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Research Article

Electrochemical Investigations on 2-amino-4, 6-diethyl-5-(4'- sulphonamoyl) azopyrimidines

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ABSTRACT

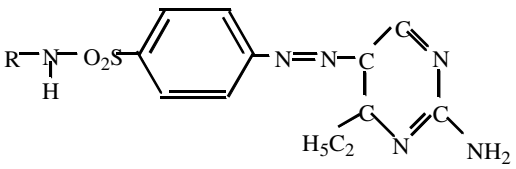
The electrochemical behaviour of 2-amino-4,6-diethyl-5-(4'-sulphonamoyl)azopyrimidines has been studied on the basis of differential pulse polarography (DPP) in phosphate buffer in pH-range 2.5 to 11.5 at dropping mercury electrode (DME), and glassy carbon electrode (GCE).The electro-reduction occurs in a single well-defined 2-e step at dropping mercury electrode. At Glassy carbon electrode also one 2e-cathodic peak is observed. The electrode process is diffusion controlled and irreversible in nature. On the Basis of differential pulse polarography (DPP), a reaction mechanism has been suggested.

Keywords: Dropping mercury electrode (DME), Glassy carbon electrode (GCE), Electrochemical behaviour, Azopyrimidine, Phosphate buffer.

1. INTRODUCTION

Pyrimidine derivatives attracted organic chemists very much because of their physiological and chemotherapeutic importance[1]. They represent a broad class of compounds found to possess, wide range of biological activities[2]. Several patents have been reported on the preparation of these heterocycles, derivatives of which are useful as bronchodilators, vasodilators, antiallergic, antihypertensive[3], anti-inflammatory, and anticancer agents[4]. In fact, there are many pyrimidine derivatives with pharmacological activities[5]. These are used as hypnotic drugs for the nervous system[6], in detecting cancer, as chemotherapeutic agents, and are central to the structure of nucleic acids in living cells[7]. Some pyrimidine derivatives have biological and diverse type of pharmacological activities[8-12].

The structures of the investigated compounds are given in Scheme (I). Moreover, most of these studies were carried out over a narrow potential range and none of these studies investigated the electrochemical properties of amino substituted pyrimidine derivatives. The effect of pH on the voltammetric characteristics of the compounds was investigated by varying the pH of the medium from pH 2.5 to 11.5.



Scheme-(I)

2. MATERIALS AND METHODS

2.1 Reagent and solution

2.0×10^{-3} M stock solutions of all the synthesized sulphonamoylarylazopyrimidines were prepare by dissolving accurately weighed quantity of compound in Purified Acetonitrile (Anal. R). Phosphate buffers in the pH range 2.5 to 11.5 were prepared by adding suitable amount of O-Phosphoric acid (H_3PO_4), potassium di hydrogen phosphate (KH_2PO_4), disodium hydrogen ortho phosphate (Na_2HPO_4), and trisodium ortho phosphate (Na_3PO_4) solution were stirred after mixing

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and left overnight to attain equilibrium. All the chemicals used were Analytical reagents and employed without further purification.

2.2 Equipments

Differential pulse polrographic (DPP) measurements were carried out using ELICO CL-362 polarographic analyser. Triple distilled mercury was used for the d.m.e. The capillary has a flow rate of 3.27s mg/sec and drop time is 2 sec is electronically controlled using a 663 VA stand from the company at zero applied potential Vs S.C.E. Polarograms are recorded using a potential rate 100 mV/s. A three electrode system composed of a working dropping mercury electrode (DME), saturated calomel elctrodeectrode (SCE), is used as reference electrode in 1.0 M KCl solution at a mercury column height of 60 c.m.All pH-metric measurement were made on a Decible DB-1011 digital pH meter fitted with a glass electrode and saturated calomel electrode (SCE) as reference electrode, which was previously standardized with buffers of known pH.

2.3 Procedure

The polarographic of all compounds were made by mixing of solution of 6.0 ml of appropriate buffer, 1.0 ml of 1.0 M KCl, 1.0 ml of stock solution of depolarizer and 2.0 ml of Acetonitrile. An inert atmosphere was maintained by passing a stream of purified N_2 gas for about 10 minutes. Pulse polarograms of newly synthesized compounds were recorded. The experiments were carried out to study the influence of different concentration of the depolarizer and different pulse amplitude on reduction process of newly synthesised 2-amino-4,6-diethyl-5-(4'-sulphonamoyl)azopyrimidines.

3. RESULT AND DISCUSSION

3.1 Differential pulse polarography

For all the compounds polarographic wave was found to be pH dependent. The plot of peak potential shifted towards more negative potential with rise in pH indicating the participation of protons in electrode process (Fig. 3.1.A_1 and A_2 Table-1]. The plots of peak height were proportional to the pulse amplitude and concentration of depolarizer confirming the diffusion controlled nature of the waves. The number of proton (p) involved in the rate determining step is calculated from the slope of $-E_p$ Vs pH plot, by following equation.

$$\partial E_{1/2} / \partial pH = 0.0591/\alpha n_a$$

The value of αn_a was obtained by the expression,

$$\alpha n_a = 0.0542 / Slope$$

The kinetics parameters heterogeneous rate constant, for electrode process was calculated from the peak current constant (I), diffusion coefficient $D^0_{1/2}$ of Differential pulse polarograms .The value of heterogeneous rate constant ($k^0_{f,h}$) has-been evaluated by Meites and Israel[13] equation.

$$E_{1/2} = -0.2412 + 0.0591 / \alpha na .log1.349\, k^0_{f,h}\, t^{1/2} D^0_{1/2}$$

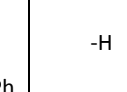
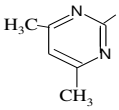
The value of diffusion coefficient has been determined by Ilkovic[14] equation.

$$id = 607\, n\, D^0_{1/2}\, m^{2/3}\, t^{1/6}\, C$$

Where n = number of electrons transferred in the process, m = rate of mercury flow in mg/s, D = diffusion constant of depolarizer in cm^2/s, t = drop time in s, C = depolarizer concentration in millimoles / litre, id = diffusion current in microamperes

The current constant (I) has been evaluated by the following expression- $I = id / c.m^{2/3}.t^{1/6}$

Table 1: Characteristics of 2-amino-4, 6-diethyl-5-(4'-sulphonamoyl) azopyrimidines at different pH, Conc. 2.0×10^{-4} M.

S. No.	Ph	-H							
		-Ep, (V)	id (µA)	-Ep, (V)	id (µA)	-Ep, (V)	id (µA)	-Ep, (V)	id (µA)
1.	2.5	0.90	3.58	0.91	3.31	0.92	4.50	0.82	3.59
2.	4.5	0.94	3.91	0.94	4.09	0.95	4.95	0.86	3.87
3.	7.0	1.06	4.45	1.08	5.16	1.10	5.85	0.91	4.87
4.	8.5	1.08	4.01	1.10	4.99	1.12	5.68	1.03	4.56
5.	10.5	1.15	3.52	1.17	4.34	1.18	4.58	1.10	3.79
6.	11.5	1.27	3.34	1.29	4.12	1.31	4.45	1.21	3.52

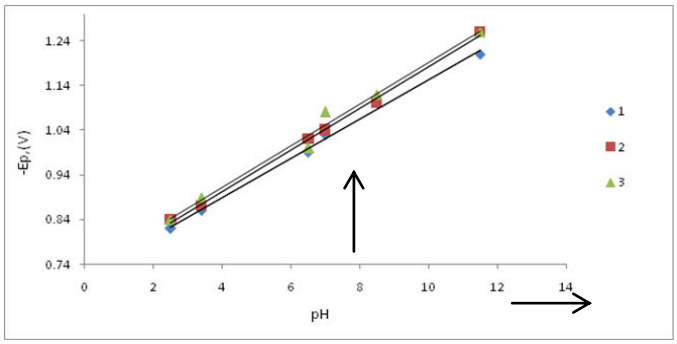


Fig. 3.1: (A_1) Plots of -Ep, (V) vs pH for

(1) 2-amino-4,6-diethyl-5-[4'-sulphanyl sulphonamoyl] azoppyrimidines.
(2) 2-amino-4,6-diethyl-5-[4'-guanidinyl sulphonamoyl] azoppyrimidines.
(3) 2-amino-4,6-diethyl-5- [4'-diazinyl sulphonamoyl] azoppyrimidines.

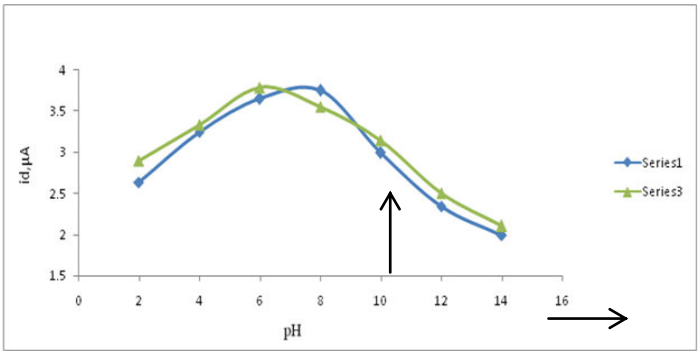


Fig. 3.1: (A_2) Plots of i_d, (µA) vs pH for

(1) 2-amino-4,6-diethyl-5-[4'-sulphanyl sulphonamoyl] azopyrimidines.
(2) 2-amino-4,6-diethyl-5-[4'-diazinyl sulphonamoyl] azopyrimidines.

3.3 Logarithmic analysis

This behavior clearly indicates towards irreversible nature of the wave, which is further confirmed by logarithmic analysis, i.e., the slope of the plot of Ed.e Vs log [i / id-i] was much higher than that of 0.0591 / n V. The plots of Ed.e. Vs log [i / id-i]-0.546 log t is given in [Fig.3.3.] and characteristics data are given in Table-3. Irreversible nature of the wave, is also further confirmed by logarithmic analysis, i.e., the slope of the plot Ed.e Vs log [i / id-i] was much higher than that of 0.0591 / nV.

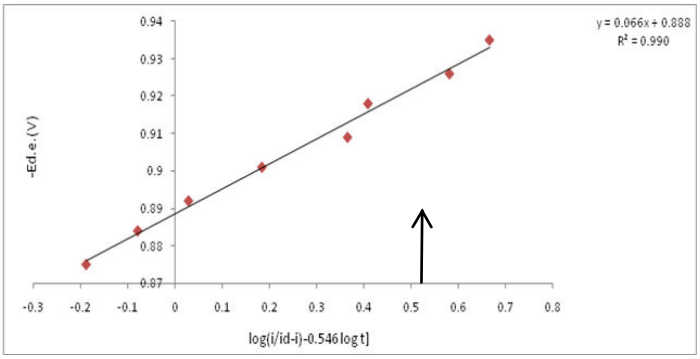
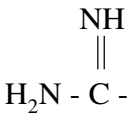
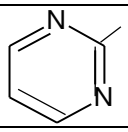
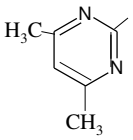


Fig 3.3: Plots of -Ed.e.(v) vs log(i /id-i)-0.546 for

(1) 2-amino-4,6-diethyl-5-(4'-sulphanyl sulphonamoyl) azopyrimidines

Table 2: Differential pulse polarographic characteristics of 2- amino-4, 6-diethyl-5-(4'-sulphonamoyl)azopyrimidines at pH 7.0, Conc. 2.0×10^{-4} M.

S. No.	-R	-Ep,V	id,µA	$\partial E_{1/2}/\partial pH$, V/pH	P	αna	I	$D_0^{1/2}\times10^{-3}$ cms^{-1}	$K^0f,h\times10^{-6}$ Cms^{-1}
1	-H	1.06	4.45	0.051	0.730	0.846	9.8	8.0	2.1
2		1.08	5.16	0.049	0.701	0.821	10.4	8.6	2.4
3		1.10	5.85	0.048	0.687	0.888	10.6	9.7	1.2
4		0.99	4.87	0.058	0.830	0.874	9.9	8.1	3.0

3.5 Reduction mechanism

In sulphonamoylazopyrimidines the possible reduction sites are >C=C, -C=N and exocyclic –N=N- out of these exocyclic –N=N bond is more susceptible to reduction because –C=N and >C=C< reduces at higher potentials. Hilson and others have reported that reduction of azo compounds takes place in 2 electron wave at the –N=N- giving hydrazono derivatives. The polarograms of the completely reduced solution did not show any reduction peak. This clearly indicates that no electroactactive species remained in the solution after complete electroreduction of compound. During the reduction, the polarized molecule formed in the first step takes a proton from the medium and gets protonated. The second step is slow and rate determining. The following scheme of the reaction of all substituted sulphonamoylazopyrimidines.

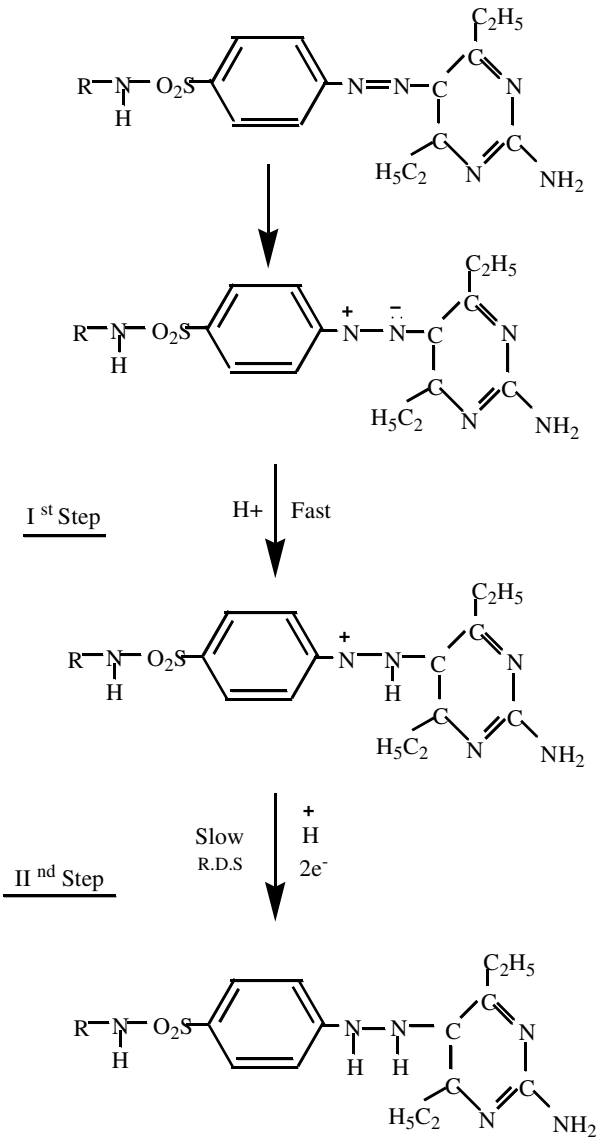


Fig.3.3: **Reaction mechanism**

3.6 Effect of ionic strength

Following equation[15] for an irreversible electrode process express the effect of double layer on -E_P values.

$$E_p = \Delta\psi_1 \left[\frac{\alpha n_a - Z}{\alpha n_a} - \frac{\partial E_{1/2}}{\partial pH} \cdot \frac{F}{2.303RT}\right]$$

Where, Z is the charge of reacting ion,Ψ is the mean electrostatic potential at the distance of an ionic redius from the surface of the electrode,α is the transfer coefficient,n is the number of electron transferred in the rate determining step. For non-ionic species the -E_p is not affected because Z=0 the first term in bracket become unity and second term in bracket is also unity, thus -Ep will be almost independent of ionic strength. For finding out the above effect polarograms of sulphonamoylazopyrimidines were recorded. No change in half-wave potential and wave height was observed (Table III). These observations indicate that peak potential of these compounds is independent of the strength of a particular supporting electrolyte.

Table 3: Effect of ionic-strenght on polarographic characteristics of 2-amino-4,6-diethyl-5-(4'-sulphonamoyl)azopyrimidines at pH 7.0, conc. =2.0×10^{-4} M, height =60 cm.

S. No.	Volume of KCl (1.0 M) , ml	-E_p ,(V)	i_d , (μA)
1.	0.50	1.06	4.45
2.	1.00	1.06	4.45
3.	1.50	1.06	4.45
4.	2.00	1.06	4.45

3.7 Effect of cation and anions

All the 2-amino-4, 6-diethyl-5-(4'-sulphonamoyl)azopyramidines were subjected to polarographic measurement using chlorides of lithium, sodium, and potassium as supporting electrolytes to determine the effect of size of the cation of the supporting electrolytes on the polarographic characteristics. The peak potential shifted towards more negative potential with increase in the size of the cation. This can be explained in terms of the structure of the double layer, although the value of peak potential is independent of Ψ_1 or ionic strength for a particular supporting electrolyte. As the size of the cation of supporting electrolyte increases the value of Ψ_1 decreases and the reaction become more difficult with the result peak potential get shifted towards more negative potential.

Table 4: Effect of cations and anions on the polarographic characteristics of 2-amino-4, 6-diethyl-5-(4'-sulphonamoyl) azopyramidines at pH 2.5, conc.2.0×10^{-4} M, height =60 cm.

S. No.	Supporting electrolyte	$-E_p$, (V)	i_d, (µA)
1.	KCl	0.90	3.58
2.	LiCl	0.92	3.58
3.	NaCl	0.95	3.56
4.	KI	0.97	3.58
5.	KNO_3	0.97	3.58

3.8. Effect of different solvents and their composition

The polarograms of sulphonamoylazopyrimidines were recorded in the minimum amout (30%) of D.M.F. The solvent concentration was then gradually increased from 30% to 70% to find out the effect of solvent composition on electrode process.It was observed that the $-E_P$ shifted towards more negative potential (Table IV) with increasing concentration of solvent. The limiting current values are, however, decreases, which may be attributed to the decrease in the magnitude of diffusion coefficient of the depolarisers as a result of an increase in viscosity of medium.

Table 5: Effect of solvent composition on the polarographic characteristics of 2-amino-4, 6-diethyl-5-(4'-sulphonamoyl)azopyramidines at pH 7.0 Conc. 2.0×10^{-4}, height = 60 cm.

S. No.	Percentage of ACN %	$-E_p$ (V)	id,µA
1	30	1.08	4.01
2	40	1.10	3.86
3	50	1.12	2.45
4	60	1.19	2.03
5	70	1.22	1.99

4. CONCLUSION

2- amino- 4,6- diethyl -5 - (4'-sulphonamoyl) azopyrimidines have been characterized electrochemically by polarography at dropping mercury electrode (DME), glassy carbon electrode (GCE). The plot of peak potential shifted towards more negative potential with rise in pH for all compounds. DPP (Differential pulse polarography) provide a sensitive and selective method for the determination. Analytical results obtained are adequate, precise and are in good agreement.

5. ACKNOWLEDGEMENT

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