POLAROGRAPHIC AND VOLTAMMETRIC INVESTIGATION OF SUDAN I

The voltammetric and polarographic reduction of the 1-phenylazo-2-naphthol (Sudan I) on a hanging mercury drop electrode (HMDE) and static mercury drop electrode (SMDE) has been studied by using several techniques including square-wave voltammetry (SWV), differential pulse polarography (DPP), direct current polarography (DCP) and cyclic voltammetry (CV) in aqueous and ethanolic Britton-Robinson buffer media. The observed shift of the compound reduction peaks to more negative potentials with increasing pH indicates that hydrogen ions are involved in the electrode reaction. The effect of scan rate and pH on the reduction peaks has been studied. From the polarographic and voltammetric data, electrochemical reduction mechanism of the azo dye has been suggested.

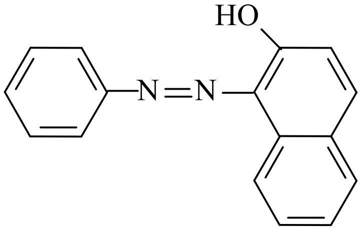
Keywords: Azo dyes, voltammetry, reduction, reaction mechanism.

1. INTRODUCTION

Sudan I (1-phenylazo-2-naphthol) is a synthetic lipid soluble azoic pigment. It has been widely used in chemical industries such as oils, fats, plastics, textiles, floor polishes and cosmetics [1]. Recently, Sudan I had been used extensively to give fascinating red color to the products such as chilli sauce, ketchup, olive oil, the New Orleans baking chicken and many other frequently eaten foodstuffs. It has been confirmed that Sudan I is a potential carcinogen for humans [1]. In 1975, Sudan I was classified as Group 3 carcinogen by the International Agency for Research on Cancer [1-3]. For these reasons, Sudan I is strictly forbidden to be added to food products according to both the Food Standards Agency and European Union [1,2].

Many analytical methods such as high performance liquid chromatography, gas chromatography-mass spectrometry, capillary electrophoresis, enzyme-linked immunosorbent assay, and electrochemical methods have been used for the determination of Sudan I [4-8]. But, many of them are time-consuming or involve a tedious extraction process before detection. In contrast, electrochemical techniques have some advantages such as rapid response, time saving, low cost, and high sensitivity [1,2,9-13]. To continue improving, the electrochemical characteristics of the reagents have been studied

In the present work, the electrochemical behavior of 1-phenylazo-2-naphthol was studied at a mercury electrode in B-R buffer electrolyte media by using SWV, DPP, DCP and CV techniques. At the same time, this study contributes to previous studies on the electrochemistry of other azo compounds. This compound has not been investigated at a mercury electrode by voltammetric methods up to now. The molecular structure of the azo compound is given below (Scheme 1).



Scheme 1. Molecular structure of the Sudan I.

2. EXPERIMENTAL

1-phenylazo-2-naphthol was purchased from Aldrich and used without further purification. 10^{-3} M stock solution of the Sudan I dye was prepared in absolute ethanol. 10^{-4} M of Sudan I solution was prepared by appropriate dilution of the stock solution with absolute ethanol. Phosphoric acid, acetic acid, boric acid and sodium hydroxide were of purity p.a. 0.04 M Britton Robinson (B-R) buffer solution (pH:2.0-12.0) was used as supporting electrolyte and 10 mL of supporting electrolyte was established into a voltammetric cell. Then 800 μL 10^{-4} M of Sudan I solution was added with a micropipette into a voltammetric cell and then square wave and cyclic voltammograms were recorded. For DPP and DCP techniques measurements, 200 μL 10^{-3} M of Sudan I solution was added with a micropipette into a 10 mL 50% B-R(0.02M) buffer-50% ethanol supporting electrolyte in the voltammetric cell.

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 (saturated KCl) reference electrode and a Pt wire auxiliary electrode. All measurements were carried out at room temperature. Voltammetric parameters were selected for an equilibrium time of 5 s, a purge time of 300 s, and at a potential step of 4 mV, a pulse height of 50 mV and a scan rate (v) of 200 mVs^{-1}. The solutions were purged with purified clean dry nitrogen for five minutes prior to the experiments in order to remove dissolved oxygen from the media.

3. RESULTS AND DISCUSSION

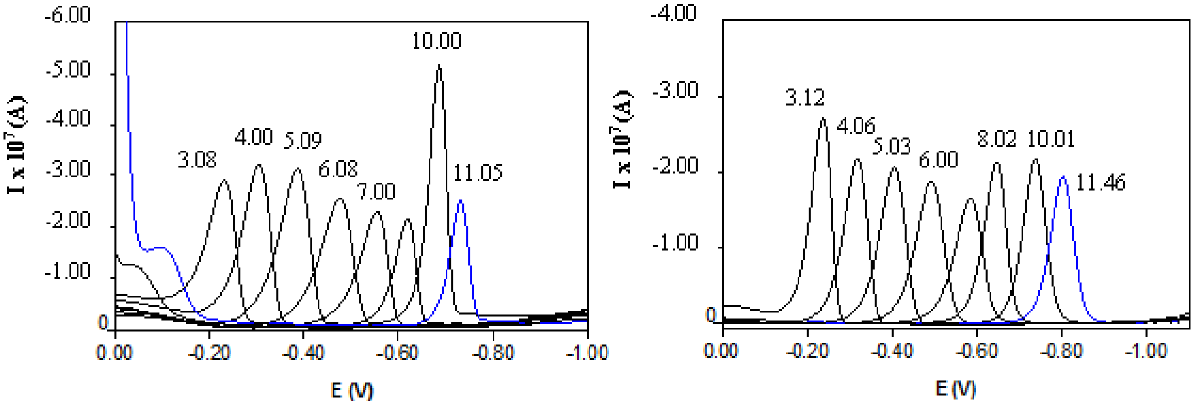


Figure 1. (a) Square wave voltammograms of 7.41×10^{-6} M Sudan I in B-R (0.04 M) buffer media (pH 3.08, 4.00, 5.09, 6.08, 7.00, 8.06, 10.00 and 11.05), v = 200 mV/s, (b) Differential pulse polarograms of 1.96×10^{-5} M Sudan I in 50% B-R (0.02 M) buffer-50% ethanol media (pH 3.12, 4.06, 5.03, 6.00, 8.02, 10.01 and 11.46), v = 4 mV/s.

The voltammograms of 7.41×10^{-6} M Sudan I in B-R (0.04 M) buffer and polarograms of 1.96×10^{-5} M Sudan I in 50% B-R (0.02 M) buffer-50% ethanol media at pH values between 2.0 and 12.0 have one reduction peak corresponding to the reduction of the azo group for SWV and DPP techniques respectively (Figure 1). As shown in Figure 1 peak currents and potentials are dependent on pH. Plots of peak potential (E_p) versus pH of Sudan I are depicted in Figure 2 for SWV and DPP techniques respectively. The observed shift of the Sudan I reduction peaks to more negative potentials with increasing pH indicates that hydrogen ions are involved in the electrode reaction [14-20].

As shown in Figure 2, peak potentials of the reduction peaks are a linear function of pH. The linear pH dependence of the peak potentials for SWV and DPP is given in Table 1. There is a linear relationship between the cathodic peak potential (E_p) and pH value, E_p(V) = -0.0435-0.0663pH for SWV and E_p(V) = -0.0499-0.0699pH for DPP techniques respectively in aqueous and ethanolic Britton-Robinson buffer media (Table 1). The slopes -66,3 mV/pH and -69,9 mV/pH are very close to the theoretical value of -59 mV per unit pH required under assumption of the $2e^-/2H^+$ or $4e^-/4H^+$ process of the electrochemical reduction of Sudan I [14].

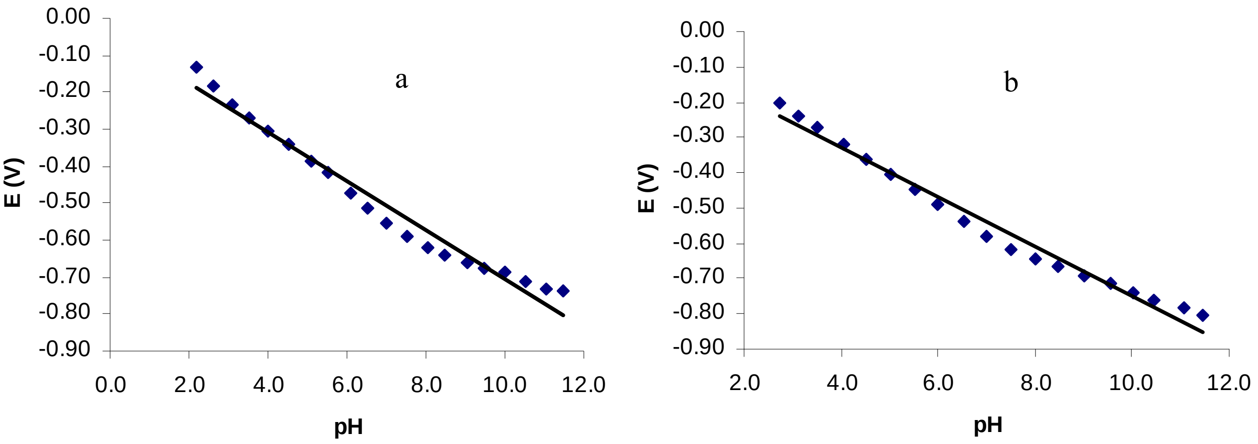


Figure 2. Dependence of cathodic peak potentials as a function of pH for Sudan I a) SWV ($7.41\text{x}10^{-6}$ M), in B-R (0.04 M) buffer, $v = 200$ mV/s, b) DPP ($1.96\text{x}10^{-5}$ M) in 50% B-R (0.02 M) buffer-50% ethanol medium, $v = 4$ mV/s.

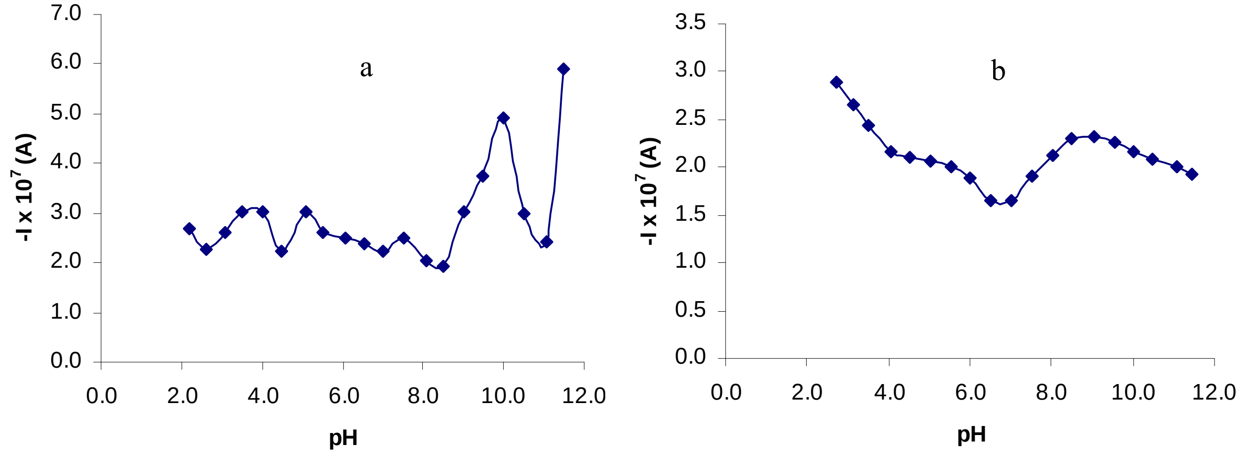


Figure 3. Dependence of cathodic peak currents as a function of pH for Sudan I a) SWV ($7.41\text{x}10^{-6}$ M), in B-R (0.04 M) buffer, $v = 200$ mV/s, b) DPP ($1.96\text{x}10^{-5}$ M) in 50% B-R (0.02 M) buffer-50% ethanol medium, $v = 4$ mV/s.

As shown in Figure 3, SWV and DPP peak currents are different from each other depending on pH. Especially in SWV, peak currents firstly decreased in the pH range of 5.0-8.5, and then increased in the pH range of 8.5-10.0. But in DPP technique, peak currents firstly decreased in the pH range of 2.7-6.5, and increased in the pH range of 7.0-8.5 and then decreased again in the pH range of 9.0-11.5.

DCP studies

Figure 4 shows typical DC polarograms of the azo compound in 50% B-R (0.02 M) buffer-50% ethanol medium, a well defined cathodic wave is seen in the pH range of 2.0-12.0 with a scan rate of 4 mV/s. Peak maxima were seen in the pH range of 2.0-12.0 at DC polarograms indicates that the adsorption of the azo compound on the electrode surface [20,21]. It can be said that the similar electrode reactions occur in acidic and basic media, due to the approximately same wave heights are obtained in acidic and basic media [21,22].

Logarithmic analyzes of the reduction waves calculated from the S-shaped DC polarograms in 50% B-R (0.02 M) buffer-50% ethanol buffer of different pH values (2.0–12.0) resulted in straight lines. Distorted polarographic waves have not been of concern for these logarithmic analyzes. The αn values were calculated according to the Heyrovsky-Ilkovic equation [23-25]. Also the Ep-pH plots for the reduction wave of Sudan I were straight lines of slopes (S) reported in Table 1. The number of hydrogen ions (a_{H+}) participating in the rate-determining step was calculated using the slope values S_1 ($S_1 = -0.05916/\alpha n$) and S_2 ($S_2 = -0.05916a/\alpha n$) of both the E versus log (I/I_d-I) and $E_{1/2}$-pH plots, respectively. The effect of pH on the half wave potential ($E_{1/2}$) of Sudan I and on the αn values involved in its reduction in 50% B-R (0.02 M) buffer-50% ethanol medium is shown in Figure 5 and Figure 6. The αn values and the number of hydrogen ions calculated indicate that the two protons and two electrons participate in the rate-determining step of the reactant centers. It is acceptable to assume that the Sudan I is reduced to corresponding amines at all studied pH values. The azo group is firstly reduced to hydrazo form and then hydrazo form is reduced to yield the corresponding amines with a two electron, two proton processes (Scheme 2) [26-30].

Table 1. Dependence of peak potentials on pH.

MEDİUM	PEAK EQUATİON	R^2	TECHNİQUE
B-R (0.04M) buffer	E_p = -0.0435-0.0663pH	0.9694	SWV
50% B-R (0.02 M) buffer -50% ethanol	E_p = -0.0499-0.0699pH	0.9775	DPP
B-R (0.04M) buffer	E_p = -0.0605-0.0681pH	0.9688	CV

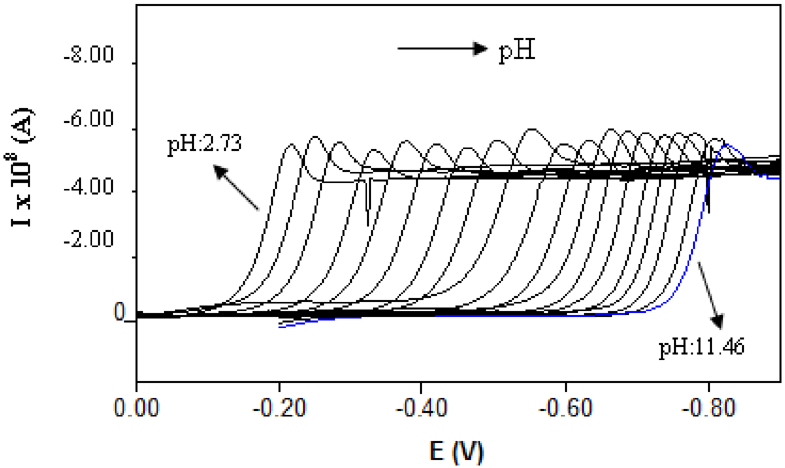


Figure 4. Polarograms of $1.96.10^{-5}$ M Sudan I in 50% B-R (0.02 M) buffer-50% ethanol solution at pH 2.0-12.0, scan rate 4 mV/s, drop time 1 s, with SMDE and Ag/AgCl reference electrode.

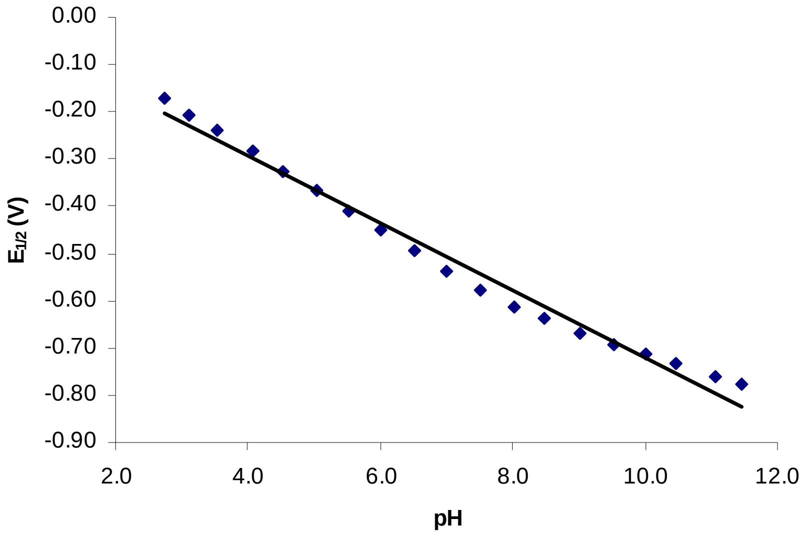


Figure 5. The dependence of $E_{1/2}$ values of Sudan I on pH in 50% B-R (0.02 M) buffer-50% ethanol medium, $v = 4$ mV/s.

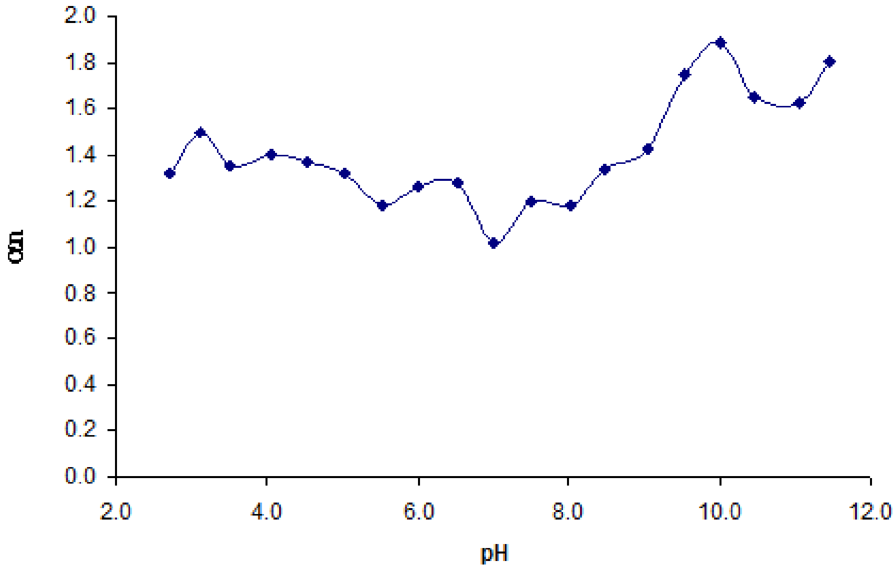


Figure 6. The change of αn with pH for the Sudan I in 50% B-R (0.02 M) buffer-50% ethanol medium.

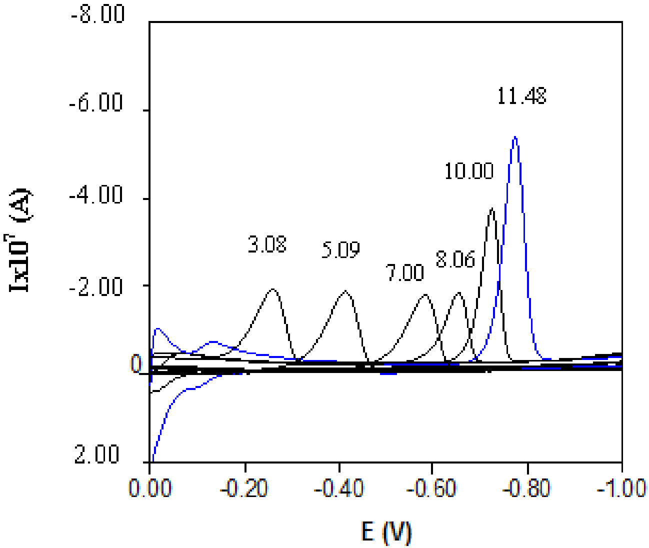


Figure 7. CV voltammograms of 7.41×10^{-6} M Sudan I in B-R (0.04 M) buffer, (pH 3.08, 5.09, 7.00, 8.06, 10.00, and 11.48, $v = 200$ mV/s).

3.4. CV Studies

CV voltammetric technique is required for explanation of electrochemical behaviour of the compound [24]. In general, pH is one of the variables that commonly and vigorously affects 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 Figure 7. The reduction of the azo group peak height is approximately constant in the pH range of 5.0-8.0 and increased in the pH range of 9.0-11.5. In the studied pH range (pH 2.0-12.0) cathodic process has been appeared to be an irreversible process as no anodic peak was observed in the reverse scan. The peak potentials (E_p) shifted to more negative values upon rise of each of the pH 2.0-12.0 which confirmed the involvement of protons in electrode reactions as SWV, DPP and DCP (Figure 2 and 5) [14-20]. Figure 8 shows a linear relationship between E_p and pH in the range of pH: 2.0-12.0 with a slope of -68.1 mV/pH as can be seen in E_p = -0.0605-0.0681pH equation. -68.1 mV/pH slope value indicates that the electrode reaction involves an equal number of electrons and protons for CV technique (Table 1) [19].

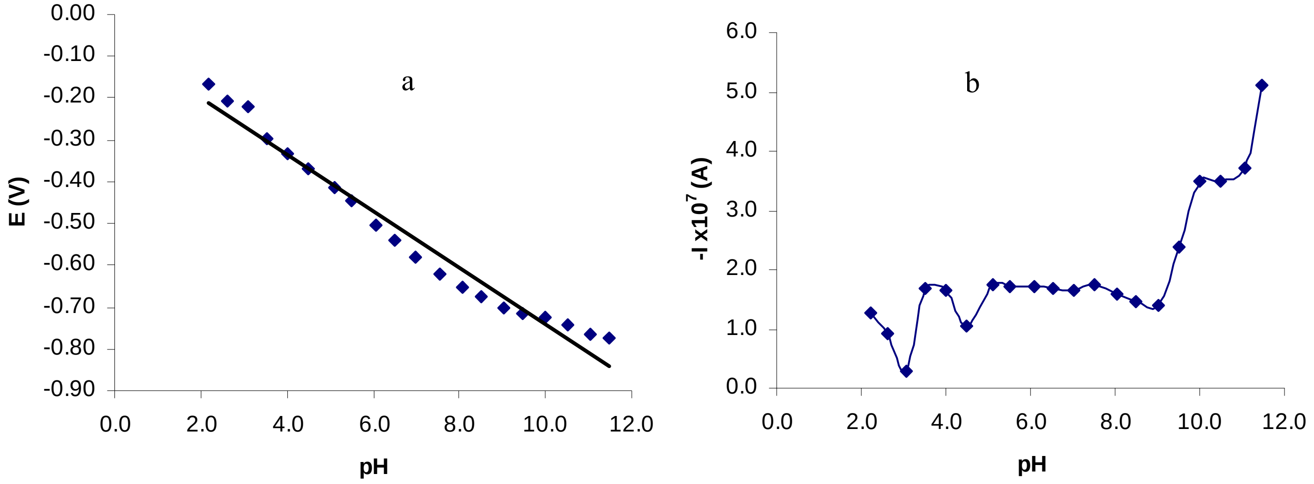


Figure 8. Dependence of a) cathodic peak potentials and b) cathodic peak currents as a function of pH in B-R (0.04 M) buffer obtained for 7.41×10^{-6} M solution of Sudan I for CV technique.

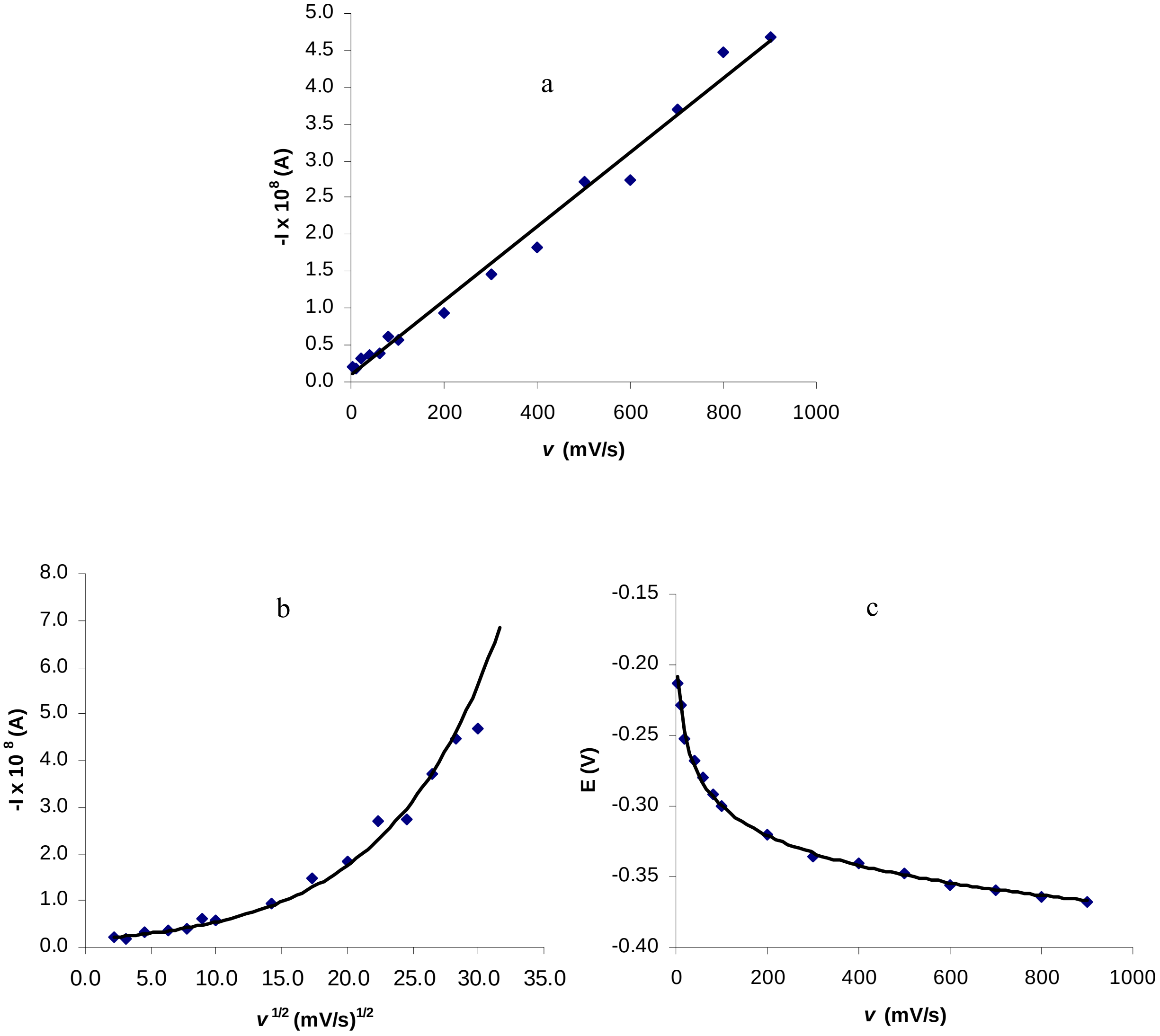
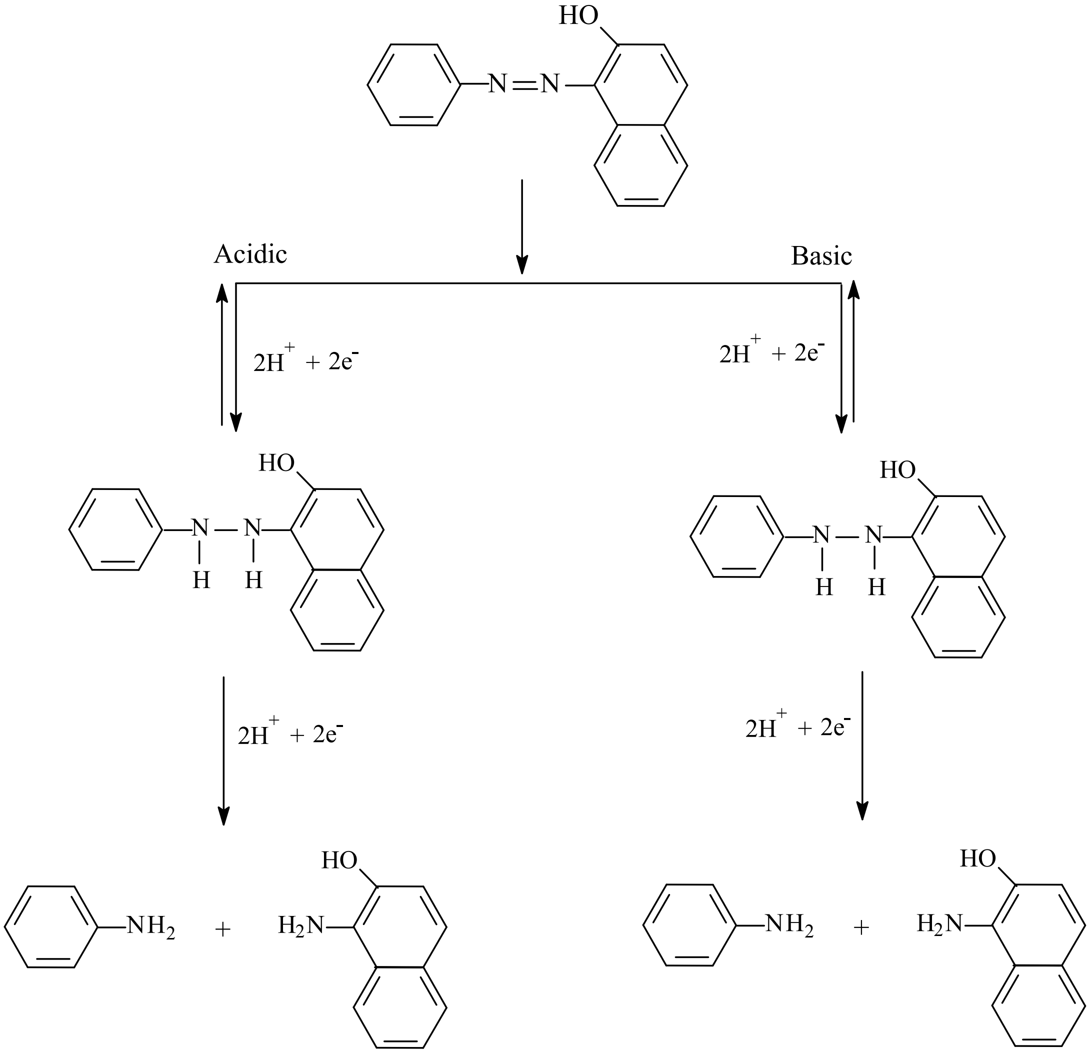


Figure 9. a) The change of cathodic peak currents of 9.90×10^{-6} M Sudan I with scan rate at pH 4.15 in B-R (0.04 M) buffer b) The change of cathodic peak currents with square root of scan rate at pH 4.15, c) The change of cathodic peak potentials with scan rate at pH 4.15, *v*=5-1000 mV/s.

For the azo group, the dependence of the peak height for the reduction (I_p) at a static mercury electrode (SMDE) on scan rate (v) was examined in B-R (0.04 M) buffer at different pH values (pH 4.15, 7.06, 9.06 and 11.01). The peak currents change linearly with scan rate (v) according to the equation $I_p = Av^x$. The x values 1.0 and 0.5 are expected for adsorption and diffusion controlled reaction, respectively. For Sudan I, the regression of log(I_p) versus log(v) gave a slope value of 0.672, 0.675, 0.841 and 0.611 for pH:4.15, pH:7.06, pH:9.06 and pH 11.06 respectively indicating that the reduction current had contributions from both diffusion and adsorption [1]. The I_p versus $v^{1/2}$ relation is not linear (Figure 9). With increasing scan rate $I_p/v^{1/2}$ slope increases. This result proves that the complex electrochemical reaction of the azo compound occurs on the electrode surface [27, 31-35]. As scan rate was increased from 5 to 1000 mV/s, the cathodic peak potential shifted toward more negative values as expected for an irreversible reduction process (Figure 9) [36-40].



Scheme 2. Reaction mechanism of the Sudan I.

Conclusions

The voltammetric and polarographic reduction of the 1-phenylazo-2-naphthol on a hanging mercury drop electrode (HMDE) and static mercury drop electrode (SMDE) has been studied by using several techniques including SWV, DPP, DCP and CV in aqueous and ethanolic Britton-Robinson buffer media. From the voltammetric data, the electrochemical reaction mechanism of the Sudan I has been suggested. Similar results were observed in previous studies [15-17, 26-28].

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