

Polarographic Behaviour of Some Sulphonic-aryl-hydrazono Pyrazolin-5-one Dyes

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Summary: Polarographic studies of some sulphonic aryl (or naphthol) hydrazono-1-phenyl-3-methyl-2-pyrazolin-5-one have been carried out in 10% ethyl alcohol B.R. buffer solutions in the pH range 1.8 - 12.0. The number of reduction waves was found to depend on the pH value of the solution and the structure of the dye stuff. All the compounds gave a single, well defined irreversible wave between pH values 2.0-9.0. The $E_{1/2}$ of this wave is pH dependent but its i_d remains almost constant throughout the entire pH range. The $E_{1/2}$ was shifted towards more negative potential showing that protonation precedes reduction. The sulphonic group causes a shift of the wave and plateau suffers a minimum at pH value higher than 9.0. The reduction corresponds to consumption of four electrons leading to the amine stage. A general mechanism for the reduction process is suggested and discussed.

Introduction

Pyrazolone and pyrazolin-5-one possess interesting antidiabetic [1-3] antineoplastic activity [4]. In view of the fact that the physiological activity of a molecule is closely related to its redox behaviour [5] in the cell membrane, therefore the study of some sulphonic arylhydrazones pyrazolin-5-one dyes were investigated at d.m.e. As a simple relationship exists between structure, half wave potential and reactivity, a better understanding of the effect of structure on the redox behaviour of these compounds can be obtained [6]. The present work summarises the electrochemical behaviour of some sulphonic aryl hydrazono-pyrazolin-5-one dyes with special reference to the effect of sulphonic group on their redox mechanisms.

Materials and Methods

The organic ligands used in the present investigation were prepared as mentioned previously [7] by coupling the diazonium salts of 4-, 3- and 2-sulphonic (4-methyl) acid compounds with pyrazolin-5-one in sodium acetate medium. Also, 2-hydroxy (4-sulphonic) naphthalene hydrazono-pyrazolin-5-one ligand was prepared by the same method [7]. The resulting dyes were recrystallized from the appropriate solvents. Elemental analysis and IR spectra confirmed the structure and purity of the compounds.

The stock solutions (0.01 M) of these compounds were prepared in 50% ethanol-50% water mixture (v/v). The

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Table-1: Effect of pH on $E_{1/2}$ and i_d of 0.5 mM. Organic Dye Solution 0.02% Gelatin in 10% Ethanol-Water at different pH's of Universal Buffer Solution.

PHP(1)					2-S(4-Me)PHP(II)					2-(OH)4-S NHP(V)				
pH	$E_{1/2}$ (V)	i_d/A	αn_a analysis	Tomas	pH	$E_{1/2}$ (V)	i_d/A	αn_a analysis	Tomas	pH	$-E_{1/2}$ (V)	i_d/A	αn_a analysis	Tomas
2.40	0.09	4.80	0.71	0.54	1.60	0.20	4.00	0.55	0.34	3.80	0.12	5.30	0.69	-
3.85	0.18	4.75	0.71	0.90	2.10	0.14	4.80	0.34	0.34	4.50	0.16	5.40	0.69	-
6.00	0.35	4.80	0.95	0.90	2.80	0.34	4.35	0.35	0.34	5.15	0.17	4.90	0.88	-
6.80	0.39	4.90	0.54	0.90	3.40	0.40	4.70	0.31	0.32	6.40	0.21	5.40	0.79	0.90
7.50	0.42	4.95	0.78	0.83	4.40	0.42	4.15	0.57	0.49	7.00	0.24	5.45	0.79	0.90
8.60	0.39	4.25	0.77	0.83	5.40	0.46	4.25	0.57	0.45	8.00	0.31	5.20	0.82	0.54
9.60	0.52	5.40	0.50	0.54	6.40	0.46	3.73	0.74	0.54	9.35	0.41	5.05	1.28	0.45
			0.40	0.54	7.30	0.47	3.80	0.53	0.68					
10.4	0.66*	3.10			8.40	0.47	4.05	0.69	0.49	10.10	0.42	4.10	0.65	0.45
	1.05**	1.10	-	-	9.00	0.55	4.10	-	0.54		0.84	3.25	0.77	0.77
					9.60	0.60	4.20	0.69	0.49					
										10.70	0.45*	3.20	0.63	0.90
											0.82**	3.70	-	0.45
					10.40	0.62**	3.72	0.31	0.54					
						1.33**	1.00	0.66	-	11.60	0.47**	0.65	-	-
											0.83	4.35	0.82	0.68
					12.00	0.62**	1.15	0.71						
						1.08	3.05	0.31	0.41	12.00	0.81**	3.75	0.69	0.60

* Parameter of 1st wave (A_1), ** Parameter of 2nd wave (A_2), + Concentration of (V). 0.1 mM.

(PHP)] whose polarogram consists of one reduction wave. The $E_{1/2}$ of this wave shifted towards more negative potentials on increasing the pH values as shown in Fig. (2a) and Table-1. A new ill defined second wave appeared at pH value 10.40.

(2) The second category comprises the compounds having sulphonic group in phenyl ring (compounds II-IV) whose polarograms consist of one well defined wave (A_1) at pH range (1.8-9.0). At pH 9.0, a new reduction wave begins to appear accompanied with a distortion of the plateau by the appearance of a minimum. The hump followed by the minimum through the reduction polarograms takes its characteristic shape in case of compounds II, III and IV at negative potential ranges between (0.7 - 1.2), (0.9 - 1.4) and (0.8 - 1.2) V., vs. SCE and at pH values 10.4, 9.0 and 9.6 respectively. As a result of this behaviour (hump followed by a minimum), a shifted rising portion leads to the formation of a new wave (A_2). The height of the first part

(A_1) decrease while that of the second part (A_2) increases with increasing pH, of the solutions (Fig. 2b).

(3) The third category is that of compound (V) which has a naphthol moiety and is different from the previous category in that its polarogram consists of one reduction wave at pH values between (3.8-8.0) and at potential range (0.0 to 0.4V) vs. SCE. Increasing pH from 8.0 to 11.6, the polarogram has a hump followed by a minimum at potential range (-0.7 to -10.0 V) vs. SCE similar to that observed through the second category was also obtained (Fig. 2 b,c). This characteristic behaviour may be attributed to the presence of sulphonic group in the dye stuff compounds (II-IV).

It is clear from (Fig. 2c Table 1) that the height of the first wave decreases while that of the second wave increases with the variation of pH from 8.0 to 11.6. Polarogram at pH 12 differs from those in the second categories as in this pH range the polaro-

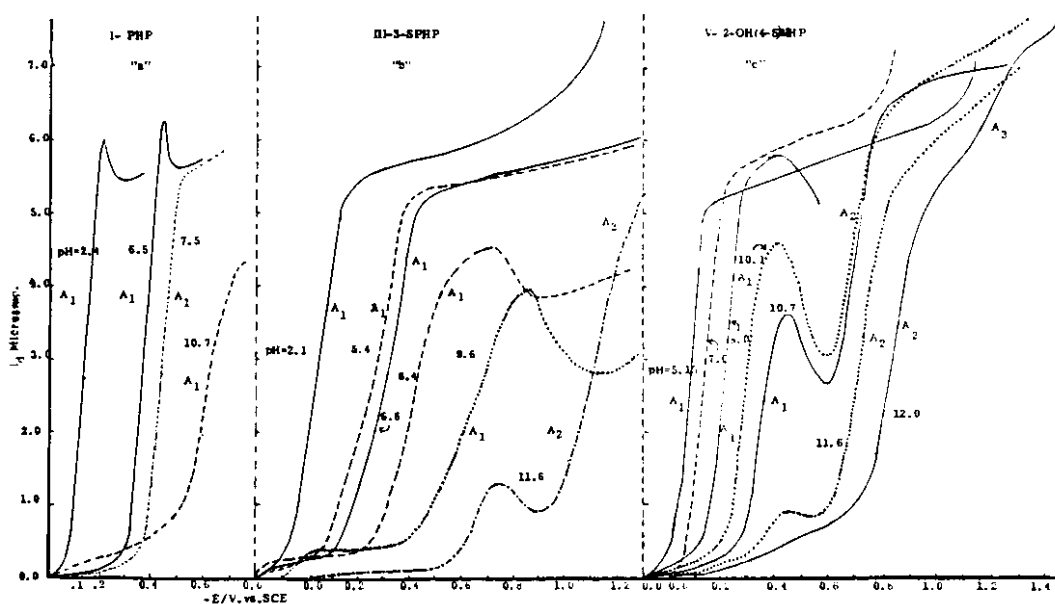


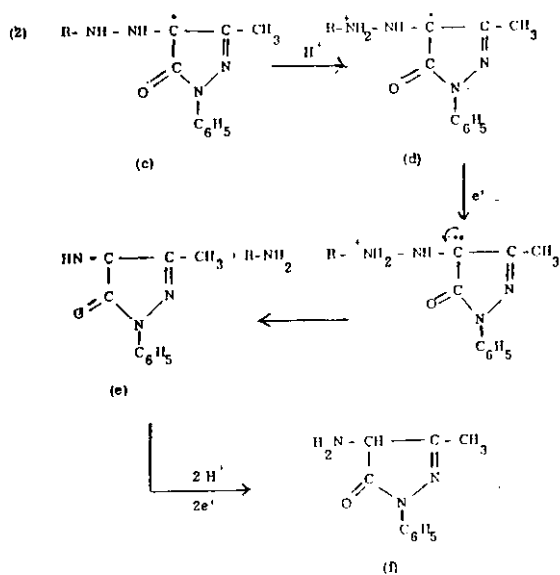
Fig.-2: Polarographic behaviour of I,II and V dyes at different pH's.

gram begins to split into two due to the ionization of hydroxyl group; the first wave nonionized species and the second wave ($E_{1/2}$ 1.16 V. vs. SCE) for ionized species.

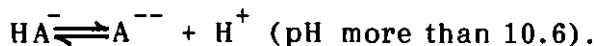
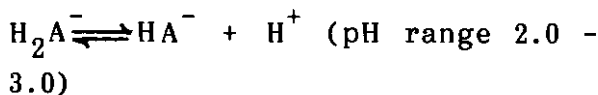
It is interesting to note that the half wave potential of the first wave obtained in case of compounds (II-V) shifts to more negative values (i.e. retarding effect) at high pH. This retarding effect was noticed in the case of compounds (II, III and IV) at pH values 9.0, and pH 8.0 for compound (V), (Fig. 2b and c). The splitting of the single wave into (A_1 and A_2) which may be due to nonionized-ionized forms or due to retardation of reduction due to adsorption of certain species. Since the values of i_d in acid medium about equal the summation of i_d of both waves in alkaline medium (Table-1). Therefore, the number of electrons consumed in both media are equal, thus favouring adsorption of certain species. The presence of a hump followed by a minimum and then a rising portion (A_1) indicates

that the reduction is hindered on the covered areas of the drop and unhindered on the bare portions [9]. The adsorbed species are the sulphonate anions probably associated with [10, 11] the buffer cation. It is clear now that the reduction behaviour of compound (I), (without sulphonic group) is not similar to that of the other dyes investigated (compounds II-V). The polarographic reduction obtained through the investigation of these compounds is similar to that obtained previously during the reduction of some 3-pyridyl azo dyes containing sulphonic group [9].

The half wave potential ($E_{1/2}$) vs. pH plots for the reduction waves obtained denote that hydrogen ions are consumed in the electrode process. The logarithmic analysis of the polarographic waves are linear plots with slopes amounting 0.07 to 0.18 denoting that the electrode process proceeds irreversibly. The effect of the mercury height (h) on the limiting current (i_d) for the investigated compounds at different pH values was studied. The plot of $\log(i_d)$ vs. $\log h$ is linear



group K_1 of the compounds (II-IV) are expected at pH value about 3.0 [17], therefore, the tendency of shifting $E_{1/2}$ to more negative potentials decrease till pH value 10.4 and an increase in $E_{1/2}$ values indicates the formation of new ionized species "reduced form"



The plots of $E_{1/2}$ vs.pH (Fig.1) is composed of interesting three segments and the pH's at points of intersection approximately equal to pK_1 and pK_2 respectively.

These data are in good agreement with results obtained by both spectrophotometric and pH-metric determination of the dissociation constant of compound (V) [7].

It is important to note that, when the depolarizer solution was tested after controlled potential electrolysis, it gave the dye test indicating that

at least one of the reduction products is an aromatic amine. Moreover, the u.v. and visible spectra of the solution was recorded during electrolysis at different time intervals. It was found that λ_{max} at 390 nm (due to $-NH-N=C$ grouping) showed gradually decrease in peak height and finally the wave disappeared after 20 hrs. supporting the reduction mechanism proposed.

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