

Cathodic Voltammetry of Nitrobenzene at Titanium in Micellar Solution

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Summary: The present study relates to electro-reduction of nitrobenzene in the presence of micellar aqueous solution of sodium dodecyl sulphate at titanium cathode, using cyclic voltammetric and titanium etching methods in a three-electrode system. Nitrobenzene gives single reduction peak (Ia) corresponding to the irreversible electrochemical reduction. However, at higher concentrations and lower sweep rates single peak splits into two cathodic peaks. These peaks correspond to reaction mechanisms, involving four-electron over-all change; first step, with one-electron transfer to form anion radical (peak I) similar to electron transfer observed in aqueous micellar media. While the second step involves protonation of anion radical followed by a three electron-addition (peak II) leading to the formation of phenylhydroxylamine. In the presence of SDS nitrobenzene solubilizes and reduces efficiently even at lower concentration; while in the absence of SDS reduction peak appears at relatively higher concentrations of nitrobenzene. This work targets the utility of titanium as cathode.

Introduction

Electro-catalytic reduction of nitrobenzene has been studied from a number of perspectives [1-12]. Various bare and modified electrodes have been investigated.

Electrochemical behavior of nitrobenzene has been studied over graphite electrode modified with carbon nano-tubes using cyclic voltammetry and constant-potential electrolysis techniques. Reduction was more efficient on modified electrode [1]. Electro-reduction in deoxygenated acid solution generates predominantly either *p*-aminophenol or aniline by generating a common intermediate, phenylhydroxylamine [2]. Cyclic voltammetry, rotating disc electrode and preparative electrolysis were applied to study the reduction of nitrobenzene by using copper and copper/mercury electrodes. Amalgamated copper was found most suitable electrode material for the reduction of nitrobenzene to *p*-aminophenol [3]. Cyclic voltammetric studies of nitrobenzene and *m*-dinitrobenzene on thermally coated titanium/titanium dioxide electrodes in acidic media indicate heterogeneous redox catalysis for both of these compounds. Significant adsorption and blocking effect of these compounds was noticed at elevated concentrations [4]. The electro-reduction of nitrobenzene was also investigated at lead, copper and mercury in aqueous organic solvents containing sulfuric acid. It was shown that the yield of *p*-aminophenol and the maximum current density for the reaction is dependent upon many factors.

Conditions for highest yield of *p*-aminophenol were mentioned [5].

Electrochemical properties of C₆₀ modified carbon paste electrode were studied in tetrabutylammonium hydroxide/methyl nitrile/water solutions. Results revealed that this electrode had a good electro-catalytic reduction response for nitrobenzene [6]. The reduction of nitrobenzene has been observed over a wide range of pH values from 4.4 to 13 at molybdenum electrodes. Constant potential coulometry along with cyclic voltammetric studies showed that under alkaline conditions the final reduction product is phenylhydroxylamine [7]. Electrochemical reduction of nitrobenzene was studied at a mercury cathode at various controlled potentials in acid electrolytes. The composition of the product mixture depends on the potential and length of electrolysis [8]. A method for the determination of nitrobenzene was applied by using a modified carbon paste electrode; at open circuit nitrobenzene was adsorbed on the electrode, and determined by differential pulse voltammetry, and cyclic voltammetry [9].

Voltammetric behavior of nitrobenzene in aqueous, micellar, micro-emulsion and aprotic media was compared on glassy carbon electrode under identical experimental conditions. A general trend of decreasing peak currents in the order i_p (micelle) > i_p (aqueous) > i_p (DMF) > i_p (μ E) was

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noticed [10]. Cyclic voltammetric behavior of nitrobenzene showed that nitrobenzene was reduced directly and easily on the surface of copper electrode rather than by the hydrogen evolved at cathode in the catalyzed iron-copper process in both acidic and basic media [11]. Process and mechanism of the electro-reduction of nitrobenzene have been investigated at titanium implanted with platinum electrode, rotating ring-disk electrode and electron spin resonance *in situ* by cyclic voltammetry in alkaline media. The results indicated that the electro-catalytic activity of implanted substrates was much more than that of the untreated and smooth platinum. The nitrobenzene anion-radical was detected as intermediate [12].

Nitro-aromatic compound have also been investigated in surfactant media [13-15].

However, so far there are only a few studies in literature related to reduction of nitrobenzene at titanium electrode [16]. Titanium is a lighter and robust metal as compared to many others, but usually it is under-utilized as cathode. Probably due to thin oxide coating over it, which we have removed [17], before voltammetric experiments were carried out. Previously we have studied the electrochemical reduction of nitrate at titanium electrode. Recent work investigates the cathodic activity of titanium for electro-reduction of nitrobenzene in the presence of SDS which could bring a higher concentration of nitrobenzene towards cathode by solubilization [18, 19], and its mechanism seems to be controlled by diffusion [20].

Result and Discussion

Voltammetry of Nitrobenzene in Aqueous SDS Micellar Solution at Titanium

The electrochemical reduction of nitrobenzene was investigated at titanium electrode,

using cyclic voltammetry. Voltammograms were recorded for 2.5 mM nitrobenzene in 20 mM aqueous sodium dodecyl sulphate at various sweep rates (0.01, 0.02, 0.025, 0.050, 0.10, 0.20 Vs⁻¹) in the potential range from -0.4 to -1.6 V.

Cyclic voltammograms were also recorded for various concentrations of nitrobenzene (2.5, 4.0, 5.0, 6.25, 7.0, 7.50, 8.25, 8.89, and 9.06 mM). Reduction started at -0.8 V by a relative increase in the total current density with the increase of the concentration of nitrobenzene as observed from the voltammetric curves but after certain concentration it is decreased due to inhibition and adsorption on the surface of electrode [4], as evident from (Table-1). A plot of cathodic peak potential versus log of concentration of nitrobenzene shows complex behavior as observed in (Fig. 2), similar results are shown by plot of cathodic half peak potential versus log of nitrobenzene concentration as revealed from values of slopes given in (Table-2).

A single cathodic peak (Ia) around 0.78-0.8 V is noticed in the micellar solution at lower concentration of nitrobenzene; the single peak also appears at higher sweep rates.

Two cathodic peaks (I and II) correspond to successive reduction steps of one electron reduction and further three electrons reduction. As anionic radical seems to persist in anionic micelles of SDS rather than in either isotropic aqueous solution or cationic micelles, so at higher concentration a separate reduction peak appears; further reduction leads to formation of phenylhydroxylamine which is the end product of nitrobenzene reduction in basic media [1-2, 7, 10, 12].

Peak current for nitrobenzene reduction was found to be a linear function of the square root

Table-1: Dependence of cathodic cyclic voltammetric peak current at 100 mVs⁻¹ on concentration of nitrobenzene at titanium cathode (0.05 cm²). Potential in volts vs. saturated calomel electrode: micellar media.

C mM	log (C) (mM)	-E _{p,1} ^c V	-i _{p,1} ^c mA	-I _{p,1} ^c mAcm ⁻²	E _{p2,1} ^c V	*E ^c V	i _{p,1} ^c /C mA/mM	α = 47.7/E ^{c*}
2.50	0.397	0.930	0.070	1.40	0.718	0.212	0.0280	225.00
4.00	0.602	0.910	0.069	1.38	0.674	0.236	0.0173	202.12
5.00	0.699	0.818	0.077	1.54	0.644	0.174	0.0154	274.14
6.25	0.796	0.800	0.081	1.62	0.646	0.154	0.0130	309.74
7.00	0.845	0.768	0.082	1.64	0.628	0.140	0.0117	340.71
7.50	0.875	0.764	0.081	1.63	0.644	0.120	0.0109	397.50
8.25	0.916	0.804	0.078	1.57	0.662	0.142	0.0095	335.92
8.89	0.949	0.836	0.078	1.56	0.708	0.128	0.0088	372.66
9.06	0.957	0.868	0.073	1.47	0.724	0.144	0.0081	331.25

Electrolyte: 20 mM sodium dodecyl sulphate aqueous solution. A steel rod was used as counter electrode. *E^c = E_{p,1}^c - E_{p2,1}^c

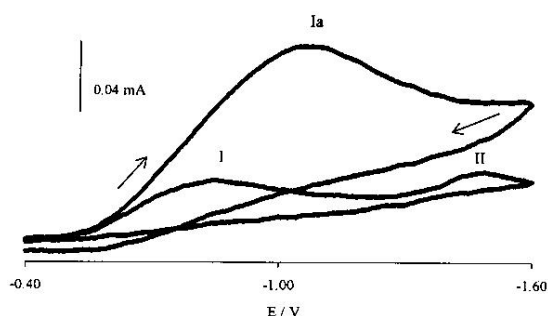


Fig.1: Cyclic voltammogram of 2.5 mM nitrobenzene in 20 mM sodium dodecyl sulphate at titanium cathode; sweep rates (upper curve) 0.2, and (lower curve) 0.02 mVs^{-1} .

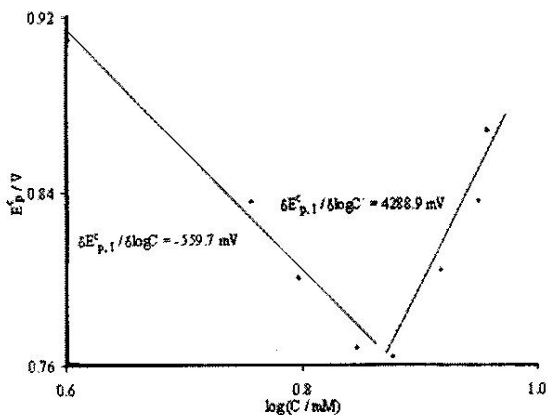


Fig.2: Variation of cathodic peak potential with logarithm of concentration of nitrobenzene in 20 mM sodium dodecyl sulphate at titanium electrode, potential in volts vs. saturated calomel electrode. Sweep rate 0.1 Vs^{-1} . $\partial E_{p,1}^c / \partial \log(C) = -559.7 \text{ mVdecade}^{-1}$. However the value of slope at $C > 7.0 \text{ mM}$ was $+4288.9 \text{ mVdecade}^{-1}$ of concentration.

Table-2: Electro-reduction of nitrobenzene at titanium cathode. Dependence of cathodic peak potential on concentration and sweep rate.

$\frac{\partial E_{p,1}^c}{\partial \log(C)}$	$\frac{\partial E_{p,2}^c}{\partial \log(C)}$	$\frac{\partial E_{p,2}^c}{\partial \log(C)}$	$\frac{\partial E_{p,2}^c}{\partial \log(C)}$	$\frac{\partial E_{p,1}^c}{\partial \log v}$	$\frac{\partial E_{p,2}^c}{\partial \log v}$
mVdecade^{-1}	mVdecade^{-1}	mVdecade^{-1}	mVdecade^{-1}	mVdecade^{-1}	mVdecade^{-1}
-559.7	4288.9	-208.3	829.4	186.5	74.3

of sweep rate as clear from (Table-3). Likewise linear dependence of cathodic peak current density versus log of sweep rate indicates that one electron reduction is diffusion controlled [20] as shown in (Fig. 3).

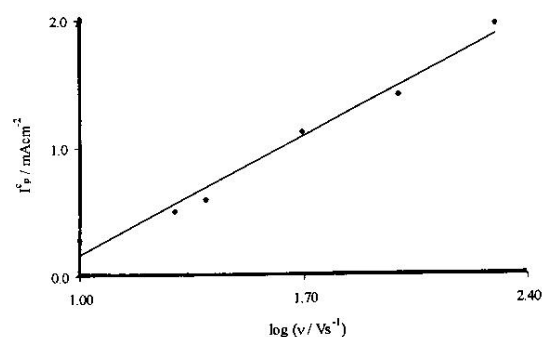
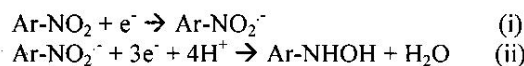


Fig.3: Influence of logarithm of sweep rate on cathodic peak current density for the cyclic voltammetry of 2.5 mM nitrobenzene in 20 mM sodium dodecyl sulphate at titanium electrode (0.05 cm^2). Potential in volts vs. saturated calomel electrode, $y = 1.3174x - 1.1536$, $R^2 = 0.9809$. Values are given in Table-3.

In anionic surfactant, SDS (which has slightly basic pH) splitting of the single peak corresponds to following overall reaction mechanism [10, 13-15];



As revealed from earlier work, in acidic and neutral medium nitrobenzene reduces directly to phenylhydroxylamine in a single step by four electrons reduction. But in basic media (pH 8) main irreversible peak for the electro-reduction of nitrobenzene in SDS was split further into two signals [10, 14].

Mono-electronic reduction of nitrobenzene to corresponding radical anion according to equation (i) corresponds to peak (I), and at more cathodic potentials a second irreversible peak (II) corresponds to three electrons transfer yielding phenylhydroxyl-amine as per equation (ii). Further investigations will involve calculating the value of diffusion co-efficient [18-19] for anionic surfactant by using various methods.

Voltammetry of Nitrobenzene in Aqueous Potassium Sulphate at Titanium

After pre-treatment of working electrode, cyclic voltammetric curves were recorded for

Table-3: Dependence of cathodic peak current on sweep rate. Cyclic voltammetry of 2.5 mM nitrobenzene at titanium electrode (0.05 cm²) vs. saturated calomel electrode: micellar media.

v	v ^{1/2}	log (v)	-E _{p,1} ^c	E _{p2,1} ^c	*E ^c	I _{p,1} ^c	-i _{p,1} ^c	i _{p,1} ^c /v ^{1/2}	α= 47.7/ E ^{c*}
Vs ⁻¹	v ^{1/2} s ^{-1/2}	(Vs ⁻¹)	V	V	V	mAcm ⁻²	mA	mA / V ^{1/2} s ^{-1/2}	
0.010	3.162	1.000	0.826	0.700	0.126	0.28	0.014	0.221	378.57
0.020	4.472	1.301	0.856	0.682	0.174	0.50	0.025	0.152	274.14
0.025	5.000	1.397	0.896	0.718	0.178	0.59	0.030	0.144	267.98
0.050	7.071	1.699	0.926	0.724	0.202	1.11	0.056	0.102	236.14
0.100	10.00	2.000	0.940	0.718	0.222	1.41	0.071	0.072	214.86
0.200	14.14	2.301	1.066	0.794	0.272	1.96	0.098	0.056	175.37

Electrolyte: 20 mM sodium dodecyl sulphate solution, steel rod used as counter electrode. *E^c= E_{p,1}^c-E_{p2,1}^c

different concentrations of nitrobenzene in 0.1 M potassium sulphate aqueous solution in the potential range -0.4 to -1.9 V using the sweep rate 0.1 Vs⁻¹ at titanium working electrodes. Saturated aqueous solution of nitrobenzene was prepared by overnight stirring of 1 mL of nitrobenzene in 25 mL of background electrolyte, having molarity *ca.* 0.163 M. Further dilutions were made by using this stock solution. Concentration dependence was studied from lower to higher concentration in range 27.08-94.70 mM nitrobenzene.

A single cathodic peak around -1.46 V is noticed in the aqueous potassium sulphate. Because aqueous media contain significantly higher concentration of water molecules in the interface, further reduction of nitrobenzene anion radical generated in the first peak region also occurs at the same potential giving rise to an overall four electron transfer process. Concentration of nitrobenzene is not a linear function of cathodic current density as shown in Table-4, revealing strong inhibition and adsorption on the surface of electrode [4, 10].

Data in Tables-1 to 4 summarize the comparison for the efficiency of electro-reduction of nitrobenzene in the presence and absence of SDS.

Table-4: Dependence of cathodic cyclic voltammetric peak current at 100 mVs⁻¹ on concentration of nitrobenzene at titanium cathode (0.05 cm²). Potential in volts vs. saturated calomel electrode: aqueous media.

C	i _p ^c	log (C)	log (i _p ^c)	I _p ^c	E _p ^c	log (E _p ^c)
mM	μA	(mM)	(μA)	μAcm ⁻²	V	(V)
27.08	0.07	0.156	-1.155	1.4	1.48	0.170
60.90	0.08	0.252	-1.097	1.6	1.49	0.173
72.20	0.07	0.269	-1.155	1.4	1.47	0.167
81.60	0.07	0.281	-1.155	1.4	1.48	0.170
88.60	0.07	0.289	-1.155	1.4	1.48	0.170
94.70	0.06	0.296	-1.222	1.2	1.48	0.170

Electrolyte: 0.1 M potassium sulphate. A steel rod was used as counter electrode

Experimental

Working Electrode Preparation

Solid titanium rod was sealed into Teflon insulation and the end abraded flat on 600-grit silicon carbide paper, resulting in a solid electrode disc surrounded by insulating Teflon. Polishing of working electrodes was done by etching in oxalic acid after ultrasonic cleaning. Thorough rinsing with double distilled water followed polishing.

Chemicals

Specification of chemicals and materials used were; nitrobenzene (Panreac), sodium hydroxide (E-Merck), oxalic acid (Riedel-de Haen), sodium dodecyl sulphate (AppliChem), potassium sulphate (E-Merck) and potassium chloride (Panreac). All the reagents used in experiments were of analytical grade and used without further purification. Solutions were not purged free of oxygen. A stock solution of nitrobenzene of 10 mM concentration was prepared in 20 mM aqueous solution of sodium dodecyl sulphate. Appropriate volume of this stock solution was used to make further concentrations in background electrolyte (sodium dodecyl sulphate aqueous solution). All the solutions were prepared with double distilled water.

Pretreatment of Titanium Working Electrode

As titanium is a valve metal and forms a passive oxide coating when exposed to elevated temperature in air (oxide layer consists of brookite, rutile, and anatase in which rutile is most common oxide). So titanium is under-utilized as cathode. Formation of titanium dioxide layer on the surface causes passivation of reaction and lowers the catalytic activity of the cathode in aqueous solution.

But after activation of titanium it may be better utilized as cathode [4, 12]. So pre-treatment was applied for the removal of oxide layer from cathode surface before acquisition of the voltammograms. Different polishing methods were used for the polishing of tarnished surface of cathode [16]. In this work etching was carried out with oxalic acid [17]. Firstly the electrode surface was polished with sand paper, and then cleaned using ultrasound for 10 min to remove any particles lodged on the electrode surface. Electrode surface was degreased in 40% sodium hydroxide solution for 2 hours at 313 K. Electrode was then pretreated by etching in boiling 10% oxalic acid for 2 hours until titanium dioxide was thoroughly dissolved. Then the titanium electrode was conserved in an aqueous solution of 1% oxalic acid to avoid re-formation of titanium dioxide layer.

Potentiostatic Studies

Cyclic voltammetry was carried out using eDAQ ER461 potentiostat. Control of the potentiostat and data acquisition were accomplished using eDAQ Echem v2, 0.9 electrochemistry research software on a dedicated P (IV) microprocessor coupled to the potentiostat. Cyclic voltammograms were acquired in a three-electrode configuration using titanium electrode as the working electrode vs. a saturated calomel electrode as reference, and a steel rod as counter electrode. Cyclic voltammograms were recorded for background and different concentrations of nitrobenzene upon addition to background solution. All experiments were carried out at room temperature. Prior to acquisition of voltammograms, the titanium electrode was subjected to pre-treatment for removal of its oxide layer and before each scan electrode was sanded with 600 grit silicon carbide paper followed by rinsing with double distilled water.

Conclusions

Nitrobenzene reduction potential depends upon its concentration, sweep rate, and micellar environments. Reduction potentials shift slightly towards more negative potentials in SDS. Linear dependence between $\log(I_p^c)$ versus $\log(\nu)$, confirms that one electron reduction (first reduction step) is diffusion controlled [20]. Diffusion in the bulk phase seems to be important for mass transfer

to cathode. When the concentration of nitrobenzene is raised in the micellar solution, it results in its significant solubilization. The breakdown of the surfactant microstructure and the formation of another structure at the electrode interface is indicated to be responsible for a complex behavior with respect to concentration as shown by (Fig. 2) and values of slopes in (Table-2). Reduction efficiencies of reaction can be compared in the absence and presence of SDS by data given in (Tables-1 to 4), respectively. In presence of SDS a higher concentration of nitro-benzene can be brought to the electrode surface at higher negative potentials.

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