Electrochemical studies of Schiff base compounds derived from antipyrine nucleus in ethanolic buffer solutions

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Abstract: The electrochemical behaviour of Schiff base compounds derived from an antipyrine nucleus was investigated in 30% (v/v) ethanolic buffer solutions (pH 3-11) using various electrochemical techniques at mercury electrode. The results showed that, the total limiting current of each of the studied compounds corresponds to 2-electron transfer process. The mechanistic pathway of the electrode reaction of the investigated compounds at mercury electrode, the effect of the medium, and the evaluation of the electrode reaction parameters were illustrated and discussed.

Key words: Schiff base, antipyrine nucleus, electrode reaction, electrochemical parameters, cyclic voltammetry.

Résumé: Opérant dans des solutions tampons (pH allant de 3 à 11) contenant 30% (v/v) d'éthanol et faisant appel à diverses techniques électrochimiques avec électrode de mercure, on a étudié le comportement électrochimique de diverses bases de Schiff dérivées du noyau antipyrine. Les résultats montrent que, le courant limite total de chacun de composés étudiés correspond à un processus de transfert d'électrons 2-. On illustre et on discute des voies mécanistiques de la réaction à l'électrode, de l'effet du milieu et de l'évaluation des paramètres de la réaction à l'électrode.

Mots clés : base de Schiff, noyau antipyrine, réaction à l'électrode, paramètres électrochimiques, voltampérométrie cyclique.

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Introduction

The electroreduction of Schiff base compounds was the subject of several interesting investigations (1-6). Generally, the electroreduction of such compounds at mercury electrode in acidic and alkaline solutions consume two electrons per reactant molecule for saturation of a carbon–nitrogen double bond or four electrons for its reductive splitting.

In this paper we report the electrochemical behaviour of some Schiff base compounds derived from an antipyrine nucleus in ethanolic buffer B.R. solutions. The electrochemical parameters of the electrode process were evaluated using dc–polarography, cyclic voltammetry and controlled potential coulometry. Verification of the electrochemical parameters determined experimentally via digital simulation method was also considered. The mechanistic pathway of the electrode reaction was discussed.

Experimental

Chemicals and solutions

The compounds under consideration were prepared by adding a solution of 4-aminoantipyrine (0.01 mol) dissolved in etha-

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nol to an ethanolic solution of 0.01 mol of salicyladehyde, *p*-hydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde, and 2-hydroxy-1-naphthaldehyde. Then, the mixture was heated and refluxed for about 2 h. On cooling the mixture, the solid compounds were separated and filtered off. The crude products were recrystallized several times from hot ethanol, washed with diethyl ether, and finally dried in a vacuum desiccator. The purity of the compounds was ascertained by crystallization until a constancy of the mp was reached. The structure of the prepared compounds were confirmed by elemental and spectral analysis. The prepared compounds have the general structure formula







Stock solutions $(2.5 \times 10^{-3} \text{ M})$ of the prepared compounds were obtained by dissolving the accurate mass of the solid compound in appropriate volume of ethanol. Britton–Robinson buffer series (pH 2–12) containing 30% (v/v) ethanol were prepared from analytical grade chemicals and used as supporting electrolyte.

Instrumentation

The dc-polarograms were recorded using a Sargent Welch polarograph model 4001. The capillary characteristics were $m = 1.03 \text{ mg s}^{-1}$, $t = 3.3 \text{ s} \text{ drop}^{-1}$ at mercury height (h) = 60 cm. The cyclic voltammograms were recorded using a polarographic Analyzer model 264A-PAR (from EG & G) and electrode assembly 303 A with a hanging mercury drop electrode (HMDE) of area = 2.6×10^{-2} cm² as a working electrode, Ag-AgCl as a reference electrode, and a Pt-wire as a counter electrode. The number of electrons consumed in the overall electrode reaction was determined using coulometry system model 380-PAR with a mercury pool cathode, saturated calomel electrode as a reference, and a Pt-wire as counter electrode. The electronic spectra were measured using Shimadzu UV-vis spectrophotometer model 160 A. Digital simulation of the extracted parameters for the cyclic voltammetric experiments were run on an PC computer using Condesim software packages (from EG & G) which allows accurate digital simulation for a wide range of mechanisms.

Results and discussion

Dc-polarography

The dc–polarographic behaviour of 2.5×10^{-4} M of Schiff base compounds (**I–IV**) was investigated in Britton–Robinson buffer solutions of pH 3–11 containing 30% (v/v) ethanol. It was found that in strong acidic solutions (pH < 3.0), the polarograms of all compounds under investigation do not

Table 1. Dc–polarographic data obtained for compounds under investigation at 25°C.

		$-E_1$	$-E_{1/2}$ (V)		$n_{\rm a} = 1$)	
Comp.	pН	$(i)^a$	$(ii)^b$	$(i)^a$	$(ii)^b$	
I	4.0	0.85		0.42		
	6.0	0.98	1.25	0.31	0.40	
	9.3		1.35		0.52	
II	4.0	1.05	_	0.29		
	6.0	1.18	1.34	0.35	0.20	
	8.6		1.48		0.49	
III	3.8	1.02		0.26		
	5.9	1.16	1.35	0.37	0.40	
	9.6		1.60		0.51	
IV	3.9	0.89		0.25		
	6.6	1.02	1.23	0.39	0.29	
	9.1	1.25	1.38	0.35	0.31	

^{*a*}(*i*) First wave.

^b(*ii*) Second wave.

show any reduction wave except the hydrogen wave which appears at a potential not more than -1.1 V. However, in solution of $3 \le pH \le 4.0$ the polarograms of the studied compounds show a single reduction wave (A) Fig. 1. At pH > 4.0a second ill-defined wave (B) appeared. This wave becomes well-defined on increasing the pH up to 7.0, its height increase at the expense of first wave (A) until the two waves merge together and become one wave. This behaviour is characteristic for compounds (I-III) while the polarograms of compound (IV) exhibit two waves of almost equal height in slightly acidic solutions and the height of the first wave decreases slightly with increasing pH. It is important to note that the total limiting current of the studied compounds corresponds to a two-electron transfer process as evidenced from coulometry studies. Figure 1 gives an example of the recorded dc-polarograms of compound (III).

The plots of i_1 for compounds (**I–III**) as a function of pH of the medium recall a dissociation curve of two steps denoting the presence of an acid–base equilibrium. The height of the reduction waves is proportional to the square root of mercury height (*h*). The straight lines obtained on plotting log i_1 vs. log *h* have slope values amounting to 0.45–0.53 revealing that the reduction process of the electrode reaction is mainly diffusion controlled (7). Also, the reduction waves of the Schiff base compounds under consideration were analyzed using the fundamental equation of irreversible polarographic waves (8)

[1]
$$E = E_{1/2} - \frac{0.0591}{\alpha n_a} \log \frac{i}{(i_d - i)}$$

The low values (<0.5) of the cathodic symmetry coefficient (α) obtained from the slope S_1 ($S_1 = 0.0591/\alpha n_a$) of the *E* vs. log ($i/i_d - i$) plots indicate the irreversible nature of the electrode process. The most probable α -values are obtained for $n_a = 1.0$ (Table 1), where n_a is the number of electrons participating in the rate-determining step.

On increasing the pH of the electrolysis solution, the halfwave potentials $(E_{1/2})$ of the polarographic wave get shifted to more negative values (Table 1), denoting that the

Table 2. Data of cyclic voltammetry for compounds under investigation at 25° C, v = 0.5 V/s.

			$E_{\rm p} - I$	$E_{\rm p}-E_{\rm p/2}~({\rm mV})$		$\alpha \ (n_{\rm a}=1)$	
Comp.	pН	Mol wt.	$(i)^a$	$(ii)^b$	$(i)^a$	$(ii)^b$	
I	5.2	307.34	112		0.42		
	10.5		120	135	0.40	0.35	
II	6.3	323.34	115		0.41		
	7.5		128		0.37		
III	6.6	307.34	110	115	0.43	0.41	
	9.6		125	130	0.38	0.36	
IV	6.6	357.39	120	126	0.40	0.38	
	10.5		132	138	0.36	0.34	

^a(i) First wave.

^b(*ii*) Second wave.

hydrogen ions are consumed in the reduction process (9). The $E_{1/2}$ -pH plots of the first reduction wave of the studied compounds give a break at pH 4.5–5.5, whereas the $E_{1/2}$ -pH plots of the second one exhibit a break at pH 8–9, indicating the protonation of -CH=N- center and the ionization of OH group of the reactants at those pH values. From the slope values of logarithmic analysis (S_1) and that of $E_{1/2}$ -pH plots (S_2) ($S_2 = (0.0591/\alpha n_a)Z_H^+$), the number of hydrogen ions participating in the rate-determining step is found to equal unity ($Z_H^+ = S_2/S_1$).

Controlled potential coulometry (CPC)

A coulometry measurement is performed by adding 10 mL of Britton–Robinson buffer (slightly acidic or alkaline) to the coulometric cell. The specified potential for each compound was applied to the cell and the electrolysis was continued until the background current attained a constant value. An amount of the reactant solution was then added (1 mL of 10^{-3} M) and the electrolysis was allowed to proceed until completion. The accumulated charge (Q) was read directly from the digital coulometer and the number of electrons (*n*) consumed for complete reduction of the reactants was calculated using the relation Q = nM/Fw), in which w is the mass (in grams) of the reactant, M is the reactant molecular weight and F is the Faraday's constant. The results obtained denoted that (*n*) equals two electrons per reactant molecule in both acidic and alkaline media.

Cyclic voltammetry

The voltammograms of the studied compounds in B.R. buffer solution at different scan rates ranging (10–500 mV/s) exhibit one or two well-defined cathodic peaks depending on the pH of the medium and nature of the substituent. In the reverse scan (anodic direction) no oxidation peaks were observed which confirms the irreversible nature of the reduction wave. The extent of the cathodic shift of the peak potential (E_p) as a function of the sweep rate, the difference between the potentials at half-peak $(E_{p/2})$ and at the peak (E_p) , confirm the irreversible nature of the electrode process (10). So, the cathodic peak potential (E_p) varies with the logarithm of the potential sweep rate according to the eq. [2] (11)

$$E_{p} = -1.14 \left(\frac{RT}{\alpha n_{a}F} \right) + \left(\frac{RT}{\alpha n_{a}F} \right) \ln \left(\frac{(k_{f,h})}{D^{1/2}} \right) - \left(\frac{RT}{2\alpha n_{a}F} \right) \ln (\alpha n_{a}v)$$

On plotting E_p or $E_{p/2}$ for the investigated compounds vs. log v, linear correlations are obtained and the cathodic symmetry coefficient (α) values at selected pH values were calculated from the slopes of these plots. Values of the symmetry coefficient (α) were also determined from the difference of peak and half-peak cathodic potentials by means of the eq. (10)

[3]
$$E_{\rm p} - E_{\rm p/2} = 1.857 (RT/\alpha n_{\rm a}F)$$

and were found to be less than 0.5 when $n_a = 1$ (Table 2), confirming the irreversible nature of the reduction process. Good agreement is found between α and n_a values calculated from the cyclic voltammetry data and their values obtained from dc–polarographic measurements.

For the irreversible charge transfer processes (12), the peak current (i_{pirr}) can be expressed by the following equation:

[4]
$$i_{\text{pirr}} = 2.99 \times 10^5 n (\alpha n_{\text{a}})^{1/2} A D^{1/2} C v^{1/2}$$

in which i_{pirr} is the peak current in amp, and C is the concentration of the reactant species which equals $1.25 \times 10^{-4} M$ in the present study, and the other terms have their usual meaning.

On plotting the i_{pirr} vs. $v^{1/2}$ at different pH values straight lines with some slight deviation from the origin are obtained revealing the diffusion character of the current (13). Table 2 revealed that the peak width $(E_p - E_{p/2})$ grows larger for the higher molecular weight compounds as well as with increasing pH of the medium, indicating increased irreversibility nature of the electrode process as the molecular weight and (or) the pH are increased (14). The E_p vs. pH plots of the first peak of the investigated compounds give two segments with slope of 60–95 mV/pH which is not much different from the values obtained from dc–polarography experiments and indicates that the species in solution undergoes a fast protonation at the interface, prior to the reduction process (14).

Diffusion coefficient (D) of Schiff base compounds was determined from the following equation (15, 16)

[5]
$$I_{\text{lim}} = \frac{i_{\text{pirr}}}{3.099(\alpha n_{a} \nu)^{1/2}}$$

Also, in the same manner, the ratio $[(dI_1/dt)_f]_{irr}/i_{pirr}$ for irreversible charge transfer can be used for determining the diffusion coefficient of the electroactive species via the following relation (16, 17)

[6]
$$\frac{[dI_1/dt)_f]_{irr}}{i_{pirr}} = 3.73 (\alpha/n_a)^{1/2} n v^{1/2}$$

where $[(dI_1/dt)_f]_{irr} = \alpha n^2 F^2 SCD^{1/2} v/3.367RT$ is the height of the forward sweep of the deconvoluted current, and the other terms have their usual meaning. Hence from relation [6], the ratio $[(dI_1/dt)_f]_{irr}$ can be determined which gives another accurate route for determination of the diffusion coefficient.

Ψ

 4.04×10^{-3}

 1.28×10^{-3}

 1.81×10^{-3}

 4.04×10^{-4}

 4.00×10^{-4}

 9.00×10^{-4}

 1.28×10^{-3}

 2.86×10^{-4}

Table 3. Values of the diffusion coefficient (D) of the compounds under consideration determined via different methods at 25°C.

Table 4. Values of $k_{\rm fh}$ determined via ref. (11) and simulation
method and its corresponding $\boldsymbol{\psi}$ of the investigated compounds
at 25°C.

Ref. (11)

 8.2×10^{-6}

 5.6×10^{-6}

 7.1×10^{-6}

 7.9×10^{-7}

 $8.5\,\times\,10^{-6}$

 9.1×10^{-7}

 6.1×10^{-5}

 6.3×10^{-7}

 $k_{\rm fh}~({\rm m/s})$

 9.5×10^{-6}

 6.2×10^{-6}

 6.8×10^{-6}

 8.5×10^{-7}

 9.3×10^{-6}

 9.4×10^{-7}

 6.3×10^{-5}

 6.1×10^{-7}

Simulation method

		<i>D</i> x10 ¹⁰ (m ² /s)			
Comp.	pН	$\overline{(i)^a}$	$(ii)^b$	(<i>iii</i>) ^c	
Ι	5.2	2.9	2.8	2.7	
	10.5	2.5	2.2	2.3	
II	6.3	3.1	2.7	2.9	
	7.5	2.3	2.2	2.5	
III	6.6	3.3	3.2	3.4	
	9.6	3.1	2.9	3.3	
IV	6.6	2.9	2.7	3.1	
	10.5	2.3	2.2	2.4	

a(i) Value of D determined from CV via eq. [4].

^b(*ii*) Value of D determined from I_{lim} via eq. [5].

^{*c*}(*iii*) Value of *D* determined from $[(dI_1/dt)_f]_{irr}$ via eq. [6].

Table 5. Values of peak characteristics, k_c , k_s , D, α , and E° determined via theoretical work at sweep rate 0.5 V/s.

Comp.	pН	i _p (uA)	$E_{\rm p}-E_{\rm p/2}~({\rm mV})$	$k_{\rm c}~({\rm s}^{-1})$	$k_{\rm s} \times 10^6 ~{\rm (m/s)}$	$D imes 10^{10} \ (\mathrm{m^{2/s}})$	α	$-E^{\circ}$ (V)
I	5.2	3.33	111	7	8.7	3.1	0.40	0.92
	10.5	5.52	121	8	6.5	1.9	0.35	1.30
II	6.3	5.31	117	5	6.1	2.9	0.42	1.13
	7.5	4.62	130	7	8.0	2.3	0.34	1.18
III	6.6	1.70	109	6	9.7	3.1	0.41	1.08
	9.6	5.35	126	8	0.9	2.6	0.33	1.24
IV	6.6	4.75	121	9	6.7	2.8	0.36	1.14
	10.5	2.91	133	10	0.62	1.9	0.32	1.26

Comp.

T

Π

III

IV

pН

5.2

10.5

6.3

7.5

6.6

9.6

6.6

10.5

Values of diffusion coefficient (D) determined via different methods (Table 3), indicate a good agreement between the values of D estimated via these methods. As a result of the disappearing of the anodic peak coupled with the cathodic one of the investigated compounds the heterogeneous rate constant $(k_{\rm fb})$ of the irreversible electrode reaction can be calculated from cyclic voltammetric data using eq. [2] (11). The plot of E_p vs. log v gives the value of the heterogeneous rate constant ($k_{\rm fh}$). Also, from the values of $E_{\rm p} - E_{\rm p/2}$ vs. the dimensionless parameter ψ , the heterogeneous rate constant is estimated. The values of $k_{\rm fh}$ is calculated by performing several simulated cyclic voltammograms with various values of $k_{\rm fh}$. The true value of $k_{\rm fh}$ is established when the values of $i_{\rm p}$, $E_{\rm p}$, and $E_{\rm p} - E_{\rm p/2}$ of the simulated cyclic voltammograms agree well with those values of the experimental one. Values of $k_{\rm fh}$ determined from these methods were reported in Table 4 confirming the agreement and the accuracy of the heterogeneous rate constant estimated via different methods.

Verification of the calculated electrochemical parameters via digital simulation

Digital simulation was used for testing the determined accurate values of the cyclic voltammetry parameters as well as obtaining the true information of the type of electrochemical process of the electrode mechanism. In general the testing of parameters is made by matching the simulated voltammogram on the experimental data, using the average experimentally determined parameters. Also, the accuracy of the electrochemical parameters can be tested via the comparison between the peak characteristics $(i_p, E_p, E_p - E_{p/2})$, of the experimental and theoretical cyclic voltammograms (18, 19). The generated cyclic voltammograms have been carried out using CONDESIM software package (from EG & G).

In this work, the nature of the electrode reaction was determined by running digital simulation for the following types of electrochemical reactions: (i) $E_{irr}C_{irr}$; (ii) $E_{rev}C_{irr}$; (iii) $E_{rev}C_{rev}$; (iv) E_qC_{irr} ; and (v) E_{irr} . The electrochemical parameters used are: (i) diffusion coefficient of the electroactive species (D); (ii) reduction potential (E°) ; (iii) concentration of the electroactive species (C); (iv) heterogeneous rate constant (k_{fh}); (v) scan rate (v); (vi) temperature (T); (vii) forward homogeneous chemical rate constant (k_f), (viii) backward homogeneous chemical rate constant (k_b) ($k_c = k_f + k_b$); and (ix) symmetry coefficient (α).

Figure 2 shows the comparison between the experimental and generated cyclic voltammograms of $E_{irr}C_{irr}$ model with its convolution and deconvolution voltammetry of the first peak of compound I at pH 6.2 and scan rate 0.2 V/s. The value of reduction potential (E°) and the values of k_c for chemical steps which following the slow charge transfer were determined using theoretical treatment and their values at the selected pH values are given in Table 5. The values of the measured peak characteristics and the electrochemical parameters used for generating the voltammograms are listed in Table 5 and confirm the accuracy of calculated parameters from experimental cyclic voltammograms. The slight deviation between the shape of experimental and simulated cyclic

Fig. 2. Matching between experimental (....) and generating (—) voltammograms of *I* (A), its convolution (B) and deconvolution voltammetry of experimental voltammogram (C) at T = 298 K, sweep rate 0.2 V/s, pH 6.2.



Fig. 3. Generating voltammograms of the models $E_{rev}C_{rev}$ (A) and $E_{rev}C_{irr}$ (B) with their convolution voltammetry at sweep rate 0.5 V/s, T = 298 K.



voltammograms (Fig. 2) is attributed to the weak adsorption of the reactant at electrode surface (20, 21). Figure 3 gives an example response of the simulated cyclic voltammogram along with its convolution voltammetry for the systems $E_{rev}C_{rev}$ and $E_{rev}C_{irr}$ at v = 0.5 V/s which indicate a discrepancy between captured CV with these models confirming the validity of the $E_{irr}C_{irr}$ mechanism.

Spectrophotometric determination of the dissociation constants

The spectra of compounds (I, III, and IV) in universal buffer solutions of varying pH values containing 30% (v/v) ethanol are studied within the wavelength range 250-600 nm.

The changes in the absorption spectra on varying the pH of the buffer solution have been used successfully for the de-

termination of the dissociation constant of azomethine group and OH group for the compounds under investigation applying the following methods:

(*i*) The half-height method (22) for which the pK is equal to the pH at half height of the absorbance–pH curve, and can be calculated from the following equation

[7]
$$pK = pH$$
 at $A_{1/2} = (A_{max} - A_{min})/2;$

(ii) limiting absorbency method (23) using the relation

[8]
$$pH = pK + \log\left(\frac{A}{A_{max} - A}\right)$$

Accordingly, a plot of the log $(A/A_{max} - A)$ vs. pH produces a straight line with intercept at log $(A/A_{max} - A) = 0$ equal to pK;

(*iii*) The modified limiting absorbency method (24, 25) in which the pK_a is calculated via the following relation

[9]
$$pH = pK_a + \log \gamma + \log \left(\frac{A - A_{\min}}{A_{\max} - A}\right)$$

where the limiting absorbency A_{\min} and A_{\max} corresponding to the absorbency of the neutral and ionized species liable to exist in the solution of the measuring wavelength and γ is the activity coefficient of the ions which are present in equilibrium. Since in very dilute solution, log $\gamma = 0.0$, then eq. [9] takes the following form

[10]
$$pH = pK_a + \log\left(\frac{A - A_{\min}}{A_{\max} - A}\right)$$

The pK value can be evaluated by plotting log $[(A - A_{\min})/(A_{\max} - A)]$ against pH. Thus, the pK value is that corresponding to the value at log $[(A - A_{\min})/(A_{\max} - A)]$ equals

Scheme 2.



Table 6. pK_a values of the compounds (I, III, and IV) determined from electronic absorption spectra methods.

Comp.	pK_1	p <i>K</i> ₂
Ι	5.2	8.70
III	5.5	9.00
IV	4.5	8.00

to zero. The values of pK obtained from the above three methods are collected in Table 6.

Electrode reaction pathway

The compounds under consideration are characterized by the presence of azomethine group $C=N^+H$. The number of electrons involved in the reduction is found to be two in acidic as well as in alkaline media as confirmed from a controlled potential coulometry experiments in acidic and alkaline media.

IR (KBr optics) studies of the electrolyzed products gave a broad band at \sim 3310 cm⁻¹ (stretching) which represent the presence of a secondary amine group in the products. Also, it was found that the mp of all the electrolyzed products in the range 338–341°C. All this experimental evidence indicates that the electrode process is irreversible and consumed two-electron reduction transferring the initial electroactive species to an inactive secondary amine (CH₂-NH-).

The $E_{1/2}$ -pH plots of the first reduction wave of these compounds give a break at pH 4.5–5.5, whereas the $E_{1/2}$ -pH plots of the second one exhibit a break at pH 8–9, indicating the protonation of the azomethine group and dissociation of the OH group of the reactants at these pH values.

On the other hand, calculation of the pK values of these compounds using spectrophotometric studies indicated the presence of two pK values (Table 6). The equilibria in solution can be represented as follows.

H₃C

CH₃

Based on the above results the mechanism of the electrode reaction of the investigated Schiff base compounds can be represented as follows: (*a*) In acidic and slightly alkaline solutions (pH < 8). Scheme 3.



The electrode reaction mechanism follows the sequence H^+ , e, e, H^+ . (b) In strong alkaline solutions (pH > 8). Scheme 4.



The electrode reaction mechanism follows the sequence e, H^+ , e, H^+ .

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