Journal of Chemical Technology and Metallurgy, 49, 4, 2014, 329-344

ELECTROCHEMICAL STUDIES OF CERTAIN ARYLAZO IMIDAZOLES

M. Sreedevi[1], A. Raghavendra Guru Prasad[2], Y.N. Spoorthy[1], L.K. Ravindranath[1]

[1]*Sri Kirshnadevaraya University,*
Anantapur, A.P., India.
E- mail: guruprasadar@yahoo.co.in
[2]*ICFAI Foundation for Higher Education,*
Hyderabad, A.P., India

Received 02 September 2013
Accepted 15 March 2014

ABSTRACT

The present investigation describes the polarographic and cyclic voltammetric behavior of certain novel (2-methyl-5-nitro-4-substituted phenyl azo-imidazol-1-y1)-acetic acid benzylidene-hydrazides. The polarographic behavior was studied at a hanging mercury drop electrode (HMDE). The cyclic voltammetric behavior was studied at a HMDE and a modified carbon paste electrode (MCPE). The electrochemical process was found to be irreversible and diffusion controlled in nature. Based on the results obtained, the reduction mechanism in an acidic as well as in a basic medium was proposed. The results from polarography and cyclicvoltammetry were compared to ascertain the findings and conclusions.

Keywords: benzene azo imidazoles, polarography, cyclicvoltammetry, HMDE, MCPE, reduction mechanism.

INTRODUCTION

Imidazole is a five membered, hetero cyclic ring containing two nitrogen atoms and two double bonds. Due to its immense pharmaceutical importance, the imidazole moiety has been extensively used in drug design. Imidazole derivatives have a wide range of pharmacological activity. Literature survey revealed that imidazole and its derivatives were reported to exhibit cardiovascular activity [1], anti-inflammatory activity [2], antimicrobial activity [3, 4], enzyme inhibition activity [5], anticovasculant activity [6] and was used in the treatment of hypertension [7, 8].

The study of electrochemical behavior is useful to understand the metabolism of the drug, as it allows the identification of metabolites with even short half-lives and which is not possible in conventional in vivo or in vitro methods [9]. Moreover, it is well established that the pharmacological properties and the structure-activity relationships of many drugs [10 - 12] are related to the electrochemical behavior of compounds. In view of the versatile medicinal applications of imidazole moiety, herein we report the synthesis and the electrochemical studies of imidazole containing compounds, in particular, the article presents a systematic and detailed investigation of the electro chemical reduction of (2-methyl-5-nitro-4-substituted phenyl azo-imidazol-1-yl)-acetic acid benzylidene-hydrazides.

EXPERIMENTAL

A CL-25 Pen Recording Polarograph manufactured by ELICO Private Limited, Hyderabad, India, was used for the polarographic studies. The cyclic voltammeter used consists of an X-Y recorder (Model RE0074), a PAR 175 Potentiostat and a PAR 175 universal programmer. The pH measurements were made with a pH meter model LI – 10 manufactured by ELICO Private Limited, Hyderabad, India.

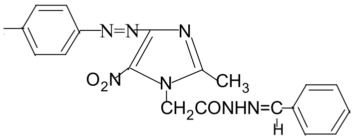
The title compounds (a-f) were synthesized by a procedure described in the literature [13].

Polarographic / Cyclic voltammetric procedure

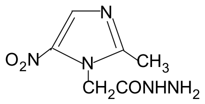
8.0 mL of the buffer solution with the desired pH (1.1 - 10.1), 2 mL of the stock solution of the substrate solution (1.0×10^{-2} M) in dimethylformamide, 6 mL of dimethylformamide and 4.0 mL of distilled water were mixed thoroughly. The polarograms/voltammograms were recorded after removing the dissolved oxygen by passing pure and dry nitrogen gas through the solution for about fifteen minutes.

RESULTS AND DISCUSSION

Polarographic behavior of (2-methyl-5-nitro-4-substituted phenyl azo-imidazol-1-y1)-acetic acid benzylidene-hydrazides (a - f)



(2-methyl-5-nitro-4-substituted phenyl cazo-imidazol-1-y1)-acetic acid benzylidene-hydrazide



2-methyl-5-nitro-imidazole-1-acetic acid hydrazide (A)

Literature survey [14 - 17] revealed that not many benzene azo imidazoles were studied for their electrochemical behavior. The polarographic investigation was carried out on (2-methyl-5-nitro-4 substituted phenyl azo imidazol-1-yl)-acetic acid benzylidene-hydrazides (a-f) in buffer solutions of pH 1.1 - 10.1. The compounds under investigation exhibit three waves in the acidic solutions of pH 1.1 - 6.1 and four waves in basic solutions of pH 8.1 - 10.1. An inspection of the structure of the compounds a-f showed that the sites susceptible for the reduction at dropping mercury electrode are the cyclic and exocyclic azomethine (>C=N-), exocyclic amide, exocyclic azo group (N=N) and exocyclic nitro group ($-NO_2$). It is well known that exocyclic azo, azomethine and nitro groups are more susceptible for reduction than the other groups. The reduction of the cyclic azomethine (>C=N-) and exocyclic amide (-CO-NH) at a dropping mercury electrode generally occurs at higher negative potentials. The polarographic behavior of 2-methyl-5-nitro-imidazole-1-acetic acid hydrazide (A), studied under similar experimental conditions revealed that the compound exhibits a well defined single reduction wave in the pH range 1.1 - 10.1. The position of the wave on the potential axis and the comparison with the reduction of nitro benzene revealed that the wave noticed for compound A was due to:

- six electron reduction of NO_2 to NH_2 in the solutions of pH = 1.1 - 6.1;

Table 1. Details of compounds synthesized.

Compound	**a**	**b**	**c**	**d**	**e**	**f**
R	-H	$-CH_3$	$-OCH_3$	-OH	$-OC_2H_5$	-Cl

Table 2. Effect of pH on – $E_{½}$ and limiting current; Medium: Aqueous dimethylformamide (40 % v/v); [Substrate] : 1×10^{-3}M.

pH	Nitro Benzene		Compound A	
	$-E_{½}$ vs SCE	Limiting Current (μA)	$-E_{½}$ vs SCE	Limiting Current (μA)
2.1	0.25	7.0	0.38	6.8
3.1	0.37	7.0	0.46	6.4
4.1	0.49	6.3	0.52	6.0
5.1	0.58	6.0	0.60	5.6
6.1	0.69	5.7	0.68	5.0
7.1	0.76	5.4	0.73	4.6
8.1	0.85	4.7	0.81	4.4
9.1	0.85	4.7	0.81	4.4
10.1	0.85	4.7	0.81	4.4

Table 3. Millicoulometric data of (2-methyl-5-nitro-imidazol-1-yl)-acetic acid hydrazide (A); [Substrate] = (0.8×10^{-4}M); Medium: Aqueous dimethylformamide (40 % v/v).

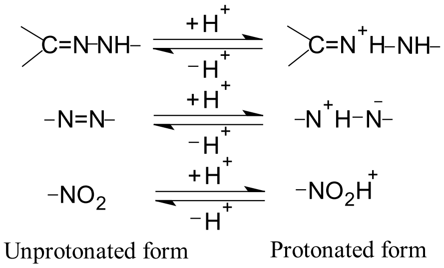
pH	Current, μA	Time, s	n-value
4.1	6.0	0	-
	5.5	7200	5.7
	5.3	10800	6.0
8.1	4.4	0	-
	4.0	7200	3.8
	3.8	10800	3.7

- four electron reduction of NO_2 to NHOH in the solutions of pH = 8.1 - 10.1;
- millicoulometric data carried out for compound A supports above observations.

The data pertaining to compound A presented in Tables 2 and 3, reveals that the reduction observed in the present investigations, is attributed to the reduction of the exocyclic nitro group. The reduction of cyclic azomethine, exocyclic amide was not observed under the chosen experimental conditions, because these groups reduce at higher negative potentials at a dropping mercury electrode. The results presented in Table 2 and 3, and their comparison with that of compounds a-f, suggest that the three reduction waves noticed for compounds a-f, are due to the reduction of the exocyclic azo group, nitro group and azomethine group.

The results in Table 4 show that the half wave potentials of the compounds under study (a-f), increase with the increase in pH in the acidic pH range, but remain unaltered in the alkaline pH range. The graph drawn between the half wave potential and pH (Fig. 1) is linear up to pH 8.1 and remains constant in solutions of higher pH. The slope of the plot E½ vs pH lies between 50 - 90 mV for all waves. The increase in half wave potentials with the increase in pH, is indicative of the participation of protons in the reduction process. The P values (number of protons) are low and non integers (Table 4). The proton transfer is a heterogeneous process [18] and the protonation of the substrate is taking place on the surface of the electrode. The shift in half wave potentials with increase of the solution pH can therefore be ascribed to the following reasons:

- Both the protonated and unprotonated forms of the depolarizer are electroactive. There is an equilibrium between the protonated form and the unprotonated form [18]. The unprotonated form is reduced at more negative potentials than protonated form [18].



- The pH dependence of the half wave potential was not only due to the antecedent acid-base chemical reaction, but was also due to the consumption of protons in the reduction process [18].
- The pH of the solution in the bulk was different from the pH at the electrode surface. In the presence of electric field, the inequality $D(P^H_S) < D(P^H_B)$ was observed.

As the equilibrium shifts towards the unprotonated form, the respective $E_{½}$ values remain constant. It is seen from Fig. 1 that the $E_{½}$ is practically constant in the alkaline pH range and is due to the fact that both the acidic and the basic forms of the depolarizer were electroactive. But in the pH range where the protonation rate decreases, the half wave potentials of both the protonated form (acidic) and the unprotonated form (basic) are so close to each other that the waves merge [19] and a single wave is observed. The – $E_{½}$ - pH relation is indicated by the following equations:

First wave

$-E_{½} = 0.10 + 0.09\ p^H$ V vs SCE for (a)
$-E_{½} = 0.12 + 0.08\ p^H$ V vs SCE for (b)
$-E_{½} = 0.18 + 0.08\ p^H$ V vs SCE for (c)
$-E_{½} = 0.22 + 0.08\ p^H$ V vs SCE for (d)
$-E_{½} = 0.16 + 0.08\ p^H$ V vs SCE for (e)
$-E_{½} = 0.08 + 0.05\ p^H$ V vs SCE for (f)

Second wave

–E½ = 0.28 + 0.05 p^H V vs SCE for (a)
–E½ = 0.26 + 0.08 p^H V vs SCE for (b)
–E½ = 0.26 + 0.08 p^H V vs SCE for (c)
–E½ = 0.28 + 0.07 p^H V vs SCE for (d)
–E½ = 0.25 + 0.07 p^H V vs SCE for (e)
–E½ = 0.24 + 0.08 p^H V vs SCE for (f)

Third wave

–E½ = 0.53 + 0.07 p^H V vs SCE for (a)
–E½ = 0.50 + 0.06 p^H V vs SCE for (b)
–E½ = 0.50 + 0.07 p^H V vs SCE for (c)
–E½ = 0.54 + 0.05 p^H V vs SCE for (d)
–E½ = 0.49 + 0.07 p^H V vs SCE for (e)
–E½ = 0.52 + 0.06 p^H V vs SCE for (f)

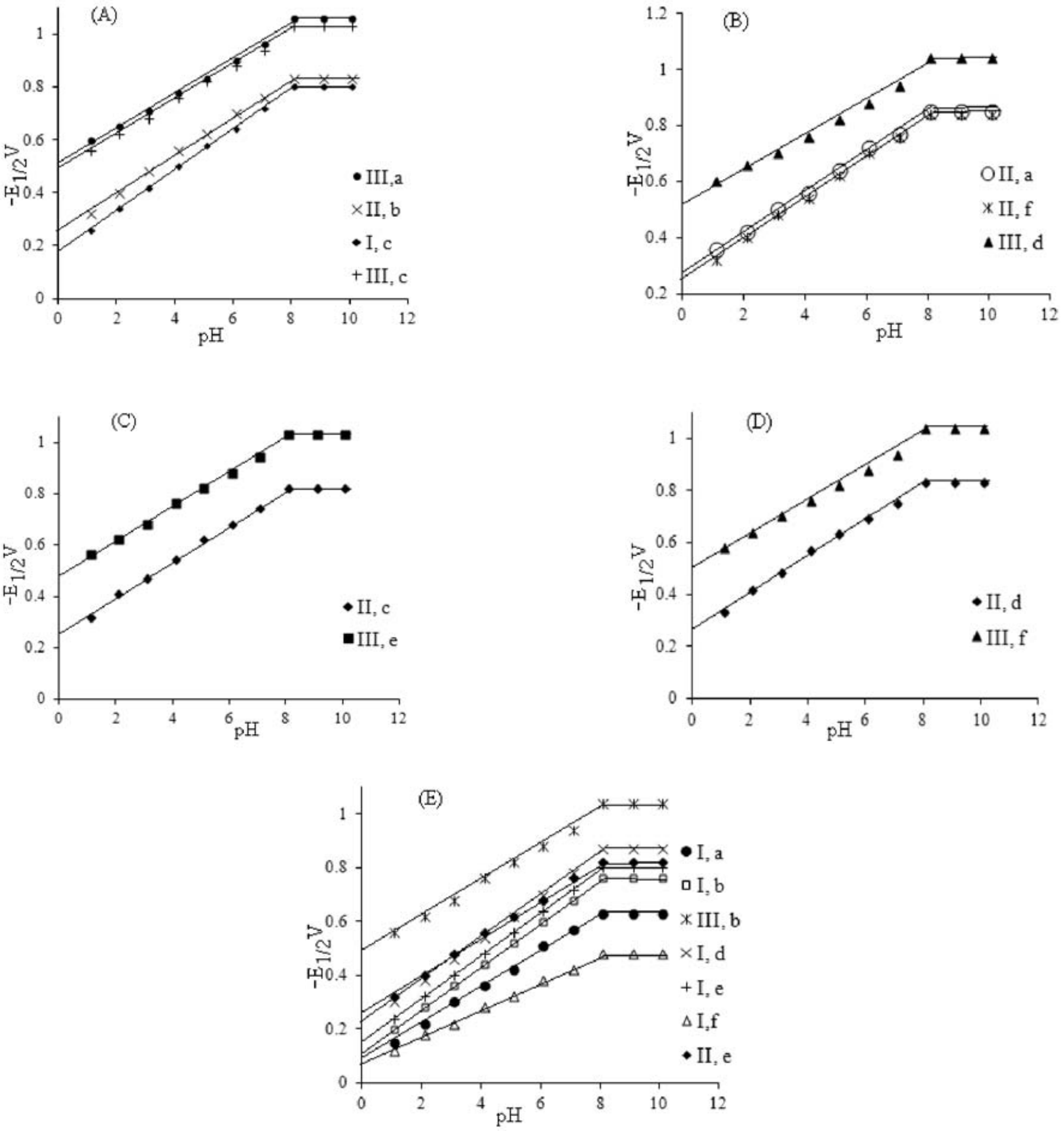


Fig. 1. (A-E). Plot of pH vs. - $E_{1/2}$. [Substrate] = 1×10^{-3} M; Medium = Dimethylformamide (40 % v/v); I indicate first wave, II - the second wave and III - the third wave.

The i_L vs $h^{½}$ plots were linear and passing through the origin (Fig. 2) indicating a diffusion controlled nature of the polarographic wave. The i_L vs concentration graphs were linear as shown in the Fig. 3 and were passing through the origin. The constancy of the $i_l/_C$ values confirms the diffusion controlled nature of the wave.

It is observed from the Table 4 that there is no significant change in the limiting current of the first wave with pH. This suggests that both the protonated form (acidic) and the unprotonated form (basic) are active

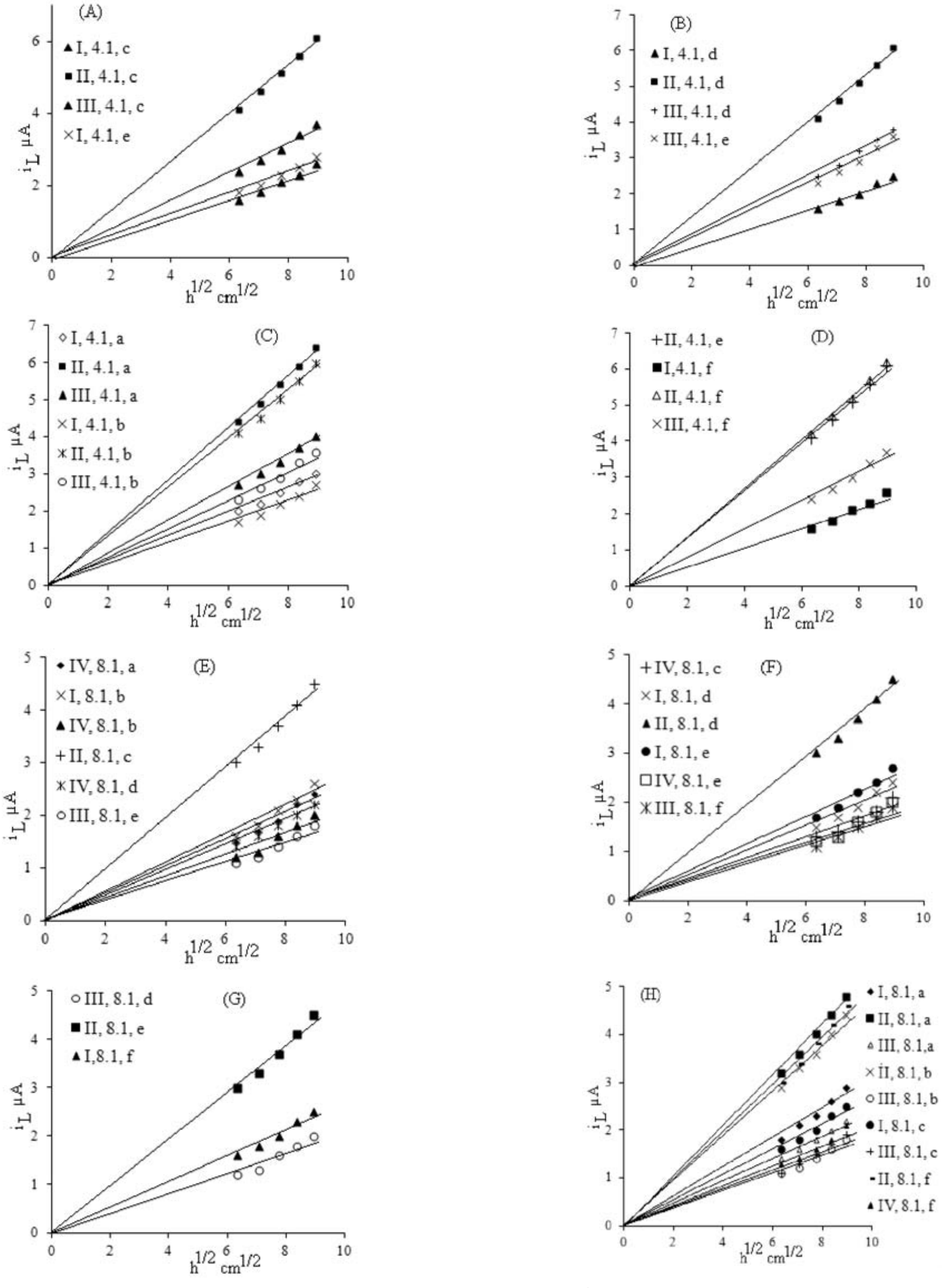


Fig. 2. (A-H). Effect of concentration on wave height. [Substrate] = 1 × 10^{-3} M; Medium = Dimethylformamide (40 % v/v); I indicate first wave, II the second wave, III the third wave and IV the fourth wave; 4.1 and 8.1 indicate the respective pH.

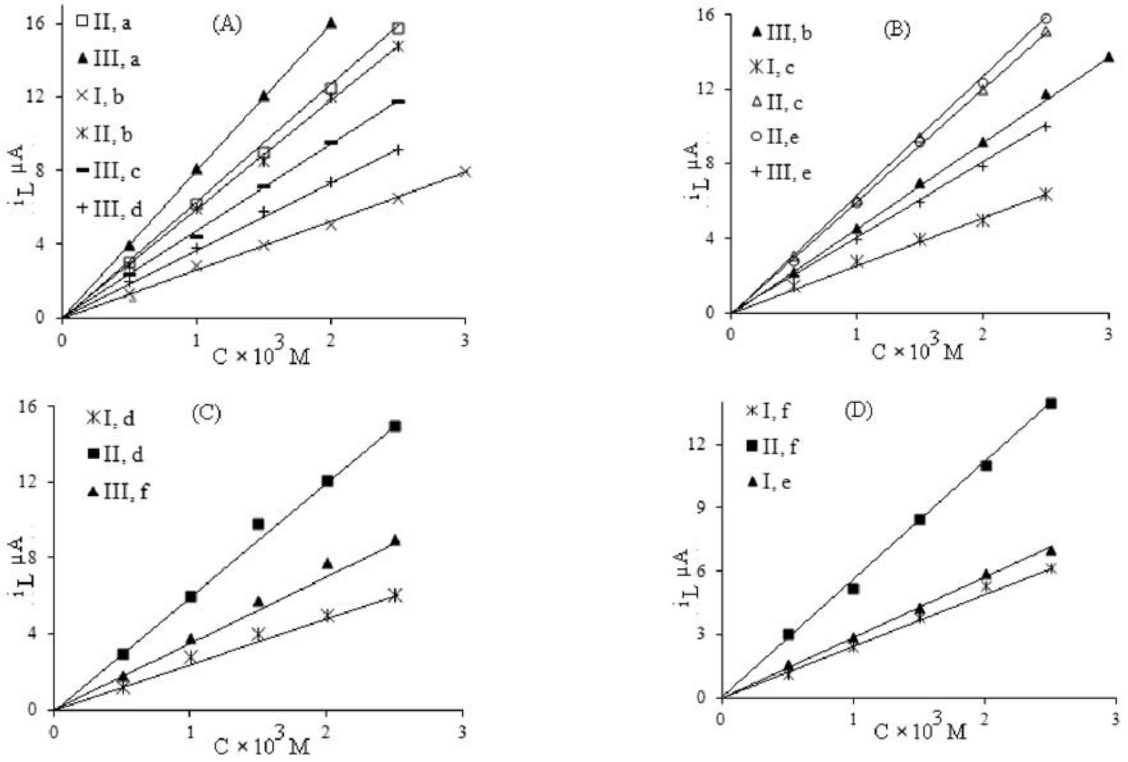


Fig. 3. (A-D). Effect of concentration on wave height. [Substrate] = 1 × 10^{-3} M; Medium = Dimethylformamide (40 % v/v); pH= 4.1; I indicate first wave, II the second wave and III the third wave.

and are transported to the electrode surface.

$$-NO_2H^+ \rightleftharpoons -NO_2 + H^+$$

Acidic active form Basic active form

The decrease in the limiting current of the second wave with increase in pH may be attributed to the difference in the number of electrons involved in the reduction of the nitro group in acidic and alkaline solutions.

$$-NO_2 + 6e^- \xrightarrow{6H^+} -NH_2 + 2H_2O \quad \text{(Acidic solutions)}$$

$$-NO_2 + 4e^- \xrightarrow{2H_2O} -NHOH + H_2O \quad \text{(Basic solutions)}$$

The change in the limiting current is attributed to the acid-base equilibrium, which results in the formation of the acidic form from the basic form or vice-versa. The limiting current remains pH independent as long as the formation of acid form from the basic form is fast enough. As the pH increases, the rate of formation of the protonated form decreases, thus the limiting current also decreases. This type of behavior was observed for the electroreduction of substituted benzene azo pyrazolin-5-ones [15] and other substituted arylazo compounds [17, 25].

The number of electrons involved in the reduction process was evaluated by millicoulometric studies [26]. The number of electrons involved in the first, second and third waves were found to be 2, 6 and 4, respectively, in a Briton-Robinson buffer solution of pH 4.1 containing 40 % (v/v) dimethyl formamide.

Nature of electrode process

The influence of concentration and mercury column height on the limiting current confirmed the diffusion controlled nature of the process.

The electrode process was found to be irreversible unlike the reversible electrode process observed for simple azo and azomethine compounds, under comparable conditions [20]. The irreversible nature of the process observed in the present investigation was further confirmed by:

- the slopes of the semi logarithmic plots (0.17 - 0.22) of the three waves were not the same as those for reversible reduction [21];
- $E_{1/2}$ shifts towards more negative potentials with increase in the depolarizer concentration [22];
- the heterogeneous rate constant ($K^O_{f,h}$), calculated

Table 4. Polarographic characteristics and kinetic parameters of arylazo imidazoles (1×10^{-3} M) at pH 4.1; Medium: Aqueous dimethyl formamide (40 % v/v).

pH	$\Delta E_{1/2}$ (mV)			$\propto n_a$			Number of protons (p)			$D \times 10^6$ $cm^2 Sec^{-1}$			$I \times 10^{-3}$			$K^0_{f,h}$			ΔG^* K cal mole^{-1}		
	I wave	II wave	III wave	I wave	II wave	III wave	I wave	II wave	III wave	I wave	II wave	III wave	I wave	II wave	III wave	I wave	II wave	III wave	I wave	II wave	III wave
(2–Methyl–5–nitro–4–phenylazo–imidazol–1–yl)–aceticacid benzylidene–hydrazide																					
2.1	0.09	0.05	0.07	0.45	0.52	0.38	0.68	0.44	0.45	2.14	1.21	1.21	1.78	4	2.67	4.31×10^{-4}	1.26×10^{-5}	0.24×10^{-6}	2.238	2.642	3.095
4.1	0.09	0.05	0.07	0.45	0.49	0.38	0.68	0.41	0.45	1.89	0.95	0.84	1.67	3.56	2.22	0.73×10^{-4}	0.96×10^{-6}	1.36×10^{-7}	2.441	2.936	3.16
6.1	0.09	0.05	0.07	0.41	0.47	0.34	0.62	0.4	0.4	1.89	0.68	0.54	1.67	3	1.78	0.80×10^{-5}	0.56×10^{-7}	0.51×10^{-7}	2.694	2.998	3.272
8.1	0.09	0.05	0.07	0.39	0.44	0.3	0.59	0.37	0.35	1.76	1.21	0.25	1.61	2.67	1.22	1.56×10^{-6}	1.39×10^{-8}	1.51×10^{-8}	2.881	3.42	3.411
10.1	0.09	0.05	0.07	0.39	0.44	0.3	0.59	0.37	0.35	1.76	1.21	0.25	1.61	2.67	1.22	1.56×10^{-6}	1.39×10^{-8}	1.51×10^{-8}	2.881	3.42	3.411
(2 – Methyl – 5 – nitro – 4*p* – tolyl azo – imidazol – 1 – yl) – acetic acid benzylidene – hydrazide																					
2.1	0.08	0.08	0.06	0.5	0.57	0.43	0.68	0.77	0.44	1.76	1.08	1.01	1.61	3.78	2.44	2.67×10^{-4}	1.31×10^{-5}	7.62×10^{-7}	2.293	2.638	2.963
4.1	0.08	0.08	0.06	0.5	0.54	0.43	0.68	0.73	0.44	1.53	0.84	0.68	1.5	3.33	2	1.11×10^{-5}	4.73×10^{-7}	6.04×10^{-8}	2.657	3.017	3.252
6.1	0.08	0.08	0.06	0.46	0.52	0.39	0.62	0.7	0.4	1.53	0.58	0.41	1.5	2.78	1.56	0.86×10^{-6}	3.02×10^{-8}	1.68×10^{-8}	2.949	3.332	3.399
8.1	0.08	0.08	0.06	0.44	0.49	0.34	0.59	0.66	0.34	1.42	1.01	0.17	1.44	2.44	1	0.71×10^{-6}	5.76×10^{-9}	4.51×10^{-9}	3.234	3.521	3.549
10.1	0.08	0.08	0.06	0.44	0.49	0.34	0.59	0.66	0.34	1.42	1.01	0.17	1.44	2.44	1	0.71×10^{-6}	5.76×10^{-9}	4.51×10^{-9}	3.234	3.521	3.549
[4–(4–Methoxy–phenylazo)–2– methyl–5–nitro–imidazol–1–y1]–aceticacid benzylidene – hydrazide																					
2.1	0.08	0.08	0.07	0.56	0.6	0.49	0.76	0.81	0.58	1.64	1.11	1.06	1.56	3.83	2.5	0.64×10^{-4}	0.87×10^{-5}	3.21×10^{-7}	2.456	2.684	3.061
4.1	0.08	0.08	0.07	0.56	0.57	0.49	0.76	0.77	0.58	1.42	0.87	0.72	1.44	3.39	2.06	1.81×10^{-6}	0.53×10^{-6}	1.8×10^{-8}	2.864	3.004	3.391
6.1	0.08	0.08	0.07	0.52	0.55	0.45	0.7	0.74	0.53	1.42	0.61	0.44	1.44	2.83	1.61	1.59×10^{-7}	2.78×10^{-8}	3.9×10^{-9}	3.142	3.341	3.566
8.1	0.08	0.08	0.07	0.5	0.52	0.41	0.68	0.7	0.49	1.31	1.06	0.19	1.39	2.5	1.06	0.92×10^{-8}	3.59×10^{-9}	6.3×10^{-10}	3.467	3.575	3.774
10.1	0.08	0.08	0.07	0.5	0.52	0.41	0.68	0.7	0.49	1.31	1.06	0.19	1.39	2.5	1.06	0.92×10^{-8}	3.59×10^{-9}	6.3×10^{-10}	3.467	3.575	3.774
4–(4–Hydroxy–phenylazo)–2–methyl–5–nitro–imidazol–1–y1]–aceticacid benzylidene–hydrazide																					
2.1	0.08	0.07	0.05	0.53	0.58	0.46	0.72	0.69	0.39	1.53	1.11	1.11	1.5	3.83	2.56	3.04×10^{-5}	0.79×10^{-5}	2.48×10^{-7}	2.541	2.695	3.091
4.1	0.08	0.07	0.05	0.53	0.55	0.46	0.72	0.65	0.39	1.31	0.87	0.76	1.39	3.39	2.11	1.02×10^{-6}	3.50×10^{-7}	3.42×10^{-8}	2.929	3.052	3.317
6.1	0.08	0.07	0.05	0.49	0.53	0.42	0.66	0.63	0.35	1.31	0.61	0.47	1.39	2.83	1.67	0.78×10^{-7}	3.17×10^{-8}	8.56×10^{-9}	3.223	3.326	3.476
8.1	0.08	0.07	0.05	0.47	0.5	0.38	0.63	0.59	0.32	1.21	1.06	0.21	1.33	2.5	1.11	1.08×10^{-8}	4.64×10^{-9}	1.45×10^{-9}	3.449	3.546	3.679
10.1	0.08	0.07	0.05	0.47	0.5	0.38	0.63	0.59	0.32	1.21	1.06	0.21	1.33	2.5	1.11	1.08×10^{-8}	4.64×10^{-9}	1.45×10^{-9}	3.449	3.546	3.679
[4–(4–ethoxy–phenyl azo)–2– methyl–5–nitro–imidazol–1–y1]–aceticacid benzylidene–hydrazide																					
2.1	0.18	0.18	0.18	0.48	0.55	0.41	1.46	1.67	1.25	1.89	1.11	1.01	1.67	3.83	2.44	1.34×10^{-4}	1.50×10^{-5}	1.03×10^{-6}	2.372	2.622	2.929
4.1	0.18	0.18	0.18	0.48	0.52	0.41	1.46	1.58	1.25	1.64	0.87	0.68	1.56	3.39	2	6.31×10^{-6}	6.32×10^{-7}	8.93×10^{-8}	2.721	2.984	3.208
6.1	0.18	0.18	0.18	0.44	0.5	0.37	1.34	1.52	1.13	1.64	0.61	0.41	1.56	2.83	1.56	5.90×10^{-7}	6.50×10^{-8}	2.77×10^{-8}	2.992	3.244	3.341
8.1	0.18	0.18	0.18	0.42	0.47	0.33	1.28	1.43	1	1.53	1.06	1.7	1.5	2.5	1	5.74×10^{-8}	1.11×10^{-9}	6.96×10^{-9}	3.258	3.446	3.499
10.1	0.18	0.18	0.18	0.42	0.47	0.33	1.28	1.43	1	1.53	1.06	1.7	1.5	2.5	1	5.74×10^{-8}	1.11×10^{-9}	6.96×10^{-9}	3.258	3.446	3.499
4–(4–chloro–phenylazo)–2– methyl–5–nitro–imidazol–1–y1)]–acetic acid benzylidene–hydrazide																					
2.1	0.05	0.08	0.06	0.43	0.48	0.36	0.36	0.65	0.37	1.64	1.14	1.06	1.56	3.89	2.5	1.96×10^{-3}	2.36×10^{-5}	1.65×10^{-6}	2.065	2.57	2.874
4.1	0.05	0.08	0.06	0.43	0.45	0.36	0.36	0.61	0.37	1.41	0.89	0.72	1.44	3.44	2.06	2.66×10^{-4}	2.13×10^{-6}	2.49×10^{-7}	2.293	2.845	3.091
6.1	0.05	0.08	0.06	0.39	0.43	0.32	0.33	0.58	0.32	1.41	0.63	0.44	1.44	2.89	1.61	6.22×10^{-5}	1.57×10^{-7}	1.0×10^{-7}	2.459	3.143	3.195
8.1	0.05	0.08	0.06	0.37	0.4	0.28	0.31	0.54	0.28	1.31	1.11	0.19	1.39	2.56	1.06	1.57×10^{-5}	4.01×10^{-8}	3.06×10^{-8}	2.617	3.299	3.33
10.1	0.05	0.08	0.06	0.37	0.4	0.28	0.31	0.54	0.28	1.31	1.11	0.19	1.39	2.56	1.06	1.57×10^{-5}	4.01×10^{-8}	3.06×10^{-8}	2.617	3.299	3.33

Table 5. Cyclic voltammetric results of (2 – Methyl – 5– nitro– 4 –substituted azo – imidazol – 1 – yl) – acetic acid benzylidene – hydrazide (1 × 10^{-3}M) at HMDE, Medium : Aqueous dimethyl formamide (40 % v/v).

pH	-R	Scan rate VS^{-1}	-E_{PCI} V	-E_{PCII} V	-E_{PCIII} V	-E_{PCIV} V	$^{i}PC_{I}$ (μA)	$^{i}PC_{II}$ (μA)	$^{i}PC_{III}$ (μA)	$^{i}PC_{IV}$ (μA)	-R	-E_{PCI} V	-E_{PCII} V	-E_{PCIII} V	-E_{PCIV} V	$^{i}PC_{I}$ (μA)	$^{i}PC_{II}$ (μA)	$^{i}PC_{III}$ (μA)	$^{i}PC_{IV}$ (μA)
2.1	**-H**	0.01	0.31	0.51	0.74	-	1.4	4.2	3	-	**-CH_3**	0.37	0.49	0.71	-	1.1	3.8	2.6	-
		0.05	0.39	0.59	0.82		3.1	9.4	6.7			0.45	0.57	0.79		2.5	8.5	5.8	
		0.1	0.43	0.63	0.86		4.4	13.3	9.5			0.49	0.61	0.83		3.5	12	8.2	
		0.5	0.59	0.79	1.02		9.9	29.7	21.2			0.65	0.77	0.99		7.8	26.9	18.4	
4.1		0.01	0.46	0.66	0.88	-	1	3.4	2.2	-		0.54	0.66	0.86	-	0.7	3	1.8	-
		0.05	0.54	0.74	0.96		2.2	7.6	4.9			0.62	0.74	0.94		1.6	6.7	4	
		0.1	0.58	0.78	1		3.2	10.8	7			0.66	0.78	0.98		2.2	9.5	5.7	
		0.5	0.76	0.94	1.16		7.1	24	15.6			0.82	0.94	1.14		4.9	21.2	12.7	
8.1		0.01	0.77	0.99	1.2	1.46	1	1.8	1	1		0.9	0.97	1.18	1.44	0.7	1.4	0.6	0.6
		0.05	0.85	1.07	1.28	1.54	2.2	4	2.2	2.2		0.98	1.05	1.26	1.52	1.6	3.1	1.3	1.3
		0.1	0.89	1.11	1.32	1.58	3.2	5.7	3.2	3.2		1.02	1.09	1.3	1.56	2.2	4.4	1.9	1.9
		0.5	1.05	1.27	1.48	1.74	7.1	12.7	7.1	7.1		1.18	1.25	1.46	1.72	4.9	9.9	4.2	4.2
2.1	**-OCH_3**	0.01	0.43	0.5	0.71	-	1	3.9	2.7	-	**-OH**	0.47	0.51	0.75	-	0.9	3.9	2.8	-
		0.05	0.51	0.58	0.79		2.2	8.7	6			0.55	0.59	0.83		2	8.7	6.3	
		0.1	0.55	0.62	0.83		3.2	12.3	8.5			0.59	0.63	0.87		2.8	12.3	8.6	
		0.5	0.71	0.78	0.99		7.1	27.6	19.1			0.75	0.77	1.03		6.4	27.6	19.8	
4.1		0.01	0.6	0.64	0.86	-	0.6	3.1	1.9	-		0.64	0.67	0.86	-	0.5	3.1	2	-
		0.05	0.68	0.72	0.94		1.3	6.9	4.2			0.72	0.75	0.94		1.1	6.9	4.5	
		0.1	0.72	0.76	0.98		1.9	9.8	6			0.76	0.79	0.98		1.6	9.8	6.3	
		0.5	0.88	0.92	1.14		4.2	22	13.4			0.92	0.95	1.14		3.5	22	14.1	
8.1		0.01	0.94	0.96	1.17	1.43	0.6	1.5	0.7	0.7		1.06	0.97	1.18	1.44	0.5	1.5	0.8	0.8
		0.05	1.02	1.04	1.25	1.51	1.3	3.4	1.6	1.6		1.14	1.05	1.26	1.52	1.1	3.4	1.8	1.8
		0.1	1.06	1.08	1.29	1.55	1.9	4.7	2.2	2.2		1.18	1.09	1.3	1.56	1.6	4.7	2.5	2.5
		0.5	1.22	1.24	1.45	1.71	4.2	10.6	4.9	4.9		1.34	1.25	1.46	1.72	3.5	10.6	5.7	5.7
2.1	**-OC_2H_5**	0.01	0.41	0.49	0.71	-	1.2	3.9	2.6	-	**-Cl**	0.27	0.49	0.73	-	1	4	2.7	-
		0.05	0.49	0.57	0.79		2.7	8.7	5.8			0.35	0.57	0.81		2.2	8.9	6	
		0.1	0.53	0.61	0.83		3.8	12.3	8.2			0.39	0.63	0.85		3.2	12.6	8.5	
		0.5	0.69	0.77	0.99		8.5	27.6	18.4			0.55	0.79	1.01		7.1	28.3	19.1	
4.1		0.01	0.58	0.66	0.86	-	0.8	3.1	1.8	-		0.38	0.64	0.86	-	0.6	3.2	1.9	-
		0.05	0.66	0.74	0.94		1.8	6.9	4			0.46	0.72	0.94		1.3	7.2	4.2	
		0.1	0.7	0.78	0.98		2.5	9.8	5.7			0.5	0.76	0.98		1.9	10.1	6	
		0.5	0.86	0.94	1.14		5.7	22	12.7			0.66	0.92	1.14		4.2	22.6	13.4	
8.1		0.01	0.94	0.96	1.17	1.43	0.8	1.5	0.6	0.6		0.62	0.98	1.18	1.44	0.6	1.6	0.7	0.7
		0.05	1.02	1.04	1.25	1.51	1.8	3.4	0.8	1.3		0.7	1.06	1.26	1.52	1.3	3.6	1.6	1.6
		0.1	1.06	1.08	1.29	1.55	2.5	4.7	1.3	1.9		0.74	1.1	1.3	1.56	1.9	5.1	2.2	2.2
		0.5	1.22	1.24	1.45	1.71	5.7	10.6	3.3	4.2		0.9	1.26	1.46	1.72	4.2	11.3	4.9	4.9

Table 6. Cyclic voltammetric results of (2 – Methyl – 5– nitro– 4 –substituted azo – imidazol – 1 – yl) – acetic acid benzylidene – hydrazide (1 × 10^{-3}M) at MCPE. Medium: Aqueous dimethyl formamide (40 % v/v)

pH	-R	Scan rate VS^{-1}	$-E_{PCI}$ V	$-E_{PCII}$ V	$-E_{PCIII}$ V	$-E_{PCIV}$ V	$^{i}PC_{I}$ (μA)	$^{i}PC_{II}$ (μA)	$^{i}PC_{III}$ (μA)	$^{i}PC_{IV}$ (μA)	-R	$-E_{PCI}$ V	$-E_{PCII}$ V	$-E_{PCIII}$ V	$-E_{PCIV}$ V	$^{i}PC_{I}$ (μA)	$^{i}PC_{II}$ (μA)	$^{i}PC_{III}$ (μA)	$^{i}PC_{IV}$ (μA)
2.1	**-H**	0.01	0.46	0.68	0.94	1.06	1	3.6	1.5	1.5	**$-CH_3$**	0.52	0.66	0.91	1.03	0.7	3.2	1.3	1.3
		0.05	0.54	0.76	1.02	1.14	2.2	8	3.4	3.4		0.6	0.74	0.99	1.11	1.6	7.2	2.9	2.9
		0.1	0.58	0.8	1.06	1.18	3.2	11.4	4.7	4.7		0.64	0.78	1.03	1.15	2.2	10.1	4.1	4.1
		0.5	0.74	0.96	1.22	1.34	7.1	25.5	10.6	10.6		0.8	0.94	1.19	1.31	4.9	22.6	9.2	9.2
4.1		0.01	0.62	0.84	1.09	1.22	0.6	2.8	1.1	1.1		0.7	0.84	1.07	1.2	0.3	2.4	0.9	0.9
		0.05	0.7	0.92	1.17	1.3	1.3	6.3	2.5	2.5		0.78	0.92	1.15	1.28	0.7	5.4	2	2
		0.1	0.74	0.96	1.21	1.34	1.9	8.6	3.5	3.5		0.82	0.96	1.19	1.32	0.9	7.6	2.8	2.8
		0.5	0.9	1.12	1.37	1.5	4.2	19.8	7.8	7.8		0.98	1.12	1.35	1.48	2.1	17	6.4	6.4
8.1		0.01	0.95	1.19	1.43	1.58	0.6	1.2	0.5	0.5		1.08	1.17	1.41	0.56	0.3	0.8	0.3	0.3
		0.05	1.03	1.27	1.51	1.65	1.3	2.7	1.1	1.1		1.16	1.25	1.49	0.64	0.7	1.8	0.7	0.7
		0.1	1.07	1.31	1.55	1.7	1.9	3.8	1.6	1.6		1.2	1.29	1.53	0.68	0.9	2.5	0.9	0.9
		0.5	1.23	1.47	1.71	1.86	4.2	8.5	3.5	3.5		1.36	1.45	1.69	0.84	2.1	5.7	2.1	2.1
2.1	**$-OCH_3$**	0.01	0.58	0.67	0.91	1.03	0.6	3.3	1.3	1.3	**-OH**	0.62	0.68	0.95	1.07	0.5	3.3	1.4	1.4
		0.05	0.66	0.75	1	1.11	1.3	7.4	2.9	2.9		0.7	0.76	1.03	1.15	1.1	7.4	3.1	3.1
		0.1	0.7	0.79	1.04	1.15	1.9	10.4	4.1	4.1		0.74	0.8	1.07	1.19	1.6	10.4	4.4	4.4
		0.5	0.86	0.95	1.2	1.31	4.2	23.3	9.2	9.2		0.9	0.96	1.23	1.35	3.5	23.3	9.9	9.9
4.1		0.01	0.76	0.82	1.07	1.2	0.2	2.5	0.9	0.9		0.8	0.85	1.07	1.2	0.1	2.5	1	1
		0.05	0.84	0.92	1.15	1.28	0.4	5.6	2	2		0.88	0.93	1.15	1.28	0.2	5.6	2.2	2.2
		0.1	0.88	0.96	1.19	1.32	0.6	7.9	2.8	2.8		0.92	0.97	1.19	1.32	0.3	7.9	3.2	3.2
		0.5	1.04	1.12	1.35	1.48	1.4	17.7	6.4	6.4		1.08	1.13	--	1.5	0.7	17.7	7.1	7.1
8.1		0.01	1.12	1.16	1.4	1.55	0.2	0.9	0.3	0.3		1.24	1.17	1.41	1.56	0.1	0.9	0.4	0.4
		0.05	1.2	1.24	1.48	1.63	0.4	2	0.7	0.7		1.32	1.25	1.49	1.64	0.2	2	0.9	0.9
		0.1	1.24	1.28	1.52	1.67	0.6	2.8	0.9	0.9		1.36	1.29	1.53	1.68	0.3	2.8	1.3	1.3
		0.5	1.4	1.44	1.68	1.83	1.4	6.3	2.1	2.1		1.52	1.45	1.69	1.84	0.7	6.3	2.8	2.8
2.1	**$-OC_2H_5$**	0.01	0.56	0.66	0.91	1.03	0.8	3.3	1.3	1.3	**-Cl**	0.42	0.86	0.93	1.05	0.6	3.4	1.3	1.3
		0.05	0.64	0.74	0.99	1.11	1.8	7.4	2.9	2.9		0.5	0.94	1.01	1.13	1.3	7.6	2.9	2.9
		0.1	0.68	0.78	1.03	1.15	2.5	10.4	4.1	4.1		0.54	0.98	1.05	1.17	1.9	10.8	4.1	4.1
		0.5	0.84	0.94	1.19	1.31	5.7	23.3	9.2	9.2		0.7	1.14	1.21	1.33	4.2	24	9.2	9.2
4.1		0.01	0.74	0.84	1.07	1.2	0.4	2.5	0.9	0.9		0.54	0.82	1.07	1.2	0.2	2.6	0.9	0.9
		0.05	0.82	0.92	1.15	1.28	0.9	5.6	2	2		0.62	0.9	1.15	1.28	0.4	5.8	2	2
		0.1	0.86	0.96	1.19	1.32	1.3	7.9	2.8	2.8		0.66	0.94	1.19	1.32	0.6	8.2	2.8	2.8
		0.5	1.02	1.12	1.35	1.48	2.8	17.7	6.4	6.4		0.82	1.1	1.35	1.48	1.4	18.4	6.4	6.4
8.1		0.01	1.12	1.16	1.4	1.36	0.4	0.9	0.3	0.3		0.8	1.18	1.41	1.56	0.2	1	0.3	0.3
		0.05	1.2	1.24	1.48	1.44	0.9	2	0.7	0.7		0.88	1.26	1.49	1.64	0.4	2.2	0.7	0.7
		0.1	1.24	1.28	1.52	1.48	1.3	2.8	0.9	0.9		0.92	1.3	1.53	1.68	0.6	3.2	0.9	0.9
		0.5	1.4	1.44	1.68	1.64	2.8	6.3	2.1	2.1		1.08	1.46	1.69	1.84	1.4	7.1	2.1	2.1

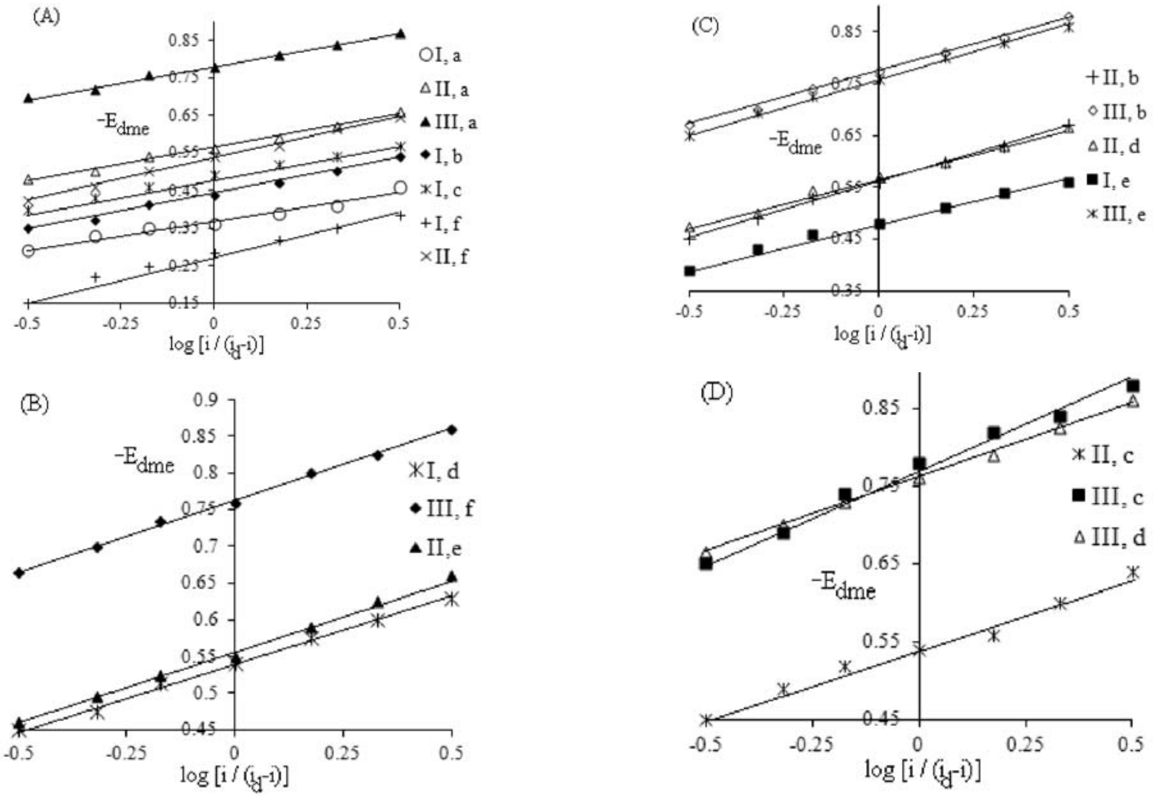


Fig. 4. (A-D). Semi log plots of arylazo imidazoles. [Substrate] = 1 × 10^{-3} M; Medium = Dimethylformamide (40 % v/v); pH = 4.1.

from the Meites-Israel equation [23] was less than 10^{-4};

The ΔG^* (activation free energy) values increase with increase of pH in the range 1.1 - 6.1 and remain unaltered in the pH range 8.1 - 10.1 [24].

These observations suggest that the reduction of N=N, $-NO_2$ and >C=N–NH groups in the compounds under investigation were irreversible. This may be due to the bulky group present at the end of N=N, $-NO_2$ and >C=N–NH groups, respectively.

The plots of $-E_{dme}$ vs $\log[i/i_d-i]$, shown in Fig. 4 at the typical pH of 4.1, were linear and the slopes were not in agreement with the theoretical values [21] (0.030, 0.015 and 0.009, respectively, for 2, 4 and 6 electron reduction) expected for the reversible waves. This indicates that the electrode reaction was irreversible. The slopes further indicate that the tendency of the irreversibility increases with increase of the pH. This was confirmed by kinetic parameters [23, 27], evaluated for the electrode reaction (decrease in $K^O_{f,h}$, the heterogeneous rate constant, increase in ΔG^*, the activation free energy, with increase in pH, as shown in Table 4). Tome's criterion [28] was also employed to confirm the irreversible nature of the polarographic waves. The ∞n_a values (∞ is the transfer coefficient and n_a is the number of electrons involved) obtained, were almost equal to the values obtained from conventional logarithmic plots (Table 4).

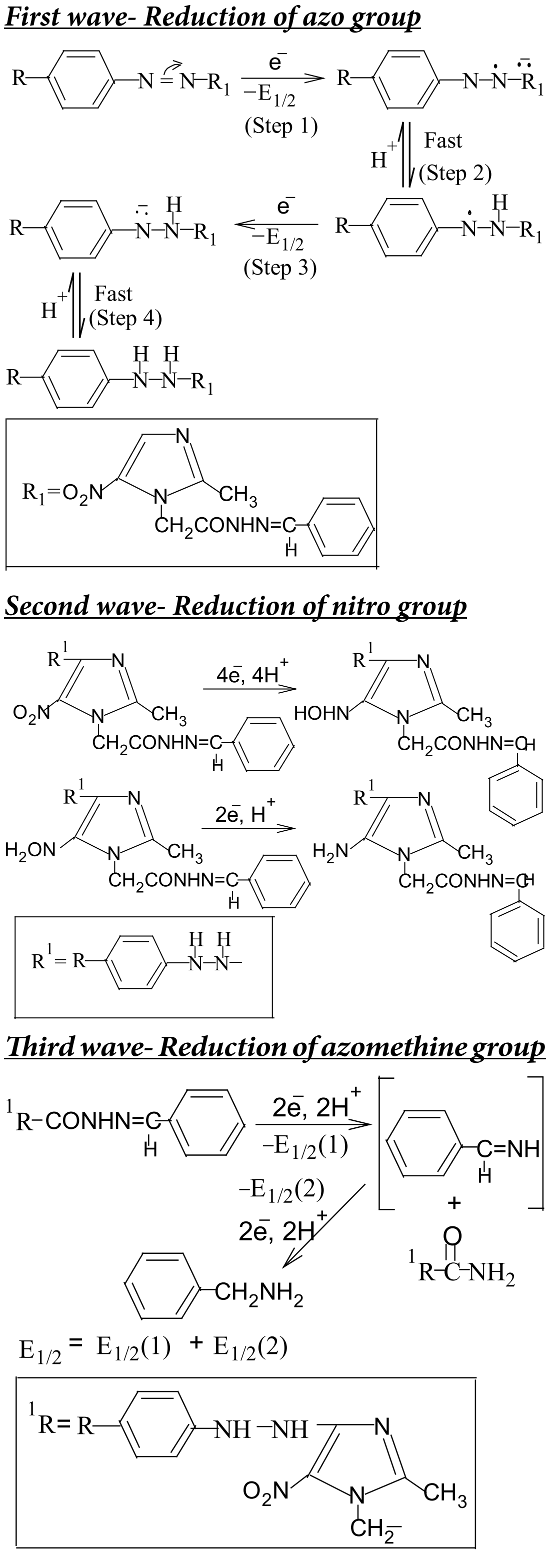
Controlled potential electrolysis

The electro-chemical reduction of (2-methyl-5-nitro-4-phenyl azoimida zol-1-yl)-acetic acid benzylidene-hydrazide (a) has been studied by the method of controlled potential electrolysis at pH 4.1. The electrolysis was followed by recording the decrease of the current with time. The number of electrons per molecule was calculated from the i-t curves [29]. The number of electrons in the three reduction steps put together was found to be 12.

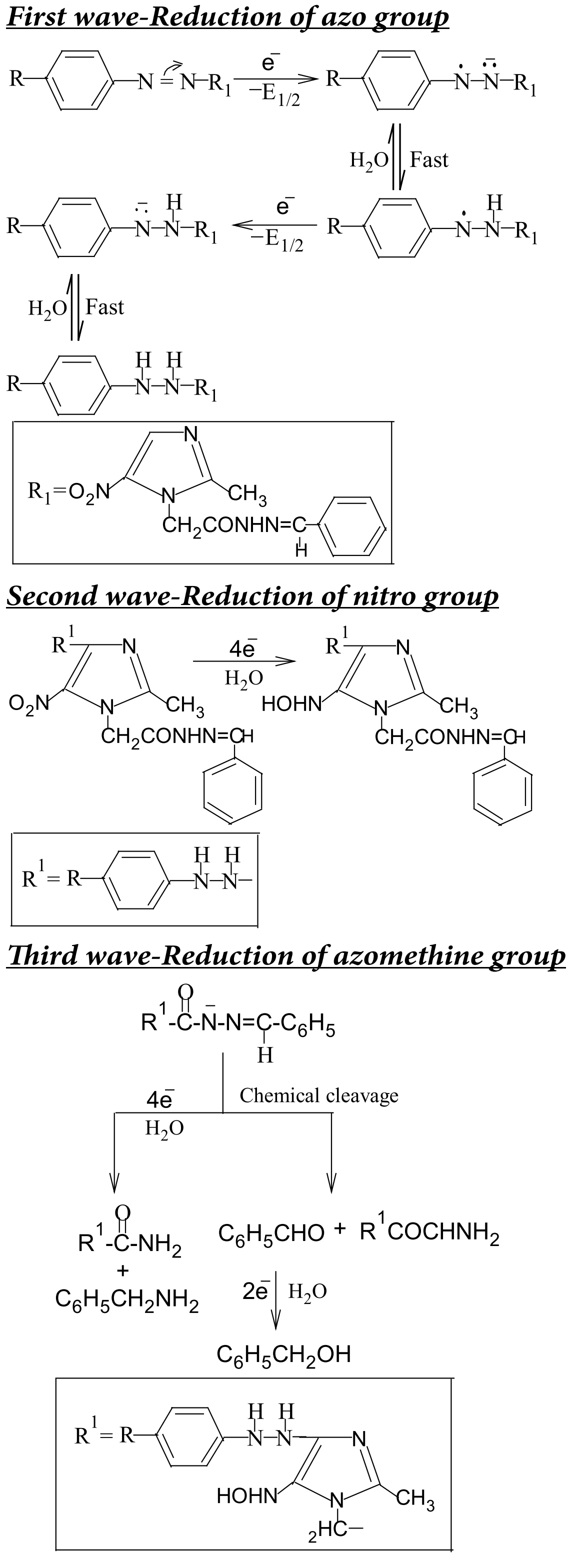
After disconnecting the electrolytic cell, 1 mL of resulting solution was withdrawn and the presence of aniline in the solution was assessed by a standard spot test [30]. The remaining reaction mixture was partially evaporated in a water bath to half its volume, cooled to room temperature and extracted with ether. The ether layer was evaporated under vacuum to obtain a yellow crystalline solid, identified as 1-(2-methyl, 3,4 diamino imidazolyl) acetamide. Based on the results obtained, the reduction mechanism, shown in Scheme 1 and Scheme 2, has been proposed for the arylazo imidazoles a-f.

Reduction of azo group

The first wave in the entire pH range of study was



Scheme 1. Reduction mechanism in acidic medium.



Scheme 2. Reduction mechanism in alkaline medium.

ascribed to the 2 electron reduction of the azo group to hydrazo stage. The results, already presented, reveal the irreversible and diffusion controlled nature of the polarographic wave. The results reported in the literature, however, show that the wave was reversible in the lower pH range for simple azo compounds under comparable conditions [31]. The irreversibility in the present studies may be due to the bulky group present at the end of the – N = N – linkage [32]. Substituent effects resulted in positive specific reaction constant (ρ) values (Table 7) suggesting that the reduction process was nucleophilic in nature under the experimental conditions. Therefore it indicates that the electron addition precedes proton addition.

The compounds exhibit a single wave in the basic pH range of study. The results, already presented, reveal the irreversible and diffusion controlled nature of the waves.

The comparison of the wave height with that of the simple azo benzene, recorded under identical conditions, and the number of electrons, evaluated from the Devries and Kroon process reveals the involvement of two electrons in the reduction process. Hence, a two electron reduction of the azo group to the hydrazo group stage is envisaged.

Reduction of nitro group

The wave height decreases with increase in the pH and remains unaltered in the alkaline pH range. The results already presented reveal the diffusion controlled and irreversible nature of the process. The fact that the half wave potential increases with increase in pH in the acid pH range suggests the involvement of protons in the reduction process.

The comparison of the half wave potentials of the second wave with those observed for nitro benzene [33] suggests that this wave was due to reduction of the nitro group to an amine in acidic medium and to phenyl hydroxylamine - in alkaline medium.

However, the half wave potential of the second wave was slightly more negative than that of the nitro group in nitrobenzene. This indicates that the heterocyclic system and the hydrazo group (NH-NH, a product formed in first reduction step) were making the nitro group reduction difficult. An additional wave, corresponding to the two electron reduction of the phenyl hydroxyl ammonium ion to aniline, was observed due to the reduction of the nitro group in acidic solutions.

The phenyl hydroxylamine was however resistant to reduction in alkaline solutions. Hence, the limiting current noticed for the second wave in alkaline solution was due to the four electron reduction of the nitro group to phenyl hydroxyl amine. But it can be seen from Table 4 that up to pH 4, the limiting current of the second wave was one and a half times greater than the limiting current for the second wave observed in the alkaline solutions of pH 8.1 - 10.1. This suggests that the second wave in acidic solutions represents a composite wave corresponding to the reduction of -NO_2 group to -NHOH and NHOH to -NH_2 group. The limiting current of the second wave in acidic solutions of pH 4.1 - 6.1 was, however, nearly same as that of the second wave noticed in the alkaline solutions of pH 8.1 - 10.1 . This suggests that all of the hydroxylamine formed was not protonated since it was the protonated species that has reduced. A similar type of observation is reported for meta nitrobenzaldehyde [34].

Reduction of the azomethine group

The third wave noticed in the present investigation was ascribed to the four electron reduction of azomethine group (CH=N-NH). The azomethine group in a-f was protonated to yield protonated azomethine. The weak (=N-NH) single bond of the hydrazide was then cleaved [35, 36] with the uptake of two electrons and two protons to form an imine intermediate. The strength of the acid or alkaline medium employed for these reductions, was approximately 0.4 %. Hence, it was not possible for the exocyclic amide linkage (O=C–NH–N) to be affected. The unstable imine intermediate produced in the above process was then reduced to an amine in a two electron process. It was reported [37, 38] that the above mentioned two steps of reduction occured at the same potential and supports the appearance of a single four electron wave, as shown in the Scheme 1.

The compounds under study exhibit four waves in the pH range 8.1 - 10.1.

The position of the wave on the potential axis indicates that the first wave was ascribed to the two electron reduction of azo group to hydrazo stage and the second wave was attributed to a four electron reduction of the nitro group to phenyl hydroxylamine. In an alkaline medium (pH > pKa) the azomethine group exists in the azomethine anionic form and the latter was undergoing a chemical cleavage partially in alkaline solution to the corresponding carbonyl compound, as shown in Scheme 2. The azomethine anionic form and carbonyl group were susceptible to reduction at the dropping mercury electrode. Therefore the third wave observed in present studies, has been ascribed to the four electron reduction of the azomethine anionic form to amine stage. A decrease in the height of the third wave with increase in pH lends support to this conclusion. The fourth wave observed was attributed to the two electron reduction of the carbonyl group to the carbinol stage.

Cyclic voltammetric behaviour at HMDE

The cyclic voltammetric experiments were conducted at the hanging mercury dropping electrode (HMDE) in buffer solutions of pH 2.1, 4.1, 6.1, 8.1 and 10.1 at different scan rates, 10 mV s^{-1}, 20 mV s^{-1}, 50 mV s^{-1} ,100 mV s^{-1}, 200 mV s^{-1}, 300 mV s^{-1} and 500 mV s^{-1} . Well defined cathodic peaks were observed at all scan rates.

The compounds under study (a-f) exhibit three cathodic peaks in the solution of pH 2.1 - 6.1 and four cathodic peaks in solutions of pH 8.1 - 10.1. The results are presented in Table 5.

A plot of $i_{pc}/\upsilon^{1/2}$ vs sweep rate was a straight line parallel to the sweep rate axis, it was contrary to behavior of a reversible system [39, 40]. The irreversible electrode process was characterized by:

- dependence of peak potential on sweep rate [41], i.e. peak potentials become more negative with increase in scan rate;
- the ratio of anodic peak current to cathodic peak current was not equal to unity [42];
- the absence of anodic peak in the reverse scan.

The above mentioned facts clearly rule out the possibility of a fast electron transfer characteristic of a reversible behavior. The linear plots of i_{pc} versus $\upsilon^{1/2}$ suggest a diffusion controlled nature of the electrode process.

Reduction mechanism

From the position of the peak on the potential axis, it was observed that the first peak obtained in acidic solutions, was due to the reduction of azo group to hydrazo stage, the second peak to the reduction of nitro group to amine stage and the third peak - to reduction of azomethine group to amine stage.

In the alkaline medium, the first peak was attributed to the reduction of azo group to hydrazo stage, second peak to the reduction of nitro group to the hydroxylamine stage and the third peak - to the reduction of azomethine anion to the amine stage and the fourth peak was attributed to the two electron reduction of carbonyl group to carbinol stage which was formed by the chemical cleavage of the azomethine anionic form. The protons required for the reduction have been taken from the aqueous solutions.

The number of cathodic peaks, noticed for compounds (a-f) in cyclicvoltammetric studies at HMDE, was the same as that in the polarographic studies conducted under similar experimental conditions at the dropping mercury electrode.

Cyclic voltammetric behavior at MCPE

The cyclic voltammetric experiments were conducted using a crown-ether modified carbon paste electrode (MCPE) in solutions of pH 2.1, 4.1, 6.1, 8.1 and 10.1 at different scan rates, 10 mV s^{-1}, 20 mV s^{-1}, 50 mV s^{-1}100 mV s^{-1}, 300 mV s^{-1} and 500 mV s^{-1}. The results are shown in Table 6.

Three well defined cathodic peaks were observed at the higher sweep rates (100 mV s^{-1}, 300 mV s^{-1} and 500 mV s^{-1}) and ill defined cathodic peaks were noticed at the lower sweep rates (10 mV s^{-1}, 20 mV s^{-1} and 50 mV s^{-1}) in solutions of pH 2.1 - 10.1. The results are presented in Table 6.

Nature of electrode process

The irreversible nature of the electrode process is characterized by:

- dependence of the peak potential on the sweep rate,
- the plot of $E_{pc} / \upsilon^{1/2}$ vs sweep rate was a straight line, parallel to the sweep rate axis,
- the absence of anodic peak in the reverse scan,
- the negative shift in the peak potential with increase in sweep rates,
- the shape of the $i_{pc}/\upsilon^{1/2}$ versus υ plot is in accordance with the Nicholson and Shain criteria Mechanism II.

The linear plots of i_{pc} versus $\upsilon^{1/2}$ suggest a diffusion controlled nature of the electrode process and the same is further confirmed by a linear plot of i_{pc} vs concentration passing through the origin. The plots of E_{pc} vs pH were similar to the $E_{1/2}$ vs pH plots and this supported the findings of DC polarography.

Substituent effect on the polarographic behaviour

The effect of a substituent on the polarographic reduction of (2-methyl-5-nitro-4-substituted phenylazo-imidazol-1-y1)–acetic acid benzylidenehydrazide was studied. The substituent effect was

Table 7. Effect of pH on specific rate constant.

pH	2.10	4.10	6.10	8.10	10.10
ρ (Polarography)	0.42	0.50	0.50	0.56	0.56
ρ (CV at HMDE)	0.40	0.50	0.53	0.70	0.70
ρ (CV at MCPE)	0.27	0.54	0.58	0.68	0.68

noticed on the polarographic reduction of the azo group to hydrazo stage. The substituent effect was not noticed for the polarographic reduction of the nitro group and the azomethine group, because the substituent was far away from the electroactive centers. The specific reaction constant (ρ) determined for the reduction of the azo group was in the range of 0.35 - 0.50. The specific reaction constant values were all positive and low, indicating the nucleophilic addition of the electrons to the substrate. This confirms that the electron uptake was the potential determining step. The same conclusion is drawn using cyclic voltammetry at HMDE and MCPE. The results are given in the Table 7.

Comparison between polarographic behavior and cyclic voltammetric behavior

The compounds a-f exhibit three well defined polarographic waves in the buffer solutions of pH 2.1 - 6.1 and four polarographic waves in the solutions of pH 8.1 - 10.1. In the cyclic voltammetric studies at HMDE, the number of cathodic peaks were the same as that of polarographic waves at the dropping mercury electrode. However, quite a different behavior was noticed with the crown-ether modified carbon paste electrode under similar experimental conditions. The first polarographic wave, noticed in the solutions of pH 2.1 - 10.1, was ascribed to the two electron reduction of azo group to hydrazo group. This wave itself manifests as the first cathodic peak at HMDE and modified CPE. The second polarographic wave was attributed to a six electron reduction of NO_2 to NH_2 in acidic solutions and a four electron reduction of NO_2 to NHOH in basic solutions. The second wave was noticed as a second cathodic peak at HMDE and at the modified carbon paste electrode. The third polarographic wave was attributed to four electron reduction of azomethine group (>C=NNH) to amine stage. This wave appeared as one cathodic peak at HMDE and two cathodic peaks at modified carbon paste electrodes in solutions of pH 2.1 - 6.1. The third polarographic wave which had appeared as third and fourth cathodic peaks at the modified carbon paste electrode, was attributed to two 2 electron reduction of azomethine group in two steps. In the first step, azomethyl is reduced to an unstable imine, which further undergoes 2 electron reduction to amine.

In solutions of pH 8.1 - 10.1, the compounds a-f exist, in azomethine anionic form. The latter in alkaline solutions was susceptible to chemical cleavage, partially into the corresponding carbonyl compound. The carbonyl compound further undergoes 2 electron reduction to carbinol stage. In polarographic studies four waves were noticed and the same number of cathodic peaks was noticed in the CV studies at HMDE. In contrast to this behavior, five cathodic peaks are noticed at the modified carbon paste electrode.

The third polarographic wave was attributed to a four electron reduction of $>C{=}N{-}\overset{\ominus}{N}{-}$ to amine stage. This wave has appeared as a third cathodic peak in the CV studies at HMDE. However, the same wave has appeared as two cathodic peaks (third and fourth) in the CV studies at the modified CPE. The fourth polarographic wave is due to a two election reduction of the carbonyl group to the carbinol stage. It appeared as a fourth peak in the CV studies at HMDE and as a fifth peak in modified CPE studies.

CONCLUSIONS

The polarographic and cyclic voltammetric behavior of certain novel (2-methyl-5-nitro-4-substituted phenyl azo-imidazol-1-y1)-acetic acid benzylidene-hydrazides were reported in this article. The polarographic behavior studied at a hanging mercury drop electrode was compared with the cyclic voltammetric behavior at HMDE and MCPE to deduce a plausible reduction mechanism in acidic as well as in a basic medium. The reduction process was found to be irreversible and diffusion controlled and involved protons.

REFERENCES

1. P.W. Erhardt, A.A. Hagdon, D. Davey, C.A. Pease, Venepalli Griffin, C.W. Gomez, R.P. Wiggins, J.R. Ingebretsen,. D. Pang, Cardiotonic agents. 5. Fragments from the heterocycle-phenyl-imidazole pharmacophore, J. Med. Chem., 32, 1989, 1173-1176.
2. F. Suzuki, T. Kuroda, T. Tamura, New antiinflammatory agents. 2. 5-Phenyl-3H-imidazo[4,5-c][1,8] naphthyridin-4(5H)-ones: a new class of nonsteroidal antiinflammatory agents with potent activity like glucocorticoids, J. Med. Chem., 35, 1992, 2863-2870.
3. M. Sreedevi, A. Raghavendra Guru Prasad, Y.N. Spoorthy, L.K. Ravindranath, Synthesis and Antimicrobial Evaluation of Certain Novel Thiazoles, Advanced Pharmaceutical Bulletin, 3, 2013, 227-230.
4. H. Jean Michael, M. Robert, S. Caoline, Synthesis and anti-leishmanial activity of new imidazoline-2-one derivatives, Eu. J. Med. Chem., 45, 2002, 711-718.
5. L.I. Kruse, V. Kaiser, J.S. Frazee, E. Garvey, E.L. Hilbert, W.A. Faulkner, K.E. Flaim, J.L. Sawyer, B.W. Berkowitz, Multisubstrate inhibitors of dopamine .beta.-hydroxylase. 1. Some 1-phenyl and 1-phenyl-bridged derivatives of imidazole-2-thione, J. Med. Chem., 29, 1986, 2465-2472.
6. D.R. Robertson, E.E. Beedle, Imidazole anticonvulsants: structure-activity relationships of (Biphenylyloxy)alkyl]imidazoles, J. Med. Chem. 36, 1987, 939-943.
7. K. Hayashi, K. Nunami, Studies on angiotensin converting enzyme inhibitors. Synthesis and inhibitory activities of 3-acyl-1-alkyl-2-oxoimidazolidine-4-carboxylic acid derivatives, J. Med. Chem., 32, 1989, 289-297.
8. Jean Chang, Fong, Khalid, Benamour, Synthesis and adrenergic binding ligand affinities of 2-imino-imidazolidine derivatives, Chem. Pharm. Bull., 48, 2000, 729-733.
9. A. Álvarez-Lueje, P. Magdalena, Z. Claudio, Electrochemical Methods for the In Vitro Assessment of Drug Metabolism: Topics on Drug Metabolism, InTech Publisher, 2012, p.222.
10. J. Rozenski, C.J. Ranter, H. Verplanken, Quantitative structure- activity relationships for antimicrobial nitroheterocyclic drugs, Quant. Struct.- Act. Relat., 14, 1995, 134-141.
11. D.I. Edwards, Comprehensive Medicinal Chemistry. The Rational Design, Mechanistic Study & Therapeutic Application of Chemical Compounds, Pergamon Press, Oxford, 1990, p. 546.
12. H. Cerecetto, R. Di Maio, M. González, Risso, G. Sagrera, G. Seoane, A. Denicola, G. Peluffo, Quijano, Stoppani, M. Paulino, C. Olea-Azar, M.A. Basombrio, Synthesis and antitrypanosomal evaluation of E-isomers of 5-nitro-2-furaldehyde and 5-nitrothiophene-2-carboxaldehyde semicarbazone derivatives. structure-activity relationships, Eur. J. Med. Chem., 35, 2000, 343-350.
13. M. Sreedevi, A. Raghavendra Guru Prasad, Y.N. Spoorthy, L.K. Ravindranath, Synthesis, characterization and antimicrobial studies on certain substituted arylazo imidazole conatinsning oxadiazoles, South. Braz. J. Chem., 20, 2012, 11-24.
14. W.U. Malik, R.N. Goyal, J. Rajeev, Polarographic reduction of some guanylpyrazoline nitrates and the effect of double layer structure on $E_{1/2}$ values, J. Electroanal. Chem., 105, 1979, 349-358.
15. L.K. Ravindranath, S.R. Rama Das, S. Brahmaji Rao, Polarographic behavior of arylazo pyrazoles, Electochimica Acta., 28, 1983, 601-603.
16. J. Rajeev, J. Indian Chem. Soc., Polarographic behaviour of some potential antidiabatic 4-arylhydrazono-N-hippuryl-3-methyl-2-pyrazolin-5-ones, LX 60, 1983, 936-940.
17. M.H. Elnagdi, H.M. Fahmy, M.A. Morsi, Polarographic Activity of The Arylhydrazones of α –Cyanoketones. As a Criterion of Their Acidity, J. Electroanal. Chem., 68, 1976, 237-242.
18. L.K. Ravindranath, S.R. Rama Das, S. Brahmaji Rao, Polarographic behaviour of arylazo pyrazoles, Electrochimica Acta, 28, 1983, 601-603.
19. P. Zuman, The Elucidation of Organic Electrode Process, Academic Press, New York, 1969, p.25.
20. J.P. Donald, Organic Polarography, Anal. Chem., 42, 1970, 139R-152r.
21. V. Suryanarayana Rao, Polarography and Allied Techniques, University Press (India) Private Limited, First Edition, 2002, p.14.
22. S. Pratihha, Ashok Kumar, S. Manisha, Synthesis and electrochemical investigations on 2-phenyl-4-[

4/-(3//-ethoxy)-phenylazophenyIJ-3-thioxo-3,4-dihydro-2H,2,4,9, IO-tetraazaphenanthrene-I-one, Indian Journal of Chemistry, 45A, 2006, 872-876.

23. L. Meites, Y. Israel, The Calculation of Electrochemical Kinetic Parameters from. Polarographic Current-Potential Curves, J. Am. Chem. Soc., 83, 1961, 4903-4906.
24. A. Raghavendra Guru Prasad, V. Seshagiri, L.K. Ravindranath, Polarographic Investigations of Certain Propiophenone benzoic acid hydrazones, Jordan Journal of Chemistry, 6, 2011, 51-*64.*
25. N.R. Bannerjee, S. Amina, H.R. Sharma, Polarographic Studies on 3,5-Dimethyl-4-(4’-sulphonamido-benzenazo)-pyrazole, Indian J. Chem., 17A, 1979, 513-516.
26. T. De Vries, J.L. Kroon, A millicoulometer method for the determination of polarographic n-values, J. Am. Chem. Soc.,75, 1953, 2484-2486.
27. R.H. Stokes, An Improved Diaphragm-cell for Diffusion Studies, and Some Tests of the Method, J. Am. Chem. Soc., 72, 1950, 763-767.
28. J. Tomes, Polarographic studies on dropping mercury electrode. Verification of the equation of polarographic wave in the reversible electro deposion of cations, Coll. Czech. Chem. Commun., 9, 1937, 12-18.
29. J.J. Lingane, Coulometric Analysis, J. Am. Chem. Soc., 67, 1950, 1916-1922.
30. F. Feigl, Spot Test, Vol. 2, Elsevier, Amsterdam, 1954, p.109.
31. B. Nygard, Azobenzene-hydrazobenzene polarographic reversibility problem, Arkiv. Kemi., 20, 1962, 163-183.
32. W.V. Malik, R.N. Goyal, J R. ain, Polarographic reduction of some arylazopyrazoles in N,N’-dimethylformamide, J. Electroanal. Chem., 87, 1978, 129-135.
33. J.E. Page, J.W. Smith, J.G. Waller, Polarographic Behavior of Aromatic Nitro Compounds. I. Mononitro Compounds, J. Phys. And Colloid. Chem., 53, 1949, 545-562.
34. I.M. Kolthoff, J.J. Lingane, Polarography, Vol. II, Interscience Publishers, 1965, p.749.
35. S. Millefiori, Polarographic reduction of azo compounds. II. 4-phenylazo- 2-naphthols, Ann. Chim. (Rome), 59, 1969, 138-154.
36. S. Millefiori, G. Campo, Polarographic reduction of azo compounds. I. 1-phenylazo-2-naphthols, Ann. Chim. (Rome), 59, 1969, 128-137.
37. Saul Patai, The chemistry of the hydrazo, azo and azoxy groups: part – I, John Wiley and Sons, Inter science publications, London, 1975, p.471.
38. P. Zuman, Topics in Organic Polarography, Plenum Press, New York, 1970, p.384.
39. A.M. Bond, Modern Polarographic Methods in Analytical Chemistry, Marcel Dekker, New York, 1980, p.195.
40. E.R. Brown, J.R. Sandifer, In Physical Methods in Chemistry, Electrochemical Methods, Second Edition, Vol II, John Wiley, New York, 1986, 273.
41. Ross, J.W. Demars, R.D. Shain, I. Analytical Applications of Hanging Mercury Drop Electrode, Anal. Chem., 28, 1956, 1768-1772.
42. H. Matsuda, Y. Ayabe, Zur Theorie der Randles-Sevčikschen Kathodenstrahl Polarographie, Z. Elektrochem., 59, 1955, 494-503.