ELECTROCHEMICAL BEHAVIOR OF NITROBENZENE IN AQUEOUS CTAB

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ABSTRACT: A mechanistic study of the electroreduction of nitrobenzene was undertaken following previously reported voltammetric investigations of nitrobenzene reduction on bare and dioctadecyldimethylammonium chloride (DODAC) covered platinum electrode. The electrochemical reduction of nitrobenzene in aqueous micellar solution of cetyltrimethylammonium bromide (CTAB) at platinum electrode using cyclic voltammetry revealed two distinct cathodic and anodic peaks with interpeak separation of about 60-65 mV indicating a reversible/quasi-reversible charge transfer reaction pertaining to one electron couple of $ArNO_2/ArNO_2^{\cdot-}$ *as reported in literature. Additional interpretation of experimental cyclic voltammogram was done by using digital simulation. Diffusion co-efficient values of nitrobenzene calculated using Randle-Sevcik equation were found close to the reported values.*

INTRODUCTION

Nitrobenzene is among extensively used compounds as solvent [1] and is an intermediate in various chemical industries. It is also used in the production of aniline, pesticides, dyes, explosives etc. [2-4]. Besides this there are many drug molecules which are of widespread pharmacological significance containing attached nitro group as their important and active part or an intermediate [5-9].

Nitrobenzene is an important nitro compound and several voltammetric studies have been reported so far in various media to investigate the electroreductive pathway of nitroaromatic compounds [1-26]; one-electron reduction step for the generation of nitro radical anion is known in various media. In most of the investigations second step is suggested to be a three- electron transfer which leads to the formation of phenylhydroxylamine at more negative potentials. However the products are substantially dependent on the reaction media whether aqueous [11-13], non- aqueous [14-17] or micellar [9, 18, 26-28].

The electrochemical behavior of nitrobenzene and nitrosobenzene in anhydrous liquid ammonia was investigated [14] by cyclic voltammetry and controlled potential coulometry. In the absence of added protonating agents, nitrosobenzene and nitrobenzene are both reversibly reduced in two one-electron transfer steps to yield radical anion and di-anion species. The overall reduction process consists of the addition of a single electron to yield a stable radical anion followed by addition of three electrons leading to the final product, different in case of protonation and without protonation [14].

Reductive electrochemistry of nitrobenzene to the corresponding anion radical and dianion has been examined [18] in anionic, cationic, and nonionic micelles. The stability of the nitrobenzene anion radical in nonionic micelles was suggested by voltammetry and supported by ESR [18].

The electrochemical reduction of four 2,5-dimethoxy nitrobenzene 6-substituted derivatives in aqueous and mixed media by cyclic voltammetry, tast and differential pulse polarography were studied [5]. In aqueous media, pH>8, it was possible to observe a polarographic peak or wave due to the nitro radical anion formation. In mixed media, all the studied compounds show a well-defined reversible couple, due to the one electron reduction of the nitro group to produce the corresponding nitro radical anion. Cyclic voltammetric studies show that the nitro radical anion generated was relatively stable, although this intermediate specie shows a tendency to undergo further chemical reactions [5].

This work reports electron transfer kinetic parameters for the electrochemical reduction of nitrobenzene in aqueous micellar media. The experimental voltammetric curves were simulated [15] using Electrochemical Simulation Package (ESP) 2.4, specifically for the reversible first electron transfer couple, $RNO_2/RNO_2^{\cdot-}$ where R is phenyl group. Diffusion coefficient of nitrobenzene was also calculated [14-15, 18, 22, 29-32].

EXPERIMENTAL

Simulations of the cyclic voltammetric reduction of nitrobenzene were performed using computer coded simulation package, Electrochemical Simulation Package (ESP) 2.4. Chemicals and their source: nitrobenzene (Panreac), γ-alumina (0.05 micron), CTAB (Merck), tetraethyl ammonium perchlorate (Alfa Aesar). The reagents were used without further purification. Solutions were not purged free of oxygen. Voltammetry of nitrobenzene was carried out using EG&G, Princeton Applied Research Corp, VersaStat II potentiostat. Data were acquired using M270 electrochemistry research software on a dedicated PII microprocessor coupled to the potentiostat. All experiments were carried out at room temperature.

All experiments were carried out in a three-electrode cell containing working electrode (platinum), a counter (platinum wire) and a reference electrode (saturated calomel electrode). Polishing of the working electrode was done on a nylon-texture synthetic cloth pad soaked with slurry of γ-alumina powder (0.05 micron) in water. Polishing was followed by thorough rinsing with distilled water.

RESULTS AND DISCUSSION

Electrochemical reduction of nitrobenzene (4mM and 6mM) was investigated in 0.1 M CTAB solution at platinum electrode using cyclic voltammetry, Fig. 1. Experiments were also performed for a specific concentration of nitrobenzene (4mM) at scan rates from 100-800 mVs^{-1} in the presence of 0.1 M CTAB/ 0.1 M TEAP (tetraethylammonium perchlorate).

Table 1: **Diffusion coefficients for nitrobenzene**

Diffusion coefficient (cm^2/s)	**Technique / Medium**
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) 7.11×10^{-6} (CTAC) 4.37×10^{-6} (Brij-35)	Single potential step chronocoulometry at hanging mercury drop electrodes in SDS, CTAC and Brij-35 [18]
3.63×10^{-7}	Cyclic voltammetry at platinum electrode in aqueous CTAB [**This work**]

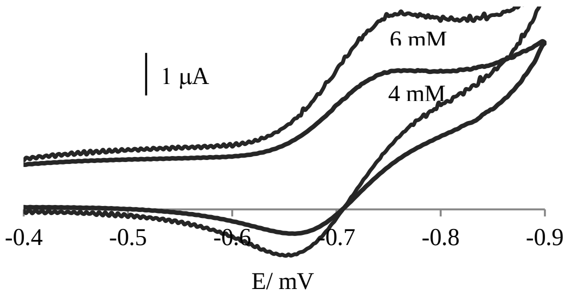

Fig. 1: Cyclic voltammetry of nitrobenzene in 0.1 M CTAB at platinum electrode. Potential vs. saturated calomel electrode at scan rate 300 mVs^{-1}. A platinum wire was used as the counter electrode. $i_p^a / i_p^c{}_{(4\ mM)} = 0.501$, $i_p^a / i_p^c{}_{(6\ mM)} = 0.273$

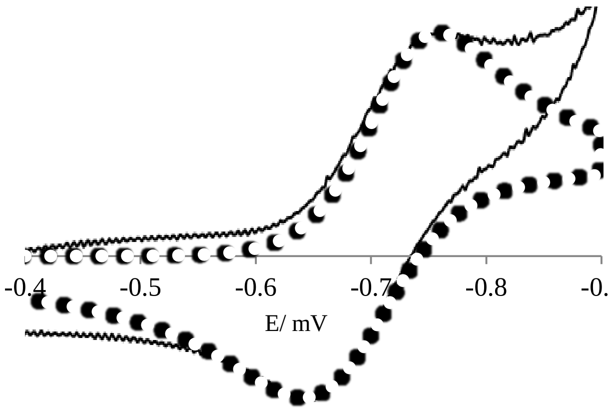

Fig. 2: Voltammetry of nitrobenzene (6 mM) in 0.1 M CTAB as per Fig. 1 above. ***Experimental curve= continuous line; Simulated curve= open circles. Parameters used in simulation were; k_h= 7 ×10^{-3} cm/s, α = 0.6.***

Simulation of experimental curves obtained for nitrobenzene reduction in micellar media using CTAB was carried out, Fig 2.

As modeled by simulation and also as reported in literature the pair of reduction-oxidation peaks is associated with one electron transfer reversible reaction leading to the formation of anion radical [5, 14-18, 20-21, 31].

Several earlier research works show the stabilization of the nitro radical anion in aprotic or mixed media, unlike in the purely aqueous media where a single irreversible four-electron reduction peak is observed indicating the generation of hydroxylamine. In micellar, non-aqueous or in mixed media with restricted proton availability, the reduction exhibits a quasi-reversible / reversible one-electron reduction to the nitro radical anion, followed by a chemical or by a further three-electron electrochemical reduction to phenylhydroxylamine or to other products depending upon the properties of the electrolyte media. 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.

Simulation of both curves obtained in Fig. 1 was carried out assuming simple heterogeneous single electron transfer mechanism; both experimental and simulated curves for 6 mM nitrobenzene are shown in Fig. 2. Displacement of simulated curve with regard to the experimental one is due to non-availability of solution resistance compensation parameter in simulation software.

Determination of diffusion coefficient

Diffusion coefficient of nitrobenzene has been calculated using Randles-Sevcik equation;

$$i_p = (2.99x105)n(\alpha n_a)^{1/2}ACD^{1/2}\nu^{1/2}$$

Where **A** the electrode area (in cm^2), **C** the concentration (in mol/cm^3), **D** the diffusion coefficient (in cm^2/s), and **ν** 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; We assumed here that $n=n_a = 1$

Table 1 summarizes values of the diffusion coefficient for nitrobenzene as reported using different experimental techniques and theoretical approaches [14, 17, 18, 30, 32].

CONCLUSION

Diffusion coefficient of nitrobenzene determined by this work as given in lower left corner of Table 1 is comparable to the corresponding values of similar molecules in micellar media [33-36].

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