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PULSE VOLTAMMETRIC DETERMINATION OF pK_a OF PARA-CHLOROANILINE

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Monochloroderivatives of aromatic amines are the degradation products of commonly used herbicides. The oxidation potential of monochloroanilines at a number of solid electrodes has been found to be dependent on the number of substituents in the ring system (Suatoni *et al* 1961). Voltammetric detection of these compounds and their separation in a mixture by liquid chromatography has been reported (Purnell and Warwick 1980; Hart *et al* 1981). Large amplitude pulse voltammetric experiments suggest that the oxidation reaction of 4-chloroaniline involves the elimination of the one electron as the initial oxidation reaction at the carbon paste anode. The experiments were performed by varying the values of rest potential, drop-time and sweep rate in large amplitude pulse voltammetry. The reasonably constant value of limiting current shows that 4-chloroaniline can be used as a standard for 1-electron oxidation for the investigation relating to the electrochemical studies of selected aromatic amines (Haque 2002). More recent work on these compounds relates to electrodegradation kinetics of *p*-chloroaniline at solid anodes (Casado *et al* 1994; Brillas *et al* 1995). The acidity and basicity of benzene and its derivatives including para-chloroaniline have been treated theoretically in terms of a new quantitative parameter (Feng *et al* 1995). Effect of potential on the adsorption of *p*-chloroaniline on silver electrodes has been studied using surface-enhanced Raman spectroscopy (Xu *et al* 1993). Haloaminobenzenes continue to be the focus of research (Freccero *et al* 2003). Recently their electrochemistry was reviewed (Haque 2003).

Normal pulse voltammetry has been used to determine pK_a of *p*-chloroaniline. The result is in close agreement with the value reported in literature. The procedure outlined in this work represents an example of a new method for the determination of pK_a of *p*-chloroaniline.

Preparation of buffers. Buffer solutions of the pH range 1.8-6.5, were adjusted to an ionic strength of 0.20 mol/dm^3 by addition of the required amount of sodium chloride. The buffer solutions used for electrochemical experiments in specific pH range and their total buffer concentrations were as follow: pH 1.8-3.1, phosphate (0.04 mol/dm^3); pH 3.7-5.7 acetate (0.04 mol/dm^3); pH 5.7-6.5, phosphate (0.04 mol/dm^3). pH was noted by using a digital pH meter and combination glass electrode (Rusling *et al* 1983).

Solutions of *p*-chloroaniline were prepared by dissolving the compound in buffers of pH 1.8-6.5, so that the final concentration of *p*-chloroaniline was 1x10^{-4} mol/dm^3. Purified nitrogen was bubbled through the solutions for five to ten minutes to remove oxygen and a nitrogen atmosphere was maintained above solutions during voltammetry.

Carbon paste electrode. The carbon paste electrode (CPE) was a disc of area 0.12 x 10^{-4} m^2 surrounded by a Teflon collar of diameter 0.3 x 10^{-2} m. The carbon paste was prepared from Fisher ACS grade graphite powder, grade no. 38 and nujol as described in literature (Adams 1969). The surface of this electrode was renewed prior to each scan.

Counter electrode. A platinum strip, A = 1 x 10^{-4} m^2, or a platinum wire was used as a counter electrode. Reference electrode (silver-silver chloride electrode): A low resistance silver-silver chloride saturated KCl, reference electrode was used for experiments in the aqueous system (Sawyer *et al* 1995). Voltammetry in a three electrode cell was done using conventional electrochemical instrumentation (Haque 1989).

The anodic normal pulse voltammetric behavior of para-chloroaniline was investigated at the carbon paste electrode over the pH range 1.8-6.5. The normal pulse voltammograms for *p*-chloroaniline in various buffers showed well formed plateaux (Haque 2002). At half the plateaux currents, E½ values were noted in various buffer solutions for the pH range 1.8-6.5. E½ vs. pH plot for 1x10^{-4} mol/dm^3 para-chloroaniline solutions in these buffers are shown in Fig 1. The first break in E½ vs. pH curve, in Fig 1, corresponds to the pKa value relating to deprotonation of the anilinium species. The value obtained 4.15 is the same as determined using spectrophotometry (Hart *et al* 1981). The first linear portion of E½ vs. pH plot shows a slope of -58 mV/pH. This value of the slope (Heyrovsky and Vavricka 1972) is consistent with the following equilibrium prior to charge transfer:

$$\text{p-ClC}_6\text{H}_4\text{NH}_3^+ \leftrightarrow \text{p-ClC}_6\text{H}_4\text{NH}_2 + \text{H}^+ \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Our results thus establish that normal pulse voltammetry affords a reliable route to the determination of pKa value of the reaction noted as in equation (1) above. For comparison, it is mentioned that cyclic voltammetric oxidation of para-chloroaniline at glassy carbon electrode gave pKa value of 5.5 in Briton-Robinson buffers of pH 1.95-12.0 containing 50%

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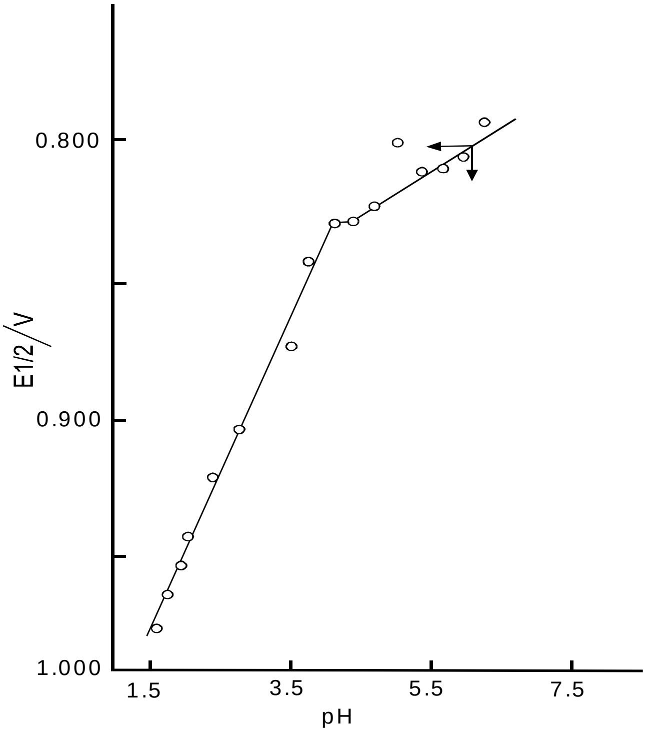

Fig 1. pH vs. half wave potential, E½ for the normal pulse voltammetric oxidation of 1x10^{-4} mol/dm^3 *p*-chloroaniline.

by volume of ethanol in water (Hart *et al* 1981). Cyclic voltammograms of 1x10^{-4} mol/dm^3 para-chloroaniline were also recorded in various buffer solutions over the pH range 1.8-6.5. The variation of Ep/2 with pH for the anodic peak of *p*-chloroaniline was linear with a break at pH equal to 4.65. This pKa value is higher than that determined by spectrophotometry (Hart *et al* 1981).

It is shown that in contrast to cyclic voltammetric method, normal pulse voltammetric method yields the correct value 4.15, for the pK_a of *p*-chloroaniline.

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