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Research Article

ELECTROCHEMICAL STUDIES OF o- AND p- ANISIDINE

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Abstract

Electrochemical oxidation of methyl substituted aniline (anisidine) has been done on both gold and platinum electrode using cyclic voltammetry. The results were compared in different supporting electrolytes such as KCl, KNO_3, H_2SO_4, HCl. Effect of pH was observed on electrochemical oxidation of o- & p- anisidine at gold and platinum electrode. During various scan single oxidation peak during first forward scan with no corresponding cathodic peak was obtained while a new anodic cathodic couple peak appears in subsequent scan obtained. Kinetic parameters like heterogeneous rate constant, transfer co-efficient and diffusion co-efficient were also calculated. A sensitive method was developed for estimation of micro quantities of anisidine by linear sweep voltammetry and hydrodynamic voltammetry.

Key words: o- and p- anisidines; cyclic voltametrically; gold electrode; platinum electrode

Introduction

Anisidines are substituted methoxy aromatic amines (methoxy aniline) and contribute to the environment as degradation product of azo dyes. According to the position of methoxy (-OCH_3) group three isomers ortho-, meta-, and para - anisidines are possible. In terms of human health hazards, o-anisidine is classified as toxic by inhalation, in contact with skin and ingestion due to its capacity to induce methemoglobin formation, as found in cats to a degree relevant for humans.

Literatures survey reveals that a lot of work has been done on anisidine polarographically but comparative study on cyclic voltammetry is reported less. Anodic oxidation of a series of p-substituted anilines in aqueous media was studied by Bacon and Adams (1968). Diffusion coefficients of a variety of aromatic amines and phenolic compounds were determined by using the voltammetric techniques with tubular graphite electrode by Sharma and Kalia (1977). Anodic differential pulse voltammetry of aromatic amines and phenols at trace levels was performed by Chey *et al.*(1977). Oxidation of p-anisidine by potential step cyclic voltammetry was studied by Baconet al. (1970). o-anisidine and p-anisidine were studied at a platinum anode by Wawzonek and McIntyre (1967). Suatoni *et al.* (1961) studied the oxidation of o-, m- and p- anisidine at a graphite electrode. 2-amino -6 methoxybenzothiozole was found to be the major product formed when p-anisidine was oxidised at a carbon anode in ammonium thiocyanide. Cyclic voltammetry of para -anisidine has been studied at GCE in aqueous medium and diffusion coefficient and heterogeneous rate constants were also calculated by Rao *et al.*.(1987). Reddy and co -workers studied anodic oxidation of ortho -anisidine (Reddy and Krishnan 1981) and para - anisidine (Reddy and Krishnan 1980) at a platinum anode using cyclic voltammetric and chronoamperommetric techniques, the diffusion coefficient of electro active species were also calculated The anodic oxidation behaviour of o - ,m - and p - anisidine was studied by sharma and kalia (1976) at the tubular graphite electrode under hydrodynamic conditions. Classical and differential pulse voltammetric determination of ortho -dianisidine was done by Barek and co -workers (1986). Mechanistic investigation of the oxidation of para -anisidine in unbuffered DMF using fast scan rates at ultra micro electrodes were carried out by Simon (1997).

The above extensive literature has shown that most of the previous studies on electro - oxidation of anisidines have been made by polarography at mercury electrode whereas studies with modern voltammetric techniques have been made in non-aqueous media . Among solid electrodes no report is there in literature on gold electrode. Therefore present work has been aimed towards a systematic, detailed and comparative electro chemical studies on ortho - and para - anisidine at gold and platinum electrode.

Materials and Methods

Cyclic voltammograms were recorded with electrochemical analyzer CV–27, from Bioanalytical System Inc. (BAS), West Lafayette, USA in combination with a Series–100, Omnigraphic X–Y recorder, Houston Instruments, Austin (USA) and a cell stand C–1 (BAS, USA) served the purpose of electrochemical cell. The instrument is easy to use, versatile reliable and has broad applicability. It can perform various electrochemical techniques like linear sweep voltammetry, cyclic voltammetry, chronoamperometry, chronocouloumetry, potentiometry, amperometry and stripping voltammetry. Instrument is designed to perform electrochemical techniques in which the potential of the working electrode is controlled and the resulting current is measured. It offers a potential range + 5.0 to – 5.0 volt (V) and scan rate ranging from 0.0001 Vs^{-1} to Vs^{-1} and current gain ranging from 0.002 mA/V to 10 mA/V. A X–Y recorder Houston, Bausch & Lomb is connected to series to the CV–27 voltammograph. The solid electrodes used as working electrode were Platinum Electrode (PtE) and gold Electrode (AuE) supplied from Bioanalytical system Inc. (BAS), USA. These electrodes have disks of highly pure electrode materials (viz. gold or platinum) embedded in CTFE plastic rod having geometric area of 1.76×10^{-2} Cm^2. Pretreatment of solid electrode surface was made by micropolishing before measurement using diamond lapping compound 1µm (Kemet, Kent, U.K.) and finally with 0.05 µm α–alumina powder on a fabric pad attached to glass plates then thoroughly rinsed by deionized water. These electrodes are found to be very useful due to their high mechanical stability, low polarity, good conductivity, inertness and usefulness over a wide potential region.

Silver–Silver chloride (Ag/AgCl) supplied by Bioanalytical systems Inc. USA was used as a reference electrode. All the potential reported in this study were measured with respect to this electrode. A platinum wire, fused to the top of the electrochemical cell served as an auxiliary electrode. A digital pH – mV temperature meter (Model PH 206) from Lutron Instrument, Taiwan was used to measure the pH values of experimental solutions. During experiment deoxygenation and inert atmosphere is maintained by passing the Nitrogen (N_2) gas over the solution (blanket mode) using BAS C–1A cell stand. Reagents used throughout the present investigation were of analytically pure grade (AR). ; o–anisidine from Loba Chemical Pvt. Ltd., India; *p*–anisidine from British Drug House, London. Acetic buffer was prepared by adding requisite amount of 0.5M sodium acetate and 0.25M acetic acid to get a buffer in the pH range of 3 to 7. A great care was taken while handling these aromatic amines. Eye, skin and clothing contacts were also avoided by wearing gloves and glasses, while preparing the solutions, inhalation of compounds was avoided by wearing a mask.

Result and Discussions

Cyclic Voltammetric studies at platinum and gold electrode:

I. *Effect of supporting electrolyte*

Cyclic voltammetric(CV) studies on anisidine has been made on different working electrode viz. platinum electrode (PtE) and gold electrode (AuE). The results were compared in different supporting electrolyte such as 0.1M KCl, 0.1M KNO_3, 0.1M potassium hydrogen phthalate, 0.1M HCl, 0.1M H_2SO_4 and Acetate buffer (pH 3 to 7). For this set of experiments an initial potential in kept 0.0 volt and final potential 1.0 Volt vs Ag/AgCl electrode, scan rate is 100 mVs^{-1}.

Electrochemical behaviour of o- anisidine as depicted in CV study revealed a single oxidation peak during the first forward scan, which showed no corresponding cathodic peak during the reverse scan. A new anodic-cathodic couple peak appears in subsequent scan. The position of oxidation peak lies between 0.57 to 0.92 V Vs Ag/AgCl electrode for different supporting electrolytes understudy. The couple peak appears in the range of 0.20 V to 0.46 V Vs Ag/AgCl (oxidation) and at 0.12V to 0.42 V (reduction). The electrochemical behaviour of o- anisidine in AuE is almost similar to that of the PtE , However the peak potential values are more electro positive in case of AuE, which is a good sign of oxidation. The current values is highest in acetate buffer (pH 5) and 0.1 M HCl as supporting electrolytes. Further studies were made in acetate buffer medium. Similar results were obtained in case of p-anisidine.

II. *Effect of pH*

Effect of rise in pH has been investigated in acetate buffer (pH 3 to 7), which also served as supporting electrolyte. The oxidation peak shifts towards less positive potential with increase in pH. Peak current is highest at pH 5. Above pH 5 the sharpness of peak decreases and current also decreases. After pH 5 the reversibility of system starts decreasing. Same pattern is found in case of gold electrode. The CV characteristics are compiled in Table 1 and 2. Effect of pH on o- Anisidine at Platinum electrode is shown in Fig. 1.

iii Determination of micro quantities of anisidine

Hydrodynamic voltammetry was performed to improve the sensitivity of voltammetric method (Table-3). This mode was achieved by stirring the solution during electrochemical reduction at a constant speed of 1700 rpm. Well-defined steady state voltammograms were obtained. The voltammetric current in hydrodynamic mode is higher than the corresponding current in linear sweep mode. Linear Sweep voltammogram of p- anisidine at different scan rate at Platinum electrode is shown in Fig.2.

Hydrodynamic curves of anisidine in acetate buffer at pH 5 were recorded at different concentration employing PtE. A comparison of voltammetric characteristics in linear sweep mode and at hydrodynamic mode was also observed. The lower limit of detection was found to be 3.2 x 10^{-5} M, which has resulted in a wave with a height of 1.6 cm. at current sensitivity of 2.0 µA/volts and at a scan rate of 100 mV /s of the instrument used.

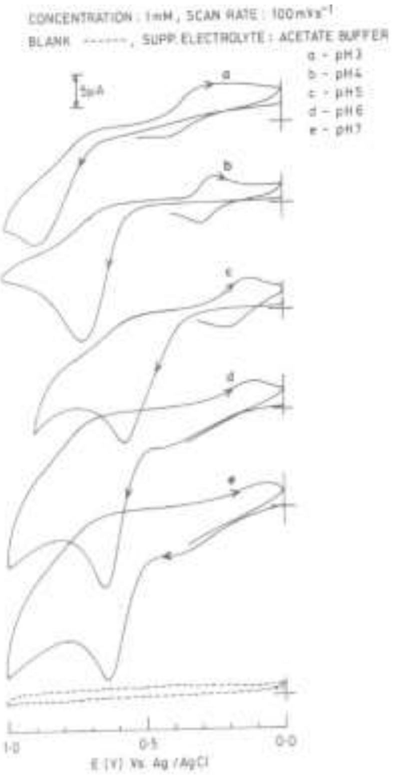

Fig 1: Voltammogram of o-Anisidine using Platinum Electrode at Different pH

Some of the notable features of these cyclic voltammetric studies are as follows:

i. Cyclic voltammogram with well-defined irreversible anodic peaks were obtained in all supporting electrolytes under study. The peak potential is in the range of +0.57 V to +0.92 V vs Ag/AgCl electrode for both the two isomers under study employing PtE as well as gold electrode.

ii. During reverse cathodic scan no cathodic peak was obtained corresponding to the main anodic peak, however at more positive potential a small cathodic peak with corresponding anodic peak during anodic scan was observe in the potential range +0.12V to +0.46V vs Ag/AgCl electrode. In p-isomer this couple peak is well defined in all the supporting electrolyte under study except 0.1M KNO_3 and 0.1M H_2SO_4, where the couple peak is absent. In case of o-anisidine appearance of on small cathodic pre peak shows tail to tail coupling in 0.1M HCl and 0.1M H_2SO_4 .

iii. pH greatly influence the characteristics of cyclic voltammogram : the sharp product couple peak was observed till pH 5 . After pH 5 the sharpness of the peaks decreases and current values also decreases .The oxidation peak shifts towards less positive potential with increase in pH. After pH 5 the reversibility of the system start decreasing at platinum electrode as well as gold electrode. Peak potential shift of the main oxidation peak was ~ 240 mV and 130 mV towards more negative potential for a 5 Unit charge of pH, at scan rate 100 mVs^{-1} for o-anisidine and p-anisidine respectively.

iv. On varying the scan rate in the range 20-300 mVs^{-1} anodic peak current increases. The peak current of product couple peak also increases on increasing scan rate. A linear relationship was observed between peak current and square root of scan rate.

v. The main oxidation peak shifts towards more positive potential. 50 mV, 20 mV for -o and -p anisidine on increasing scan rate from 20 mVs^{-1} to 300 mVs^{-1} at platinum electrode.

vi. The anodic peak current is found to increase with concentration in the range of 10^{-5} M to 10^{-3} M. The sensitivity of voltammetric assay is improved by performing hydrodynamic voltammetry.

vii. Thus the electrochemical studies on anisidine at solid electrodes (platinum and gold) have resulted in determination of important kinetic and thermodynamic parameters, rate constant of heterogeneous charge transfer related to electrochemical oxidation of both the two isomers of anisidine. The additional advantage of the present study is the development of optimum condition for micro-level determination of anisidines, which are quite significant environmentally.

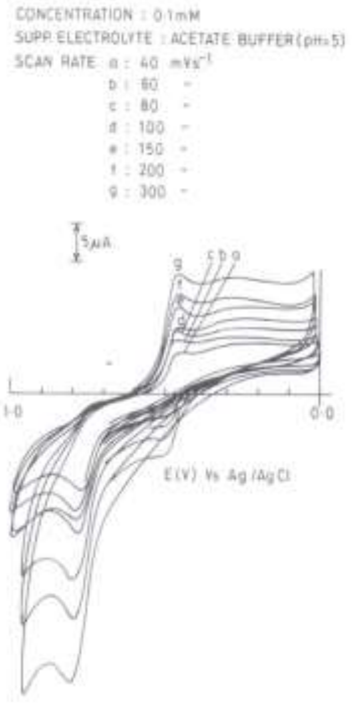

Fig 2. Liner Sweep Voltammogram of p- anisidine at Different Scan rate using Platinum Electrode

Table 1: Cyclic voltammetric characteristics of o- anisidine at different pH at different working electrode Reference electrode: Ag-AgCl, Concentration: 1 mM, Supp. Electrolyte: Acetate Buffer (pH 3), Scan Rate: 100 mVs^{-1}

pH	**Irreversible Oxidation Peak**		**Product Couple Peak**					
			Cathodic		**Anodic**			
	Epa *(V)*	**Ipa** *(µA)*	**Epc** *(V)*	**Ipc** *(µA)*	**Epa** *(V)*	**Ipa** *(µA)*	**ΔEp** *(mv)*	**Ipa/ Ipc**
			Platinum Electrode					
3	0.88	14.5	0.30	4.0	0.40	3.0	100	
4	0.73	22.0	0.24	3.0	0.29	3.0	50	1.0
5	0.64	28.5	0.18	4.0	0.25	3.5	70	0.9
6	0.65	23.0	0.12	3.5	0.40	5.0	280	1.4
7	0.64	20.0	-	-	-	-		
			Gold Electrode					
3	0.86	14.O	0.25	3.0	.019	2.5	-60	0.83
4	0.70	24.0	0.23	3.5	0.30	3.0	70	0.9
5	0.66	23.0	0.19	3.5	0.25	3.0	60	0.9
6	0.65	22.0	0.07	2.5	0.35	2.5	280	1.0
7	0.64	17.0	-	-	-	-	-	-

Table 2: Cyclic voltammetric characteristics of p- anisidine at different pH at different working electrode Reference electrode: Ag-AgCl Concentration: 1 mM,Supp. Electrolyte: Acetate Buffer (pH 5) Scan Rate: 100 mVs^{-1}

pH	**Irreversible Oxidation Peak**		**Product Couple Peak**					
			Cathodic		**Anodic**			
	Epa *(V)*	**Ipa** *(µA)*	**Epc** *(V)*	**Ipc** *(µA)*	**Epa** *(V)*	**Ipa** *(µA)*	**ΔEp** *(mv)*	**Ipa/ Ipc**
			Platinum Electrode					
3	0.62	4.0	0.22	1.5	0.29	1.5	70	1.0
4	0.49	5.0	0.12	2.0	0.25	2.0	130	1.0
5	0.44	6.0	0.10	3.0	0.15	2.0	50	0.7
6	0.51	5.5	0.15	2.5	0.20	2.5	50	1.0
7	0.50	5.0	0.10	1.5	0.16	2.0	60	1.3
			Gold Electrode					
3	0.63	4.5	0.24	2.5	0.3	2.0	60	0.8
4	0.49	4.5	0.16	2.5	0.20	1.5	40	0.6
5	0.45	6.0	0.12	3.5	0.17	2.0	50	0.6
6	0.51	5.0	0.15	3.5	0.20	2.5	50	0.7
7	0.51	5.0	0.11	3.0	0.15	2.0	40	0.7

Table 3: Comparison of linear sweep voltammetric and hydrodynamic mode during electro-oxidation of Anisidine

Concentration (Molar)	**Linear sweep mode**		**Hydrodynamic mode**	
	Epa (V)	**Ipa (µA)**	**E $_{1/2}$ (V)**	**I $_{LIM}$ (µA)**
		o-Anisidine		
1.1x 10 $^{-5}$	-	-		
3.2x10 $^{-5}$	0.88	3.2		
5.2x10 $^{-5}$	0.88	3.6		
1x10 $^{-4}$	0.89	6.0		
		p-Anisidine		
1.1x10 $^{-5}$	-	-	0.74	1.8
5.2x10 $^{-5}$	-	-	0.73	3.6
1.1x10 $^{-4}$	-	-	0.74	2.0

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