

Electrochemical Studies and Thermodynamic Parameters of Citrazinic Acid Azo Dye and its Nitro Derivatives in DMF-Aqueous Solutions

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Abstract

The electrochemical behavior of citrazinic acid azo dye derivatives (I-V) was recorded in aqueous buffer solutions containing 10% (v/v) DMF using DC-polarography and cyclic voltammetry. The DC-polarograms displayed one or two reduction waves depending on the nature of substituent and the pH of the electrolyte solution. The reduction process takes place irreversibly and diffusion controlled at the electrode surface through the uptake of four electron/molecules for compound I and eight electron/molecules for each of compounds II-V. The recorded cyclic voltammograms displayed two irreversible cathodic peaks at different pH values. The kinetic parameters of the electrode process such as, αn , heterogeneous rate constant (k_s) and activation energy (ΔG^\ddagger) were evaluated and discussed from cyclic voltammetry. Also, the electrode reaction mechanism is proposed and discussed. The effect of introducing substituents on the half-wave potential of the reduction process is illustrated. The different thermodynamic parameters such as activation energy (ΔG^\ddagger), enthalpy change (ΔH^\ddagger) and entropy change (ΔS^\ddagger) revealed the endergonic nature of the electrode reaction.

Keywords: citrazinic azo dyes, polarography, cyclic voltammetry, thermodynamic parameters.

Introduction

Azo dyes and Schiff bases have acquired wide interest in application to biological systems [1-3], indicators in complexometric titrations [4] and analytical chemistry [5]. The polarographic reduction of azo compounds was the subject of several studies [6-9], but no study has been extended to azo compounds containing citrazinic acid nucleus. Therefore, the present paper is devoted to study the electrochemical behavior of a series of new prepared citrazinic acid azo compounds (I-V) using DC-polarography and cyclic voltammetry techniques. Also, the mechanism of the electrode reaction is

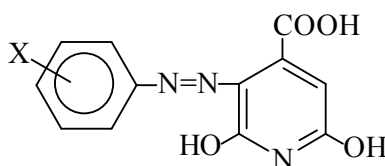
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proposed and discussed. The effect of substituent on the half-wave potential was also studied. The different thermodynamic parameters of the electrode reaction were determined and discussed.

Experimental

Solid compounds

Citrazinic acid azo dye derivatives were prepared by coupling of the diazotized amine derivatives with citrazinic acid in alkaline solutions [10,11]. The crude products were then re-crystallized from a mixture of acetone and water; the purity of the compounds was tested by constant melting point. The elemental and structural analysis such as C, H and N microanalysis as well as IR and $^1\text{H-NMR}$ spectra confirmed the following structural formula:



where X = 2,4-dimethyl- (I), 2,6-dichloro-4-nitro- (II), 2-cyano-4-nitro- (III), 2-chloro-4-nitro- (IV) and 3-(2,6-dibromo-4-nitrophenylazo) citrazinic acid (V).

Solutions

A series of Britton-Robinson buffer solutions of different pH values ranging from 2.0 - 12.0 was prepared and used as supporting electrolyte in electrochemical measurements. Stock solutions 5×10^{-3} M of each of the prepared citrazinic acid azo compounds I-V were dissolved in pure dimethylformamide (DMF). By appropriate dilution the final concentration in the electrolysis cell was adjusted at 1.5×10^{-4} M containing 10% DMF volume at the selected pH. The pH of the solution was corrected for the presence of 10% DMF. The electrolyte solution was then deaerated by passing a stream of nitrogen gas for 10 min to remove oxygen traces.

Apparatus

The DC-polarograms were obtained using Sargent Welch Polarograph Model 3001. The reference electrode used is the saturated calomel electrode, SCE. The capillary tube possessed the following characteristics in bi-distilled water at zero applied potential: $m = 1.41$ mg/s and $t = 4.0$ sec at $h = 60$ cm Hg. The potential is scanned at 0.5 V/min. Electrochemical analyzer model HQ 2030 was used for cyclic voltammetric (CV) measurements. A three compartment cell was used for CV measurements consisting of glassy carbon electrode (GC) as working electrode, Pt-wire as auxiliary electrode, and saturated calomel electrode as reference electrode. The area of the glassy carbon electrode used is 0.067 cm².

The controlled potential coulometry (CPC) was performed to determine the number of electrons (n) consumed in the reduction process using a large mercury

pool cathode. The coulometry system model is 380 PARC and consists of a digital coulometer model 179 and a cell system model 377A. The potential of the electrolysis was selected at a value that corresponds to the limiting current of the polarographic wave using a potentiostat.

A digital pH-meter Orion research model 601A digital ionalyzer was used to measure the pH of the solutions. All measurements were performed at 25 ± 1 °C using HAAke A81 water circulator bath unless otherwise is specified.

Results and discussions

1- The polarographic behavior

The DC-polarograms of 1.5×10^{-4} M of citrazinic acid azo compounds I-V were recorded in aqueous Britton-Robinson buffer solutions containing 10% (v/v) DMF of different pH values in the range from 2.0 to 12.0. The polarograms recorded of compound I at different pH values displayed only single reduction waves of almost equal heights corresponding to the electroreduction of $-N = N-$ center, while compound (III) displayed single reduction wave in solutions of $\text{pH} < 7.98$. At higher pH values the single wave is splitted into two polarographic waves, Fig. 1. The height of the second wave increases at the expense of the first one. The total limiting current (i_L) of the reduction process remains nearly constant over the entire pH range of investigation.

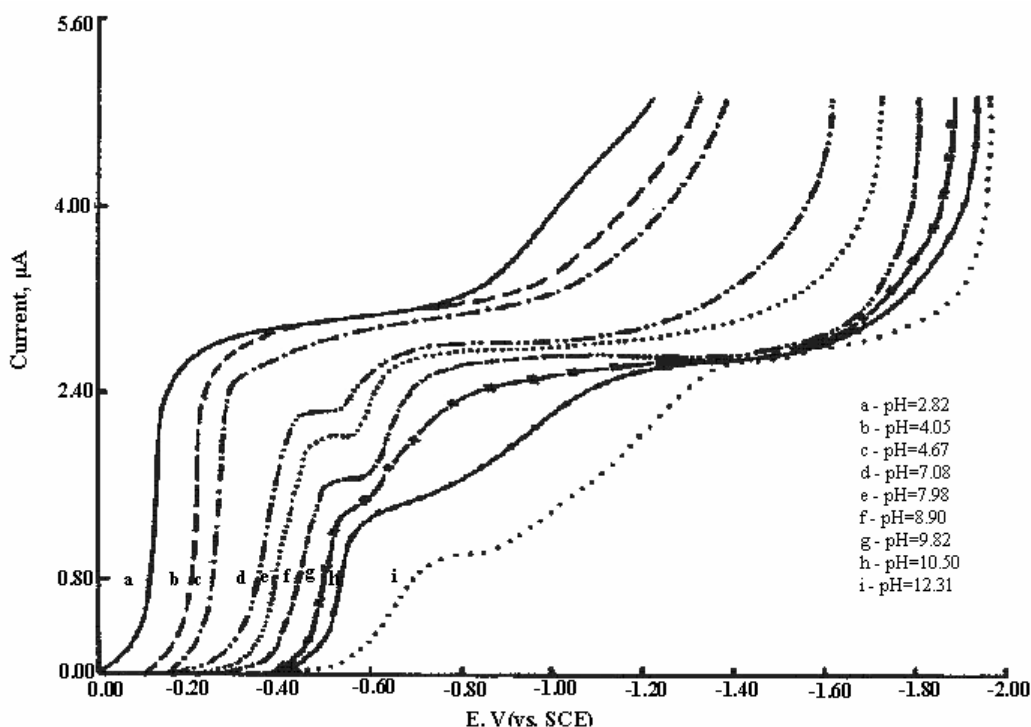


Figure 1. DC – polarograms of 1.5×10^{-4} M citrazinic acid azo dye (III) in universal buffer solutions containing 10 % (v/v) DMF of different pH values.

On the other hand, compounds II, IV and V displayed two polarographic waves of equal heights at all pH values corresponding to the reduction of the two electroactive centers, nitro ($-\text{NO}_2$) and azo ($-\text{N}=\text{N}-$) groups, respectively, where

the nitro-group is known to be more easily reduced than -N = N- center [12]. Although compound (III) contained both electroactive centers, it displayed a single reduction wave in acidic solutions while in alkaline ones this wave is splitted into two waves suggesting the presence of an acid-base equilibrium [13]. This behavior indicates that the non-protonated species formed in alkaline solutions is hardly reducible and a separation in half-wave potentials ($E_{1/2}$) due to the reductions of both $-\text{NO}_2$ and $-\text{N} = \text{N}-$ active centers occurs. While in acidic solutions the protonated form of the azo center is easier reducible than the non-protonated one with no sufficient change in $E_{1/2}$, appearing to be very close to that of $-\text{NO}_2$ group, displaying single reduction wave.

The plots of i_L versus pH of the electrolysis solution for compounds (I, II, IV and V) showed constancy of the limiting current with no practical changes, while for compound III, a dissociation curve is obtained, Fig. 2. This behavior denotes that an acid-base equilibrium is present and the total limiting current i_L is pH-independent, while the slight decrease is attributed to the increased viscosity of the medium.

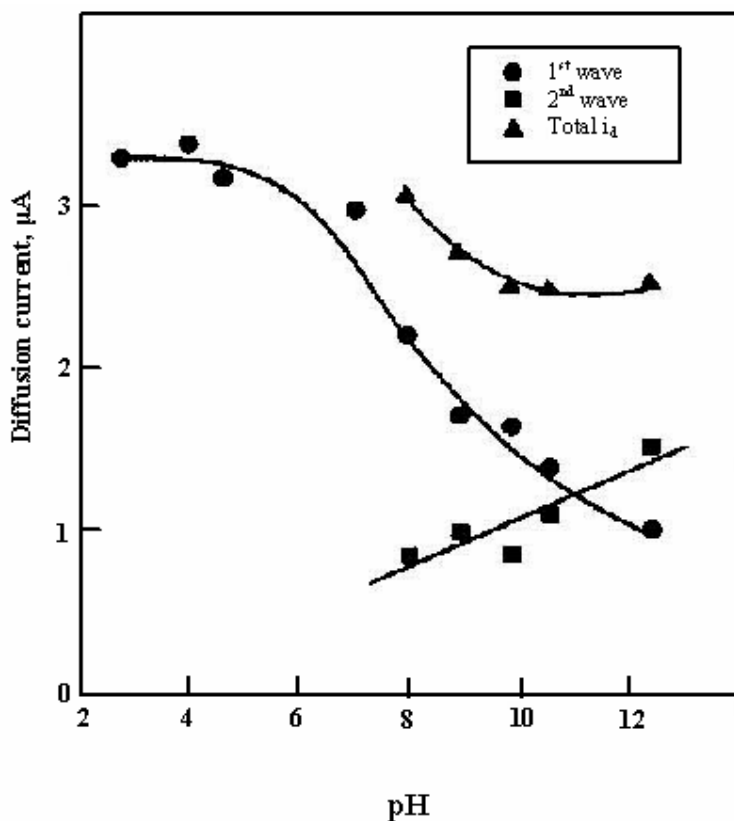


Figure 2. Plots of i_d versus pH for the reductions of citrazinic acid azo dye (III).

Nature of the polarograms

i- Nature of the current produced in the electrochemical cell

The effect of mercury height, h , on the limiting current, i_L , of the polarographic waves of all compounds (I-V) was recorded at pH values 2.82, 7.08 and 9.82. The values of the exponent x in the relation $i_L = Kh^x$ [14] were found in the range

0.47-0.55 in different media, Table 1. Inspection of these values denotes that the reduction process is mainly a diffusion-controlled process.

Table 1. DC-polarographic data obtained for citrazinic acid azo compounds (I-V) in 10% DMF-aqueous solutions at 25 °C.

| Compound | pH | $-E_{1/2}/V$ | x | S_1/mV | S_2/mV | p | α | |
|----------|------|--------------|------|-------------------|----------|-------------------|-------------|-------------|
| | | | | | | | $n_a = 1.0$ | $n_a = 2.0$ |
| I | 2.82 | 0.130 | 0.48 | 44.0 | 59 | 1.34 | 1.34 | 0.67 |
| | 7.08 | 0.420 | 0.50 | 45.0 | 59 | 1.31 | 1.31 | 0.66 |
| | 9.82 | 0.561 | 0.52 | 43.0 | 59 | 1.37 | 1.37 | 0.69 |
| II | 2.82 | 0.058 | 0.50 | 50.0 ^a | 53 | 1.06 ^a | 1.18 | 0.59 |
| | | 0.235 | 0.49 | 52.9 ^b | 61 | 1.15 ^b | 1.33 | 0.67 |
| | 7.08 | 0.283 | 0.50 | 39.1 ^a | 53 | 1.36 ^a | 1.51 | 0.76 |
| | | 0.500 | 0.52 | 44.3 ^b | 61 | 1.38 ^b | 1.33 | 0.67 |
| | 9.82 | 0.400 | 0.52 | 41.0 ^a | 56 | 1.36 ^a | 1.44 | 0.72 |
| | | 0.610 | 0.50 | 53.7 ^b | 61 | 1.13 ^b | 1.10 | 0.55 |
| III | 2.82 | 0.130 | 0.47 | 45.0 | 61 | 1.35 | 1.31 | 0.65 |
| | 7.08 | 0.384 | 0.49 | 66.5 | 61 | 0.92 | 0.89 | 0.45 |
| | 9.82 | 0.450 | 0.53 | 38.3 ^a | 37 | 0.99 ^a | 1.54 | 0.77 |
| | | 0.630 | 0.50 | 51.9 ^b | 36 | 0.70 ^b | 1.14 | 0.57 |
| IV | 2.82 | 0.123 | 0.49 | 52.0 ^a | 72 | 1.38 ^a | 1.13 | 0.57 |
| | | 0.310 | 0.50 | 70.8 ^b | 67 | 0.95 ^b | 0.83 | 0.42 |
| | 7.08 | 0.425 | 0.52 | 78.2 ^a | 72 | 0.92 ^a | 0.75 | 0.38 |
| | | 0.586 | 0.49 | 48.0 ^b | 67 | 1.39 ^b | 1.23 | 0.61 |
| | 9.82 | 0.490 | 0.55 | 47.7 ^a | 42 | 0.88 ^a | 1.23 | 0.62 |
| | | 0.675 | 0.51 | 57.4 ^b | 46 | 0.80 ^b | 1.03 | 0.52 |
| V | 2.82 | 0.080 | 0.50 | 41.0 ^a | 58 | 1.41 ^a | 1.44 | 0.72 |
| | | 0.237 | 0.52 | 42.4 ^b | 59 | 1.39 ^b | 1.39 | 0.70 |
| | 7.08 | 0.320 | 0.52 | 42.0 ^a | 58 | 1.38 ^a | 1.40 | 0.70 |
| | | 0.480 | 0.49 | 43.0 ^b | 59 | 1.37 ^b | 1.37 | 0.69 |
| | 9.82 | 0.420 | 0.53 | 38.3 ^a | 37 | 0.99 ^a | 1.54 | 0.77 |
| | | 0.600 | 0.51 | 51.9 ^b | 36 | 0.70 ^b | 1.14 | 0.57 |

$S_1 = 0.0591/\alpha n_a$, $S_2 = \Delta E_{1/2}/\Delta pH$, $x = \Delta \log i_1/\Delta \log h$. ^a and ^b are referring to the first and second waves, respectively.

ii- Reversibility test of the electrode process

Logarithmic analysis of the polarographic waves is of quite importance for testing the thermodynamic reversibility of the electroreduction process. By applying the fundamental equation of Meites [15], the plots of $\log [i/(i_d - i)]$ versus $E_{d,e}$ showed linear correlations for all compounds (I-V) at the different pH values. From the slopes (S_1) of these plots the values of the transfer coefficient (α) were obtained. Values of the transfer coefficients (α) are found to be less than 0.77 at $n_a = 2.0$ in different media, Table 1, where n_a is the number of electrons involved in the rate-determining step. Therefore, it is concluded that the

reduction process takes place irreversibly and the rate-determining step should involve two electrons.

The irreversibility of the electrode process is further confirmed from the cathodic shift of the half-wave potentials ($E_{1/2}$) of all azo compounds (I-V) on increasing the pH of the electrolyte solution. This behavior could be attributed to the participation of hydrogen ions in the electrode process and the proton uptake precedes the electron transfer step [13]. The number of protons p participating in the rate-determining step was calculated from the rate change of $E_{1/2}$ versus pH using the following equation [15]:

$$d(E_{1/2})/d(\text{pH}) = [(0.05915)p]/\alpha n_a \quad (1)$$

The plots of $E_{1/2}$ versus pH for compound I showed a straight line of slope amounting to 59 mV, whereas the plots for compounds II-V showed breaks at pH values corresponding to their $\text{p}k_a$. The values of $\text{p}k_a$ were estimated and found to be in good agreement with those reported from our previous potentiometric investigations [2].

From the slope values of both $E_{1/2}$ -pH plot (S_2) and those of logarithmic analysis (S_1), the number of protons (p) involved in the rate-determining step was found to be unity for all compounds at different pH values, Table 1.

2- Cyclic voltammetry

The cyclic voltammograms of 1.0×10^{-4} M of citrazinic acid azo dye derivatives (I-V) were recorded in aqueous Britton-Robinson buffer solutions containing 10% DMF at pH values 2.82, 7.08 and 9.82. The voltammograms recorded at different scan rates (20-500 mV/s) consisted of two cathodic peaks in different media corresponding to the first and second waves observed in DC-polarography, as represented in Fig. 3 as a typical example. The absence of any anodic peaks on the reverse scan indicates the irreversibility of the reduction process. The irreversibility of the electrode process is further confirmed from the negative shift of the cathodic peak potentials (E_p) on increasing the scan rate (ν) for all compounds under consideration. For an irreversible electron transfer process the peak potential (E_p) is related to the scan rate (ν) by the following equation [16]:

$$E_p = - 1.14 (RT/\alpha n_a F) + (RT/\alpha n_a F) \ln (k_s/D^{1/2}) - (RT/2\alpha n_a F) \ln (\alpha n_a \nu) \quad (2)$$

where α is the transfer coefficient, ν is the scan rate (V/sec), D is the diffusion coefficient (cm^2/sec), k_s is the standard rate constant of the electron transfer process (cm/sec), and other parameters have their usual meanings. By plotting E_p versus $\ln \nu$ straight lines were obtained. The values of αn_a parameters were evaluated from the slopes of such plots. The transfer coefficient (α) values were determined and found to be less than unity at $n_a = 2.0$, indicating the irreversibility of electrode process, Table 2.

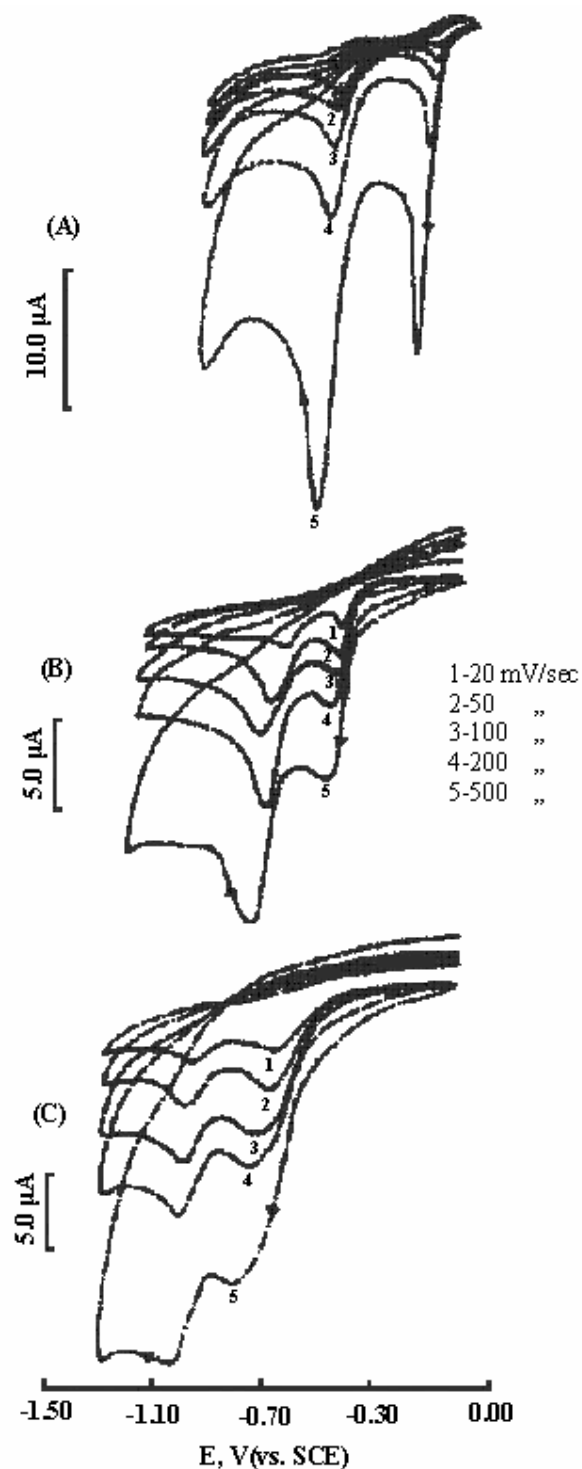


Figure 3. Cyclic voltammograms recorded at different scan rates of 1×10^{-4} M citrazinic acid azo dye (V) in universal buffer solutions containing 10% (v/v) DMF at: a- pH= 2.82, b- pH =7.08 and c- pH=9.82.

On the other hand, the plots of peak current (i_p) versus square root of scan rate, $v^{1/2}$, showed linear correlations. The straight lines obtained were found to pass

through the origin indicating the diffusion-controlled current [17], as illustrated from DC-polarographic data.

Table 2. Cyclic voltammetric data and kinetic parameters of citrazinic acid azo compounds (I-V) in 10% DMF-aqueous solutions at 25 °C.

| Compound | pH | $-E_p^*/V$ | αn_a | $k_s / (cm/s)$ | $\Delta G^\ddagger / (kJ/mol)$ |
|----------|------|--------------------|--------------|------------------------|--------------------------------|
| I | 2.82 | 0.182 _a | 1.27 | 3.30×10^{-3} | 183.1 |
| | | 0.551 _b | 0.49 | 2.08×10^{-6} | 260.4 |
| | 7.08 | 0.384 _a | 0.42 | 1.31×10^{-4} | 216.9 |
| | | 0.763 _b | 0.43 | 2.47×10^{-7} | 282.7 |
| | 9.82 | 0.756 _a | 0.51 | 5.29×10^{-8} | 298.9 |
| | | 1.038 _b | 1.22 | 1.59×10^{-20} | 601.3 |
| II | 2.82 | 0.318 _a | 0.86 | 4.75×10^{-5} | 227.6 |
| | | 0.727 _b | 0.58 | 1.87×10^{-8} | 309.8 |
| | 7.08 | 0.472 _a | 0.61 | 4.79×10^{-6} | 251.6 |
| | | 0.750 _b | 0.62 | 5.00×10^{-9} | 323.6 |
| | 9.82 | 0.731 _a | 0.65 | 5.57×10^{-9} | 322.5 |
| | | 0.985 _b | 0.73 | 8.81×10^{-13} | 414.3 |
| III | 2.82 | 0.182 _a | 0.77 | 4.30×10^{-3} | 180.3 |
| | | 0.723 _b | 0.55 | 4.04×10^{-8} | 301.7 |
| | 7.08 | sh _a | - | sh _a | - |
| | | 0.781 _b | 0.68 | 6.11×10^{-10} | 345.7 |
| | 9.82 | 0.658 _a | 0.56 | 1.30×10^{-7} | 289.5 |
| | | sh _b | - | sh _b | - |
| IV | 2.82 | 0.184 _a | 0.82 | 4.42×10^{-3} | 180.0 |
| | | 0.532 _b | 0.85 | 4.43×10^{-8} | 300.7 |
| | 7.08 | 0.441 _a | 0.66 | 5.95×10^{-6} | 249.3 |
| | | 0.735 _b | 0.75 | 4.51×10^{-10} | 348.9 |
| | 9.82 | 0.710 _a | 0.56 | 4.32×10^{-8} | 301.0 |
| | | 0.986 _b | 0.67 | 4.13×10^{-12} | 398.1 |
| V | 2.82 | 0.184 _a | 1.10 | 4.39×10^{-3} | 180.1 |
| | | 0.527 _b | 0.76 | 1.53×10^{-7} | 287.7 |
| | 7.08 | 0.464 _a | 0.55 | 1.09×10^{-5} | 243.0 |
| | | 0.725 _b | 0.76 | 4.79×10^{-10} | 348.2 |
| | 9.82 | 0.722 _a | 0.41 | 7.12×10^{-7} | 271.6 |
| | | 1.018 _b | 0.91 | 6.01×10^{-16} | 490.8 |

* at 100 mV/sec. ^a - first peak; ^b - second peak; sh = shoulder.

Kinetic parameters of the electrode reaction

The heterogeneous rate constant (k_s) of citrazinic acid azo compounds (I-V) were computed from cyclic voltammetry measurements [16] at different pH values using equation 2. From both the slope values and intercepts of the $E_p - \ln v$ plots at different pH values using equation 2, the values of αn_a and subsequently k_s were calculated. The necessary values of the diffusion coefficients were calculated

using Ilkovic equation. The energy of activation (ΔG^\ddagger) of the electrode process was determined using k_s values according to the following equation [18]:

$$\Delta G^\ddagger = 5778.8 (5.096 - \log k_s) \quad (3)$$

It is concluded that k_s is decreased on increasing the pH of the electrolysis medium, whereas the activation energy (ΔG^\ddagger) is increased, Table 2. This behavior can be explained by the fact that the protonated or neutral molecules existing in media of lower pH values can readily diffuse to the electrode surface, which in turn decreases the activation energy ΔG^\ddagger . At higher pH values the non-protonated forms of the reducible species required higher activation energy. The increased values of ΔG^\ddagger indicate that the electrode reaction becomes more irreversible.

Mechanism of the electrode reaction

The results obtained from both DC-polarography and cyclic voltammetry techniques showed that citrazinic acid azo compounds (I-V) were reduced in an irreversible and diffusion-controlled manner. The number of electrons consumed in the reduction process is calculated with the aid of Ilkovic equation. The corrected values of the diffusion coefficients of the azo compounds under investigation were determined using Stock's equation [19]. By applying in Ilkovic equation, it was found that four electrons per molecule were consumed in the reduction of N = N center of compound I to the amine stage. While for compounds II-V, the number of electrons were found to be eight per molecule, corresponding to the cleavage reduction of N = N center by four electrons, in addition to the reduction of -NO₂ group to the hydroxylamine stage (-NH-OH) through four electrons [17] in both acidic and alkaline solutions. These results were confirmed using controlled potential coulometry; the accumulated charge (Q) during electrolysis was taken directly from the digital coulometer at a potential corresponding to the limiting current value. By applying the Faraday's law related to the measured charge Q (Coulombs) transferred to the amount of material electrolyzed:

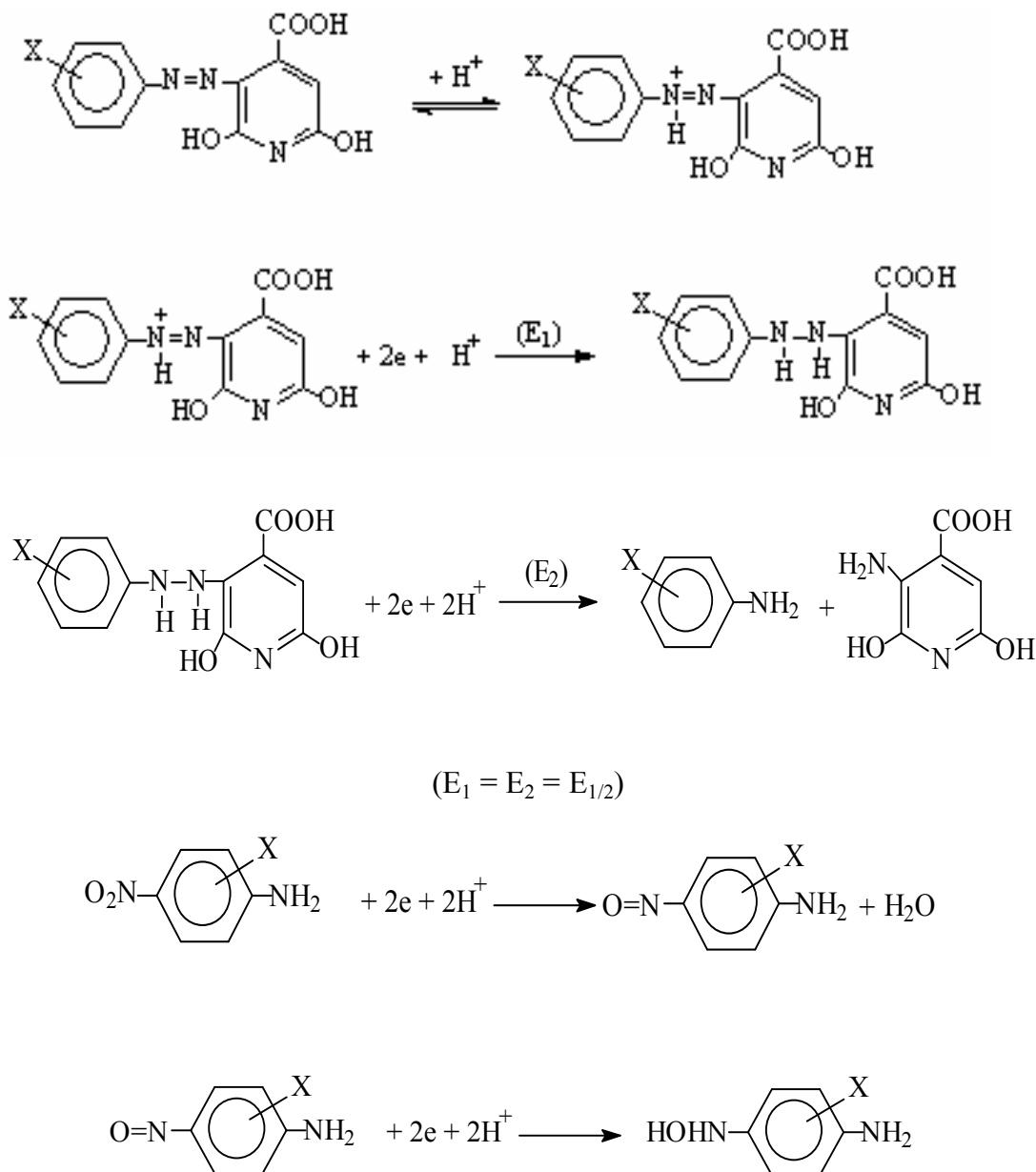
$$Q = nFW/M \quad (4)$$

where W is the sample weight in grams and M is its molecular weight. The average number of electrons was found to be four for compound I and eight for compounds (II-V) in acidic and alkaline solutions of pH values 3.0 and 10.0.

Thin layer chromatography (TLC) was applied on the completely electrolyzed solutions of compounds I and IV to characterize the final products of the reduction process. The electrolyte solution was concentrated and the buffer ingredients were then removed by extraction with ether. By comparing the TLC of the ethereal extract of compound I with authentic 2,4-dimethylaniline it was found to be one of the electrolysis products. This indicates that the four electrons were consumed in the reductive cleavage of -N = N- center. In the case of compound IV, the remaining four electrons were used in the reduction of -NO₂

group containing compound to the hydroxyl amine stage (-NHOH), which is supported later from the effect of Hammett substituent constant (σ_x). The reduction of $-\text{NO}_2$ group takes place by accepting H^+ and two electrons followed by H^+ to form the dihydroxyl amine derivative, $-\text{N}(\text{OH})_2$. This intermediate is very unstable and very fast loose water molecule to form nitroso derivative ($-\text{N}=\text{O}$).

Depending on the forgoing facts and structural genesis of the investigated compounds, the reduction mechanism may be summarized as follows:



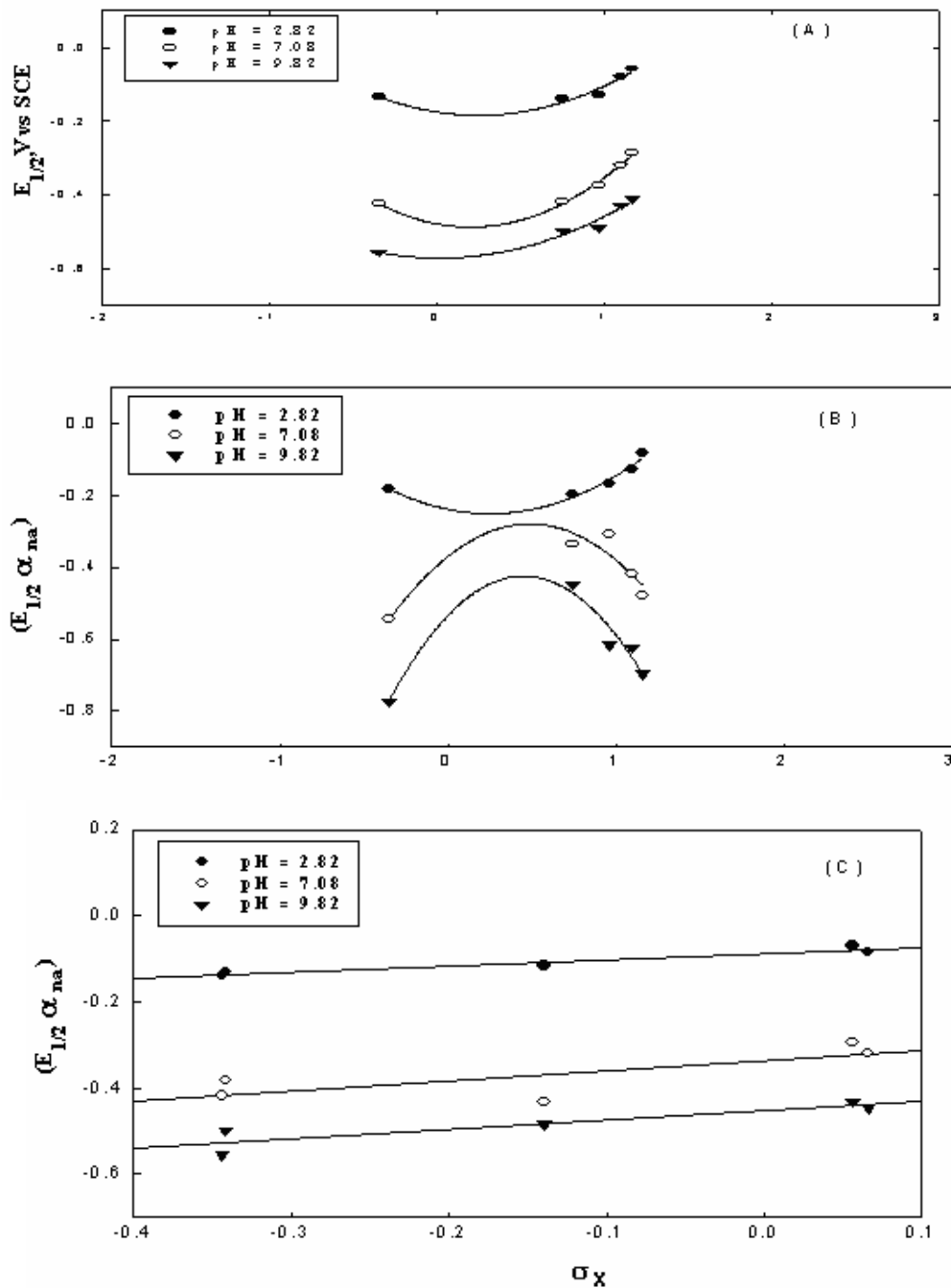


Figure 4. The effect of Hammett substituent on the half-wave potentials at different pH values. A – $E_{1/2}$ vs. σ_x , B – $(E_{1/2} \cdot \alpha_{na})_x$ vs. σ_x , and C – $(E_{1/2} \cdot \alpha_{na})_x$ vs. σ_x , using polar substituent constant of σ_{NHOH} .

The linearity of $(E_{1/2} \cdot \alpha_{na})_x$ vs. σ_x using the value of σ_{NHOH} instead of σ_{NO_2} suggested that $-\text{NO}_2$ group is reduced first and contributes to the electrode reaction of citrazinic acid azo dyes as $-\text{NHOH}$ rather than $-\text{NO}_2$ group [18]. This behavior supported the suggested electrode reaction mechanism. The general

trend of these compounds revealed that compounds containing electron donating groups were reduced at more negative potentials, whereas compounds containing electron withdrawing groups were reduced at lower potentials. Subsequently, the electrode reaction is hindered in compounds containing electron donating groups and it is facilitated by electron withdrawing groups.

Thermodynamic parameters of electrode process

The thermodynamic parameters $\Delta G^\#$, $\Delta H^\#$ and $\Delta S^\#$ of the electrode reaction were determined by studying the effect of temperature on the cyclic voltammograms of citrazinic azo compounds (I-V) at pH 9.82. The cyclic voltammograms recorded at 298.15, 308.15 and 318.15 K are essentially similar displaying two irreversible cathodic peaks. The cathodic peak potential (E_p) remains nearly constant on increasing the temperature, while the observed changes of peak currents are attributed to the viscosity changes of the electrolysis medium. The diffusion coefficients were estimated from the slopes of the plot of $I_p \nu^{-1/2}$ utilizing values of αn_a obtained from the $E_p - \ln \nu$ plot. The diffusion coefficients of citrazinic acid azo compounds (I-V) were found to increase on increasing the temperature and the temperature coefficient ranges from 1.30 to 1.82 % using the Stokes-Einstein equation [19], Table 3.

The heterogeneous rate constant k_s of the electron transfer process was determined at different temperatures from the slopes and intercepts of the $E_p - \ln \nu$ plots using equation (3). The values of k_s were found to increase on increasing the temperature.

On using Arrhenius type equation, the plots of $\log k_s$ versus $1/T$ is linear with a correlation coefficient exceeding 99.5%. The slopes of the Arrhenius plots were used to estimate the apparent activation energy (E_a). The enthalpy change of activation ($\Delta H^\#$) was determined according to the following relationship:

$$\Delta H^\# = E_a - RT \quad (5)$$

The corresponding activation energy ($\Delta G^\#$) of the electrode process was determined according to equation (3). The corresponding entropy change ($\Delta S^\#$) was calculated using the well-known relationship:

$$\Delta G^\# = \Delta H^\# - T\Delta S^\# \quad (6)$$

The calculated thermodynamic parameters are listed in Table 3. Inspection of the values revealed the following conclusions:

- 1- Positive enthalpy change ($\Delta H^\#$) accompanied the reduction process revealed the endergonic nature of the electrode process.
- 2- Negative entropy change ($\Delta S^\#$) observed indicates that an ordered electrode reaction becomes less ordered on increasing the temperature.
- 3- The decreased values of the activation energies ($\Delta G^\#$) indicate that the reduction process becomes easier and the degree of irreversibility is decreased at higher temperatures.

Table 3. Thermodynamic parameters for citrazinic acid azo compounds (I-V) obtained from cyclic voltammetry at different temperatures.

| Comp. | T / K | $\Delta G^\#$ /(kJ/mol) | $\Delta H^\#$ /(kJ/mol) | $-\Delta S^\#$ /(J/mol) | Temp. Coeff. |
|-------|--------|-------------------------|-------------------------|-------------------------|--------------|
| I | 298.15 | 298.8 _a | 13.2 | 229.2 | - |
| | | 601.3 _b | 53.5 | 439.6 | |
| | 308.15 | 295.4 _a | 13.1 | 219.2 | 1.38 |
| | | 585.4 _b | 53.4 | 413.3 | |
| | 318.15 | 290.5 _a | 13.0 | 208.7 | 1.75 |
| | | 571.7 _b | 53.3 | 389.8 | |
| II | 298.15 | 322.5 _a | 48.5 | 919.2 | - |
| | | 414.3 _b | 73.6 | 142.8 | |
| | 308.15 | 316.4 _a | 48.4 | 869.9 | 1.30 |
| | | 405.2 _b | 73.5 | 1076.3 | |
| | 318.15 | 310.8 _a | 48.3 | 825.1 | 1.65 |
| | | 396.8 _b | 73.4 | 1016.6 | |
| III | 298.15 | 289.4 _a | 39.5 | 838.1 | - |
| | | - | - | - | |
| | 308.15 | 284.3 _a | 39.4 | 794.6 | 1.34 |
| | | - | - | - | |
| | 318.15 | 279.8 _a | 39.3 | 755.7 | 1.67 |
| | | - | - | - | |
| IV | 298.15 | 301.0 _a | 17.5 | 950.9 | - |
| | | 398.1 _b | 29.0 | 1237.7 | |
| | 308.15 | 295.3 _a | 17.4 | 902.0 | 1.37 |
| | | 389.3 _b | 28.9 | 1169.6 | |
| | 318.15 | 290.5 _a | 17.3 | 858.6 | 1.71 |
| | | 381.5 _b | 28.8 | 1108.1 | |
| V | 298.15 | 271.6 _a | 14.3 | 863.2 | - |
| | | 490.8 _b | 40.6 | 1509.8 | |
| | 308.15 | 266.9 _a | 14.2 | 820.1 | 1.38 |
| | | 478.9 _b | 40.6 | 1422.5 | |
| | 318.15 | 262.7 _a | 14.1 | 781.2 | 1.82 |
| | | 467.9 _b | 40.5 | 1343.9 | |

^a - first peak; ^b - second peak

Conclusion

Citrazinic acid azo dyes (I-V) were reduced irreversibly in one or two reduction steps depending on the nature of the substituent and the pH of the electrolysis solution. Cyclic voltammetry confirmed this phenomenon and showed two irreversible cathodic peaks. The number of electrons consumed in the electrode process was evaluated and found to be 4-electron/molecules for compound I whereas 8-electron/molecules were consumed for the electroreduction of compounds II-V. The electrode kinetics such as αn_a , k_s and $\Delta G^\#$ were determined. The effect of pH, substituent and temperature on the values of

kinetic parameters and electrode reaction was also discussed. The different thermodynamic parameters of the electrode reaction revealed the endergonic nature of the electrode reaction.

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