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# Electrochemical Oxidation of *p*-Chloroaniline at a Platinum Electrode

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**Anodic oxidation of *p*-chloroaniline in aqueous solutions has been carried out at a platinum electrode using the techniques of cyclic voltammetry and chronoamperometry. Mechanism for the oxidation process has been proposed and is consistent with the electrochemical data and the products of the reaction. The data is also utilized in the evaluation of the transfer and diffusion coefficients of the electroactive species under consideration. The nature of adsorption involved is discussed.**

LORD and Rogers[1] have carried out the conventional voltammetric studies on the oxidation of anilines by recording polarograms at gold, graphite, platinum and lead dioxide electrodes. Anodic voltammetry at an impregnated graphite electrode has been applied to study the effect of ring substitution on the half-wave potentials of phenol and aniline and to determine whether the half-wave potentials of disubstituted anilines and phenols could be reliably predicted from the values of monosubstituted compounds[2]. Bacon and Adams[3] have carried out cyclic voltammetric studies of a series of substituted anilines, including *p*-chloroaniline, in acid media at a carbon paste electrode and postulated that these compounds undergo a head to tail coupling giving the corresponding 4'-substituted *p*-amino diphenylamines. Santhanam[4] showed that the process involved removal of only one electron with the formation of 4,4'-dichloroazobenzene as the product of oxidation. Wawzonek and McIntyre[5] reported that when *p*-substituted anilines were oxidized in acetonitrile in the presence of pyridine, N-N coupling occurred to give hydrazobenzenes which further underwent oxidation to the substituted azobenzenes.

In the present investigation, an attempt is made to understand the nature and mechanism of the electrochemical oxidation of *p*-chloroaniline at a platinum electrode using cyclic voltammetry and chronoamperometry. The data obtained by these techniques have been made use of in the evaluation of transfer and diffusion coefficients of the above species in the media of different *p*H values.

The theoretical principles and various applications of the cyclic voltammetric and chronoamperometric techniques have been described in detail in the literature[6,7].

## Materials and Methods

*p*-Chloroaniline used was a Burgoyne sample melting sharply at 70°. Solution of *p*-chloroaniline was prepared by first dissolving it in the minimum quantity of ethanol and then diluting with water to the required volume.

The supporting electrolytes used were: (i) Clarks and Lubs buffer of *p*H 1·3, prepared by mixing 200 ml of 0·1*N* hydrochloric acid and 250 ml of 0·2*N* potassium chloride and diluting to 1000 ml. (ii) Phosphate buffer of *p*H 6·6, prepared by mixing 178 ml of 0·1*N* sodium hydroxide and 500 ml of 0·1*N* potassium dihydrogen phosphate and making up the resulting solution up to 1000 ml. Other supporting electrolytes (0·1*N* sodium carbonate, 0·1*N* sodium hydroxide and 1*N* sulphuric acid) were prepared using BDH Analar grade samples.

A multi-purpose electrochemical instrument which could function as a polarograph, a potentiostat, a cyclic voltammeter and a galvanostat, constructed by Bhagat and Santhanam[8] at the Tata Institute of Fundamental Research, was employed in the present work. It could provide automatic cycling between the potentials needed for cyclic voltammetric work with the facility to hold the instrument at any desired value. A Mosley-135AM X-Y recorder of Hewlett & Packard was employed for recording both the cyclic voltammograms and chronoamperometric curves. Fortran IV computer IBM system 360/44 was used for the computation of data.

*Procedure* — Equal volumes (~100 ml) of the supporting electrolyte were taken separately in a 400 ml beaker and in a porous vessel of convenient size kept in the beaker. The supporting electrolyte in the porous vessel was rendered free of dissolved oxygen by passing nitrogen gas. The solution was also kept under nitrogen atmosphere to avoid atmospheric oxidation. A platinum wire electrode of radius 0·5 mm was kept immersed in the solution in the porous vessel and a spiral platinum rod counter electrode was placed outside in the solution in the beaker. A known volume of the electroactive species under study in solution at known concentration was added and cyclic voltammograms recorded at the required sweep rates. Cyclic voltammograms were obtained at different concentrations of the electroactive species. Before every run the solution was stirred by bubbling nitrogen gas for 5 min. Cyclic voltammograms for the supporting electrolytes were also recorded in order to evaluate the exact contributions of the electroactive species.

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In the chronoamperometric experiments, the electrolytic cell was prepared in the same manner as above and after the supporting electrolyte was saturated with nitrogen gas, a known amount of the electroactive species was added and the current-time curves recorded at the required potentials. The current-time curves were also taken for the supporting electrolyte at the potentials at which the current-time curves were recorded for the species. Saturated calomel electrode was used as a reference electrode in all the above measurements.

Performance of the working electrode was checked by carrying out the cyclic voltammetric and chronoamperometric studies using potassium ferrocyanide as a test substance in 2$M$ potassium chloride as the supporting electrolyte, in view of its known behaviour in terms of reversibility and absence of adsorption at the electrode. Chronoamperometric data of this system have been employed to evaluate the electrochemical area of the working electrode which in the present case was found to be 1·326 sq. cm.

## Results and Discussion

*Cyclic voltammetric results* — Typical cyclic voltammograms of *p*-chloroaniline in sulphuric acid and Clarks and Lubs buffer are presented in Fig. 1. The electrochemical oxidation of *p*-chloroaniline takes place at +0·98 V (vs SCE) in sulphuric acid (Fig. 1a) and at +0·96 V (vs SCE) in Clarks and Lubs buffer (Fig. 1b). The anodic peak potentials (vs SCE) observed in phosphate buffer, sodium carbonate and sodium hydroxide are +0·94 V (Fig. 2a), +0·75 V (Fig. 2b) and +0·68 V (Fig. 2c) respectively. The peak potential values given above refer to particular sweep rates and concentrations of the species. Table 1 gives the cyclic voltammetric data for *p*-chloroaniline with reference to the peak potential values at different sweep rates and *p*H values. $E_p$ has been found to vary with *p*H. The shift of peak potentials with sweep rate in the different media employed and the absence of current in the reverse scan suggests the process to be irreversible.

Besides the regular oxidation peaks discussed earlier, additional redox couples were also noticed in the subsequent sweeps in certain media as revealed by the data in Table 2. The redox couples were not noticed for the potential range employed

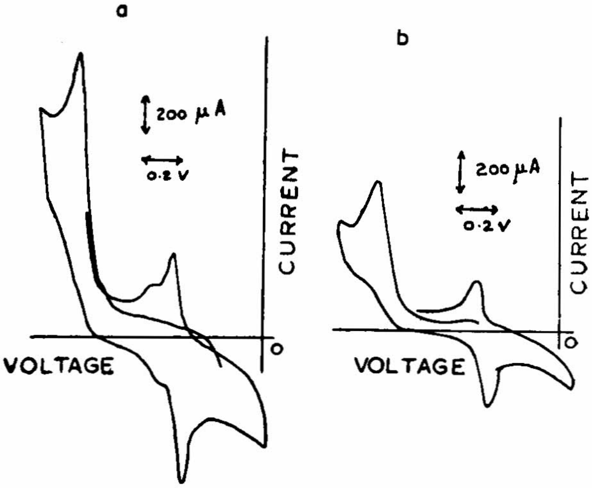

Fig. 1 — Cyclic voltammograms of *p*-chloroaniline in (a) H$_2$SO$_4$ (1·5 m$M$, sweep rate = 0·72 V sec$^{-1}$), (b) Clarks and Lubs buffer (1·5 m$M$, sweep rate = 0·28 V sec$^{-1}$)

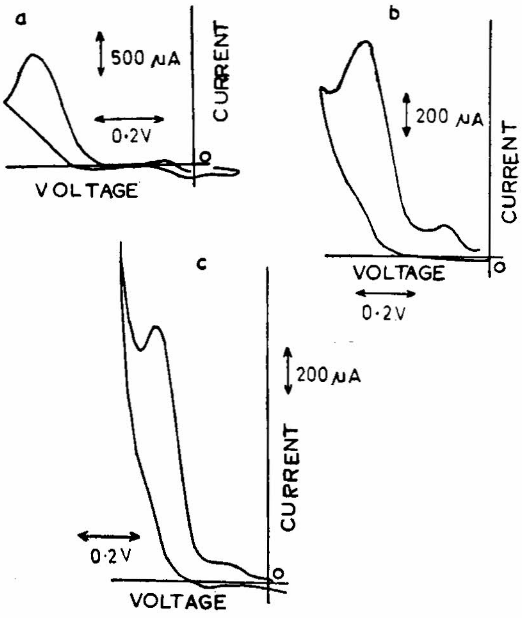

Fig. 2 — Cyclic voltammograms of *p*-chloroaniline in (a) phosphate buffer (4·32 m$M$), (b) Na$_2$CO (2·9 m$M$), (c) NaOH (2·9 m$M$) [sweep rate in all the cases = 0·13 V sec$^{-1}$]

TABLE 1 — PEAK POTENTIAL VALUES ($E_p$) AT DIFFERENT SWEEP RATES IN DIFFERENT SUPPORTING ELECTROLYTES IN CYCLIC VOLTAMMETRY OF *p*-CHLOROANILINE

(Conc. of *p*-chloroaniline = 1·5 m$M$)

| Sulphuric acid | | CL buffer | | Phosphate buffer | | Sodium carbonate | | Sodium hydroxide | |
|---|---|---|---|---|---|---|---|---|---|
| $v$/V sec$^{-1}$ | $E_p$/V | $v$/V sec$^{-1}$ | $E_p$/V | $v$/V sec$^{-1}$ | $E_p$/V | $v$/V sec$^{-1}$ | $E_p$/V | $v$/V sec$^{-1}$ | $E_p$/V |
| 0·05 | +0·96 | 0·04 | +0·92 | 0·04 | +0·79 | 0·04 | +0·64 | 0·04 | +0·59 |
| 0·14 | +0·96 | 0·14 | +0·95 | 0·13 | +0·84 | 0·13 | +0·72 | 0·13 | +0·65 |
| 0·28 | +0·97 | 0·28 | +0·96 | 0·29 | +0·88 | 0·26 | +0·72 | 0·26 | +0·66 |
| 0·35 | +0·97 | 0·35 | +0·96 | 0·37 | +0·89 | 0·36 | +0·73 | 0·35 | +0·68 |
| 0·49 | +0·97 | 0·49 | +0·97 | 0·49 | +0·90 | 0·51 | +0·74 | 0·51 | * |
| 0·72 | +0·98 | 0·71 | +0·99 | 0·70 | +0·92 | 0·72 | +0·78 | 0·72 | * |

*Well-defined peaks are not obtained.

TABLE 2 — ADDITIONAL PEAK POTENTIALS IN THE CYCLIC VOLTAMMETRY OF *p*-CHLOROANILINE

| Supporting electrolyte | Sweep width employed/V | Additional peak potentials/V | |
|---|---|---|---|
| | | Anodic | Cathodic |
| Sulphuric acid | 0 to 1·22 | +0·48 | +0·40 |
| Clarks and Lubs buffer | −0·06 to +1·16 | +0·40 | +0·34 |
| Phosphate buffer | +0·15 to +1·18 | +0·18 | +0·06 |
| Sodium carbonate | −0·01 to +0·97 | — | — |
| Sodium hydroxide | −0·1 to +0·90 | — | — |

TABLE 3 — VALUES OF THE PARAMETER $i_p/v^{\frac{1}{2}}c$

| Sweep rate/V sec$^{-1}$ | Conc./m*M* | Current/μamp | $i_p/v^{\frac{1}{2}}c$ |
|---|---|---|---|
| | SULPHURIC ACID | | |
| 0·04 | 1·5 | 320 | 1080 |
| | 2·9 | 600 | 1023 |
| | 4·3 | 780 | 895 |
| | CLARKS AND LUBS BUFFER (*p*H 1·3) | | |
| 0·04 | 1·5 | 320 | 1054 |
| | 2·9 | 560 | 933 |
| | 4·3 | 830 | 931 |
| | PHOSPHATE BUFFER (*p*H 6·6) | | |
| 0·04 | 1·5 | 420 | 1384 |
| | 2·9 | 700 | 1165 |
| | 4·3 | 980 | 1098 |
| | SODIUM CARBONATE (*p*H 11·4) | | |
| 0·04 | 1·5 | 415 | 1436 |
| | 2·9 | 710 | 1241 |
| | 4·3 | 930 | 1094 |
| | SODIUM HYDROXIDE (*p*H 13·0) | | |
| 0·04 | 1·5 | 420 | 1427 |
| | 2·9 | 790 | 1399 |
| | 4·3 | 1060 | 1264 |

TABLE 4 — DIFFUSION COEFFICIENT (*D*) DATA FOR *p*-CHLOROANILINE AT 24°

(Conc. of *p*-chloroaniline = 1·5 m*M*)

| Medium | $\alpha n_a$ | $10^5D$ (cm$^2$ sec$^{-1}$) | |
|---|---|---|---|
| | | Cyclic voltammetric | chronoamperometric |
| 1*N* sulphuric acid | 0·69 | 1·450 | 0·739 |
| Clarks and Lubs buffer | 0·80 | 1·015 | 1·018 |
| Phosphate buffer | 0·53 | 0·984 | 0·573 |
| Sodium carbonate (0·1*N*) | 0·40 | 1·883 | 0·667 |
| Sodium hydroxide (0·1*N*) | 0·44 | 1·663 | 0·667 |

TABLE 5 — CHRONOAMPEROMETRIC DATA FOR *p*-CHLOROANILINE*

(Conc. of *p*-chloroaniline = 1·5 m*M*)

| Time/s (sec) | Current (μamp) in | | | | |
|---|---|---|---|---|---|
| | Sulphuric acid | Clarks and Lubs buffer | Phosphate buffer | Sodium carbonate | Sodium hydroxide |
| 2 | 205 | 244 | 355 | 382 | 355 |
| 4 | 150 | 172 | 250 | 246 | 220 |
| 5 | 136 | 150 | 225 | 213 | 189 |
| 6 | 128 | 136 | 205 | 194 | 170 |
| 7 | 1211 | 124 | 192 | 166 | 152 |
| 8 | 114 | 112 | 175 | 158 | 135 |
| 9 | 110 | 108 | 166 | 140 | 121 |
| 11 | 100 | 96 | 152 | 117 | 101 |
| 13 | 95 | 88 | 136 | 100 | 87 |
| 15 | 93 | 86 | 127 | 90 | 74 |
| 16 | 88 | 82 | 124 | 82 | 72 |
| 18 | 85 | 78 | 115 | 76 | 59 |
| 20 | 80 | 72 | 110 | 66 | 57 |

*Potentials employed +1·10, +1·0, +0·90, +0·85 and +0·70 V in sulphuric acid, CL buffer, phosphate buffer, $Na_2CO_3$ and NaOH respectively.

in sodium carbonate and sodium hydroxide supporting electrolytes. It is interesting to note that the product of oxidation is itself involved in the formation of redox couples in the subsequent sweeps. This is supported by the fact that the cyclic voltammograms of the electro-oxidized product of *p*-chloroaniline (electro-oxidized for 1 hr and then the cyclic voltammograms taken) show the evidence of the presence of redox couple even in the first sweep.

In the calculation of *n* value using the basic equation for peak current

$$i_p = 2\cdot98\times10^5 . n(\alpha n_a)^{1/2}\, AD^{1/2}V^{1/2}C$$

the diffusion coefficient of *p*-methoxyphenol, a similar sized molecule (reported[9] in the literature as $0\cdot70\times10^{-5}$ cm$^2$ sec$^{-1}$) has been employed for the computation of $i_p/v^{1/2}\,c$ values for comparing with those obtained from the experiment (vide Table 3). The $\alpha n_a$ values employed are calculated from cyclic voltammetric results (Table 4). The number of electrons involved in the electrochemical oxidation of *p*-chloroaniline in sulphuric acid and Clarks and Lubs buffer is evaluated to be one and in the other media to be two.

In acidic solutions, the anodic reaction pathway for *p*-chloroaniline may probably be given as shown in Scheme 1 and the linearity of $i_p$ vs $v^{1/2}$ plot for *p*-chloroaniline in sulphuric acid suggests that the electrode process is diffusion-controlled.

Bacon and Adams[3] had observed a redox couple having an anodic peak at +0·25 V and cathodic peak at +0·275 V (vs SCE) for a sample of 4-amino-4′-chlorodiphenylamine at *p*H 3·1 at carbon paste electrode. This suggests that the additional redox couples noticed in the different media, which were found to shift with *p*H, are probably due to the 4-amino-4′-chlorodiphenylamine, the product of oxidation of *p*-chloroaniline.

In the alkaline media reaction (1) yielding 4,4′-dichloroazobenzene can be suggested.

$$2(p\text{-Chloroaniline}) \rightarrow 4,4'\text{-dichloroazobenzene} + 4H^+ + 4e \quad \ldots(1)$$

The formation of 4,4′-dichloroazobenzene as a product of oxidation has been confirmed by the absorption spectrum of the product collected after 30 min at the potential +0·70 V (vs SCE).

*Chronoamperometric results* — Current-time data for the electrochemical oxidation of *p*-chloroaniline in the different media and the potential steps employed are presented in Table 5. These values refer to a

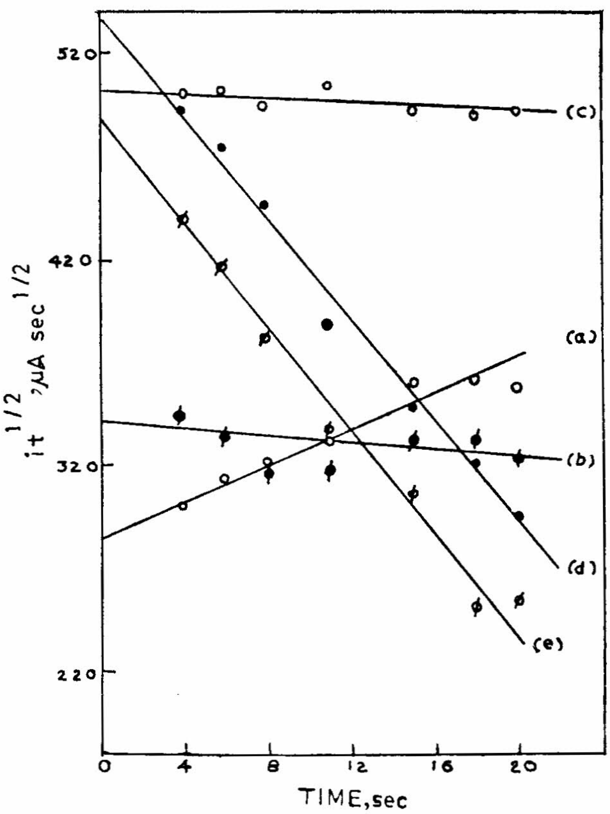

Fig. 3 — $it^{1/2}$ vs $t$ plots of $p$-chloroaniline in (a) $H_2SO_4$, (b) Clarks and Lubs buffer, (c) phosphate buffer, (d) $Na_2CO_3$ and (e) NaOH

particular concentration, and as the data follow similar pattern at other concentrations studied, they are not shown here. $it^{1/2}$ vs $t$ plots of $p$-chloroaniline (Fig. 3) show that the results are affected in phosphate buffer, sodium carbonate and sodium hydroxide. The decreasing trend in the variation of $it^{1/2}$ with time suggests complications due to adsorption on the electrode in these media. The pre-peaks obtained in sodium carbonate and sodium hydroxide (100 to 125 mV cathodic of the regular peaks) indicate that a strong adsorption of the product of oxidation may be responsible for reducing the effective area of the electrode and hence the discrepancy in results[10].

The diffusion-coefficient data for $p$-chloroaniline evaluated using both the techniques are presented in Table 4.

The diffusion-coefficient values obtained by chronoamperometric method are preferred to cyclic voltammetric values for the following reasons: (i) Cyclic voltammetric evaluation of diffusion-coefficient requires the knowledge of $\alpha n_a$ and $i_p/v^{1/2}c$ values. $\alpha n_a$ is extremely sensitive to the surface state of the electrode and $i_p/v^{1/2}c$ values are also influenced by adsorption. (ii) Chronoamperometric evaluation of the diffusion-coefficient requires a knowledge of $(it^{1/2})_0$ values. Since these values are calculated by extrapolation of $it^{1/2}$ values to zero time, the diffusion-coefficient values obtained by this method are not likely to be affected by the complications associated with the surface state of the electrode.

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