Electroreduction of some Arylazomethine Hydrazine Glyoxalic Acid Compounds

Y.I. Moharram and M.M. Ghoneim

Chemistry Department, Faculty of Science, Tanta University, Tanta, EGYPT.

Electrochemical behaviour of arylazomethine hydrazine glyoxalic acid compounds are studied using DC polarography , cyclic voltammetry, chronoamperometry and chronopotentiometry. Values of symmetry coefficient (α) and the hetergeneous rate constant (k_s) of the electron transfer are evaluated. Using digital simulation CONDECON software, the halfwave potential ($E_{1/2}$) value is determined by a fitting procedure. Convolution-deconvolution analysis of recorded cyclic voltammetric current data allows the determination of diffusion coefficient (D). The effect of medium and substitutent on the electrode reaction are examined. The reduction follows ECEC mechanism in slightly acidic and neutral media and EC mechanism in alkaline solutions.

In cyclic voltammetric technique, electrochemical information is mostly obtained from the peak potentials and peak current values. The convolution and deconvolution procedures using data at other points from the CV experiments provide excellent criteria for understanding the electrochemical mechanism and parameter determination. The convolution I_1 (eq.1) is a semi-integral of the current i(u) measured at time u, and t is the total time elapsed [1,2]

$$I_1 = \frac{1}{\pi^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}}\, du \quad \ldots \quad (1)$$

The deconvolution of I_1 is simply the differential dI_1/dt.

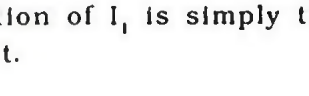
In recent years, there is a considerable interest in the electrochemical reduction of hydrazones and azomethine compounds [3-9]. The present work concerns with the study of the electrochemical behaviour of arylazomethine hydrazine glyoxlic acid compound and some of its derivatives at a mercury cathode.

EXPERIMENTAL

Materials

Arylazomethine hydrazine glyoxalic acid compounds (Compounds I to V) were prepared by the method recommended for hydrazone and Sciff bases. For this purpose, hydrazine glyoxalic acid was

Arylazomethine hydrazine glyoxlic acid compound (I) and some of its derivatives



X=H (I), p-CH_3 (II), p-OCH_3 (III), p-Br (IV), p-Cl (V)

© E.C.S.I. Bangalore

refluxed with the required quantity of the amine derivatives in ethanol. On allowing the reaction mixture to cool, the solid separated out. This was filtered and recrystallized several times from ethanol and preserved in a desiccator over silica gel.

Phosphoric, acetic and boric acids (A.R. Grade) were used to prepare Britton Robinson buffers covering the pH range 2.8-11.5 [10]. A 1:1 sodium hydroxide solution (Vickers Laboratories Limited) was prepared and used for adjustment of pH of the buffer solution. Analar ethanol (99.8%, BDH) was used without any further purification.

Voltammetric Measurements

The polarograms were recorded on a pen recording polarograph (Model 1004 SARGENT-WELCH) using a two electrode (DME-SCE) polarographic cell [11].

A controlled potential coulometry system (Model 373A from EG&G) consists of a potentiostat Model 173. The electrometer probe (Model 178) connects the cell assembly to the front panel of the Model 173 potentiostat. A potentiostat / galvanostat model PAR-362 (from EG&G) was used in the electrochemical measurement to generate the current flowing in the electrochemical cell. The hanging mercury drop assembly (303A electrode assembly from EG&G) consists of HMDE (area = 1.2×10^{-6} m^2) as a working electrode, Ag/AgCl as reference electrode and Pt wire as counter electrode. This was used during the cyclic voltammetry, chronoamperometry and chrono-potentiometry measurements.

The ORION pH-meter Model 201 with sensitivity $\pm$ 0.02 pH units was used for pH measurements.

CONDECON 300, a software marketed by EG&G, was used to determine both electrochemical and chemical parameters of the electrochemical reaction.

RESULTS AND DISCUSSION

DC Polarography

The polarographic reduction of aryl-azomethine hydrazine glyoxalic acids (I to V) is investigated in B.R. buffer solution of pH 4.5-11.90, containing 40% (v/v) ethanol. The compounds do not show any well-defined reduction wave in media of pH < 5.5. Here H_2 evolution preceeds all other reductions. In media of higher pH, the polarogram consists of a single reduction step (Fig.1 shows the polarographic

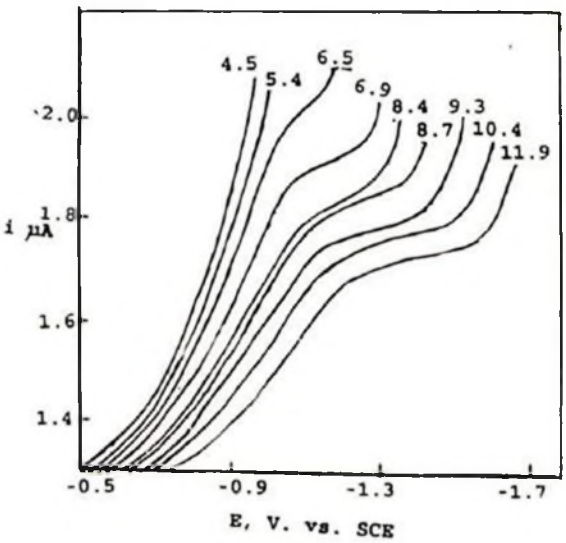


Fig.1. Polarograms for the reduction of I at a mercury drop electrode,
(DME characterstics: m= 1.549 mgs^{-1} & t= 4.5 s at mercury height 60 cm).
Concentration = 1 x 10^{-4} M; T = 17°C.

response of the parent compound and is typical of the compounds). The limiting current decreases gradually at higher pH range (8-10). In strongly alkaline solutions (pH > 10), the limiting current is half of its height in lower pH. The number of electrons transfered in the electro-reduction in neutral / slightly acidic solutions is 4 (controlled potential electrolysis experiments - Table 1). The TLC of the etherial extract of the completely electrolysed solution shows acetohydrazine as one of the main products indicating a cleavage of -C=N- bond (uptake of 4 electrons). At pH > 10, only two electrons are consumed in the electron transfer process.

Table 1

Controlled Potential Electrolysis Data for the Arylazomethine Compounds

Media 40 % ethanol; T = 17°

pH	Reduced at	n
Compound I (H)		
6.8	-1.35 V	3.92 4
11.40	-1.60 V	1.98 2
Compound II (p-OCH_3)		
7.01	-1.40 V	3.84 4
11.4	-1.60 V	1.89 2
Compound IV (p-Cl)		
6.80	-1.40 V	3.72 4
11.4	-1.55 V	1.87 2

The plots of log i_l *vs* log h (i_l = limiting diffusion current and h = mercury height) at different pH values give straight lines. The slope values (in the range 0.44-0.68) indicate the effect of chemical and adsorption components in the electron transfer reaction. Logarithmic analysis of polarographic currents [11] indicates higher slope value showing that the electron transfer rates are slow. Values of symmetry coefficient (α) can be determined assuming the probable values of n_a as one or two. The value of α calculated using $n_a = 2$ appears to be in the correct range at all pH values (Table 2). So, the number of electrons involved in the rate-determining step (n_a) at all pH values is taken as two. The polarographic half-wave potential ($E_{1/2}$) shifts to more negative values with increasing pH of the medium. This indicates the involvement of protons in the rate-determining step and the proton transfer precedes the electron transfer process.

Table 2

Values of (α) and (α n_a) of the Azomethine compounds

calculated from the Reciprocal slopes (S) of log $i/(i_l - i)$ *vs* E plots; Slope (S) = 0.059 /α n_a

Conc. 1×10^{-4}M; Medium 40% ethanol; T = 20°C;

pH	Slope, mV	α n_a	α $n_a = 1$	α $n_a = 2$
Compund I(H)				
6.85	96	0.616	0.616	0.308
8.42	89	0.664	0.664	0.332
10.63	91	0.650	0.650	0.325
Compound (II) (p-OCH_3)				
6.90	92	0.640	0.640	0.320
8.70	94	0.628	0.628	0.314
10.35	109	0.542	0.542	0.271
Compound (III) (p-Br)				
6.75	100	0.591	0.591	0.296
8.60	100	0.591	0.591	0.296
9.90	109	0.542	0.542	0.270

Direct comparison of experimental with simulated cyclic voltammograms

Cyclic voltammetric experiments were carried out at 17°C in 40% ethanol solution containing $1x10^{-4}$ depolariser. The data was captured on floppy discs using the CONDECON system, to study the nature of electron transfer process, substitutent effects and to evaluate electrochemical parameters. Cyclic voltammogram of the parent compound (Fig.2) is typical of all the compounds; fig 2A shows two unidirectional voltammetric peaks at different sweep rates ranging from 50 to 500 mV/s at pH = 7.7. The electron transfer process is totally irreversible, probably because of a very rapid chemical reaction involving the product of the electrode reaction (EC_{irrev} mechanism).

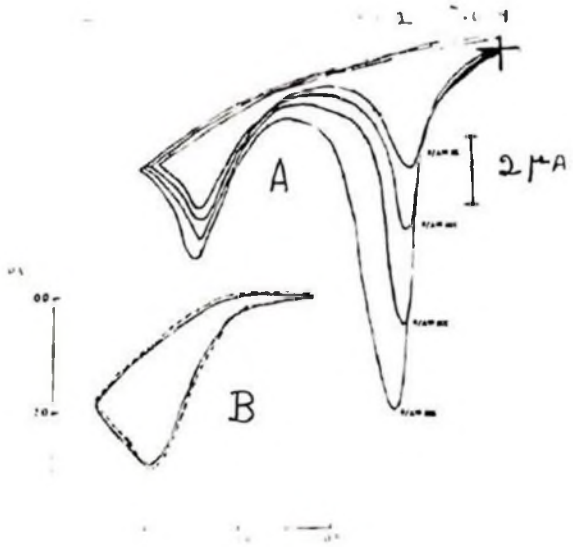


Fig.2. Cyclic Voltammograms for the parent compound. at HMDE
Concentration = 1 x 10^{-4} M; T = 17°C.
(A) Both the peaks at scan rates 50 - 500 mV/s; pH = 7
(B) Voltammogram for the first reduction wave only
pH = 8.1; Scan rate 100 mV/s:
Dashed curve is theoretical
sweep rate 100 mV/s, pH = 8.1

Fig.2B shows the cyclic voltammetric response of the first reduction step of arylazomethine hydrazine glyoxalic acid at HMDE in buffer solutions of pH = 8.1 at a sweep rate of 100 mV/s. It also displays a digitally simulated curve for EC_{irrev} system superimposed on this. The fit between experimental and simulated voltammograms is very sensitive to the values of α (symmetry coefficient) since it affects the shape and the magnitude of the theoretical current potential curves. Values of symmetry coefficients calculated from reciprocal slope were used in the curve fitting procedure.

Values of symmetry coefficients are calculated from the breadth of the cyclic voltammetric response ($E_p - E_{p/2}$), for the first voltammetric peak using the following equation for irreversible system [12]:

$$E_p - E_{p/2} = (0.048/\alpha n_a)\ \text{mV at } 25^\circ \quad \ldots (2)$$

For the first voltammetric peak, values of heterogeneous rate constant k_s of electron transfer of the depolarizers under consideration are evaluated using equation:

$$E_p = E^\circ - 1.14\ \frac{RT}{\alpha n_a F} + \frac{RT}{\alpha n_a F} \ln \frac{k_s}{D_A^{1/2}} - \frac{RT}{2\alpha n_a F} \ln \alpha n_a v \quad \ldots\ldots (3)$$

The results are recorded in Table 3

It seems that the higher the pH value, the lower is the value of k_s. This probably indicates that the reaction becomes more sluggish with increase in pH value.

Table 3

The Electrochemical Parameters

Extracted from Cyclic Voltammetry at Scan rate 100 mV/Sec (CV), Digital Simulation (DS), Chronopotentiometry (CP) and Chronocoulometry (CC)

Method	k_s m/s	I_{lim} $\mu A/s^{1/2}$	Dx10 m^2/s	α	$E_{1/2}$
Compound I					
pH = 6.8					
CV	3.02×10^{-8}	3.57	1.25	0.52	
DS	3.00×10^{-8}	—	1.24	0.54	0.21
CP			1.19		
CC			1.21		
pH = 10.5					
CV	7.62×10^{-12}	3.52	1.23	0.52	
DS	7.60×10^{-12}	-	1.18	0.54	0.26
CP			1.19		
CC			1.24		
Compound III					
pH = 6.9					
CV	4.23×10^{-8}	3.41	0.93	0.52	
DS	4.20×10^{-8}		0.91	0.53	0.27
CP			0.92		
CC			0.95		
pH = 10.2					
CV	5.62×10^{-11}	3.39	0.89	0.53	
DS	5.60×10^{-11}		0.89	0.50	0.33
CP			0.94		
CC			0.92		
Compound IV					
pH = 6.7					
CV	4.55×10^{-8}	3.49	1.01	0.51	0.25
DS	4.50×10^{-8}		1.06	0.52	
CP			0.99		
CC			1.02		
pH = 9.85					
CV	8.75×10^{-11}	3.47	0.91	0.55	
DS	8.70×10^{-11}		0.89	0.56	0.31
CP			0.94		
CC			0.95		

It appears that the simulated EC_{irrev}[13] results of the first reduction wave of compound I and some of its derivatives are similar to the experimental ones. The kinetic and thermodynamic parameters of the compounds in question were obtained by fitting the experimental CV curves with theoretical ones generated by variation of parameters. One might doubt if the reported values represent a unique solution or simply they are one of a family of solutions. However the following points clarify the position.

Assuming an equality of the diffusion coefficients of electrochemical species and knowing values of k_s and α obtained from experimental current-potential curves, the voltammograms at a hanging mercury drop electrode were simulated at different values of ($E_{1/2}$), until an acceptable fit was obtained for the electrochemical data. These assumed ($E_{1/2}$) values were used to simulate the theoretical CV data. This confirms that the ($E_{1/2}$) values are correct (Table 3). The slight deviation of the shape of experimental voltammograms from the simulated ones (Fig.2B) indicates that adsorption of either the reactant or the product [14] slightly affects electron transfer kinetics.

Convolution and Deconvolution Treatments

All data captured for the compounds I to V show the same response toward quantitative analysis using the convolution and deconvolution procedures [15-18].

The convoluted current (I_t) (calculated for the current given in Fig.2B) is shown in Fig.3. It is observed from the convoluted data (graph in fig 3) that I_t does not return to zero in the reverse half of the sweep. In

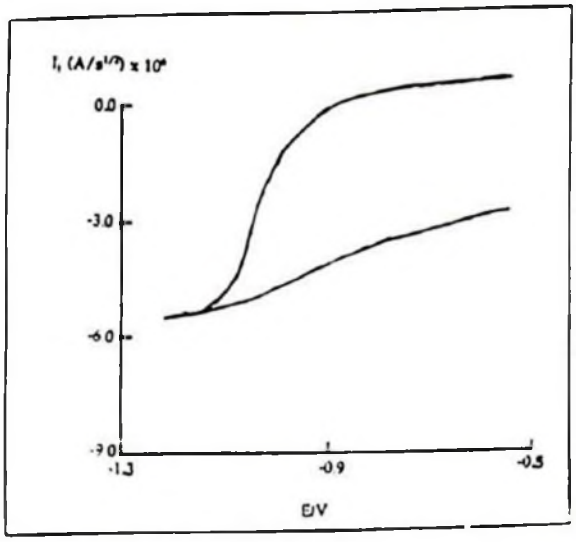


Fig.3. Connvoluted current for the first reduction wave of I
sweep rate of 100 mV/s; pH = 8.1; concentration = 1 x 10^{-3}; T = 17°C.

case of EC behaviour [13], the diffusional fields of both reactant and electrochemical product are affected by the chemical reaction. This in turn results in a relative lowering of their concentrations, when the electrode returns to the starting potential. The latter is directly related to the failure of I_l to return to 0 after the wave. So the non return to zero of i_l, indicates a following chemical reaction [13]. The clear gap in I_l between the sweep halves (for all the azomethine compounds under investigation) supports the slow electron transfer nature of the electrode reaction. Under diffusion controlled conditions [19], $[A]_{(0,t)} = 0$, (where $[A]_{(0,t)}$ is the concentration of the electroactive reactant species A at the electrode surface), the maximum convoluted current can be expressed as [20]:

$$I_{lim}^{\Lambda} = n\ F\ a\ D_A^{1/2}[A]^* \qquad \ldots (4)$$

where I_{lim}^{Λ} is the limiting convoluted current in A/s$^{1/2}$, n is the number of electrons involved in the electron transfer process, $[A]^*$ is the concentration of electroactive species A in the bulk solution, F is Faraday's constant, "a" is the electrode area and D_A is the diffusion coefficient of the depolarizer species "A". Assuming that diffusion coefficients of electrochemical species is equal to the diffusion coefficient of the compounds under consideration, D_A was evaluated (Table 3) using equation 4.

Semidifferentiation of EC_{irrev} voltammetric data (dI_l/dt) shows voltammograms of unequal heights (Fig.4) for all the compounds under investigations. The backward peak is much broader than forward peak. The deconvolutions dI_l/dt are now well displayed on either side of the half wave potential. The values of half-peak width (the width of the peak at half of its height), $W_{1/2}$, are 123 and 267 mV at sweep rates of 0.05 and 1 V/s, respectively in solution of pH = 8.1. These differ from the value for reversible one electron transfer

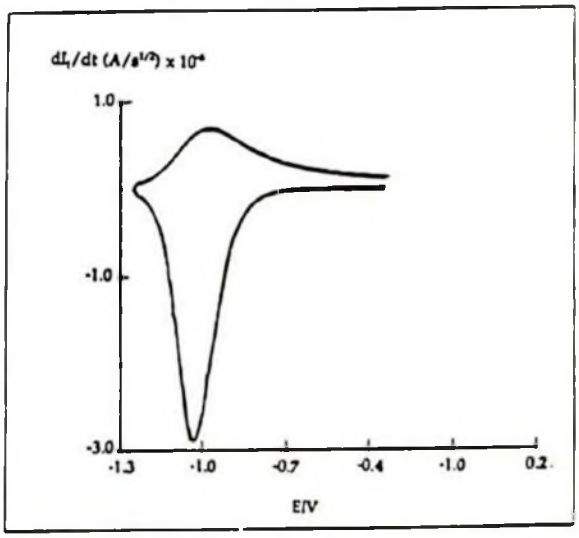


Fig.4. Deconvoluted current for the first reduction wave of I-A
sweep rate = 100 mV/s, pH = 8.1, concentration = 1 x 10^{-4} & T = 17°C.

(88.09 mV at 17°C) [19]. These results mean that the electron transfer process is slow and confirm that the system is EC_{irrev} [13].

Chronoamperometry, Chronocoulometry and Chronopotentiometry

Chronoamperometric experiments are performed under conditions similar to cyclic voltammetry. Current/time capture and subsequent treatment, are provided by the CONDECON software package. The duration of polarization was 0.355 s.

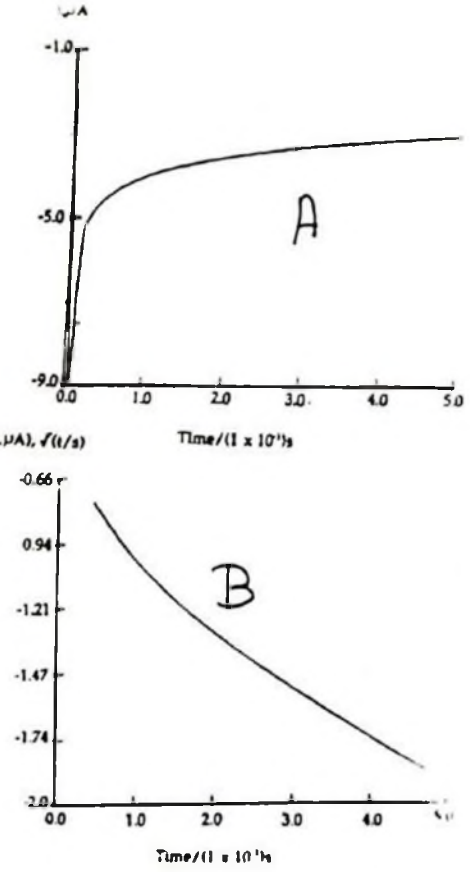


Fig.5.Chronoamperogram for the first reduction wave of I
pH = 7.5, concentration = 1 x 10^{-4} & T = 17°C.
(A) chronopotentiogram trace; (B) Cottrel plot

Fig.5A, shows the profile of the captured data at overpotentials more negative than the corresponding cyclic voltammetric peak potential. The slow rise in current is due to a slight excess of damping. The plot of $i.t^{1/2}$ *vs* t (Fig.5B) show that Cottrell relationship [18] is not obeyed.

The diffusion coefficients are evaluated from chronocoulometric data in a given solution of electroactive reactant using the following equation [18].

$$Q = [2\ n\ F\ a\ [A]^*\ D_A^{1/2}\ t^{1/2}] / \pi^{1/2} \quad \ldots \quad (5)$$

Fig.6, shows chronopotentiogram for the parent azomethine compound under conditions similar to cyclic voltammetry. The chronopotentiometric technique has been used to measure the diffusion coefficient values using the Sand equation [20].

$$D_A^{1/2} = I_{lim}^{A} / [n\ F\ a\ [A]^*]$$

$$= 2\ i_c(t_s/\pi)^{1/2} \quad \ldots \quad (6)$$

The D_A values obtained from different techniques (Table 3) are in good agreement.

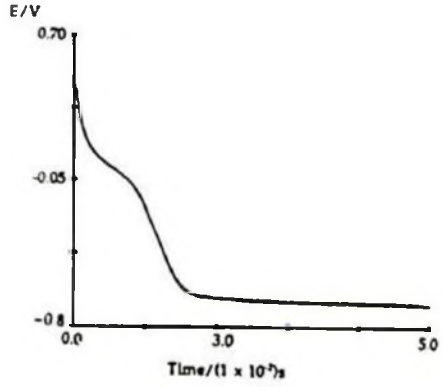
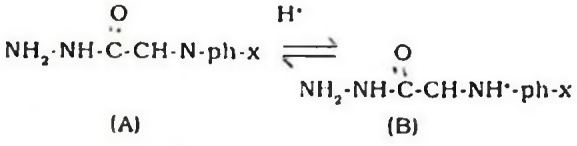


Fig.6. Chronopotentiogram for the reduction wave of I-A.
pH = 7.5, conc = 1 x 10^{-4}M & T = 17°C.

Electrochemical Reaction Mechanism

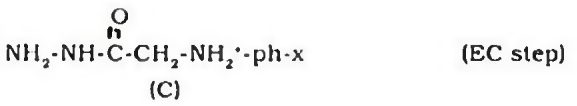
On the basis of the above results, the following scheme, can be written for the electroreduction of the azomethine centre in the compounds:

In neutral and slightly acidic solutions



(A) (B)

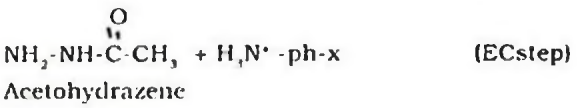




(EC step)

(C)



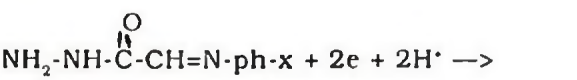


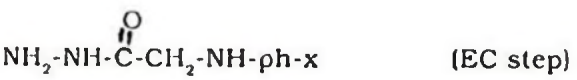
(ECstep)

Acetohydrazene

In acidic media the first step is a fast protonation - deprotonation equilibrium coupled with an ECEC process; the electron trnasfer rate is slow; this is coupled with a following rapid chemical reaction.

In strongly alkaline solutions





(EC step)

In alkaline solutions, the electrochemical reduction follows the EC reaction. The slow electron transfer is followed by rapid chemical reaction.

Structural Effects

The polarographic $E_{1/2}$'s as a function of the Hammett substituent constant (σ_x) are linear for the azo compounds under investigation at two pH values (7.1 and 10.3) with slope values ($\rho_{s.R}$) being +0.12 to + 0.14 V. This indicates that the electroreduction process of the -C=N- group corresponds to nucleophilic attack in the potential-determining step. Plots of the peak potential E_p's (scan rate of CV = 200 mV/s) as a function of the Hammett substituent constant (σ_x) for the compounds under consideration at different pH values (7.5 and 10.5) are also linear with slope ranging from 0.12 to 0.16. This indicates that the reduction of -C=N- group corresponds to nuelophlic attack at the potential determing step and effect of the substituents on the reaction centre is mainly inductive [21].

REFERENCES

1. K.S. Oldham. *Anal. Chem.*, **44** (1972) 196, 1121.
2. J.C. Imbeaux, and J.M. Saveant. *J.Electroanal. Chem.*, **44** (1973) 169.
3. R.N. Goyal and R. Jain. *J.Electroanal Chem.*, **84** (1977) 141.
4. R.N. Goyal, R. Bhushan and Agarwal. *J.Electroanal. Chem.*, **174** (1979) 281.
5. W.U. Malik and P.N. Dua. *Indian J. Chem.*, **21(A)** (1982) 114.
6. R. Jain, J. *Indian Chem. Soc.*, **Vol. LX** (1983) 936.

7. C. Olmedo, L. Deban, D. Vazquez, R. Pardo and S. Palmera, *Electroanalysis*, **6(8)** (1994) 694.

8. M.A. Ahlam, A.M. Morsi and H.M. Elnagdi, *Collect. Czech. Chem. Commun.*, **59(8)** (1994) 1572.

9. N. Harsha, D. Prajapati and S. Jagir, *J. Chem. Res., Synop* **6** (1994) 228.

10. H.T.S. Britton, *Hydrogen ions*, (4th ed). **Chapman and Hall, London,** (1952) 388.

11. L. Meites, *Polarographic Techniques*, **Interscience, New York,** (1965) 240.

12. A.J. Bard and L.R. Faulkner, *Electrochemical Methods - Fundamentals and Applications*, **John Wiely and Sons. New York** (1980).

13. J.M. Saveant and D. Tessier, *J. Phys. Chem.*, **82** (1975) 1723.

14. R.S. Lawton and A.M. Yacynch, *Anal. Chem.*, **53** (1981) 1523.

15. C.P. Andrieux and J.M. Saveant, *J.Electroanal. Chem.*, **26** (1970) 147.

16. J.C. Imbeaux and J.M. Saveant, *J.Electroanal. Chem.*, **63** (1975) 429.

17. J. Leddy and A.J. Bard, *J.Electroanal. Chem.*, **189** (1985) 203.

18. F.G. Cottrell, *Z. Physik. Chem.*, **42** (1902) 385.

19. Y.I. Moharram, *Ph.D. Thesis*, **Tanta University** (1991).

20. H.J. Sand, *Phil- Mag.* **1** (1902) 45.

21. L.P. Hammett, *Chem. Rev.*, **17** (1935) 125.