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Research Article

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Electrochemical studies of some new adipic acid dihydrazide combining benzaldehyde derivatives

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ABSTRACT

The electrochemical behavior of arylidene adipic acid dihydrazide derivatives (I-VII) was investigated in Britton-Robinson buffer solutions containing 50% (v/v) ethanol using three different electrochemical techniques namely: DC-polarography, cyclic voltammetry and chronocoulometry. DC-polarograms displayed only one irreversible diffusion-controlled reduction waves overall the pH range studied from 2.0 to 11.0 except VII, which showed two irreversible reduction waves. The diffusion current of the reduction waves in acidic solutions is almost twice that in alkaline ones. Cyclic voltammograms showed one or two irreversible reduction peaks depending on the pH of the electrolysis solution and the nature of substituent. Chronocoulometry indicated that the compounds under study are not adsorbed on the electrode surface. The kinetic parameters of the electrode reaction and the effect of substituent on the half-wave potential were determined and discussed. Also, the electrode reaction mechanism was proposed and discussed.

Key words: Arylidene adipic dihydrazide, derivatives, polarography, cyclic voltammetry, kinetic parameters.

INTRODUCTION

Adipic acid dihydrazide is an important molecule by possessing the two symmetrical amido groups containing carbonyl and terminal amino groups, it is used as homo bifunctional linker in biconjugate chemistry to prepare active forms originally mannans from the pathogenic yeasts, Candida tropicalis, Candida glabrata and Candida albicans (durana and Bystricky, 2002). Earlier in 1994, the final progress report approved the safety assessments of adipic acid dihydrazide in cosmetic formulations, fragrance and ingredients (SAGE, 1994). Adipic acid dihydrazide is used in the binding and coupling of the basement membrane glycoprotein laminin to glycosaminoglycans by the formation of Schiff base with the N-terminal group. Molecules are conceivably exposed to the hydrophilic environment in an available similar to that existing physiologically (Fransson *et al*, 1980 and Rosso *et al*, 1981).

Synthesis of immunogenicity of meningococcal B polysaccharide conjugated to tetanus toxoid via ADH spacer (Bartoloni *et al*, 1995), and the binding of monoclonal antibodies α (2→8) polysialicacid conjugated to outer membrane vesicle was formulated using ADH (Sarvarnangala *et al*, 1996).

ADH used as a linker to prepare hydrogel nanoparticle networks for controlled drug release (Haung *et al*, 2004). Hydrazide modified carboxymethyl dextran with aldehyde modified dextran or carboxymethylcellulose hydrogels were proven for pharmaceutical and biomedical applications (Van Tomme *et al*, 2008, Ito *et al* 2007 , Dizerega and Campeau 2001).

The developing of an injectable hydrogel composed of oxidized hyaluronic acid and adipic acid dihydrazide and incorporated it with nucleus pulposus cells to reverse nucleus degeneration (Su *et al*, 2010). Novel crosslinking hydrogels incorporated ADH were prepared and used for the controlled release of bioactive molecules specially pharmaceutical proteins and the encapsulation of living cells (Hennink and Van Nustrum 2012, Barash *et al*, 2012 and Chen *et al*, 2010). ADH hydrogels, microgels and nanogels emerging platform for drug release of HIV/AIDS (Agrahari *et al*, 2013), incorporate cisplatin for peritoneal dissemination of gastric cancer (Emoto *et al*, 2013) and for developing tissue engineering (Jiang *et al*, 2014, Mateen and Hoare, 2014).

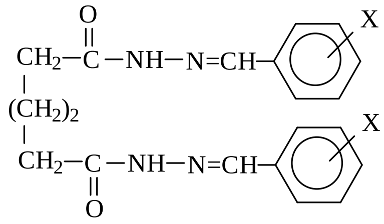
Aryl hydrazides and hydrazone compounds have a special interest due to their biological and medicinal importance (Harmon *et al*, 1968 and Swamy *et al*, 1990). Some of these compounds exhibited antifungal activity (Swamy *et al*, 1990 and Garg and Sharma, 1969). The study of their electrochemical behavior is a subject of great importance, which has attracted much attention (Goyal and Jain, 1983, 1977, Laud, 1959, Temerik and Abu Zuhri, 1980). Numerous hydrazide and hydrazone compounds of mono-carboxylic acids have been studied (Ghoneim *et al*, 1978, 1989, 1992, Issa *et al*, 1986, Scott and Jura, 1967, Ready and Roa, 1991, Jain and Gupta, 1995, Elaskalany *et al*, 1995 and Jain *et al*, 1997). The majority of workers agreed that this class of compounds were reducible polarographically in the protonated form from acidic solutions via 4-electron step to yield aromatic amines. But, there is no sufficient information of the detailed mechanistic pathway of the electrochemical behavior of the dihydrazides derived from dicarboxylic acids.

Due to the highly importance of adipic acid diydrazides as cross linking agent in several hydrogels, membranes, drug delivery systems and in the tissue engineering manufacturer it is of considerable interest to study the role of electron transfer process of some new synthesized adipic acid dihydrazide combined benzaldehyde derivatives I-VII. The mechanism and kinetics of the exchange of electrons and protons are not yet fully understood. The sequence of addition of electrons and protons, the kinetic of various steps and the nature of final product depend on various parameters. To give insight on the electrode reaction mechanism as well as the effect of introduced substituents into the phenyl ring on the reduction process.

EXPERIMENTAL SECTION

2.1 Methods of preparations

Arylidene adipic acid dihydrazide derivatives were prepared by condensation of the adipic dihydrazide with some aromatic aldehydes in absolute ethanol according to the method of Struve (Mohammed *et al*, 2009). The purity of the prepared compounds was checked by constancy of melting point. Structural elucidation of the prepared compounds using C,H and N, I.R and ^{1}Hnmr analysis confirmed the following structural formula:



where X = H (I), p-Cl (II), p-Br (III), p-OH (IV), p-OCH$_3$ (V), p-CH$_3$ (VI) and p-NO$_2$ (VII).

2.2 Solutions

Stock solutions of $5x10^{-3}$ M of compounds (I-VII) were prepared by dissolving the accurate weight of the solid material in absolute ethanol (analytical grade, BDH). Britton-Robinson buffer solutions of different pH values in the range from 2.0 to 11.0 containing an appropriate volume of absolute ethanol (to ensure complete solubility of compounds under investigations) were used as the supporting electrolyte. The calculated volume of stock solution of arylidene adipic acid dihydrazide was then introduced into the electrolysis cell. The solution was freed from oxygen by bubbling a stream of pure nitrogen gas for 10 min. All experiments were carried out at 25 ± 1°C.

2.3 Instruments

The DC-polarograms were recorded with a Sargent Weilch Polarograph model 3001. The capillary characteristics in 0.1 M KCl at open circuit are: t = 4.5 sec/drop, m = 1.1 mg/sec at mercury height (h) = 60 cm. A Polarographic Analyzer model 264A, (EG&G) Instrument was used in recording cyclic voltammograms. The electrode assembly model 303A with a hanging mercury drop electrode (HMDE) of 0.026 cm^2 area was used as a working electrode. The cyclic voltammetric measurements were carried out in a three-compartment glass cell containing the working electrode, a platinum counter electrode and Ag/AgCl as a reference electrode. A coulometry system (model 380

PARC) which consists of a digital Coulometer model 179 and a cell system model 377A was used for controlled potential coulometry measurements. The chronocoulometric measurements are performed using Potentiostat model HQ-2030. A digital pH-meter model 201 accurate to ± 0.05 pH unit was used for measuring the pH of the electrolysis solutions.

RESULTS AND DISCUSSION

3.1.1 DC-Polarographic Studies

The polarographic behavior of $1.25x10^{-4}$ M of adipic acid dihydrazide derivatives (I-VII) was investigated in Britton-Robinson buffer solutions of pH 2.0-11.0 containing 50% (v/v) ethanol. In strong acidic solutions (pH < 3.0), the plateau of the polarographic wave obtained for all the investigated compounds is ill-defined due to the early hydrogen evolution. In buffer solutions of higher pH values, the polarograms of compounds (I-VI) exhibited a single polarographic wave of almost equal height (Fig. 1a). On the other hand, compound VII (nitro derivative) showed two waves within the entire pH range (Fig. 1b). The limiting current (i_l) of the reduction wave in acidic solutions is almost twice that in alkaline ones, while in neutral solutions the limiting current has an intermediate value. In order to investigate the effect of pH of the electrolysis solution on the limiting current value, the latter is plotted against the pH value. A dissociation curve is obtained for all compounds under investigation (Fig. 2), revealing that the limiting current is pH-dependent and the number of electrons involved in the reduction process in acidic solutions is doubled that uptaken in alkaline ones (Zuman, 1969).

3.1.2 Nature of the polarographic waves

The effect of mercury pressure (h) on the limiting current (i_l) of the polarographic wave at different pH values revealed that the reduction process of the arylidene adipic acid dihydrazide derivatives (I-VII) is controlled by diffusion. This suggestion is achieved from the straight lines obtained from the plotting of log (i_l) vs. log (h), according to the relation: $i_L = Kh^x$ (Heyrovesky and Kuta, 1965) which denoted slope values of 0.49 to 0.59 for all compounds under investigation.

For testing the thermodynamic reversibility of the electrode processes, the logarithmic analysis of the polarographic waves was performed according to the fundamental equation of Meites (Meites, 1969). The plots of $E_{d.e}$ versus log $i/(i_d - i)$ for all compounds (I-VII) showed linear correlations at different pH values. From the slopes (S_1) of these plots the values of the transfer coefficient (α) were obtained and found to be less than 0.7 at $n_a = 2.0$ in acidic solutions whereas in both neutral and alkaline solutions its value is less than 0.7 at $n_a = 1.0$ (Table 1). Consequently, it is concluded that the reduction process of all compounds takes place irreversibly and the rate-determining step should involve two electrons and one electron in acidic and alkaline solutions, respectively.

Further inspection of the data of Table 1 indicates that the half-wave potential ($E_{1/2}$) of the polarographic wave is shifted to more negative values on increasing pH of the solution. This behavior reveals that hydrogen ions are consumed in the reduction process and the proton uptake precedes the electron transfer (Zuman, 1969). Linear correlations consisting of two segments were obtained on plotting $E_{1/2}$ versus pH of all compounds as represented in Fig. 3 as a typical example. The rate change of $E_{1/2}$ with pH can be used to calculate the number of hydrogen ions (p) involved in the rate-determining step using the following equation (Craw and Westwoed, 1968):

$$[dE_{1/2}]/[d(pH)] = [(0.05915)\ p]/\ \alpha n_a \qquad (1)$$

From the slope values of the $E_{1/2}$-pH plots (S_2) and those of logarithmic analysis (S_1), the number of hydrogen ions (p) involved in the rate-determining step was found to be unity. These results denoted that, in acidic solutions the rate-determining step is pH-dependent and involves two electrons and one proton whereas in neutral and alkaline ones it involves one electron and one proton (Table 1).

3.2 Cyclic voltammetry

Cyclic voltammograms of $1.0x10^{-4}$ M of all compounds (I -VII) were recorded in buffer solutions containing 50% (v/v) ethanol at different pH values. The voltammograms recorded at different sweep rates (20-500 mV/sec) are essentially similar and showed one or two cathodic peaks depending on both the pH of the solution and the nature of substituent (Fig. 4). There is no peaks observed in the reverse scan (anodic direction) revealing the irreversibility of the reduction waves. On increasing sweep rate the peak current is linearly related to the square root of sweep rate according to Delahay equation (Delahay, 1954) for irreversible electrode processes.

$$i_p = 3.01x10^5 n(\alpha n)^{1/2} A D^{1/2} \upsilon^{1/2} C \qquad (2)$$

The straight lines obtained from the plots of i_{pc} versus $\upsilon^{1/2}$ are passing through the origin indicating that the electrode reaction is controlled by diffusion (Bard and Faulkner, 1980). This experimental result is in good agreement with that obtained from DC-polarographic measurements. Moreover, the cathodic peak potential (E_{pc}) is shifted to more negative potentials on increasing the sweep rate which is further confirmation for the irreversible nature of the electrode process. The variation of peak potential with the sweep rate (υ) has given by the following equation (Galus, 1976):

$$E_p = E^o - 1.14[RT/\alpha n_a F] + [RT/\alpha n_a F] \ln (k_s/D^{1/2}) - [RT/2\alpha n_a F] \ln \alpha n_a \upsilon \quad (3)$$

Therefore, on plotting E_p vs. ln υ, linear correlations are obtained. From the slopes of these plots, the transfer coefficient (α) values for all arylidene adipic dihydrazones were evaluated at the selected pH values and listed in Table (2). The α-parameter values were also determined using the relationship that relates E_p and i_p as following (Gokhshtein and Gokhshtein, 1960):

$$E_p = [2.3\ RT/\alpha n_a F] \log i_p + \text{Constant} \quad (4)$$

On plotting E_p vs. log i_p, linear correlations were obtained. The transfer coefficient (α) values were calculated from the slopes of these plots and given in Table (2). It is illustrated that α is less than unity at $n_a = 2.0$. These results ascertain the good agreement of α values obtained using the different methods which confirm the irreversible nature of the reduction peaks.

3.3 Chronocoulometry (CC)

Chronocoulograms were recorded in the same solution composition and the predetermined potential range used in cyclic voltammetric measurements. In case where the reactant but not the product is adsorbed, the difference between the intercepts of the forward and reverse steps provides the amount of adsorbed reactant (Anson, 1966, Anson and Osteryoung, 1983) which amounts to $nF\Gamma$, where Γ is the amount adsorbed reactant in mole cm^{-2}. This amount was found in the range of $1.0x10^{-14}$ M which could be considered as a negligible quantity as compared to the original concentration of electroactive species ($1.25\ x10^{-4}$ M). Also, the slope values were used in determining the diffusion coefficients of arylidene adipic dihydrazones (I-VII). Values of the diffusion coefficients were found in good agreement with those obtained from Ilkovic equation.

3.4 Heterogeneous rate constant from cyclic voltammetric data

The heterogeneous rate constant, k_s, of arylidene adipic acid dihydrazides (compounds I-VII) was calculated from cyclic voltammetry in solutions of different pH values. The intercepts of the plots of E_{pc} vs. ln (υ) was used for the determination of αn_a and subsequently k_s using equation 3 (Table 2). The necessary values of the diffusion coefficients of the depolarizers (compounds I-VII) were calculated using Ilkovic equation. Also, the corresponding energy of activation $\Delta G^{\#}$ of the electroreduction process was determined according to the following equation (Anson and Osteryoung, 1983):

$$\Delta G^{\#} = 5778.8\ (5.096 - \log k_s) \quad (5)$$

Inspection of the data given in Table (2), reveals that the formal rate constant, k_s, was decreased on increasing the pH of the solution. The electrode reaction becomes more difficult and the irreversibilty of the system is increased for all compounds (I-VII). Simultaneously, the activation energy, $\Delta G^{\#}$, is increased on increasing the pH of the electrolysis solution revealing that the reduction process is irreversible. Increasing the pH of the solution required higher energy of activation to achieve reduction which in turn increases irreversibilty. This behavior is common for both species formed in solution corresponding to the first and second peaks.

The effect of introducing substituents (x) in the para-position of the homocyclic phenyl ring on the half-wave potential ($E_{1/2}$) of the dihydrazide compounds was correlated with Hammett substituent constant, σ_x. Values of σ_x were taken directly from the tabulation of Ritchie and Sager (Sakla *et al*, 1978). The plots of $E_{1/2}$ vs. σ_x at different pH values showed linear correlations of positive slopes indicating the nucleophilic attack in the potential-determining step. The plots of $E_{1/2}$ vs. σ_x showed linear correlations with a small positive slopes amounting to 0.132 and 0.208 at pH 5.0 and 9.0, respectively as shown in Fig. 5. The deviation of σ_{NO2} from linearity indicates that p-NO_2 group is contributed to the electroreduction of arylidene adipic acid dihydrazides as NHOH group (Ritchie and Sager, 1964). The use of σ_{NHOH} value instead of σ_{NO2} was found to fits linearity supporting our reaction mechanism, which is proposed below. The general observed trend is the negative shift of $E_{1/2}$ of the arylydene adipic acid dihydrazide derivative (I) on introducing electron-donating substituents such as p-OH (IV), p-OCH_3 (V) and p-CH_3

(VI). Whereas electron-withdrawing substituents such as p-Cl (II), p- Br (III) and p-NO_2 (VII) showed a positive-shift by decreasing the basicity of the unprotonated nitrogen atom linked to the aryl moeity. This behavior indicates that electron-donating substituents hindered the electrode reaction and required higher energy. On the other hand electron-withdrawing substituents facilitated the electrode process and lower energy is required.

3.5 Controlled potential coulometry (CPC)

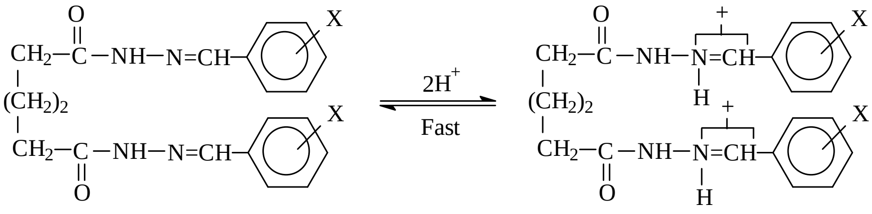
To suggest the electrode reaction mechanism it is important to determine the number of electrons consumed in the reduction processes. The number of electrons was determined with the aid of Ilkovic equation using values of diffusion coefficients obtained from chronocoulometric studies and confirmed experimentally using controlled potential electrolysis.

Controlled potential coulometry was performed to calculate experimentally the total number of electrons involved in the electroreduction process. Firstly, the potential of the working electrode (mercury pool) was adjusted with a value just at the top of the polarographic limiting current. The background current was measured (10 ml buffer + 10 ml pure ethyl alcohol). Then 2 ml ($1.0x10^{-3}$ M) of the depolarizer were introduced into the coulometric cell and the electrolysis was continued to completion. The amount of charge (Q) in coulombs was readed directly from the digital coulometer. Also, the number of electrons (n) was determined using the relation:

$$Q = nFw/M \qquad (6)$$

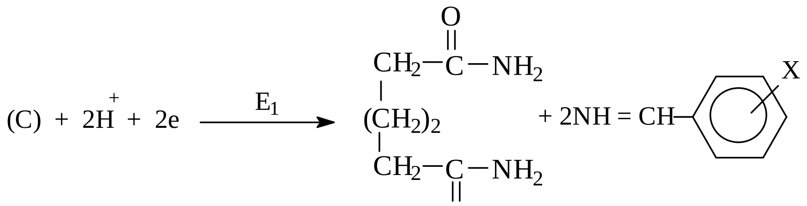
where w is the weight of depolarizer in grams and M its molecular weight. The experiment was performed in solutions of pH 3.5 and 8.0 and the total number of electrons consumed in the electroreduction of compounds (I-VI) was found to be (8 and 4) ± 0.2 electrons, respectively. In case of compound (VII), which contained two symmetrical electroactive nitro groups, 16 and 12 ± 0.2 electrons were involved in the reduction process in solutions of pH 4.0 and 8.1, respectively.

The completely electrolysed solution of compound (VI) was concentrated to half its volume by evaporation on water-bath and the buffer ingradients were removed by extraction with ether. The TLC of the etheral extract revealed that two spots were obtained for the completely electrolysed solution of pH 3.5 whereas one spot was observed for the other solution (pH 8.0). On comparing the two spots (pH 3.5) with the authentic p-methylbenzylamine, the latter was found to be one of the main electrolysis products, which confirmed the cleavage of the N - N bond in acid solutions. Depending on the forgoing results and in terms of structural genesis the reduction mechanism could take place as follows:



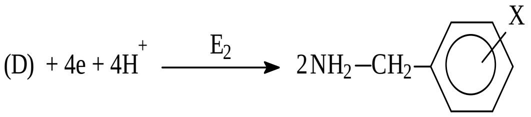
(A) (B)

In acid media:

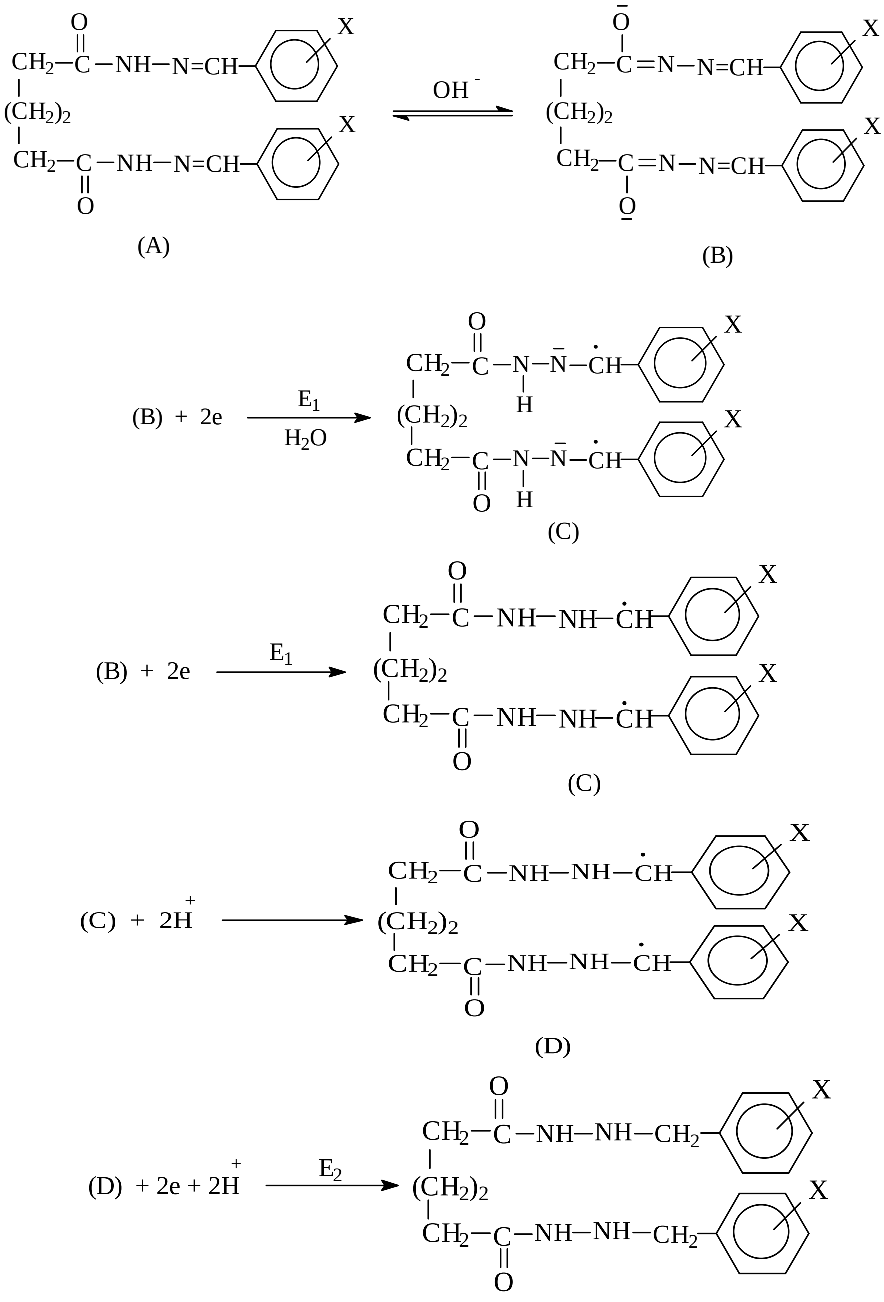


(D)

($E_1 = E_2 = E_{½}$ = single wave)



In alkaline media:



(E_1 = E_2 = $E_{½}$ = single wave)

For p-NO_2 derivative, the reduction of the –NO_2 group can be given as follows:

In acidic media:
$2(\text{-NO}_2) + 8\,e + 8H^+ \rightarrow 2(\text{-NHOH}) + 2H_2O$

In alkaline media:
$2(\text{-NO}_2) + 8\,e + 6H^+ \rightarrow 2(\text{-NHOH}) + 8OH^-$

Table 1: Electrochemical data obtained from the reduction of arylidene adipic acid dihydrazide derivatives (I-VII) using DC-polarographic technique

Compound	pH	i_d (μA)	$-E_{1/2}$ (V)	S_1 (mV)	S_2 (mV)	p	αn_a $(Volt)^{-1}$	$\Delta \log(i_L)/\Delta \log(h)$
I	3.5	1.65	1.013	58.3	55.9	0.96	1.01	0.59
	7.0	1.00	1.223	96.0	77.0	0.80	0.62	0.51
	9.1	0.86	1.335	104.0	77.0	0.74	0.57	0.58
II	3.5	1.44	1.010	73.4	50.6	0.69	0.81	0.58
	7.0	0.68	1.180	103.3	67.0	0.75	0.42	0.59
	9.0	0.72	1.320	84.2	67.0	0.80	0.70	0.56
III	3.2	1.38	0.983	61.4	49.9	0.81	0.96	0.59
	7.2	0.85	1.200	108.8	69.9	0.64	0.42	0.59
	9.2	0.68	1.275	104.1	69.9	0.67	0.48	0.59
IV	3.3	1.55	1.123	53.6	56.3	1.10	1.10	0.59
	7.1	1.02	1.310	108.5	63.0	0.58	0.43	0.59
	9.1	0.75	1.430	105.3	63.0	0.60	0.47	0.59
V	3.2	1.50	1.080	55.4	58.9	1.06	1.07	0.58
	7.0	1.12	1.293	103.0	78.9	0.77	0.57	0.58
	9.1	0.76	1.415	105.4	78.9	0.79	0.39	0.54
VI	3.3	1.45	0.983	71.3	61.0	0.86	0.83	0.59
	7.1	1.16	1.260	91.4	81.0	0.87	0.65	0.58
	9.2	0.72	1.363	104.5	81.0	0.79	0.42	0.59
VII	3.9	1.14	0.425	51.0	52.1	1.02	1.16	0.53[a]
		1.12	1.190	85.0	59.0	0.69	0.62	0.49[b]
	7.2	1.08	0.628	51.1	52.1	1.02	1.16	0.49[a]
		1.07	1.334	64.1	59.0	0.92	0.92	0.50[b]
	10.	1.00	0.777	50.3	52.1	1.04	1.18	0.51[a]
	4	0.60	1.446	89.4	59.0	0.66	0.66	0.51[b]

a- Firt wave
b- Second wave

Table 2: Kinetic parameters and data obtained from cyclic voltammetry for the electroreduction of arylidene adipic acid dihydrazide derivatives (I-VII) at 25°C

Compound	pH	α^1	α^2	$Dx10^{-6}$ (cm^2/sec)	k_s (cm/sec)	ΔG* (KJ/mol)
I	3.5	0.35	0.34	5.10	$1.08x10^{-7}$	291.4[a]
		0.43	0.42		$3.53x10^{-9}$	327.3[b]
	7.0	0.55	0.58	5.00	$2.37x10^{-13}$	428.1
	9.1	0.64	0.66	5.00	$8.15x10^{-15}$	463.4
II	3.5	0.32	0.29	5.20	$5.07x10^{-7}$	275.2[a]
		0.30	0.28		$2.12x10^{-7}$	284.3[b]
	7.0	0.30	0.49	5.10	$1.52x10^{-8}$	312.0
	9.1	0.32	0.51	5.10	$2.31x10^{-10}$	331.7
III	3.3	0.39	0.26	4.90	$2.48x10^{-8}$	306.8[a]
		0.31	0.24		$9.31x10^{-8}$	293.0[b]
	7.1	0.48	0.47	4.80	$4.58x10^{-12}$	397.0
	9.1	0.50	0.51	4.80	$8.66x10^{-11}$	366.2[a]
		0.60	0.62		$1.08x10^{-13}$	436.3[b]
IV	3.2	0.49	0.41	5.60	$5.81x10^{-10}$	346.2[a]
		0.46	0.41		$3.22x10^{-10}$	352.4[b]
	7.0	0.43	0.76	5.40	$2.57x10^{-12}$	403.1
	9.1	0.54	0.53	5.40	$2.96x10^{-14}$	449.9
V	3.2	0.33	0.32	5.40	$9.65x10^{-8}$	292.3[a]
		0.39	0.37		$5.45x10^{-9}$	322.7[b]
	7.0	0.39	0.35	5.30	$1.32x10^{-11}$	385.9
	9.1	0.62	0.60	5.30	$1.50x10^{-15}$	481.2
VI	3.3	0.36	0.31	5.50	$2.60x10^{-8}$	306.3[a]
	7.1	0.46	0.44		$6.88x10^{-10}$	344.4
	9.2	0.57	0.53	5.40	$2.14x10^{-14}$	453.3
		0.60	0.63	5.40	$1.31x10^{-14}$	458.5
VII	3.9	0.48	0.46	5.30	$1.83x10^{-4}$	213.4[a]
		0.34	0.33		$5.46x10^{-10}$	346.9[b]
	7.2	0.51	0.52	5.10	$1.13x10^{-5}$	242.6[a]
		0.42	0.43		$1.11x10^{-10}$	363.6[b]
	10.4	0.54	0.52	5.10	$7.55x10^{-7}$	271.0[a]
		0.55	0.53		$6.93x10^{-12}$	392.7[b]

a- 1st. peak
b- 2nd. Peak
1- Using equation 3
2- Using equation 4

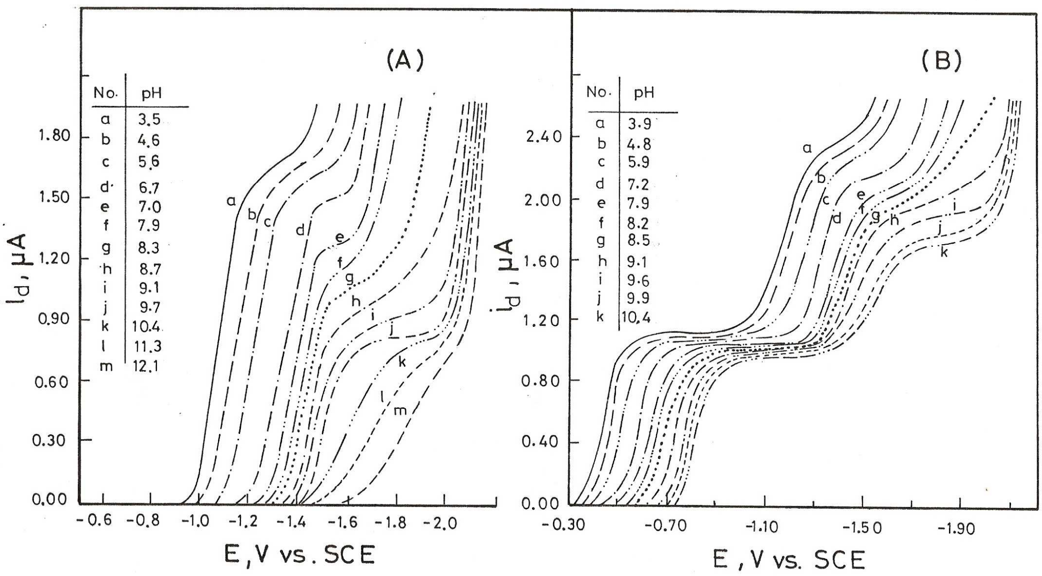


Fig. 1

Fig. 1. DC-polarograms of $1.25x10^{-4}$ M of arylidene derivatives of adipic dihydrazide in universal buffer solutions containing 50% ethanol at different pH values:
(A) p-OCH_3 derivative and (B) p-NO_2 derivative.

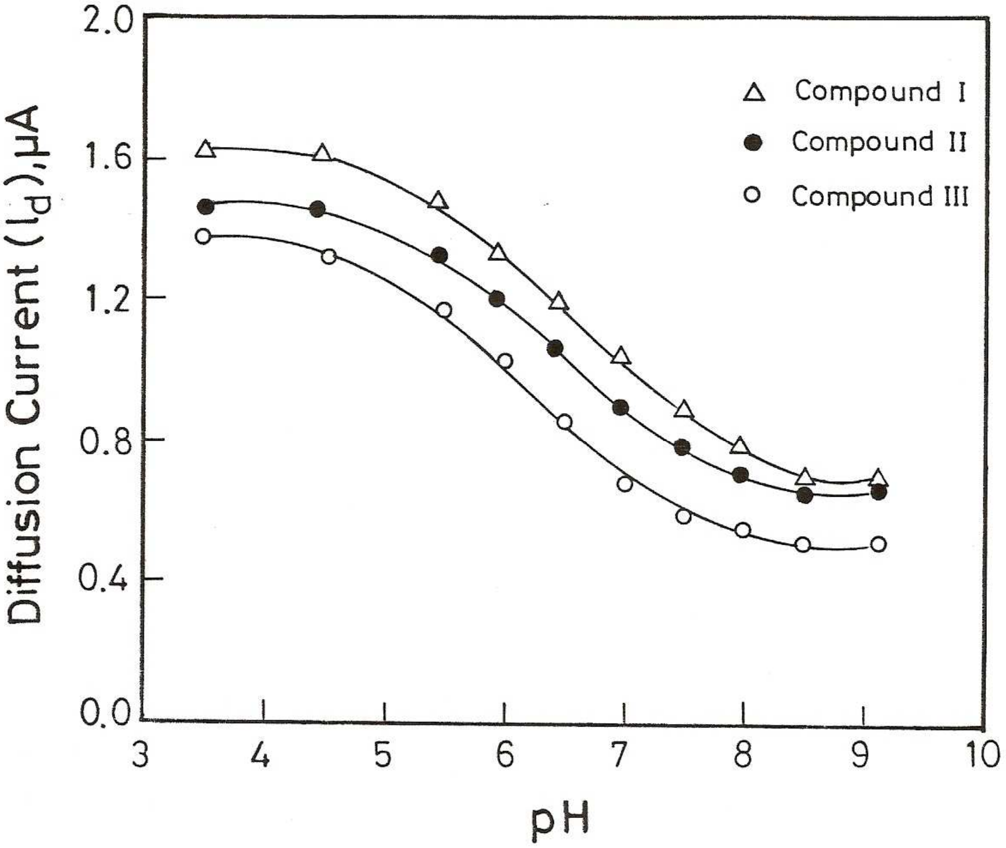


Fig. 2

Fig. 2. The effect of pH of electrolysis solution on the values of the diffusion current

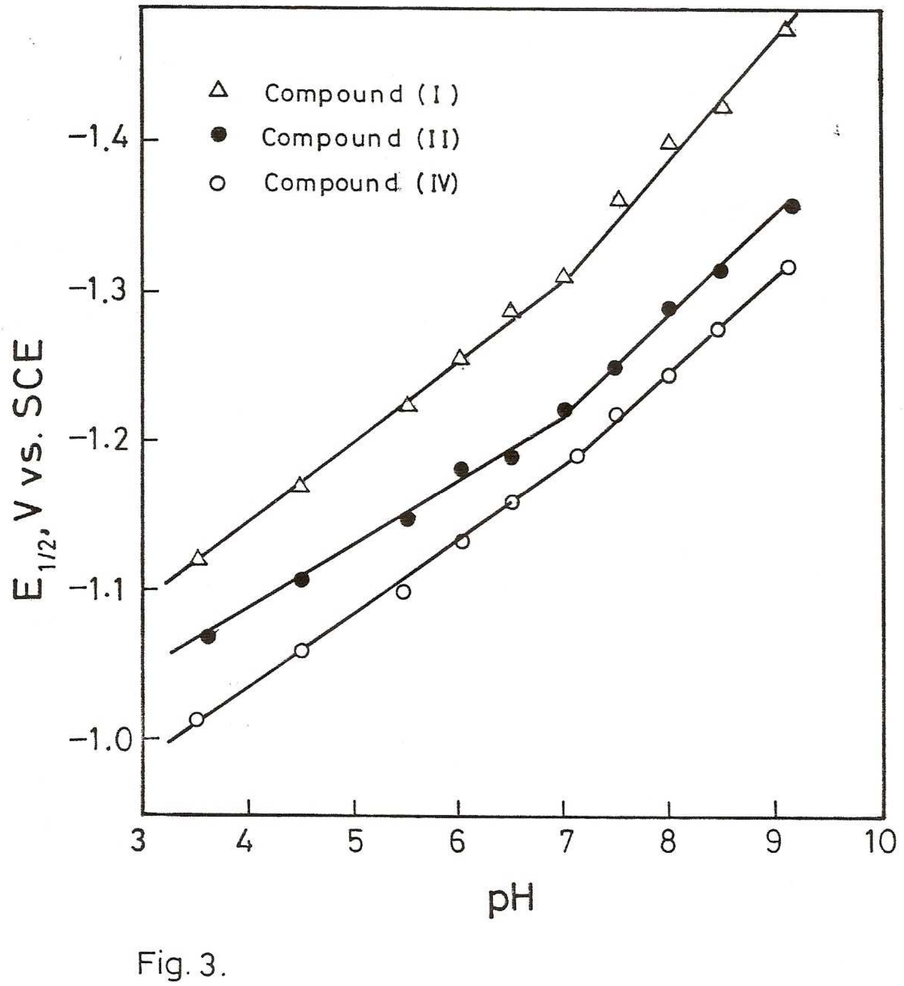


Fig. 3. The effect of pH of electrolysis solution on the half-wave potentials

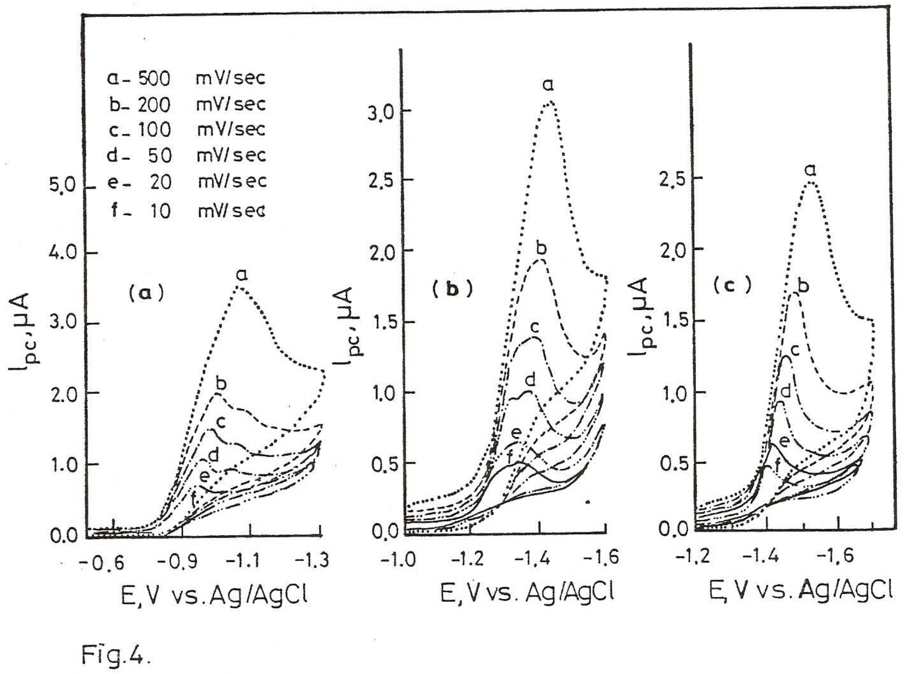


Fig. 4. Cyclic voltammograms for 1.0x10^{-4} M of p-CH$_3$ derivative at different scan rates and different pH values: (A) pH = 3.3, (B) pH = 7.1 and (C) pH = 9.2

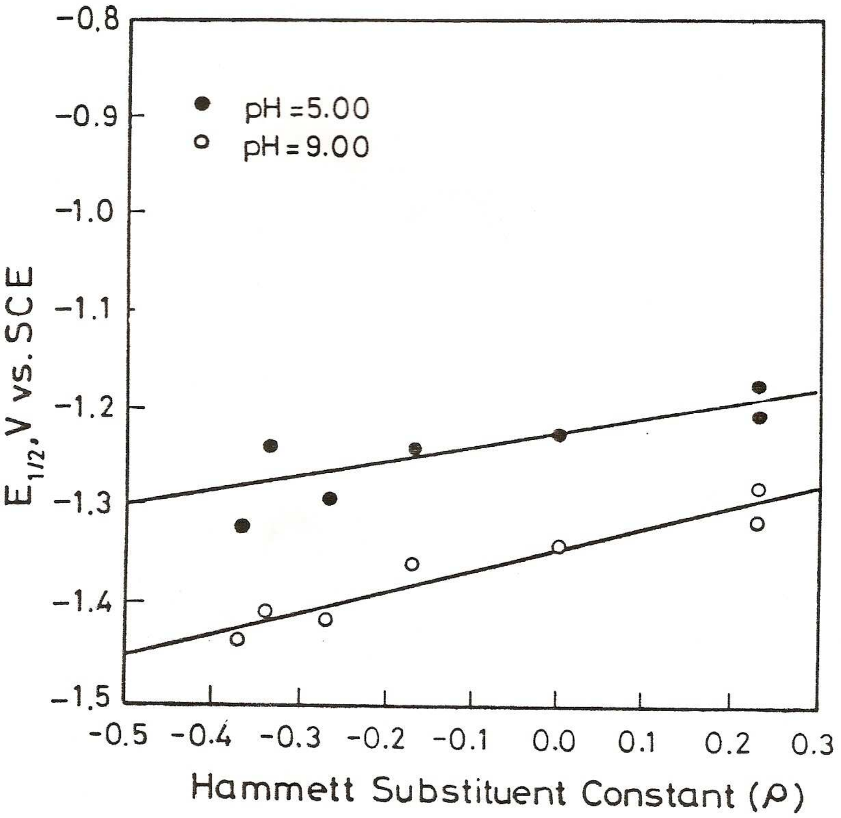


Fig. 5

Fig. 5. The effect of Hammett substituent constant on the half-wave potential of the unsubstituted compound (I)

CONCLUSION

Adipic acid dihydrazide derivatives (I-VI) were reduced at mercury electrode irreversibly through the uptake of 8 and 4 electrons in both acidic and alkaline solutions, respectively. Whereas p-NO_2 derivative (VII) it was found to be reduced through the uptake of 16 and 12 electrons in acid and alkaline media, respectively. The irreversibility of electrode reaction was ascertained from both DC-polarography and cyclic voltammetry techniques. The transfer coefficient (α) was determined using different methods and found to be less than 0.7 indicating the irreversibility of the electrode process. The kinetic parameters of the electrode reaction were calculated and discussed. The mechanistic pathway of the electrode reaction follows the sequence H^+, e, e, H^+ in acidic solutions whereas in alkaline solutions the sequence is e, H^+, e, H^+.

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