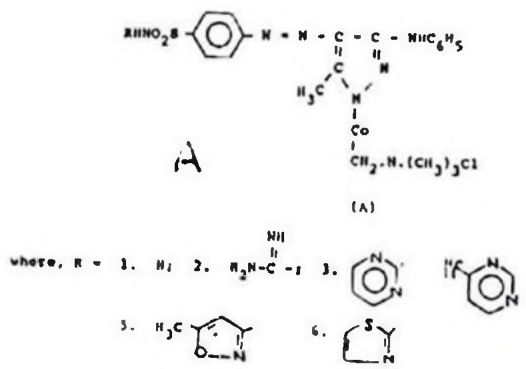
Voltammetric Studies on Some Sulphonamoyl Azopyrazoles

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The electrochemical behaviour of 1 - (carboxymethyl) trimethylammoniumchloride,3-aminophenyl,5-methyl,4-(4'-sulphonamoyl), azopyrazoles have been carried out in B.R. buffers of pH range 2.5-12.0 using 0.1M KCl as supporting electrolyte at d.m.e. and g.c. electrodes. For all these compounds a single, two - electron, diffusion-controlled, irreversible wave corresponding to the reduction of azo group was observed. The mechanism of reduction has been postulated on the basis of DCP, CV, coulometry and end product analysis. The effect of ionic-strength and solvent composition on the electrode process has also been studied.

The redox chemistry of azo compounds [1] is of immense importance due to their medicinal and other various applications. In view of the biological activities displayed by azopyrazoles and sulphonamides and usefulness of electrochemical techniques in studying compounds of biological importance, some azopyrazoles have been studied comprehensively at d.m.e. and g.c. electrodes.



1 - (carboxymethyl) trimethylammo-niumchloride, 3-aminophenyl,5-methyl,4-(4'-substituted sulphonamoyl), azopyrazoles

EXPERIMENTAL

All the compounds were synthesised in the laboratory [2] and purified by recrystallisation. The structure of these compounds was confirmed by elemental and spectral analysis. Stock solutions ($2.0X10^{-4}$ M) of all compounds were prepared in dimethylformamide (AR). Buffer Stock solutions at pH 2.5-12.0 and potassium chloride (1.0 M) solution were prepared in double distilled water from AR grade chemicals. The equipment used and experimental details are reported elsewhere [3].

RESULTS AND DISCUSSION

D.C. Polarography

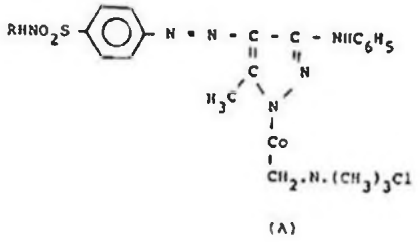
All the 1 - (carboxymethyl) trimethylammo-niumchloride,3-aminophenyl,5-methyl,4-(4'-

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substituted sulphonamoyl), azopyrazoles (compounds A 1 - 6) were reduced in a single, well-defined, two-electron step in the pH range 2.5-12.0. The electrochemical characteristics of the compounds are compiled in Table 1.

Table 1

Polarographic Characteristics of 1-(Carboxymethyl)trimethyl-ammoniumchloride, 3-aminophenyl,5-methyl,4-[4'-(substituted) sulphonamoyl] azopyrazoles



(A)

pH = 4.7; Conc = 2.0 x 10^{-4} M

Comp. No.	$-E_{1/2}$ V	i_d mA	$\frac{dE_{1/2}}{dpH}$	Ix10^{-3}	P	αn_a
1	1.20	2.54	0.08	0.47	1.10	0.79
2	1.12	2.30	0.06	0.40	0.59	0.59
3	1.12	3.80	0.08	0.69	1.03	0.73
4	1.04	4.05	0.08	0.55	1.00	0.73
5	1.06	3.45	0.07	0.62	0.74	0.59

The low values of temperature coefficient (< 1.62%/deg.) and direct proportionality beween i_d *vs* concentration & i_d *vs* $h^{1/2}$ clearly established the diffusion-controlled nature of the electrode process. The shift in $E_{1/2}$ towards more negative potential with concentration and logarithmic analysis confirmed the irreversible nature of the electrode process [4]. The value of αn_a and the number of protons (P) involved in the rate determining step are calculated using following expressions:

$$E_{3/4} - E_{1/4} = 0.0517/\alpha n_a \quad \text{and}$$

$$\frac{dE_{1/2}}{dpH} = \frac{0.05917}{\alpha n_a} \times P$$

Linear Sweep and Cyclic Voltammetry

Voltammetric reduction at glassy carbon electrode in the entire pH range (2.5 - 12.0) indicates irreversible nature of the electrode process [6] by the negative shift in the peak potential with increasing sweep rate (50-20 mV/sec). The plots of i_d *vs* concentration and i_p *vs* $v^{1/2}$ are linear (Fig.1) indicating the diffusion-controlled nature [5] of the

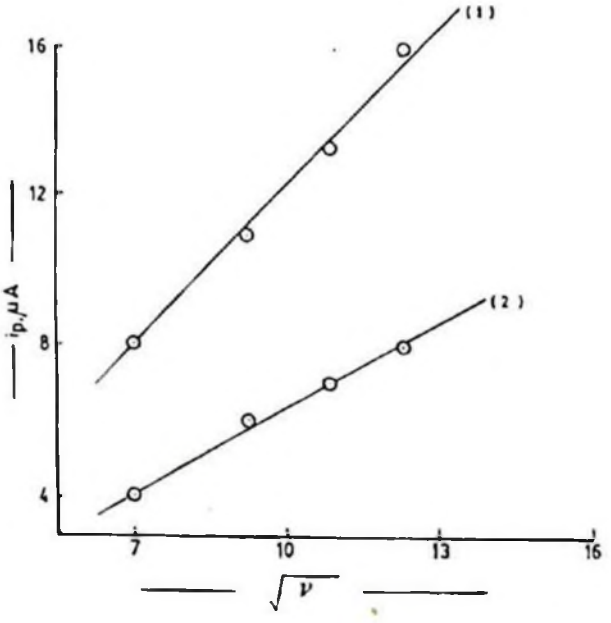


Fig. 1: Plots of i_p, μA Vs $\sqrt{\nu}$ for 1- (Carboxymethyl) trimethylammoniumchloride - 3 - aminophenyl - 5 - methyl - 4 - (1) [4' - pyrimidinylsulphonamoyl], (2) [4'- (4'', 6''- dimethylpyrimidinylsulphonamoyl) azopyrazole at pH 4.2, Conc 2 x 10^{-4} M

electrode process. These results thus, confirmed the D.C.polarographic result. The plots of E_p *vs* pH are almost identical to $E_{1/2}$ vs pH plots.

Coulometry

Coulometric measurements [7] showed that the number of electrons taking part in overall electrode process was found to be two. With progress of electrolysis at the controlled potential, the colour of the solution gradually faded away and finally a colourless solution was obtained, indicating reduction of azo group.

Mechanism of Reduction of azo Group

On the basis of number of electrons involved in the electrode process and number of protons involvedved in the rate determining step, following mechanism [8] may be postulated for the reduction of these compounds.

R'-N=N-R"

⇕

R'-N⁺=N⁻-R"

Fast +H⁺

↓ H

R'-N⁺=N-R"

Slow 2e⁻ H⁺

↓

R'-NH -NH-R"

Where R' = 

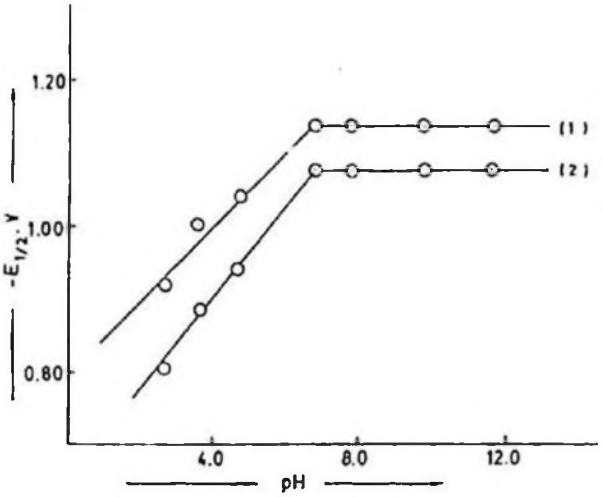
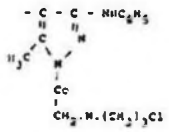


Fig.2: Plots of $-E_{1/2}$, V Vs pH for 1- (Carboxymethyl) trimethyl-ammoniumchloride - 3 - aminophenyl - 5 - methyl- 4 - (1) (4'-methoxazolylsulphonamoyl) ; (2) (4", 6"-dimethyl - primidinylsulphonamoyl) azopyrazole at Conc. 2.0×10^{-4} M.

and R" = 

This mechanism is supported by shift of $E_{1/2}$ with pH (Fig 2). Both acidic and basic forms of the depolarizer are electro-active but in the pH range where protonation rate decreases, their $E_{1/2}$s are so close to each other that the waves merge [9 a], hence $E_{1/2}$ is constant above 7.7 pH. Below this pH, only the acidic form is undergoing reduction.

Effect of Double Layer

Ionic Strength

Ionic strength affects double layer and the latter affects the kinetics of the electrode process. In the present case, $E_{1/2}$ is found to be independent of ionic strength in the range 0.5 M to 2.0 M KCl; i_d also is independent.

Mairanovsky [10] has given an expression for $\Delta E_{1/2}$ consisting of two terms- the first depending on the charge of the electroactive species and the second term depending on pH dependence of $E_{1/2}$. Compounds under study are adsorbed at the mercury surface and their preprotonation is also a surface reaction - they are present chiefly in non-ionised state in bulk; adsorbed species change to protonated form on the surface just before discharge. Thus for all practical purposes, charge on the reacting species may be considered as zero. Thus the first term in Mairanovsky expression for $\Delta E_{1/2}$ becomes unity. The second term could be just cancelling the first resulting in $\Delta E_{1/2} = 0$.

Effect of Different Ions

The size of the ions in the medium also is expected to influence double layer. To evaluate this, the effect of different anions and cations on the polarogram was studied by repeating the measurements in 0.1 M solutions of KBr, KI, KCNS & KNO_3 and LiCl, NaCl, CsCl & tetraethylammonium bromide as supporting electrolytes. No change in i_d and $E_{1/2}$ values was observed in case of anion variation, but $E_{1/2}$ shifted towards more negative values and i_d was found to be constant with increase in cation size (Table 2). The structure of double layer does not change with size of the anions [11] since cations predominate in the electrical double layer at these potentials. Increase in the size of the cations lead to decrease in Ψ potential making reaction more difficult [12]; This results in a shift of $E_{1/2}$ towards more negative values.

Table 2

Effect of Cations, Anions and Solvent Concentration on the Polarographic Characteristics

Depolarizer: 1-(Carboxymethyl)-trimethylammoni umchloride, 3-aminophenyl,5-methyl,4-[4'-(substituted) sulphonamoyl] azopyrazole
pH = 4.7; Conc = 2.0 x 10^{-4} M; Solvent DMF
Supportmg Electrolyte Concentration = 0.1 M

Supp. Electrolyte	% DMF	$-E_{1/2}$ V	i_d mA
Effect of Anions			
$(C_2H_5)_4NBr$	30% DMF	1.18	2.58
KBr	30% DMF	1.18	2.30
KI	30% DMF	1.18	2.30
KNO_3	30% DMF	1.18	2.30
KCNS	30% DMF	1.18	2.30
Effect of Cations			
LiCl	30% DMF	1.16	2.64
NaCl	30% DMF	1.18	2.60
KCl	30% DMF	1.20	2.54
Effect of Solvent Concentration			
KCl	30% DMF	1.20	2.54
KCl	40% DMF	1.22	2.58
KCl	50% DMF	1.24	2.40
KCl	60% DMF	1.26	2.30
KCl	70% DMF	1.30	1.80

Effect of Solvent Composition

On increasing the concentration of DMF from 30 - 70%, both $E_{1/2}$ and i_d decreased. At very high concentration of the solvent, ill defined waves were observed. The protonated species

get discharged on the electrode surface. The increase in solvent results in increase in pH [13] and dissociation constant of the protonated species [14]. Both these factors lower protonation; consequence is the shift in $E_{1/2}$ [14]. Schwabe assumed a shift in $E_{1/2}$ as due to inhibition of electrode process by the adsorbed solvent molecules [15]. A decrease in adsorbability (and hence surface concentration) of the depolariser with increasing concentration of the organic solvent in aqueous - organic mixture would also retard the electrode process [9 b]. Decrease in i_d could be due to increase in viscosity of the solvent.

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