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Studying the effect of substituent on the electrochemical reduction of nitrobenzene and its Derivatives

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Abstract:

This paper reports a comprehensive study about electrochemical reduction of nitrobenzene and its derivatives ortho- meta- para-nitroaniline and para-nitrobenzaldehyde in mixed aqueous organic media (5% methanol,KCl 0.5 M) by polarographic cyclic voltammetry on Dropping Mercury Electrode(HDME). The results showed that all derivatives gave a sharp irreversible well-defined peak on (Hg) Hanging Dropping Mercury Electrode(HDME) in a reaction involving four electrons to give the hydroxylamine derivative. In this medium meta-nitroaniline is easier reduced in approximately 80 mV than that of the ortho-nitroaniline. It was observed that para- nitrobenzaldehyde is easier reduced than para-nitroaniline because it has electron- withdrawing substituent.

Key words: polarography, cyclic voltammetry, nitrobenzene, Hanging Dropping Mercury Electrode (HDME).

1. Introduction:

Nitrobenzene (NB) is an important raw material and solvent in the manufacturing of aniline, dye, pesticide, explosives, and pharmaceuticals [1] .A large amount of NB has been released into the environment annually due to excessive use and improper handling of the wastewater[2]. Because of the toxicity on human and the environment, NB has been listed as one of the 129 priority pollutants by USEPA and its maximum permissible concentration for wastewater is 1 mg/L [3].

Nitrobenzene is very stable due to its structure and chemical properties. The electron withdrawing group – NO2 attached to the benzene ring makes it more difficult to be oxidized than to be reduced [4]. Therefore, more effort has been focused on the reductive approaches over the past decades, such as physical adsorption, biological reduction, chemical reduction and electrochemical reduction[5-6]. Electrochemical reduction method has received much attention, because it is cleaner, more efficient and compact, and the cost is comparable with other techniques [7].

It has been reported that NB reduction resulted in a variety of products via various path-ways depending on the electrode and electrolyte applied. Among those products, AN was reported to be of lowest toxicity and a more favorable end product[8-11].

The electrochemical reduction for a lot of Substituted nitrobenzene have been studied Particularly, 4-(nitrophenyl)- substituted, p-nitrobenzophenone, 1,4-dihydropyridines(DHP) which have involved the electroreduction of the nitroaromatic group present in these molecules [12–16]. The electrochemical reduction of some 1,4-DHP derivatives in aqueous media follows the general pattern of nitroaromatic compounds involving a single 4-electrons step producing the hydroxylamine derivative [16–17]. Our effort is focused on the use of electrochemical techniques to extract the maximum possible information on the reduction characteristics of the ortho- meta-and para- nitroaniline derivatives.

2. Materials and methods:

Nitrobenzene(NB)99%, ortho-nitroaniline(o-NA) 99% , meta- nitroaniline(m-NA) 99% ,para- nitroaniline(p-NA)98% and para-nitrobenzaldehyde(p-NBA)98% Were purchased from Merck Laboratories. All the chemicals used in the experiments were of analytical grade and used without further purification. The water utilized in all studies was double-distilled and deionized.

The polarograms were obtained with ampere-metric station model (Metrohm Comutrace 797 VA) Swiss Mitrom company production. A three-electrode cell contained a DME, an Ag/AgCl reference electrode, and a platinum wire auxiliary electrode.

2.1.Experimental Procedure:

The general procedure for obtaining polarograms was as follows:

NB(10^{-3}M),o-NA(10^{-3}M),m-NA(10^{-3}M),p-NA(10^{-3} M),and p-NBA(10^{-3}M)) were prepared by weighing suitable amounts of these compounds and dissolving them in methanol(5 ml). Then the solutions were transferred to volumetric flask (100-ml) and diluted to the mark using distilled water that contains KCl(0.5 M).

At first, 25 ml of each solution prepared was put into the poloragraphic cell. Then the solutions were purged with nitrogen for 5 min. The polarograms were recorded by applying a negative going scan over the potential range from 0 to −2000 mV. The obtained polarograms were used for further calculations. All measurements were made at 25◦C.

3. Results and discussion

3.1. Electrochemical reduction of NB in aqueous media

The electrochemical reduction of NB on (Hg) Hanging Dropping Mercury Electrode(HDME)
in aqueous media(KCl 0.5 M supporting electrolyte) was studied. As shown inFig.(1), the reduction of NB started at around 0 V in 0.5 M KCl solution , with one cathodic peak occurred at −845 mV, attributing to NB reduction to phenylhydroxylamine (PHA).followed by an anodic peak appeared in the return cycle at 112 mV, It represented the two-electron reversible transformation between PHA and nitrosobenzene (NSB).

$$\text{Ar-NO2+ 4e-+4H+} \rightarrow \text{Ar-NHOH + H2O}$$

$$\text{Ar-NHOH} \rightarrow \text{Ar-NO + 2e-}$$

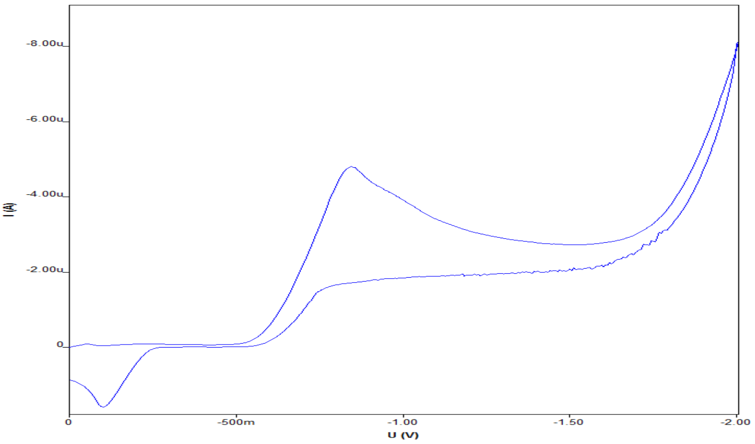


Figure 1 cv curve of (HDME) in 0.5 M KCl, in the presence of 10^{-3} M NB

3.2. Effect of NB concentration and scan rate

Fig. 2(a) shows the NB concentration effect on the reduction reaction as measured by cyclic voltammetry on (HDME)electrode. As could be noticed, NB reduction started almost at the same potential within the investigated concentration range. The current increased at a faster speed and the NB reduction peak potential shifted towards the more negative direction with the increase of NB concentration, meanwhile the reduction peak current increased to some extent. The change of reduction peak current with NB concentration was also plotted. Fig. 2(b) shows a good linear relationship with a R value of 0.9822 suggests the reaction could follow zeroth order kinetics with respect to NB concentration.

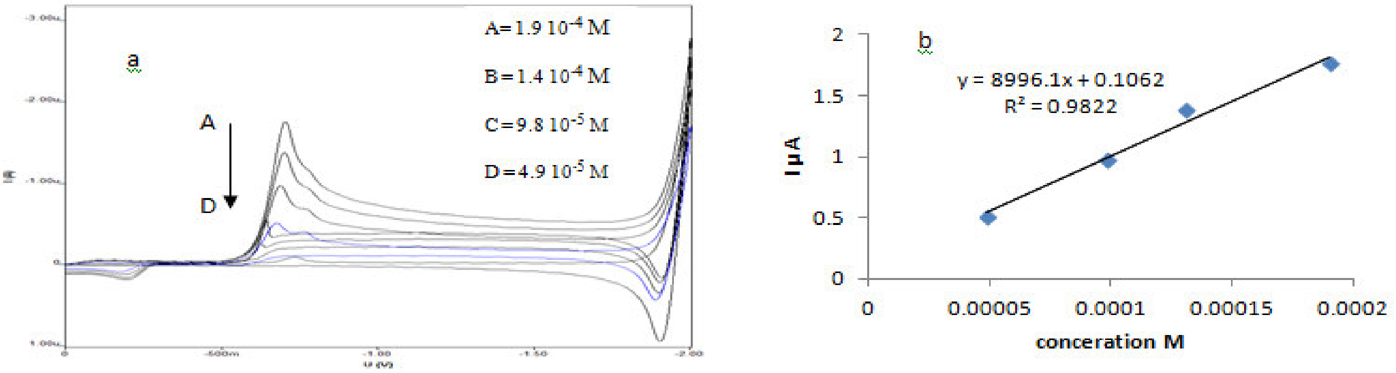


Figure 2 (a) CV curves of(HDME) in 0.5 M KCl at various NB concentrations , Figure2 (b) a good liner relationship between current and conceration

Fig. 3(a) showed NB reduction on (HDME)at various scan rates. It was cleared that, the curves showed one irreversible cathodic reduction peaks at all scan rates; and this reduction peaks shifted towards the positive direction with the decrement of peak current(denoted asipc) as the scan rate slowed down. The effect of v1/2 on ipc was depicted in inset of Fig. 3(b), clearly. The current function correlated linearly with the square root of the scan rate.This indicates that the electrochemical reduction of nitrobenzene on (HDME)is a diffusion-controlled process. However, adsorption might still play a significant role in the process .[18]

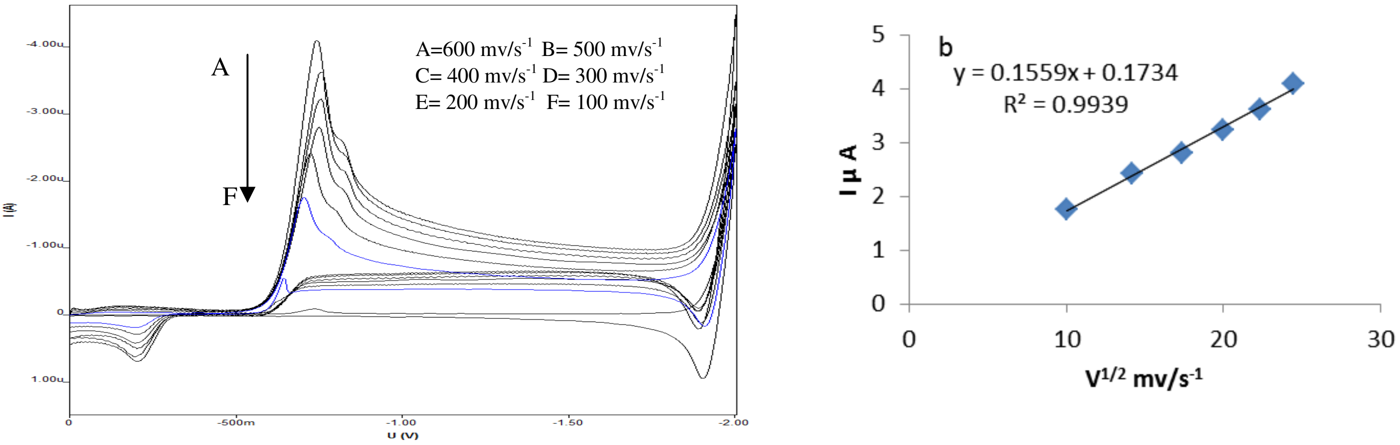


Figure 3(a) **cv curvesof (HDME) in 0.5 M KCl with 10^{-3} M NB at different scan rates, 3(b) The NB reduction peak current as a function of scan rate**

3.3. Effect of substituent on NB reduction:

All the derivatives of nitrobenzene. were reduced at (HDME) at the same concentrations were prepared in mixed media of (0.5 M KCl, methanol).The compounds showed a similar polarographic behavior with well-defined waves or peaks depending on the cyclic voltammetry modes. All of the derivatives exhibited one cathodic peak (Fig. 4). This peak appears in all polarograms. The polarograms of nitro aniline derivatives were compared to the polarogram of nitrobenzene, it was found that the ratio of their limiting currents was close to the same result, confirming that the reduction of these derivatives is also due to a four-electrons, four protons reduction as nitrobenzene.

$$\text{Ar-NO2+ 4e-+4H+} \rightarrow \text{Ar-NHOH + H2O} \qquad (1)$$

All NB derivatives gave a sharp irreversible well-defined peak (Fig.4), which corresponds to the reduction of the nitro group to hydroxylamine group according to reaction (1).

However this irreversible peak of meta-NA (Epc= -857 mv) was reduced at less cathodic potentials in approximately (70-100) mV compared with the ortho-NA derivative (-916 mv)and para-NA derivative(-1040 mv). A plausible explanation for these results could be ascribed to the more electron-donating and mesomeric properties of the (-NH2) group, which affected the electron density of the nitro moiety in the ortho-position and para- position compared with the meta-position.

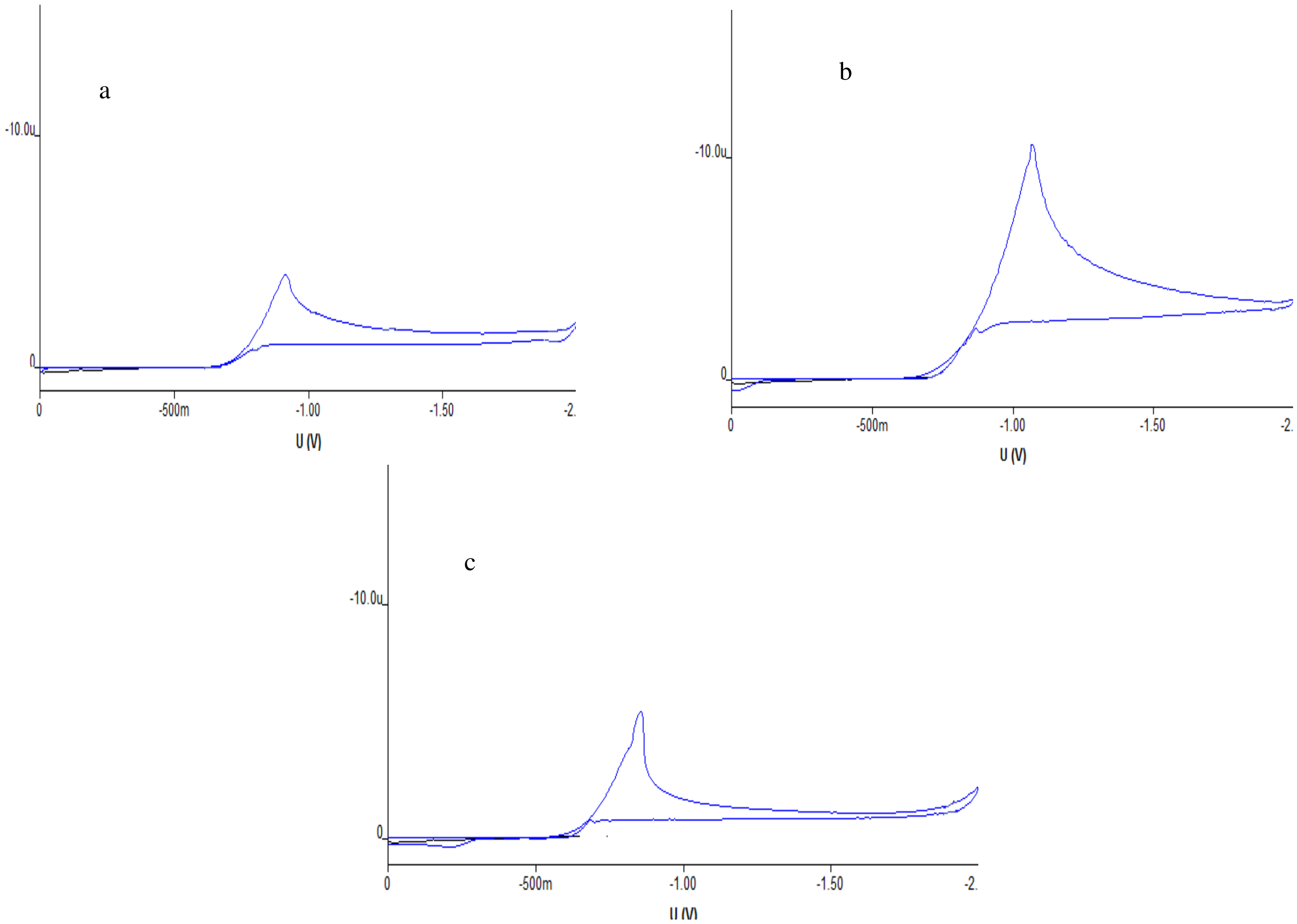
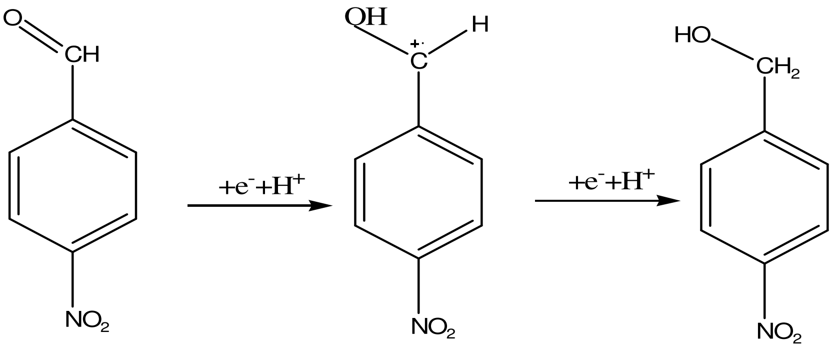


Figure 4 cv curves of (HDME) in 0.5 M KCl with 10^{-3} M (a)O- NA, (b)P-NA , (c) m-NA

The compared of the para- nitro aniline(p-NA) polarogram with the para-nitrobenzaldehyde(p-NBA) polarogram also achieved. Both derivatives gave a sharp irreversible well-defined peak (Fig.5), which corresponds to the reduction of the nitro group to hydroxylamine group according to reaction (1).

The data showed that para-nitrobenzaldehyde was reduced at less cathodic potentials (-547mv) than para-nitroaniline(-1040mv). A reasonable explanation for these results could be ascribed to the more electron-withdrawing and mesomeric properties of the (-COH) group, which affected the electron density of the nitro moiety in the para-position, so it was easier to reduce.

Furthermore; it was observed two cathodic peaks occurred at (−1350 mV,-1680 mv). This could be attributed to the (-COH) group reduction, which usually gives one peak, but it was separated into two peaks according to reaction (2). Each peak corresponds to one electrone, it may due to the presence of nitro substituent, which was adsorbed on the surface of the electrode.



(2)

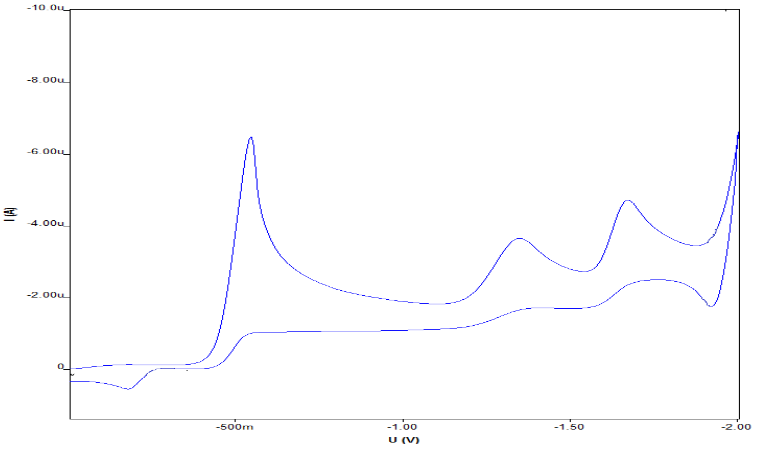


Figure 5 cv curve of (HDME) in 0.5 M KCl, in the presence of 10^{-3} M p-NBA

4. Conclusions:

It was found that the electrochemical reduction of NB in mixed aqueous organic media:

1. The nitrobenzene and its derivatives gave a sharp irreversible well-defined peak on (Hg) Hanging Dropping Mercury Electrode(HDME) in a reaction involving four electrons to give the hydroxylamine derivative at different potentials [E_{PC}(NB) = - 845 mv, E_{PC}(m-NA) = - 857 mv, E_{PC}(o-NA) =-916mv, E_{PC}(p-NA) = -1040mv, and E_{PC}(p-NBA) = - 547mv].
2. It could follow the zeroth order kinetics with respect to NB concentration, and that electrochemical reduction of nitrobenzene on (HDME) is a diffusion-controlled process.
3. It was noticed that the presence of electron- donating groups(-NH_2) affected the electrochemical behavior of nitrobenzene and made it more difficult to reduce.
4. the presence of electron-withdrawing groups(-COH) affected the electrochemical behavior of NB in mixed aqueous organic media and made it easier to reduce.

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