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Polarographic and voltammetric investigation of 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinoline sulfonic acid

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Abstract

The behaviour at HMDE and SMDE of 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinolinesulfonic acid has been studied by several techniques including Square wave voltammetry (SWV), Differential pulse plarography (DPP), Direct current polarography (DCP) and Cyclic voltammetry (CV). Current–potential curves recorded at HMDE and SMDE electrode provide information on electrode reaction mechanism. The reduction of a pre-protonated azo group involving a four-electron process and two peaks or waves, gives amine derivatives in acidic solutions. In alkaline solution the reduction process occurs at more negative potential with the formation of a stable hydrazo compound. The electrochemical reduction mechanism of the azo compound is suggested using SWV, DPP, DCP and CV techniques in aqueous solutions of varying pH.

Keywords: Azo; Polarography; Voltammetry; Reaction mechanism

1. Introduction

Azo compounds are widely used in industry as textile dyes, colouring agents in foods and pharmaceuticals etc. As a result they can enter the body through the intake of certain foods and drugs that contain these azo compounds. Concern has been voiced about the potential carcinogenicity of compounds containing azo group. Therefore, a study of the mechanism of the polarographic and voltammetric reduction of azo compounds is worthy of investigation [1–4].

The electrochemical behaviour of a variety of azo compounds has been investigated for the years. A detailed study of the polarography of azobenzene and its *p*-sulphonic acids was reported in previous studies. Some azo compounds are known to be reduced to the amines via a four electron reaction. *p*-Dimethylaminoazobenzene showed that the two number of electrons involved in the reduction are pH dependent. Below pH 7.0 the step height corresponded to four electrons and basic media to little more than two. In previous studies some monoazobenzene derivatives showed a complex electrode reaction mechanism. Especially, in acidic media irreversible electrode reaction mechanism was observed. In basic media anodic peak in CV voltammograms were found. Electrode reaction mechanism depends on solution media, pH and substituent effects [5–12].

In this study polarographic and voltammetric behaviour of 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinolinesulfonic acid was investigated. The aim of this

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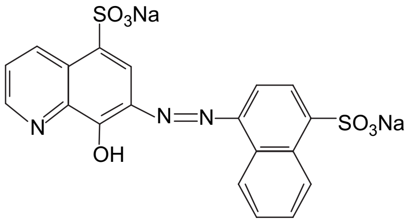
study is to explain the electrochemical reaction mechanism for the azo compound using Square wave voltammetry (SWV), Differential pulse polarography (DPP), Direct current polarography (DCP) and Cyclic voltammetry (CV) in different media. At the same time, this study contributes to previous studies on the electrochemistry of other azo compounds [9–16]. This compound has not hitherto been investigated by polarographic and voltammetric methods. Chemical structure of the azo compound is given as below:



2. Experimental

Stock solution of 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinolinesulfonic acid ($c = 10^{-3}\ \mathrm{mol\,dm^{-3}}$) was prepared by dissolving an exactly weighed amount of the pure substance (from Merck products) in triple distilled water. This stock solution was stored in a dark bottle. Phosphoric acid, acetic acid, boric acid, ammonia and sodium hydroxide were of purity p.a. The water used was triple distilled. Buffer solutions used are Britton Robinson buffer (pH 2.0–12.0), acetate buffer (pH 3.5–5.5), phosphate buffer (pH 6.0–8.0), borate buffer (pH 7.0–10.0), ammonia buffer (pH 8.5–10.5). pH values of buffer solutions were adjusted to the required pH with sodium hydroxide stock solutions.

The polarographic and voltammetric experiments were carried out using a computer controlled electroanalysis system (Metrohm 757 VA Computrace Electrochemical Analyser). A three electrode combination system was used. This consisted of a Multi Mode Electrode (DME, SMDE and HMDE), an Ag/AgCl reference electrode and a Pt wire auxiliary electrode. All the measurements were carried out at room temperature.

A Jenway 3040 model ion analyser was used to monitor the pH of buffer solutions in the range of 2.0–12.0, standardised with pH 7.00 and pH 4.00 stock buffer solutions.

The solutions were purged with purified clean dry nitrogen for 5 min prior to the experiments in order to remove dissolved oxygen from the media and blanketed thereafter.

3. Results and discussion

The electrochemical behaviour of 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinolinesulfonic acid was investigated over the wide pH range (pH 2.0–12.0) in different aqueous buffer solutions by using SWV, DPP, DCP and CV techniques. DPP and SWV polarograms and voltammograms were recorded for the azo compound in Britton Robinson buffer (pH 2.0–12.0), acetate buffer (pH 3.5–5.5), phosphate buffer (pH 6.0–8.0), borate buffer (pH 7.0–10.0), and ammonia buffer (pH 8.5–10.5) solutions. In this study, reduction of azo group in the azo compound was investigated. Polarograms and voltammograms of the compound in Britton Robinson buffer solutions are shown in Fig. 1. At pH < 5.0 for SWV and pH < 8.0 for DPP, a sharp reduction peak and a small shoulder peak for the compound appear in the polarograms and voltammograms. At higher pH range, single reduction peak was observed which depends on pH and solution media. Therefore, systematic studies were made at large pH range (2.0–12.0) by different voltammetric techniques such as SWV, DPP, DCP and CV.

Generally the polarographic and voltammetric reduction of an organic compound can be represented by

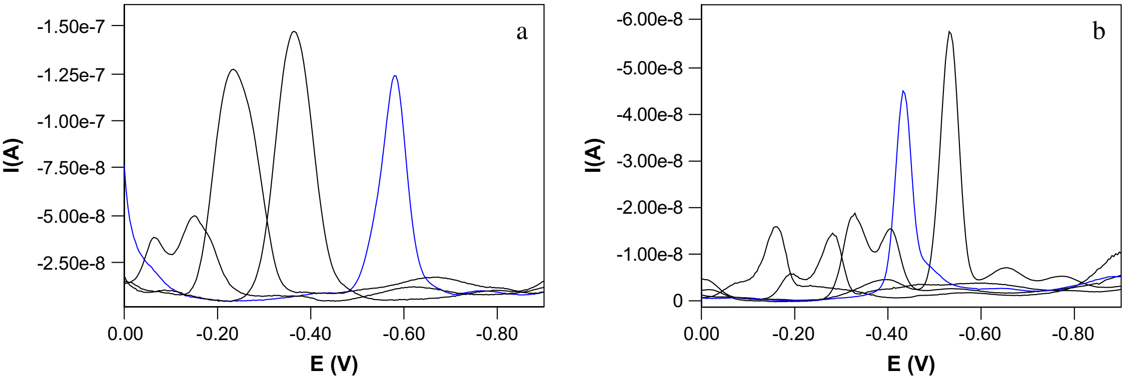


Fig. 1. Voltammograms and polarograms of the azo compound in Britton Robinson Buffer solutions. (a) SWV (pH 3.16, 5.15, 7.16, 10.67); (b) DPP (pH 3.13, 5.04, 7.10, 9.25, 10.88).

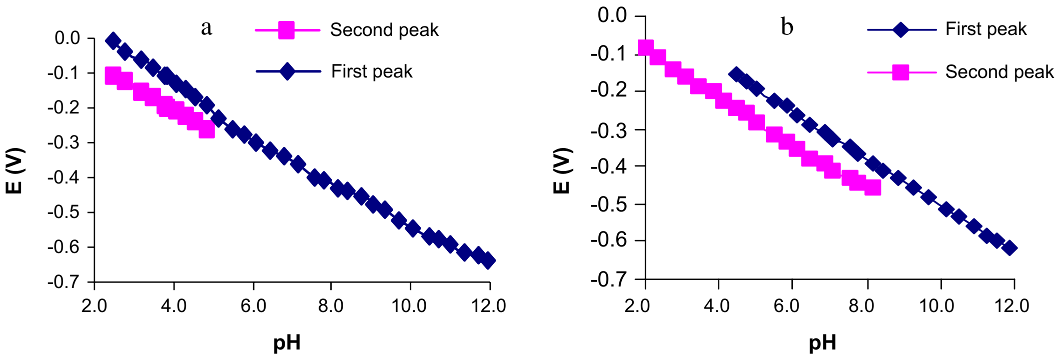


Fig. 2. Change in peak potential of the azo compound with pH in Britton Robinson Buffer solution. (a) Scan rate 200 mV/s for SWV, (b) scan rate 4 mV/s, drop time is 1 s for DPP and Ag/AgCl is reference electrode.

$$O + aH^+ + ne^- = RHa$$

The approximate relationship between E_p and pH for a reversible reaction at 25 °C is

$$E_p = E^0 - 0.059(a/n)\ \mathrm{pH}$$

A plot of E_p against pH should be linear with a slope of $0.059a/n$ and an intercept corresponding to E^0 [17,18]. The effect of pH on the polarographic and voltammetric peak potential of the compound is shown for BR buffer in Fig. 2.

The E_p–pH plots change linearly in the pH range 2.0–12.0 for the azo group. The observed shift of the compound peaks to more negative potentials with increasing pH is in agreement with the following relationship for different voltammetric techniques in the pH range 2.0–12.0 (in different buffer) as below (Table 1).

Reduction peak potentials of the compound in polarograms and voltammograms shift to more negative potentials revealing the H^+ ions exist in the reduction process. Within pH range 3.0–8.0 DPP, SWV and CV peaks split depending on the pH (Fig. 1 for DPP).

Two waves were observed at DCP polarograms in acidic media (Fig. 3). As seen from SWV and DPP (Fig. 2), single wave has been observed at higher pH values. The values of electron numbers were calculated by Heyrovsky–Ilkoviç equation. The slope of E versus $\log I/I_d - I$ is $0.059/\alpha n$ and the intercept of the graph equals the value of the $E_{1/2}$ [17,18] which is the potential corresponding to the $I_d/2$. The results of αn values are given in Table 2.

It can also be seen from Figs. 3 and 4 that the limiting current of the two waves are equal in the acidic media. With increasing pH, second wave decreased and disappeared at higher pH values. These results support that first cathodic wave belongs to reduction of the azo group to hydrazo form, second wave hydrazo form to corresponding amines.

CV voltammetric technique is required for explanation of electrochemical behaviour of the compound [12,19,20]. In general, pH is one of the variables that commonly and strongly influences the shapes of voltammograms, and therefore it is important to investigate the effects of pH on electrochemical systems. The pH dependence of the cyclic voltammogram of the azo compound obtained in acidic, neutral and basic media are given in Fig. 5. Two reduction peaks have been seen in the range of pH 2.0–7.0 and one reduction peak in the range of pH 7.0–12.0. At the same time, as anodic peak potential of the azo compound increases, the second cathodic peak decreases. However, in acidic medium the two cathodic processes (E_{pc}) appear to be irreversible processes as no current (or small current) is observed in reverse scan.

Table 1
Dependence of peak potentials on pH

Medium	I. Peak equation	*r*	II. Peak equation	*r*	Technique
BRb	$E_p = 0.1337 - 0.0672$ pH	0.9964	$E_p = 0.0501 - 0.0637$ pH	0.9988	SWV
BRb	$E_p = 0.1221 - 0.0626$ pH	0.9998	$E_p = 0.0323 - 0.0618$ pH	0.9985	DPP
BRb	$E_p = 0.0714 - 0.061$ pH	0.9994	$E_p = 0.0079 - 0.0639$ pH	0.9987	CV
Borate	$E_p = 0.0939 - 0.064$ pH	0.9979			SWV
Borate	$E_p = 0.0697 - 0.062$ pH	0.9996			CV
Phosphate	–		$E_p = -0.0308 - 0.0476$ pH	0.9930	SWV
Phosphate	–		$E_p = 0.0765 - 0.0627$ pH	0.9987	CV
Ammonia	–		$E_p = -0.1078 - 0.0458$ pH	0.9933	SWV
Ammonia	–		$E_p = -0.0856 - 0.0483$ pH	0.9971	CV

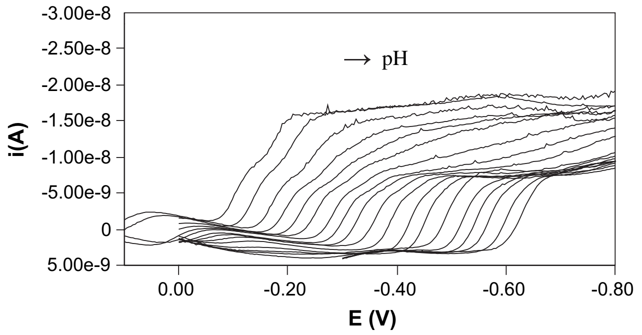


Fig. 3. Polarograms of the azo compound in Britton Robinson Buffer solution (pH 2.0–12.0, scan rate 4 mV/s, drop time 1 s, with SMDE and Ag/AgCl reference electrode).

Table 2
αn Values of the azo compound in BR buffer

pH	2.71	3.71	5.08	5.99	7.18	8.17	9.18	10.49	11.00	11.84
1. Wave	1.90	2.10	1.93	1.86	1.89	1.49	1.71	1.46	1.57	1.74
2. Wave	2.10	2.10	1.58	1.61	–	–	–	–	–	–

For characterization of two peaks in acidic media, the direction of sweep was reversed at different potentials, and anodic peak was observed in reverse scan as shown in Fig. 6. According to these results (Figs. 5 and 6), it has been observed that reduction of the azo group in the dye does not stop at hydrazo stage but further reduction leads to the cleavage of –NH–NH– linkage to give amino compounds as the final products. It can be said that two cathodic peaks belong to reduction of the azo group to hydrazo (first peak) and hydrazo to alkyl amines (second peak) in the pH range 2.0–7.0 [7,8,12,15,16,21–25]. At higher pH values the reduction mechanism stops hydrazo step because only one cathodic peak and anodic peak were observed. These results are in agreements with as described in other techniques.

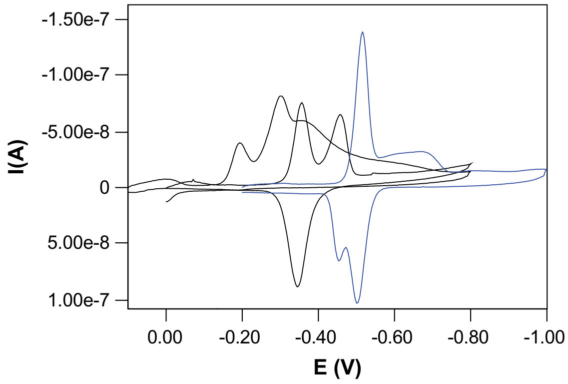


Fig. 5. CV voltammograms of the azo compound in BR buffer (pH 4.86, 6.77, 8.40, scan rate 200 mV/s).

The effect of several parameters on the electrochemical reaction mechanism in CV, such as scan rate and the probable adsorption on the surface of mercury drop, about reversibility of reaction on the voltammetric signal was studied (Fig. 3) [19,20].

In order to gain more information for elucidating the kind of electrochemical controlled processes taking place in different buffer solutions, the effect of scan rate on the peak potential and peak current was studied by cyclic voltammetry on a HMDE. Upon analysis of the effect of scan rate between the root square of scan rate and peak intensity were established within the range of scan rates studied (5–1000 mV/s). The change of I_p versus $v^{1/2}$ is not linear. With increasing of scan rate, $I_p/v^{1/2}$ slope increases. This situation proved that the complex electrochemical electrode reaction of the azo compound occurs on the electrode surface. Such behaviour is adopted as indicative of EC mechanism in previous studies [6–16,22–25]. CV voltammograms show an adsorption effect on the electrode surface because cathodic peak is broad, and anodic peak intensity is higher than cathodic peak intensity (Fig. 5).

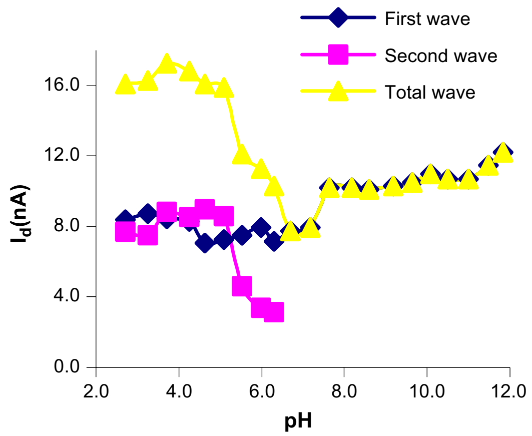


Fig. 4. The change of I_d with pH for the azo group.

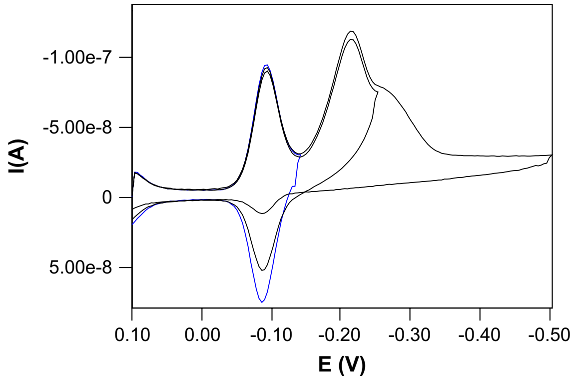
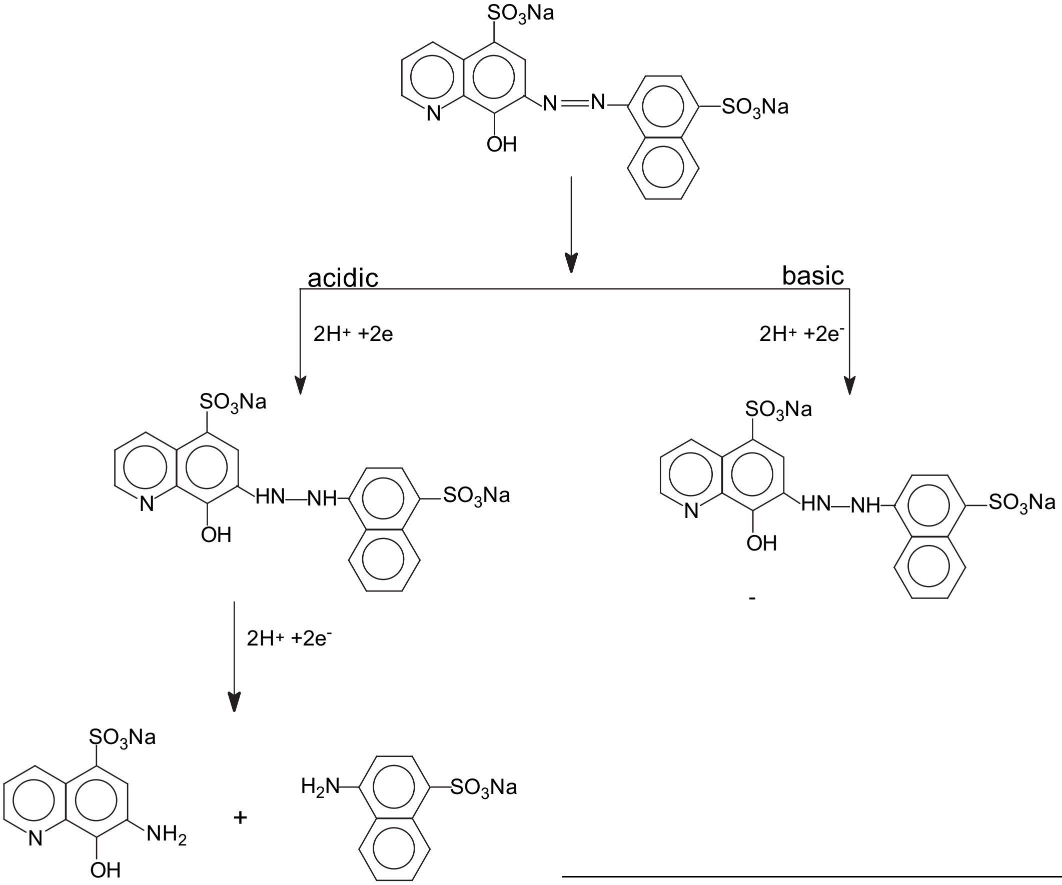


Fig. 6. CV voltammograms of the azo compound in BR buffer (1. final potential: –0.140, 2. final potential: –0.250, 3. final potential: –0.500).

3.1. Electrode reaction mechanism of the azo compound

According to these results, it can be said that the reduction of the azo centre takes place via four electrons to the aniline derivative in acidic media and two electrons to the hydrazo derivative in basic media. These concepts are in agreement with earlier findings on the polarographic and voltammetric behaviour of other azobenzene derivatives [1–8]. Overall electrode reaction mechanism for the azo compound from the DPP, SWV, DCP and CV data are given as below:



Similar electrode reaction mechanism for other azo compounds were obtained in previous studies [5–16,26].

The redox property of the azo compound on the electrode is influenced by the variations of pH values. Therefore pH is a critical factor for determination of the azo compounds. On the other hand the pH of the test solution also affects both linear range and detection power.

The applicability of the proposed square wave voltammetric procedure as an analytical method for the determination of the azo compound was examined by measuring the cathodic peak current as a function of the concentration of the depolarizer. The calibration graphs were constructed at different buffer solutions and potassium nitrate media. Optimum pH value was selected as 6.0. The dependency existed between peak current and the concentration of the azo compound was linear within the range 9×10^{-8}–2×10^{-5} M. The concentration for which the SW voltammetric signal just disappeared as the concentration decreased is defined as the detection limit. The detection limit of the azo compound was found to be 9×10^{-8} M.

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