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An electrochemical investigation and reduction mechanism of 3, 5-Dinitrobenzoic acid at a glassy carbon electrode: A voltammetric study

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ABSTRACT

The voltammetric behavior of 3, 5-Dinitrobenzoic acid (3, 5-DNBA) has been studied at a Glassy carbon electrode (GCE). 3, 5-DNBA was found to produce two reduction peaks in the forward scan i.e. 0.0 V to −0.1 V. In acidic medium there were no peaks in the reverse scan, indicating irreversible system and diffusion controlled process. The effect of different parameters such as pH, scan rate, concentration, surfactants, repeatability and reproducibility was studied. Based on the results obtained a reduction mechanism was proposed for 3, 5-DNBA. The limits of detection (LOD) and limit of quantification (LOQ) values were found to be 0.68×10^{-6} M and 2.26×10^{-6} M respectively. The total number of electrons (n), diffusion coefficient (D), charge transfer coefficient (α), the number of electrons involved in rate determining step (n_α) and area of the working electrode (A) were calculated as 12, 3.897×10^{-3} cm^2/s, 0.46, 2, 0.3743×10^{-3} cm^2 respectively. The electrochemical impedance spectroscopic (EIS) studies of 3, 5-DNBA at GCE and Pt electrode were also studied.

1. Introduction

3, 5-Dinitrobenzoic acid (3, 5-DNBA) is an organic compound, which is having a carboxylic acid group and two nitro groups at meta positions. The two nitro groups have positive charge on Nitrogen (N) atom and negative charge on Oxygen (O) atom, due to this the 3, 5-DNBA compound forms many charge–transfer complexes with metals and acts as a π-acceptor in the charge–transfer complexes [1,2]. 3, 5-DNBA was used as corrosion inhibitor and also used in photography [3,4]. This was an important intermediate in pharmaceutical industry [5] for the synthesis of sulphachrysolidine and for the detection of ampicillin [6,7]. The derivatives of 3, 5-DNBA were used as radiation sensitizers for tumor treatment [8,9].

The vibrational spectral analysis of 3, 5-DNBA was studied by Amalanathan et al. [9]. To the best of our knowledge a complete voltammetric investigation on 3, 5-DNBA was not made. Hence there was a need for the development of simple and sensitive voltammetric methods for the determination of 3, 5-DNBA. Cyclic voltammetry is an important voltammetric technique and widely used for studying the electrochemical behavior of electro active species. This technique was mainly used for the study of redox reactions and stability of reaction products. This technique was based on monitoring the current, by changing the applied potential in both forward and reverse scans at a working electrode. In this work, we have studied the electrochemical determination of 3, 5-DNBA using voltammetric techniques such as CV and Differential pulse voltammetry (DPV) at the glassy carbon electrode (GCE). The developed method was found to be of simple procedure and of high sensitivity. The electrochemical impedance spectroscopic method for the determination of 3, 5-DNBA was proposed.

2. Experimental

2.1. Apparatus

All electrochemical experiments were carried out by using a model CHI-660D (CH-Instruments). The experiments were done with a conventional three electrode electrochemical cell. The three electrode system consisted of Glassy carbon electrode (GCE) as a working electrode, Pt-wire and saturated calomel electrode (SCE) as a counter and reference electrodes respectively. A model LI 120 (ELICO) pH meter was used for the preparation of various pH buffer solutions.

2.2. Chemicals

3, 5-DNBA was obtained from SIGMA and dissolved in methanol to prepare 10 mM/L standard stock solution. Sodium dodecyl sulfate (SDS), N, N, N, N-Cetyl trimethyl ammonium bromide (CTAB) and Triton-X 100 (TX-100) were dissolved in double distilled water to make 1% solutions. 0.2 M phosphate buffer solution was prepared from $NaH_2PO_4\cdot2H_2O$ and Na_2HPO_4. All other chemicals were of analytical grade quality.

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3. Results & discussion

3.1. Voltammetric behavior of 3, 5-DNBA

The voltammetric behavior of 3, 5-DNBA in 0.2 M phosphate buffer solution (PBS) of pH-6.0 was examined at GCE between the potential sweep window of 0.0 V to −1.0 V. Two well defined reduction peeks were observed at −0.62 V (R_1) and −0.82 V (R_2) at a scan rate of 30 mV/s and no peaks were observed in the reverse scan, suggesting that the electrochemical response of 3, 5-DNBA at GCE was entirely an irreversible process. The first peak (a) refers to the reduction of nitro groups into corresponding hydroxylamine and second peak (b) refers to reduction of hydroxylamine groups into amino groups. The reduction mechanism of 3, 5-DNBA was shown in Scheme 1. Based on the results obtained, we have proposed a detailed reduction mechanism for 3, 5-DNBA at GCE (Scheme 2). The elaborated mechanistic proposal includes, first the negatively charged oxygen atoms of each nitro group take protons and form an adduct, later it takes four electrons to form a negative charge on other oxygen atom of nitro group followed by addition of protons and removal of water leads to the formation of corresponding nitroso compound. The formed nitroso compound was unstable and it takes two protons followed by the four electrons and two protons to form 3, 5-Dihydroxylaminebenzoic acid. All the above processes correspond to the first reduction peak (R_1). Under the acidic conditions 3, 5-Dihydroxylaminebenzoic acid takes two protons followed by removal of two water molecules, addition of four electrons and two protons and forms a final product 3, 5-Diaminobenzoic acid (second reduction peaks R_2) [10–13]. CV and DPV of 3, 5-DNBA at pH-6.0 were shown in Fig. 1a & b respectively.

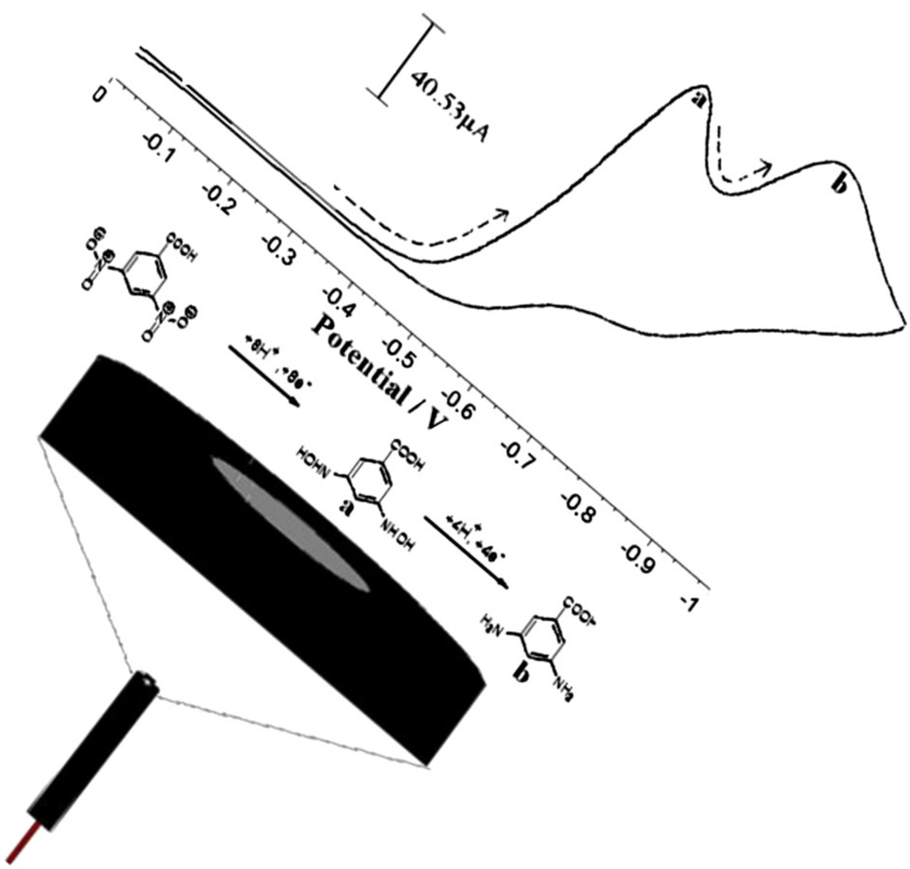
3.2. Effect of pH

The effect of pH was studied by using CV technique. The influence of pH on 1×10^{-3} M solution of 3, 5-DNBA at GCE was examined by using PBS with the pH ranging from pH 5.0 to pH 10.0. Fig. 2a explains the effect of pH on 3, 5-DNBA. As the pH increases there was a shift of peak (R_1) potentials towards more negative side, and in basic medium there was a decrease in peak currents of second peak (R_2). This behavior was due to the fact that as the pH of the buffer increases the availability of protons decreases [14], hence further reduction of second system (i.e. hydroxylamine group into amine group) decreases. From Fig. 2a as the pH of the buffer solution increases from acidic to basic medium the reversibility of the second peak (R_2) was increased and this was due to the conversion of hydroxylamine group into nitroso group [15]. It was observed that at pH-6.0 the peak currents of two reduction peaks were good, therefore we concluded that at pH-6.0 of PBS as a good supporting electrolyte for the determination of 3, 5-DNBA. From the plot E_p vs pH and through the Nernst Eq. (1), we have calculated the total number of electrons (n) involved in the reduction process as 11.749 (≈12) [16]. Fig. 2b shows the plot of pH versus peak currents (in 10^{-5} A) and peak potentials (in V) of first reduction peak (R_1), the linear regression equation for the pH verses peak potentials was E (in V) = 0.58462 + 0.00503 pH.

$$E = E_0 – (0.0591 \ \ pH/n). \qquad (1)$$

3.3. Effect of scan rate

The effect of scan rate on 1×10^{-3} M solution of 3, 5-DNBA was studied at GCE by using pH-6.0 of PBS as a supporting electrolyte



Scheme 1. The mechanism of reduction for 3, 5-DNBA at the surface of the GCE.