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ELECTROCHEMICAL REDUCTION OF p-AMINOAZOBENZENE ON GLASSY CARBON ELECTRODE

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The electrochemical reduction of p-aminoazobenzene was investigated on glassy carbon electrode in aqueous methanolic solution of less acidic and alkaline pH using voltammetry techniques. Single wave was observed both at pH 3.0 and in alkaline pH conditions. Cyclic voltammetric data showed that the reduction process was kinetically controlled irreversible process at pH 3.0 and diffusion controlled irreversible process at alkaline pH. Product analysis of the preparative electrolysis experiments confirmed that the reduction was a two electron transfer process.

Key words: Voltammetry, p-aminoazobenzene, glassy carbon electrode, electroreduction

INTRODUCTION

Azo and diazocompounds are important substances which are used in dye industry and pharmacy [1, 2]. These compounds are also used to prepare hydrazo and amino compounds by reduction. Reduction of azo, azoxy and diazo compounds are generally carried out by chemical methods.

Electrochemical reduction of these azo compounds are also studied in different media (acidic, neutral, basic aqueous, mixed aqueous-organic media and aprotic media) on a number of electrode materials [3-5] and has been reviewed [6]. The polarographic reduction of azobenzene has been studied in the pH range 1-13 and reported to be pH dependent. In acid medium (pH below 4), two reduction waves are observed where the second wave is due to the further reduction and cleavage of hydrazobenzene with the formation of aniline. Only one reduction wave observed in the pH range 4-13 indicates that prior protonation of the two nitrogen atoms present in hydrazobenzene is a prerequisite for further reduction. With increase in acidity of the medium below pH 4.0, the wave height of the second wave increases and reaches the height of the first wave at pH 2.0, at the same time changing from a kinetically controlled to a diffusion controlled wave. It has been reported that further increase of acidity leads to a decrease of the second wave height due to the benzidine rearrangement of hydrazobenzene in acid medium

$$C_6H_5 - N = N - C_6H_5 \overset{2H^+}{\underset{2e^-}{\rightleftharpoons}} C_6H_5 - NHNH - C_6H_5 \quad \ldots(1)$$

$$C_6H_5 - NHNH - C_6H_5 \overset{+H^+}{\rightleftharpoons} C_6H_5\overset{+}{N}H_2NHC_6H_5 \quad \ldots(2)$$

$$C_6H_5\overset{+}{N}H_2NHC_6H_5 \overset{+H^+}{\rightleftharpoons} C_6H_5\overset{+}{N}H_2\overset{+}{N}HC_6H_5 \quad \ldots(3)$$

$$C_6H_5\overset{+}{N}H_2\overset{+}{N}H_2C_6H_5 \overset{+2e^-}{\rightleftharpoons} 2C_6H_5NH_2 \quad \ldots(4)$$

Substituent effect in the electrochemical reduction of substituted azobenzenes [7-10] are extensively studied and found that electron withdrawing substituents such as $-COOH$, $-SO_3H$ decrease the basicity of nitrogen atoms in azobenzene and thus hinders the further reduction of the hydrazobenzene whereas electron donating substituents in the ortho or para-position increase the basicity of nitrogen atoms in azobenzene and favour further reduction. Preparative scale reduction of p-aminoazobenzene to p-phenylene diamine is also reported [11].

Azobenzene and substituted azo compounds undergo electroreduction in DMF on dropping mercury electrode (DME) with two one electron steps [12-14] wherein the first electron transfer is reversible. This paper reports mainly the results of the voltammetric studies of the reduction of p-aminoazobenzene (p-AAB) at slightly acidic and alkaline medium on glassy carbon electrode (GCE) and preparative experimental studies for product identification.

EXPERIMENTAL

Cell

An H type glass cell with three electrode system was used for these experiments except for the preparative electrolysis. This cell was divided into two compartments by a fine porous glass frit. The working glassy carbon disc electrode of 5 mm diameter was connected to the saturated calomel electrode (SCE) acting as reference electrode by a capillary containing agar-agar-potassium chloride bridge. Platinum sheet electrode was used as the counter electrode. All the other details of the cell and instrumentation are same as reported earlier [15, 16].

Double distilled water and methanol were used for preparing solutions. Analytical grade sodium hydroxide-sodium acetate and sulphuric acid were used for the preparation of supporting electrolyte. p-amino-azobenzene was prepared from diazoaminobenzene [17], recrystallised and used.

Electrochemical measurements

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 the inert atmosphere within the cell. The working glassy carbon electrode tightly inserted into a glass tube, finished and polished mechanically was used for voltammetric studies. The above electrode was degreased with trichloro-ethylene, washed with double distilled water and positioned into the cell containing solvent supporting electrolyte. Both catholyte and anolyte were the same. All the experiments were done at a constant tempertaure of 303K.

Potentials were applied from a potential scan generator through a potentiostat and the current output 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 −0.2V to −1.6V vs SCE for a few minutes before actual recording of the current.

Preparative electrolysis experiments were done in a divided cell of 500 ml capacity. 400 ml of the catholyte was used and it was separated by a cation exchange membrane diaphragm and catholyte was stirred by a mechanical stirrer during electrolysis. 20 cm^2 area GCE was used as cathode and stainless steel plate as anode. The temperature of the cell was maintained at 295-297 K.

RESULTS AND DISCUSSION

Acid pH (3.0)

Steady state voltammetry

Figure 1 shows the typical voltammogram obtained for the reduction of 0.2515×10^{-3} p-aminoazobenzene on GCE in 1:1 methanol water mixture containing 0.1M sodium acetate hydrochloric acid buffer of pH 3.0. Well defined voltammogram with single peak at a potential of −400mV vs SCE is obtained under unstirred condition.

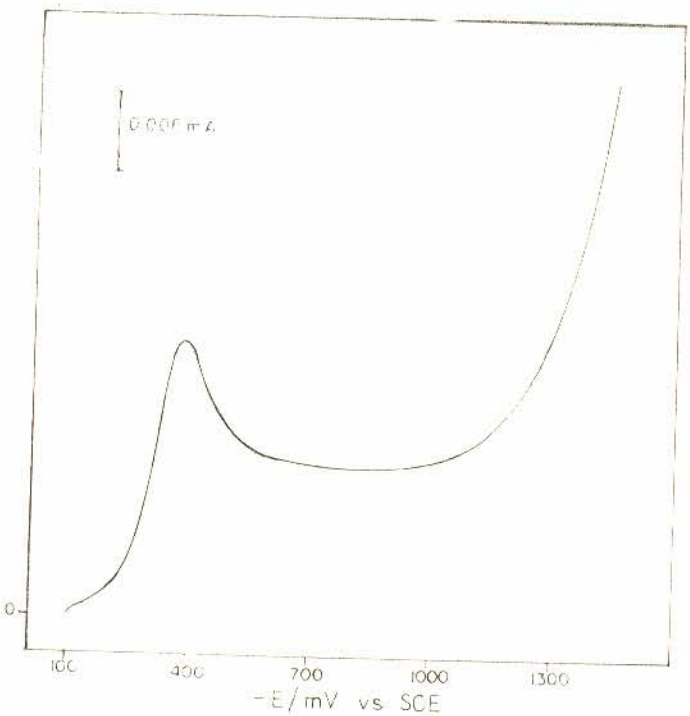

Fig. 1: Typical voltammogram recorded for the reduction of 0.2515×10^{-3} M p-AAB on GCE. pH 3.0. Sweep rate 20 $mV.s^{-1}$

Potential, E vs log current density plots are derived from the steady state voltammograms (Fig. 2) and Tafel slope analysis of these plots give Tafel slope value of 110-120 mV per decade change of current. This value has indicated that the first electron transfer is irreversible under the above conditions.

Cyclic voltammetry

Figure 3 shows the cyclic voltammograms recorded for the reduction of 2.012×10^{-3}M p-aminoazobenzene on GCE. Voltammograms with single cathodic peak or wave is observed in the forward scan and no complementary anodic peak or wave is observed on reverse scan. Figure 3 again shows the effect of sweep rate on the voltammograms. Peak current, i_p, is found to increase with sweep rate. But $i_p/V^{1/2}$ values are not constant. Peak potential, E_p, is found to shift in the cathodic direction with increase in sweep rate. This observation along with the absence

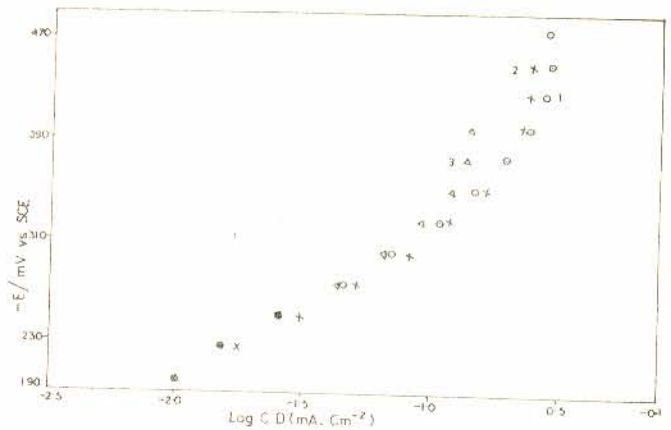

Fig. 2: E vs log c.d. plots for the reduction of p-aminoazobenzene at GCE. pH 3.0 Temp. 303K
(1) 2.012×10^{-3} M (2) 1.509×10^{-3} M (3) 1.006×10^{-3} M

of anodic wave on reverse scan and the decrease of $i_p/V^{1/2}$ values have suggested that the overall process is kinetically controlled in an irreversible process.

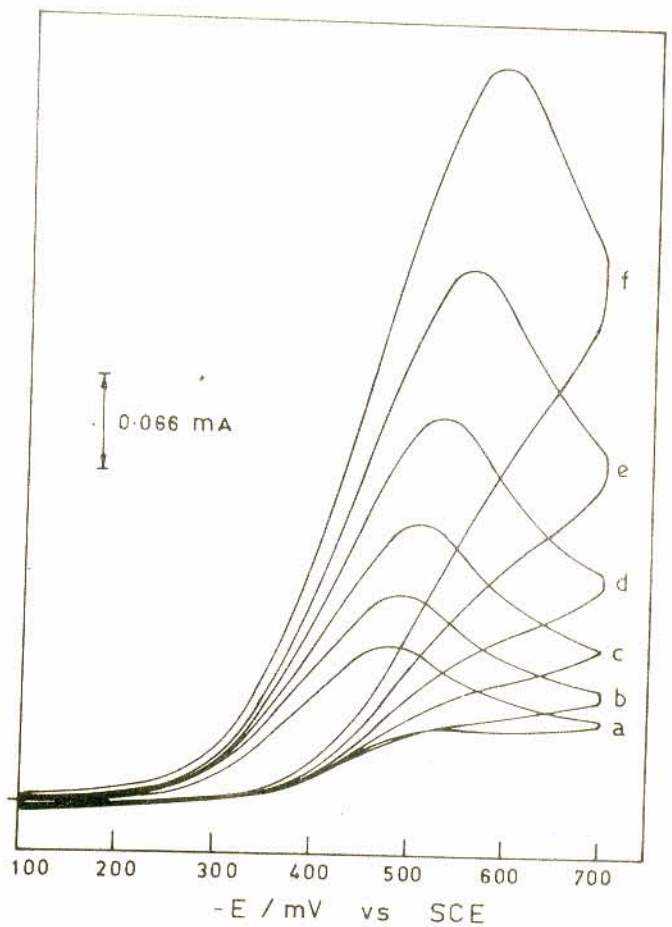

Fig. 3: Effect of sweep rate on the cyclic voltammograms obtained for the reduction of 2.012×10^{-3} M p-aminoazobenzene on GCE. Temp. 303K, pH 3.0
(a) 10 $mV.s^{-1}$ (b) 20 $mV.s^{-1}$ (c) 40 $mV.s^{-1}$ (d) 80 $mV.s^{-1}$ (e) 160 $mV.s^{-1}$ (f) 320 $mV.s^{-1}$

Alkaline pH

Steady state voltammetry

Voltammograms are recorded at 3 $mV.s^{-1}$ for the reduction of p-aminoazobenzene on glassy carbon electrode in 1:1 methanol-water mixture containing 0.25M sodium hydroxide. Well defined peak shaped voltammogram with single peak is obtained under unstirred condition.

Potential, E vs log current density plots are derived from the voltammograms (Fig. 4) and Tafel slope analysis of these plots gives the Tafel slope value of 110mV per decade change of current. This value gives an indication that the first electron transfer is irreversible.

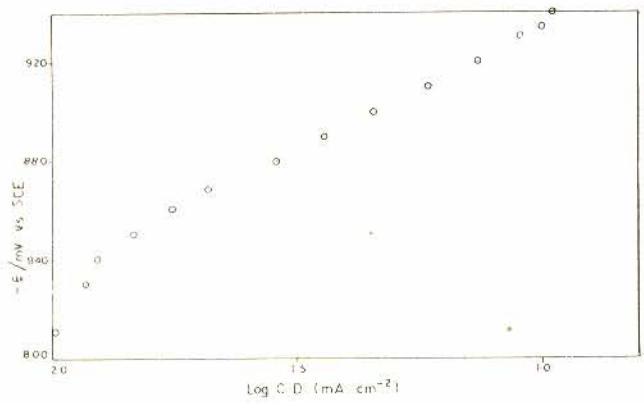

Fig. 4: E vs log c.d. for the reduction of p-aminoazobenzene (1.257 x 10^{-3} M) on GCE in alkaline methanol medium. Temp. 303K

Cyclic voltammetry

Figure 5 shows the typical cyclic voltammogram recorded for the reduction of 1.257 x 10^{-3}M p-aminoazobenzene on GCE in alkaline medium at 80 $mV.s^{-1}$. Well defined single cathodic peak with two small anodic waves on scan reversal is observed.

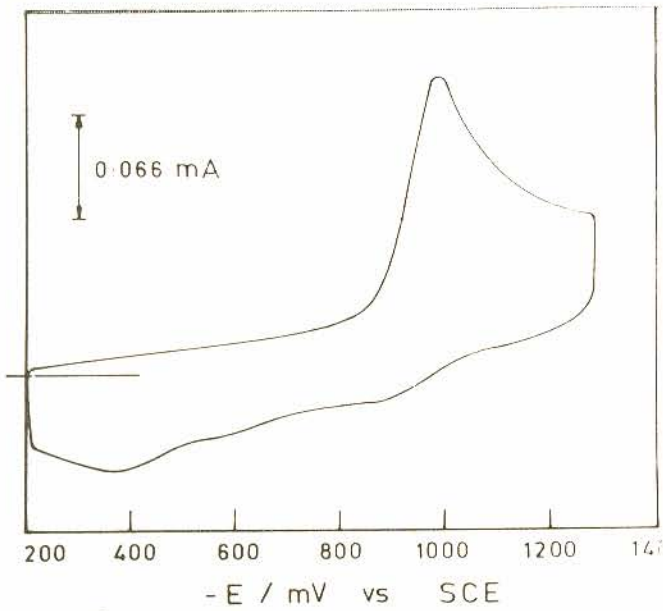

Fig. 5: Typical cyclic voltammogram recorded for the reduction of 1.257 x 10^{-3}M p-aminoazobenzene on GCE in 1:1 methanol water mixture containing 0.25 N NaOH. Temp 303 K, Sweep rate 80 $mV.s^{1}$

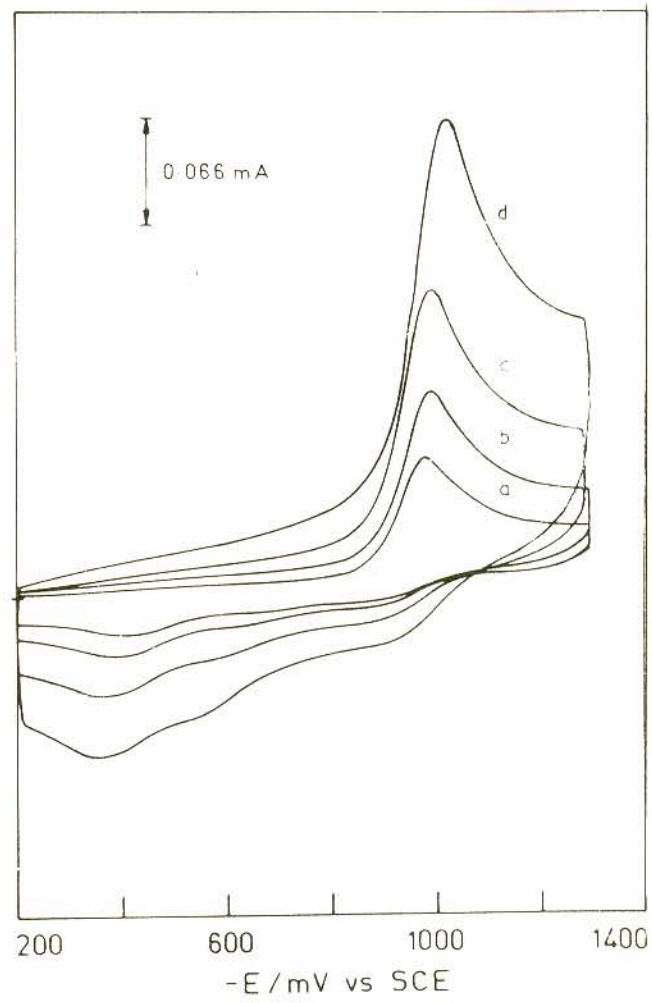

Fig. 6: Effect of sweep rate on the cyclic voltammograms recorded for the reduction of 0.7545 x 10^{-3}M p-aminoazobenzene on GCE in 0.25N NaOH. Sweep rate: (a) 20 $mV.s^{-1}$ (b) 40 $mV.s^{-1}$ (c) 80 $mV.s^{-1}$ (d) 160 $mV.s^{-1}$ (e) 320 $mV.s^{-1}$

Effect of sweep rate

Cyclic voltammograms are recorded for the reduction of p-amino-azobenzene at different sweep rates. Figure 6 shows the effect of sweep rate on the cyclic voltammograms obtained for the reduction of 1.258 x 10^{-3}M p-aminoazobenzene on GCE in alkaline medium. Cathodic peak current i_p is found to increase with sweep rate and $i_p/V^{1/2}$ values are almost constant as shown in Table I. This observation has indicated that the reduction process is diffusion controlled process. Peak potential (E_p) is found to shift in the cathodic direction even though anodic waves are observed on reverse scan which are not well defined and the anodic current increases with increasing sweep rate. The current values are very low as compared to the cathodic current values. Therefore, the reduction process is found to be quasireversible.

CONCLUSION

Comparison of the voltammetric data obtained at pH 3 and alkaline pH indicate that peak current is slightly higher at acidic pH under identical conditions and this is in accordance with the polarographic data which has shown that there is a transition from

TABLE-I: Cyclic peak parameters for the reduction of 1.258×10^{-3}M p-aminoazobenzene in 1:1 methanol water mixture containing 0.25N NaOH on glassy carbon electrode

Temperature 301 - 303 K

Sweep rate $mV.s^{-1}$	i_p (mA)	$i_p/V^{1/2}$	$-E_p$ (mV)
20	0.0693	0.4900	975
40	0.0990	0.4950	985
80	0.1452	0.5134	990
160	0.1914	0.4785	1015

four electron reduction to two electron reduction when the pH of the solution changes from acidic to alkaline. The observed fact that the reduction of p-aminoazobenzene is kinetically controlled under acidic pH (3.0) shows that slow protonation of the reactant before electron transfer controls the overall process and unprotonated p-aminoazobenzene undergoes electron transfer under alkaline pH conditions.

Preparative electrolysis experiments carried out in a divided cell in aqueous methanolic alkaline condition using 20 cm^2 area GCE have confirmed the formation of two electron reduction product, namely p-aminohydrazobenzene. As quantitative analysis of the experimental results has not been made, the results are not presented.

The following is the proposed reduction mechanism of p-aminoazobenzene on GCE in aqueous methanolic alkaline solution:

$$p - H_2N - C_6H_4 - N = N - C_6H_5 \xrightleftharpoons{e^-}$$

$$pH_2N - C_6H_4 \overset{(=)}{\underset{=}{N}} - \underset{-}{N} - C_6H_5 \qquad \ldots(5)$$

$$p - H_2N - C_6H_4 - \overset{(-)}{\underset{-}{N}} - \underset{-}{N} - C_6H_5 \xrightleftharpoons{e^-}$$

$$p - H_2N - C_6H_4 \overset{(-)}{\underset{-}{N}} - \underset{-}{\overset{(-)}{N}} - C_6H_5 \qquad \ldots(6)$$

$$p - H_2N - C_6H_4 - \overset{(-)}{\underset{-}{N}} - \underset{-}{\overset{(-)}{N}} - C_6H_5 \xrightarrow{2H_2O}$$

$$p - H_2N - C_6H_4NHNHC_6H_5 + 2OH^- \qquad \ldots(7)$$

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