value was 120 - 140 mV and it reached to 60 mV in alkaline pH per decade change of current. These values have indicated that the first electron transfer is an irreversible charge transfer process and in alkaline medium the same electron transfer is a reversible one.

The half wave potential ( $E_{1/2}$ ) values obtained at 3 mV.s<sup>-1</sup> under different pH conditions were found to shift in the cathodic direction with increasing pH and the limiting current was found to increase with pH and after a particular pH, it decreased as shown in Table I. The shift in  $E_{1/2}$  values in the cathodic direction with increasing pH has indicated that protonated molecules are involved in the electron transfer reaction. The increase of the peak current with pH under constant concentration of furfural and constant sweep rate condition has suggested that the concentration of electroactive species is increased with pH and indirectly indicated

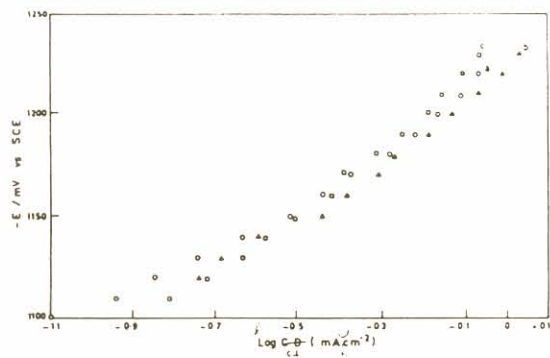


Fig. 1:  $E$  vs log current density plots for the reduction of furfural on GCE, pH 5.96 (a)  $4.83 \times 10^{-2}M$ , (b)  $7.24 \times 10^{-2}M$ , (c)  $9.66 \times 10^{-2}M$

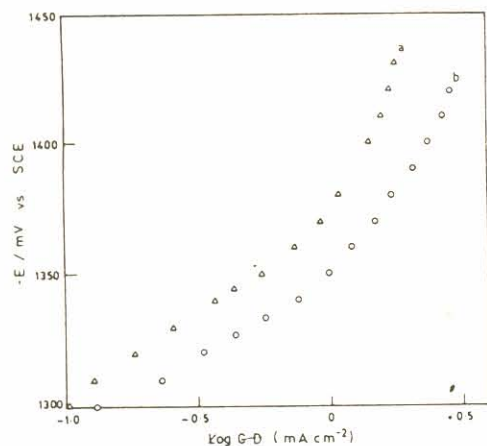


Fig. 2:  $E$  vs log current density plots for the reduction of furfural on GCE, pH 10.2 (a)  $2.4 \times 10^{-2}M$ , (b)  $4.8 \times 10^{-2}M$

TABLE-I: Effect of pH on half wave and peak current values for the reduction of  $4.828 \times 10^{-2} M$  furfural on GCE under steady state condition

pH	$E_{1/2}$ (mv)	$i_p$ (mA)
5.96	1270	0.450
7.00	1310	0.500
10.20	1370	0.540
12.70	1360	0.430

the involvement of a preceding chemical reaction which generates electroactive species and the chemical reaction is catalysed by alkali.

#### Cyclic voltammetry

The cyclic voltammetric reduction behaviour of furfural was recorded on GCE. Figure 3 shows the typical cyclic voltammogram recorded for the reduction of furfural in phosphate buffer of pH 5.96 at  $20 \text{ mV.s}^{-1}$ . Well defined single peak was formed with an  $E_p$  of  $-1420 \text{ mV vs SCE}$ . The wave may be a two electron or one electron wave.

#### Effect of sweep rate

The sweep rate was varied from  $20 \text{ mV.s}^{-1}$  to  $320 \text{ mV.s}^{-1}$ . Figure 4 shows the effect of sweep rate on the cyclic voltammograms obtained for the reduction of furfural on GCE at

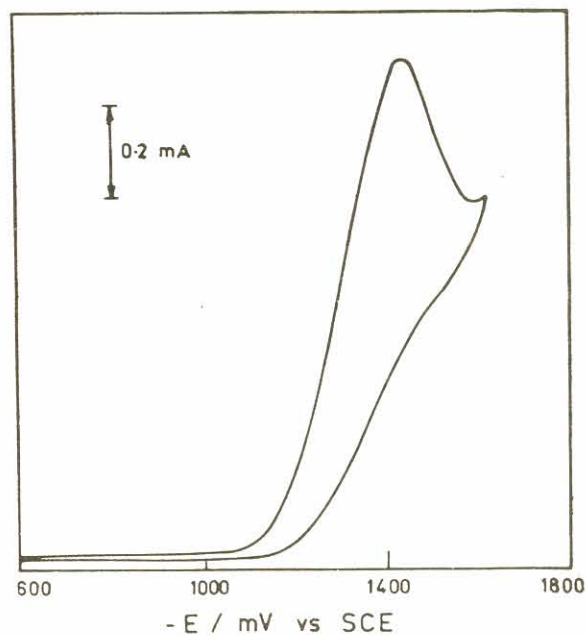


Fig. 3: Cyclic voltammogram recorded for the reduction of  $4.8 \times 10^{-2}M$  furfural on GCE, pH 5.96. Sweep rate  $20 \text{ mV.s}^{-1}$ .

pH 10.2. Peak current was found to increase with increasing sweep rate but  $i_p/v^{1/2}$  values were found to be decreasing with increasing sweep rate irrespective of the pH conditions. The decreasing  $i_p/v^{1/2}$  values indicate that the overall process is kinetically controlled. The controlling chemical reaction may be a dehydration reaction of the hydrated furfural molecule or protonation of the furfural molecule or the intermediate species.

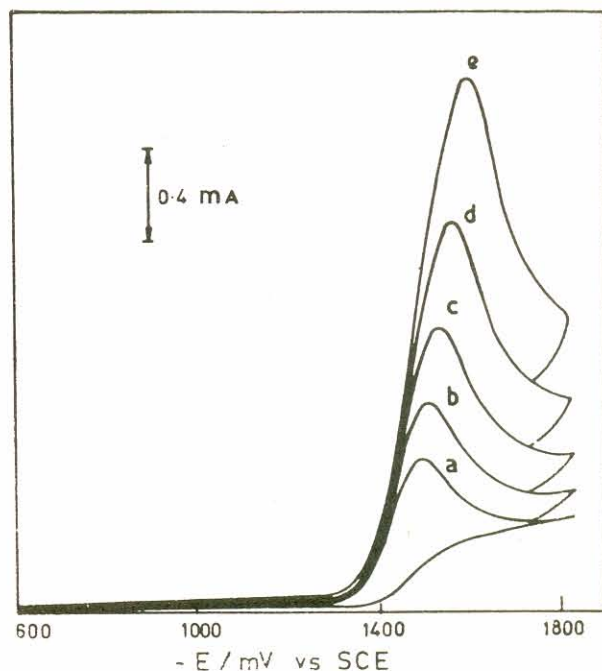


Fig. 4: Effect of sweep rate on the cyclic voltammograms recorded for the reduction of  $2.414 \times 10^{-2}M$  furfural on GCE, pH 10.2. Sweep rate (a)  $20 \text{ mV.s}^{-1}$  (b)  $40 \text{ mV.s}^{-1}$  (c)  $80 \text{ mV.s}^{-1}$  (d)  $160 \text{ mV.s}^{-1}$  (e)  $320 \text{ mV.s}^{-1}$ .



### Effect of concentration

The concentration of furfural was varied from 0.024 M to 0.24 M and its effect on the cyclic voltammetric reduction behaviour was recorded. It was found that the peak current increased with increasing concentration while potential shifted to more cathodic values with. This effect was more pronounced around neutral pH. This may be due to blocking effect of furfural molecules adsorbed over electrode surface.

### Effect of pH

Cyclic voltammetric behaviour of the reduction of furfural was recorded at different pH conditions in the pH range 4.75 to 12.7. A single wave was observed at pH 4.75, 5.98 and at alkaline pH. Two waves were observed at pH 7.0 particularly at higher concentrations of furfural. No anodic wave was observed in the reverse scan in the whole pH range studied.

The peak current ( $i_p$ ) was found to increase with increasing pH upto 10.2.  $E_p$  and  $E_{p1/2}$  values were found to shift in the cathodic direction with increasing pH. Table II shows the effect of pH on cyclic voltammograms obtained for the reduction of  $4.8 \times 10^{-2}$  M furfural on GCE at  $40 \text{ mV}\cdot\text{s}^{-1}$ . Increase of peak current with pH has indicated that the concentration of electroactive species is increased as the pH of the electrolyte increased and therefore a preceding chemical reaction is controlling the charge transfer reaction and the chemical reaction is catalyzed by alkali. At the same time, shifting of  $E_p$  and  $E_{p1/2}$  values to cathodic side observed with increasing pH has suggested that only protonated molecules are involved in the charge transfer reaction and the preceding chemical reaction which is controlling the overall process may be the dehydration reaction which is controlling the overall process may be the dehydration reaction, reaction hydrated furfural molecules.

TABLE-II: Effect of pH on cyclic peak parameters obtained for the reduction of furfural on glassy carbon electrode Sweep rate  $40 \text{ mV}\cdot\text{s}^{-1}$

pH	$i_p$ (mA)	$-E_p$ (mV)	$-E_{p1/2}$ (mV)
4.75	1.10	1580	1410
5.96	1.29	1465	1320
7.0	1.52	1520	1390
10.2	1.565	1530	1430
12.7	1.450	1460	1390

This type of increase of current with increasing pH has already been observed with the reduction of formaldehyde [7 and 8], glycolaldehyde [9], glyoxylic acid [10] with exist in the hydrated form and decrease of peak current or limiting current observed beyond a particular pH was also explained by the formation of electroinactive geminol diol anion ( $\text{RCHOHO}^-$ ) from the hydrated molecule as follows.

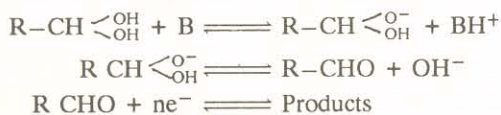


Figure 5 shows the cyclic voltammograms recorded at pH 7.0 for the reduction of  $1.2 \times 10^{-1}$  M furfural on GCE at different sweep rates. Two waves were observed under the above condition. The current value of the total wave height was very less when compared to the current obtained for  $0.48 \times 10^{-1}$  M furfural at  $40 \text{ mV}\cdot\text{s}^{-1}$ . The first wave height was increasing with sweep rate but the second wave height was almost independent of sweep rate.  $E_{1/2}$  values of the first wave and  $E_{p1/2}$  that of the single wave formation for lower

concentration of furfural at pH 7.0 are almost the same. Therefore, the electrode process occurring in the first wave formation was the same as that observed with a single wave at other pH conditions except for the blocking of the electrode surface by adsorption of furfural molecules and this was indicated by the very low value of the peak current of the first wave and the second wave was due to the second electron transfer to the adsorbed intermediate.

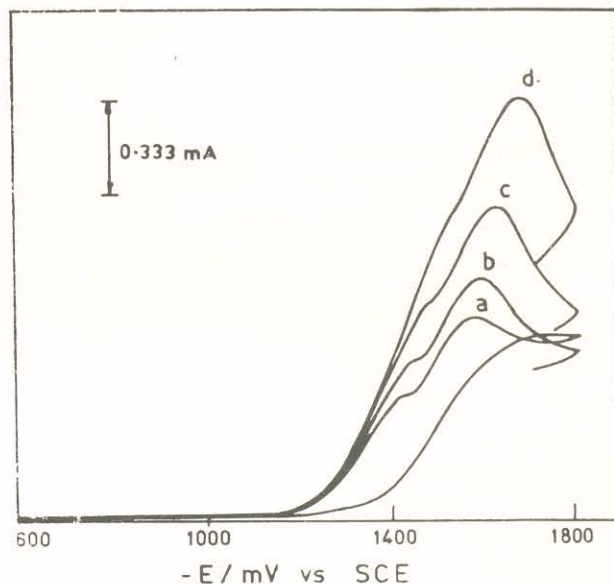


Fig. 5: Effect of sweep rate on the cyclic voltammogram recorded for the reduction of  $1.2 \times 10^{-1}$  M furfural on GCE. pH 7.0. Sweep rate (a)  $10 \text{ mV}\cdot\text{s}^{-1}$  (b)  $20 \text{ mV}\cdot\text{s}^{-1}$  (c)  $40 \text{ mV}\cdot\text{s}^{-1}$  (d)  $80 \text{ mV}\cdot\text{s}^{-1}$ .

The voltammetric and cyclic voltammetric study of the pH effect on the reduction behaviour of furfural has shown that the protonated molecules are involved in the reduction and the overall electrode process is a two electron irreversible reduction process which is controlled by the preceding chemical reaction (dehydration). The following is the reaction scheme for furfural.



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