Engineering and Technology Journal for Research and Innovation (ETJRI)
ISSN 2581-8678, Volume II, Issue I

Electrochemical Studies on Some Synthesized Anils

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***Abstract*- Series of synthesized 4-[({2-hydroxy-5-[2-(substituted methyl phenyl) diazen-1-yl] phenyl} methylidene) amino] N-(1,3-thiazol-2 yl)/ 4-amino-N-(n-acetyl-5-methyl-1,2-oxazol-3-yl) 2-chlorobenzene-1-sulphonamides were analyzed for their voltametric behaviour on dropping mercury (DME) and solid electrodes using differential pulse polarography, cyclic voltammetry and Coulometry techniques. The data revealed that the electrode process is irreversible, and diffusion controlled. The kinetic parameters i.e. charge transfer coefficient (α_{n_a}), formation constant ($k^{\circ}_{f,h}$) and diffusion coefficient were calculated.**

Keywords: **Sulphonamide Azomethines, differential pulse polarography, cyclic voltammetry, Coulometry.**

I. INTRODUCTION

Sulphonamide drugs paved way for the antibiotic revolution in medicine. They are the basis of several groups of drugs. First and second-generation sulfonyl urea include potent hypoglycemic agents [1-4]. In addition to remarkable antimalarial activity, sulphonamides exhibit diuretic [5], anti-carbonic anhydrase [6], anti-thyroid [7] and anti-tumor activities [8-11]. Sulphonamides possessing a thiourea scaffold are reported to be efficient inhibitors of carbonic anhydrase. Sulphonamides hinder pyrimidine nucleotide biosynthesis through the carbonic anhydrase-facilitated carbamoyl phosphate biosynthesis. Sulphonamide azomethines have acquired wide interest in application to biological systems [12-14]. Azo and Imine linkages characterized by –N=N- and -N=CH- respectively exhibit a broad spectrum of pharmacological and biological properties. Electrochemical behaviour of imines has drawn the attention of scientists. Fry and Reed [15] investigated the reduction mechanism of various imines in DMF using polarography, cyclic voltammetry, coulometry and preparative scale electrolysis. Half wave potential of various imines of the type ArCH=NAr have been compiled by Scott and Jura [16], Martinet et al. [17] and Andrieux et al. [18]. Reduction potential of various imines was stated to be dependent on the size of aromatic group at either side of the --CH=N- group [19], the type of substituent attached to the aromatic ring [20-22] and intramolecular hydrogen bonds [23-24].

II. DIFFERENTIAL PULSE POLAROGRAPHY

Differential pulse polarographic studies of the azomethines were carried out with chosen buffers in suitable pH range. The polarographic reduction was found to be dependent on pH. A typical pulse polarogram is shown in Fig. 1 and polarographic characteristics have been compiled in Table 1.0.

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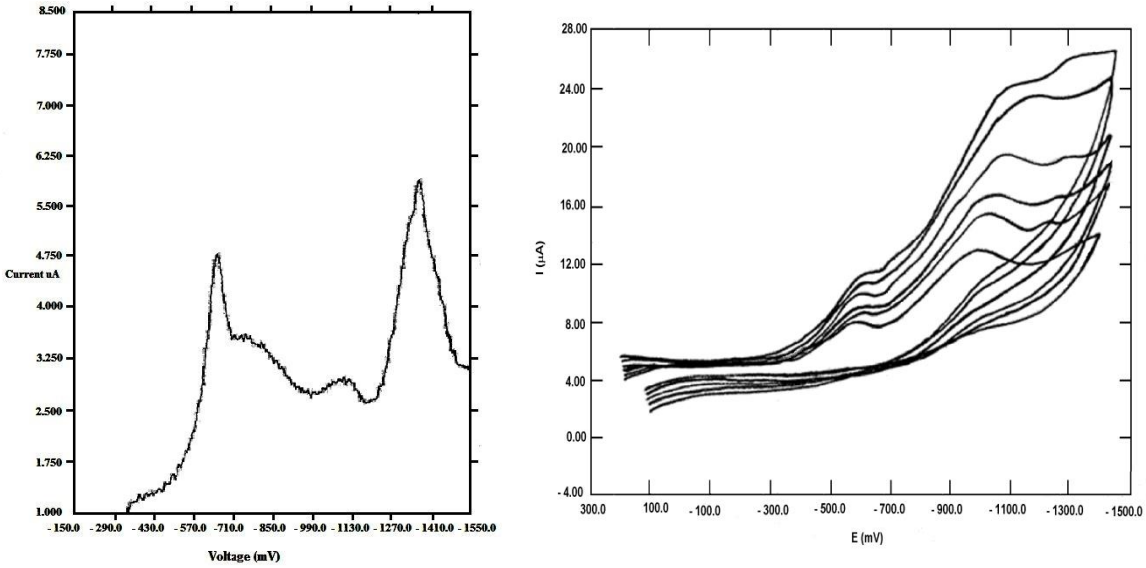

Fig.1 (a,b) : Differential pulse polarogram and cyclic voltammogram of 4-[({2-hydroxy-5-[2-(*m*-substituted methyl phenyl) diazen-1-yl] phenyl} methylidyne) amino]-N-(5-methyl-1, 2-oxazol-3-yl) 2 chloro benzene-1-sulphonamides at standardized conditions.

The peak potential shifted towards more negative values with the rise in pH for all tested compounds. (fig. 2). Plot of i_d vs. pulse amplitude (fig.3) and i_d vs. concentration (fig. 4) are linear, confirming the diffusion based electrode reaction. Reversibility of the electrochemical process was established by recording polarograms at different concentrations of the azomethines and it was observed that $-E_{1/2}$ modulated towards negative for rise in concentration. The logarithmic analysis of [$-E_{d.e}$. vs log ($i/i_d - i$) – 0.546 log t] being greater than 59.2/n mV, here t is drop time (fig.5).

The number of protons (*p*) involved in the rate determining step is calculated from the slope of $-E_{1/2}$ vs. pH plot using the following expression:

$$\frac{\partial E_{1/2}}{\partial \text{pH}} = \frac{0.0591}{\alpha n_a} \qquad \text{(i)}$$

Diffusion coefficient ($D_0^{1/2}$) and heterogeneous rate constant ($K^0_{f.h}$) values were calculated as:

$$E_{1/2} = -0.2412 + \frac{0.0591}{\alpha n_a} \log \frac{1.34 K^o_{f.h} t ½}{D_0^{1/2}} \qquad \text{(ii)}$$

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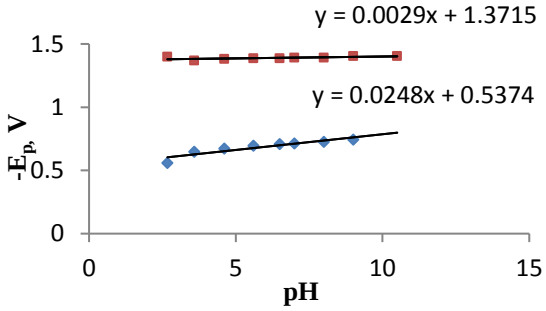

Fig. 2

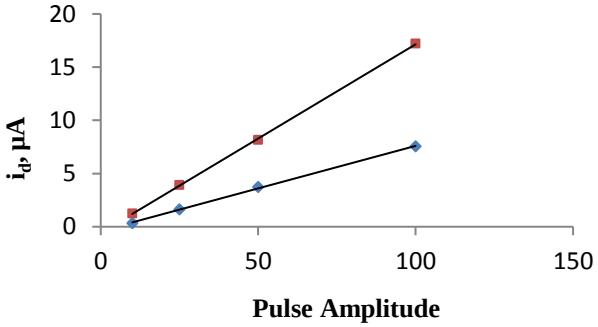

Fig. 3

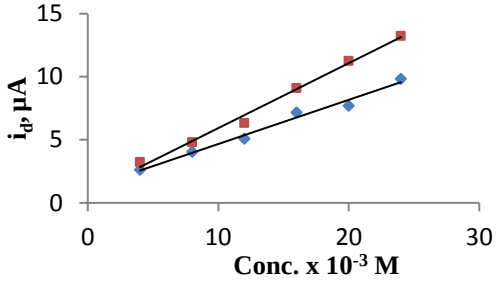

Fig. 4

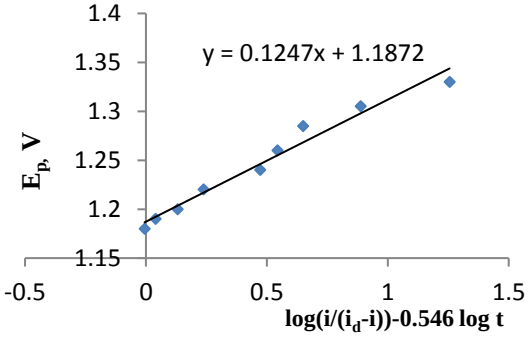

Fig. 5

TABLE -I: DIFFERENTIAL PULSE POLAROGRAPHIC CHARACTERISTICS OF SOME 4- [({2-HYDROXY-5- [2-(*M*-SUBSTITUTED METHYL PHENYL) DIAZEN-1-YL] PHENYL} METHYLIDENE) AMINO]-N-(SUBSTITUTED) 2-CHLORO BENZENE-1- SULPHONAMIDES, REPRESENTATIVE FOR THE BEHAVIOR OF THE STUDIED AZOMETHINES.

S No	R	Bond	E_p V	i_d µA	α_{n_a}	I x10^2 µA	$\partial E_{1/2}/\partial pH$, V/pH	$D_o^{1/2}$, cm^2sec^{-1}	$k^o_{f,h}$, cm sec^{-1}
1	*o*-CH_3	-N=N-	0.672	4.568	0.14	1.73	0.024	$7.12x10^{-8}$	$4.598x10^{-7}$
		CH=N-	1.380	5.276	0.162	2.97	0.002	$1.64x10^{-7}$	$9.310x10^{-6}$
2	*m*-CH_3	-N=N-	0.762	4.055	0.192	1.53	0.023	$6.32x10^{-8}$	$1.57x10^{-6}$
		CH=N-	1.380	4.812	0.248	1.82	0.004	$1.50x10^{-7}$	$1.00x10^{-4}$
3	*p*-CH_3	-N=N-	0.762	4.372	0.178	1.65	0.008	$6.82x10^{-8}$	$1.00x10^{-6}$
		CH=N-	1.386	5.887	0.214	2.23	0.002	$1.83x10^{-7}$	$3.91x10^{-5}$

III. CYCLIC VOLTAMMETRY

Cyclic voltammetry obeys Randles- Sevic equation, which implies that the process is diffusion controlled.

A. Experimental

Sulphonamides were obtained from Fluka Chemicals Co., USA. Other chemicals were obtained from Sigma Aldrich Chemie

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Gmbh, Germany. IR spectra were recorded on a Shimadzu, Japan model Prestige IR 20 spectrophotometer. The differential pulse polarographic (DPP) measurements were carried out using the ELICO CL362 polarographic analyzer (India). The drop time of 1 s was electronically controlled using a 663 VA stand from the company. Cyclic voltammetry was performed using a Potentiostat Versastat EG and G II Princeton Applied Research Model 273 coupled with 270/250 research electrochemistry software 4.30.

B. Reduction Mechanism

On the basis of differential pulse polarography, cyclic voltammetry and Coulometry, a mechanism has been postulated for the reaction. In the reduction of the azo group $2e^-$, $2H^+$ irreversible reduction is proposed to take place. Protons are not involved in the rate determining step. A $2e^-$, $2H^+$ reduction is proposed to take place by addition of the electron first, followed by H^+ and subsequently, the next electron adds followed by the proton rendering the 2-chloro benzene -N-(substituted) benzene-1-sulphonamide molecule free. (Scheme-I)

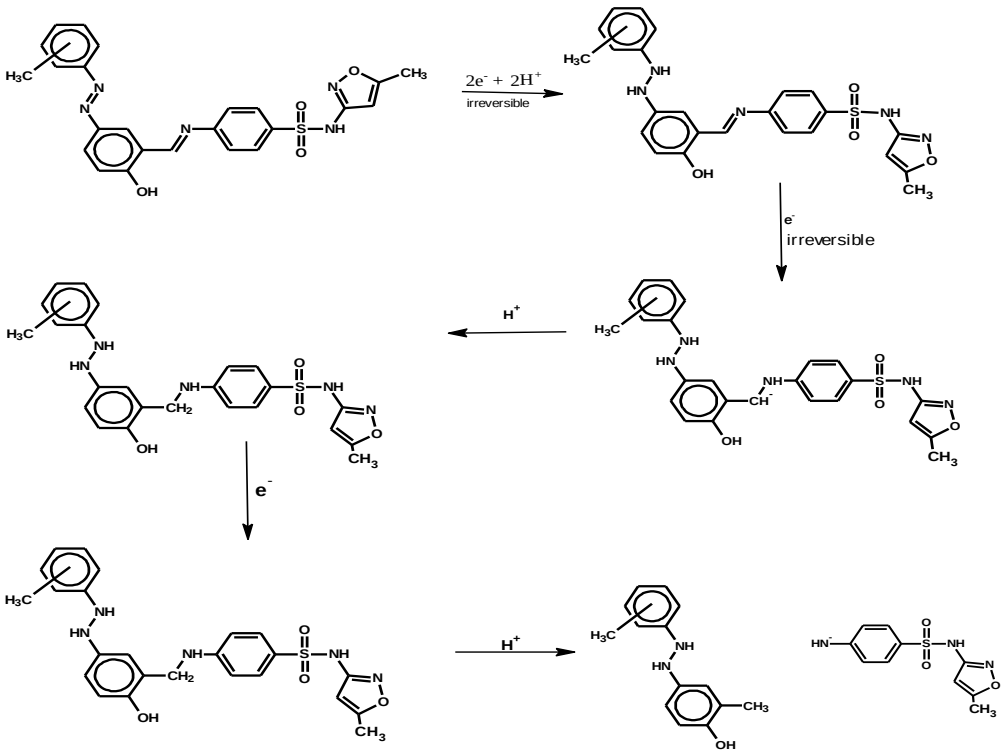

Fig. 6: Scheme-I

IV. RESULTS AND DISCUSSION

The ease of reduction of the azo moiety was favored in acidic media, The $–CH_3$ group at the *o*, *m*, *p*, positions alters the strength of the azoic linkage which is clearly depicted by the id_1 values at the pKa of the azomethines. The sulphonamides studied indicate the participation of protons in the

electrochemical reduction at the azoic site. The influence of the catalytic hydrogen wave but disorganizes the reduction peak of the imine site which is significant when the medium turns progressively basic. The electrode process is diffusion controlled and irreversible as demonstrated by polarographic analysis. Reductive cleavage of the bioactive sulphonamides is pH dependent with change in the pKa of the parent sulphonamide (sulphamethoxazole pka-6.5,sulphacetamide -7.0) towards more acidic side (4.61 and 3.58 respectively) indicating their altered redox characteristics. It may lead to altered biochemical activity facilitating the development of a novel sulfa drug with better medicinal value, lesser toxicity towards the host and possibly a lower residence time of its residue in the ecosystem. Natural attenuation through biodegradability may also get altered due to the incorporation of the azo & imine moieties which are potentially bioactive pharmacophores prominently reported in literature.

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