Polarographic Studies on Arylazopyrazoles with Special Reference to the effect of Surfactants

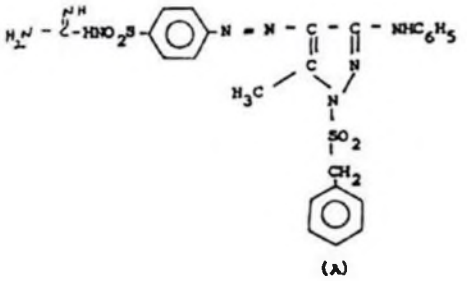
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The importance of surface active agents in the suppression of polarographic maxima is well known. A variety of compounds like gelatin, agar, glue, peptones, gum arabic, methyl red, fuchsin, and cationic, anionic & non - ionic soaps has been cited in the literature as maximum suppressors in polarographic analysis. However, only few of them (such as gelatin, methyl red and triton x-100) have found universal application. In the last few decades, many new suppressors have been recommended. To cite a few - poly acrylamide [1], thiobarbiturates [2] and sulphonated aryl stearic acids, dodecyl pyridinium bromide, isothiourea & dodecyl ether hydrobromide [3]. Studies by other workers include the work of Reilley [4] and Smoler [5] on the effect of surface active agents on polarographic current, as well as Holleck and Exner [6] on the effect of such compounds on the mechanism of reduction of organic compunds.

Amongst the new suppressors recommended, mention may be made of the use of polyoxyethylene lauryl ether by Tamamushi and Yamanaka [7], dimethyl dodecyl amine oxide by Barradas and Kimmerle [8,9], dodecyl ammonium and tetrabutyl ammonium perchlorate by Kolthoff and Khallafella [10] and soaps, dodecyl benzene sulphonates, dodecyl pyridinim bromide by Malik and Haque [3]. Although a number of workers have studied the effect of surface active agents in polarography, little attention has been paid to the exact role of surface active agents in the suppression of polarographic maxima.

The present paper deals with the effect of surfactants on the polarographic maxima on the heterocyclic compound 1-phenyl methyl sulphonyl 3-aminophenyl-5-methyl-4 (4'-guanylsulphonamoyl) azopyrazole (A).



(A)

EXPERIMENTAL

Polarographic measurements were carried out on ELICO DC CL - 25 polarograph. Dropping mercury electrode was used as working

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electrode and saturated calomel electrode (SCE) as reference electrode. Potentiometric studies were made on DP510 Digital pH Meter with glass electrode which was previously standardised with buffers of known pH in acidic and alkaline range.

Stock solution ($2.0x10^{-3}$M) of the azopyrazole (A) was prepared in purified DMF (AnalaR). Potassium chloride (Analar) solution (1.0M) was prepared in doubly distilled water. B.R. buffers of varying pH were prepared in doubly distilled water using A.R. grade chemicals. Surfactants like tween-20, sodium dodecyl sulphate, cetylpyridinium chloride having concentration 0.1% in distilled water were used to study their effect on polarographic maxima.

Working solutions were prepared by mixing 1.0 ml of stock solution of aopyrazole (A), 2.0 ml of DMF, 1.0 ml of KCl and 6.0 ml of appropriate B.R. buffer. Six such solutions were prepared with increasing amounts (0.1 ml to 0.5 ml) of 0.1% surfactant solution while keeping final volume 10 ml and maintaining concentration of depolariser at $2.0x10^{-4}$ by reducing the volume of B.R. buffer (from 5.9 to 5.5 ml). The solutions were deareated by passing a stream of purified nitrogen gas for 15 minutes before recording the polarograms and a blanket of nitrogen gas was maintained throughout the experiment in all the cases.

RESULTS AND DISCUSSION

The azopyiazole (A) gave a single, two electron reduction wave in the B.R. buffers of pH range 2.3 to 11.8. The polarographic wave was diffusion-controlled (i_d *vs* $h^{1/2}$ and i_d *vs* concentration plots linear) and inreversible ($E_{1/2}$ for the reduction of azo group was found to be pH dependent, Table 1 and shifted towards more negative potential with increasing concentration of the depolariser).

Table 1

Polargraphic characteristics of 1-phenylmethyl-sulphonyl,3-aminophenyl,5-methyl,4-(4'-guanylsulphonamoyl) azopyrazole at Different pH

Conc. = $2.0x10^{-4}$M

pH	$-E_{1/2}$ V	i_d μA
4.5	0.65	1.98
6.5	0.68	1.92
7.5	0.70	1.88
11.5	0.72	1.88

A maximum was observed in the polarogram. Surfactants tween-20, sodium dodecyl sulphate and cetylpyridinium chloride were added to suppress maximum. It is known that surfactants even in trace quantities can exert a strong effect on the electrode process and adsorption of such substances at the electrode process may inhibit the electrolytic process, deform the polarographic current voltage curves, bring about irregularity in the polarograms, shift the wave to more negative potential or even split the wave [9]. All the three types of surfactants - anionic (e.g., sodium dodecyl sulphate), cationic (e.g.,

cetylpyridinium chloride) and non-ionic (e.g., tween-20) - were used and in different concentrations in this study to suppress the polarographic maxima. Maximum in the polarogram of compound (A) gets suppressed in the prsence of all the three types of surfectants. It was observed that the maxima get suppressed at lower concentrations of surfactants, but at higher concentrations, the $E_{1/2}$ shifted towards more negative potential and i_d decreased. Surfactants above critical micellar concentration (CMC) got absorbed at the electrode surface. This lowers the surface concentration of the depolariser. The combined effect of adsorption and change in double layer structure lower the rate of electrode process resulting in cathodic shift of half-wave potential and decrease in the value of limiting current.

When tween-20 was added to the solution at the lower concentration (when 0.1 ml of 0.1% tween -20 was used), the polarographic maxima disappeared. But at the concentration in the range 0.1 ml to 0.2 ml, the halfwave potential shifted towards more negative potential and limiting current decreased. These effects were more at higher concentration (Table 2). Similar observations were recorded in the case of anionic surfactant, 0.1% sodium dodecyl sulphate and cationic surfactant, 0.1% cetylpyridinium chloride (Table 2).

Table 2

Polargraphic characteristics of 1-phenylmethyl-sulphonyl,3-aminophenyl,5-methyl,4-(4'-guanylsulphonamoyl) azopyrazole at Different Concentrations of Surfactants

pH = 4.5; Conc. = 2.0×10^{-4}M
Stock Solution of Surfactant Used 0.1 %

Vol	$-E_{1/2}$	i_d	$-E_{1/2}$	i_d	$-E_{1/2}$	i_d
case	V	μA	V	μA	V	μA
Surfactant	**Tween 20**		**Na Dodecyl Sulphate**		**Cetyl Pyridinium Cl**	
0.0	0.65	1.98	0.65	1.98	0.65	1.98
0.1	0.66	1.96	0.66	1.96	0.68	1.96
0.2	0.68	1.92	0.68	1.94	0.68	1.96
0.3	0.68	1.90	0.70	1.92	0.70	1.92
0.4	0.70	1.86	0.70	1.89	0.72	1.84
0.5	0.72	1.84	0.72	1.86	0.72	1.86

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