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On Electroreduction of Nitrobenzene: Nominal Simulation of Voltammograms

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Abstract

A mechanistic study of electroreduction of nitrobenzene was carried out in cationic micellar solutions of cetyltrimethylammonium bromide (CTAB) at platinum electrode using cyclic voltammetry. Distinct cathodic and anodic peaks were observed with inter-peak separation of about 60-65 mV suggesting a reversible/quasireversible charge transfer reaction pertaining to one electron redox couple $\text{ArNO}_2/\text{ArNO}_2^-$. Digital simulation was used for interpretation of the charge transfer reaction. A simple electrochemical mechanism is proposed for the mono-electron charge transfer step. An electrochemical-chemical-electrochemical (ECE) mechanism is indicated for the voltammograms involving nitrobenzene reduction on dioctadecyldimethylammonium chloride (DODAC) covered platinum. Calculated diffusion coefficient values of nitrobenzene (D) are reported.

1. Introduction

Nitrobenzene is a widely used solvent [1]. It is employed in the production of aniline, pesticides, dyes, explosives [2-4]. Many drug molecules of pharmacological significance contain the nitro group [5-9]. Numerous voltammetric investigations have been reported in various media relating to the electro-reductive pathways of nitroaromatic compounds [1-26] and one electron reduction step, for the generation of anion radical is proposed in various media. In most of the investigations second step is suggested to be a three-electron transfer leading to the formation of phenylhydroxylamine at more negative potentials. The products are substantially dependent on the reaction media, be it aqueous [11-13], non- aqueous [14-17] or micellar [9, 18, 26-28].

Coulometric and cyclic voltammetric studies have been carried out [14] to study the electrochemical behavior of nitrosobenzene and nitrobenzene in anhydrous liquid ammonia. Both nitrobenzene and nitrosobenzene are reversibly reduced in the absence of added protonating agents, and follow the two one-electron transfer steps to yield the stable species of anion radical and dianion. The overall process of reduction consists of the addition of a single electron to yield an anion radical followed by addition of subsequent three electrons to give final products. Electro-reduction of nitrobenzene to the nitro anion radical and dianion has been studied [18] in cationic, anionic and nonionic micellar media. Voltammetric studies suggested the formation of nitro anion radical in nonionic micellar solution further supported by Electron Spin Resonance Spectroscopy.

Differential pulse and TAST polarography together with cyclic voltammetry were used to examine electro-reduction of four 6-substituted derivatives of 2,5-dimethoxynitrobenzene in mixed and aqueous media [5]. A polarographic wave for

radical anion was detected in aqueous media at pH greater than 8. While a definite reversible couple of peaks was observed in mixed media in case of all investigated compounds, mechanism involves one-electron reduction of the nitro group to produce the related anion radical. Studies using cyclic voltammetry have exhibited the relative stability of nitro anion radical produced in the process, which is prone to chemically combine with other reactive species [5].

This work relates to electron transfer mechanism for the electrochemical reduction of nitrobenzene at platinum in micellar media and on DODAC coated platinum.

Experimental voltammetric curves were simulated [15] using Electrochemical Simulation Package (ESP) 2.4. Simulations focused on the first and reversible electron transfer step ($\text{RNO}_2/\text{RNO}_2^-$ couple). Diffusion coefficient (D) of nitrobenzene was calculated [14-15, 18, 22, 29-37].

2. Results and Discussion

Figure 1 shows cyclic voltammetric curves of nitrobenzene in CTAB. A couple of redox peaks is observed at the two indicated concentrations.

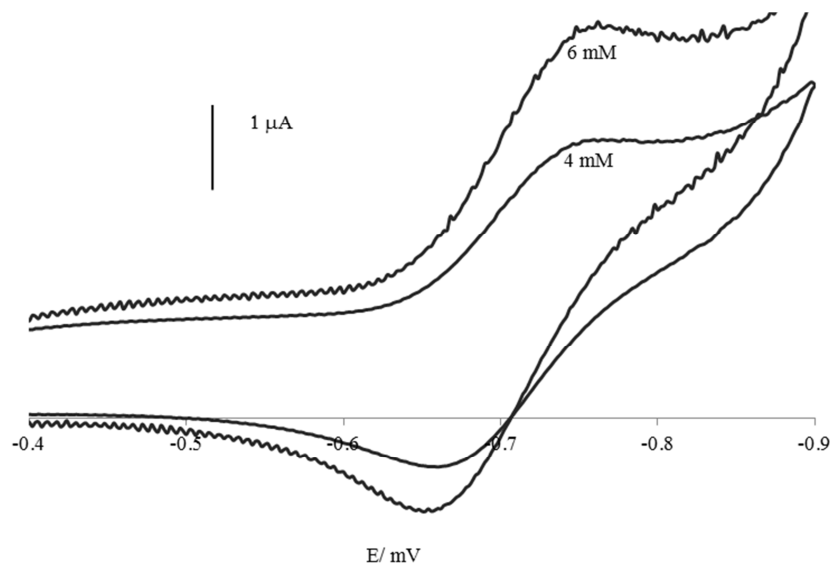


Figure 1. Cyclic voltammetry of nitrobenzene in 0.1 M CTAB at platinum electrode vs. saturated calomel electrode, scan rate 300 mVs^{-1} . Platinum wire was used as a counter electrode. $i_p^a/i_p^c (4 \text{ mM}) = 0.501$, and $i_p^a/i_p^c (6 \text{ mM}) = 0.273$.

Simulation of curves in Figure 1 was carried out assuming heterogeneous single-electron transfer mechanism. Experimental and simulated curves for 6mM nitrobenzene are shown in Figure 2.

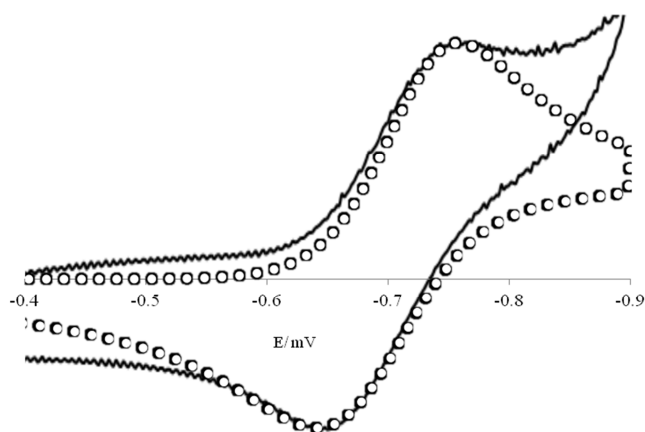


Figure 2. Voltammetry of 6 mM nitrobenzene in 0.1 M CTAB on platinum electrode vs. saturated calomel electrode, scan rate 300 mVs^{-1} . Platinum wire was used as a counter electrode. Experimental curve = continuous line; Simulated curve = open circles. Parameters used in simulation: $kh = 7 \times 10^{-3} \text{ cm/s}$, $\alpha = 0.6$.

As observed by simulation the couple of reduction-

oxidation peaks is associated with one electron transfer quasi-reversible reaction featuring formation of anion radical from nitrobenzene [5, 14-18, 20-21, 31].

Figure 3 displays an overlay of simulated and experimental cyclic voltammograms at DODAC covered platinum electrode [33] in nitrogen-saturated 1:1 water/propanol mixture.

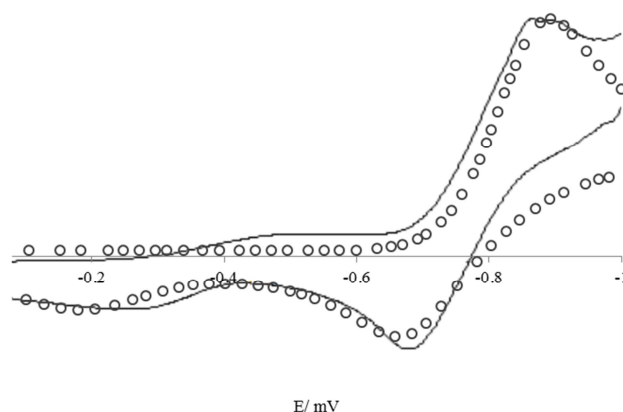


Figure 3. Cyclic voltammetric curves of nitrobenzene (2.27 mM) in 1:1 water-propanol mixture at DODAC covered platinum electrode ($8 \times 10^{-4} \text{ cm}^2$). Sweep rate, $v = 300 \text{ mVs}^{-1}$. Experimental curve = continuous line; Simulated curve = open circles. Open circles curve obtained assuming ECE mechanism using simulation parameters as; $k_{h1} = 5 \times 10^{-4} \text{ cm/s}$, and $k_{h2} = 1 \times 10^{-5} \text{ cm/s}$, $\alpha_1 = 0.5$, and $\alpha_2 = 0.55$, $k_f = 3 \times 10^{-1} \text{ s}^{-1}$, $k_b = 0.0 \text{ s}^{-1}$.

In addition to the reversible/quasi-reversible peaks, a second anodic peak is obtained on the reverse scan. The couple of anodic and cathodic peaks involves anion radical via single electron transfer reaction. The anion-radical formed in the first step undergoes a chemical reaction to an intermediate subsequently leading to a product that is oxidized in the second anodic peak. This nominal ECE mechanism is suggested for the experimental [33] cyclic voltammogram.

Previous research work shows a stabilization of the anion radical in mixed or aprotic media, unlike in purely aqueous media, where an irreversible single peak is observed pertaining to four electron reduction step engendering

hydroxylamine. Whereas in micellar, non-aqueous or in mixed media with limited proton availability, the reduction follows a quasi-reversible/reversible one-electron reduction to produce nitro anion radical. The generation of mono-electron reversible couple is highly dependent on the characteristics of reaction media. Acidic and basic media also affect the stability of nitro radical anion.

Cathodic peak currents of both experimental and simulated voltammograms of nitrobenzene reduction on DODAC coated platinum were plotted against square root of scan rate, Figure 4. There is reasonable agreement between experiment and simulation for intermediate values of the scan rate.

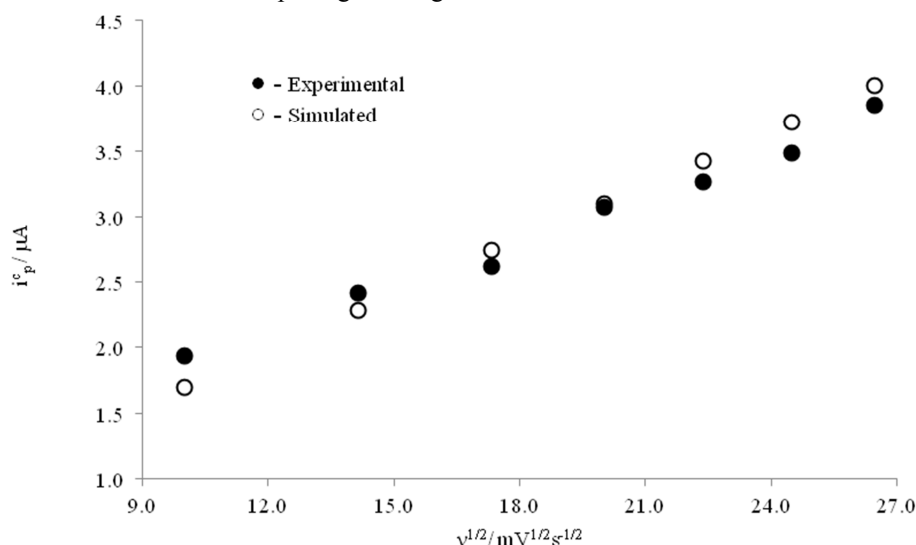


Figure 4. Dependence of cathodic peak current on square root of scan rate for the electrochemical reduction of 2.27 mM nitrobenzene in 1:1 water /propanol mixture at DODAC covered platinum electrode using cyclic voltammetry.

Diffusion coefficient of nitrobenzene was calculated using Randles–Ševčík equation [34].

$$i_p = (2.99 \times 10^5) n(n_a)^{1/2} A C D^{1/2} v^{1/2}$$

Where A the electrode area (in cm^2), C the concentration (in mol/cm^3), D the diffusion coefficient (in cm^2/s), and v the

scan rate (in V/s). While; n= number of electrons in stoichiometric equation and n_a = number of electrons involved in the charge-transfer step, assuming $n=n_a=1$

Values of diffusion coefficient Table 1 were found to be comparable with those reported in literature [14, 17, 18, 30, 32].

Table 1. Diffusion coefficients for nitrobenzene.

Diffusion coefficient (cm^2/s)	Technique/Conditions
2.8×10^{-5}	Cyclic voltammetry at gold microelectrode in anhydrous liquid ammonia [14]
$3.4 \pm 0.1 \times 10^{-9}$	Chronoamperometry at Platinum micro disk in room temperature ionic liquid [17]
6.97×10^{-6} (SDS)	Single potential step chronocoulometry at hanging mercury drop electrodes in SDS, CTAC and Brij-35 [18]
7.11×10^{-6} (CTAC)	
4.37×10^{-6} (Brij-35)	
3.63×10^{-7}	Cyclic voltammetry at platinum electrode in aqueous CTAB [34]
6.11×10^{-5} Bare Pt	Cyclic voltammetry at bare and DODAC covered platinum electrode in 1:1 water /propanol mixture [33, this work].
1.09×10^{-4} DODAC covered Pt	

3. Experimental

Simulations of the electrochemical reduction of nitrobenzene are performed using computer coded simulation package: Electrochemical Simulation Package (ESP) 2.4. Experimental curves of nitrobenzene electroreduction in 1:1 water/propanol mixture at bare and DODAC

(dioctadecyldimethylammonium chloride) coated platinum [33] and those obtained in CTAB were simulated.

Nitrobenzene (Panreac), γ -alumina (0.05 micron), CTAB (Merck), tetraethyl ammonium perchlorate (Alfa Aesar) were of analytical grade and used without further purification. Voltammetric experiments were carried out using potentiostat: EG&G, Princeton Applied Research Corp, VersaStat-II. Electrochemistry research software (M270) was

used to acquire data on a dedicated computer coupled with the main instrument. Solutions were not purged free of oxygen. All experiments were performed in a set-up consisting of three electrodes: a working electrode (platinum), a counter electrode (platinum wire), and the reference electrode (a saturated calomel electrode).

4. Conclusions

It is shown that electro-reduction of nitrobenzene at DODAC covered platinum electrode surface predictably yields higher diffusion coefficient as compared to corresponding values for the case of bare platinum electrode surface. The stabilization of nitro radical anion in the presence of cationic CTAB micelles and DODAC film is indicated. Digital simulations are supportive of the stabilization of the nitro radical anion in the media employed in this investigation of the electroreduction of nitrobenzene

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