

## Polarographic Behaviour of Some 3-Pyridylazo Dyes

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The polarographic behaviour of some azo dyes containing 3-pyridyl moiety has been investigated in 40% ethanolic buffers covering the pH range 3-12. The number of waves depends on the part of the dye attached to the 3-pyridylazo moiety. If this part is 8-quinolinol, two waves are observed, while one wave is obtained if it is a phenol or naphthol derivative. However, this one wave splits into daughters in compounds containing sulphonic acid group due to adsorption of the dye molecules and reduction of the adsorbed molecules at lower potentials. The reduction corresponds to the consumption of four electrons leading to the amine stage. The second wave in the quinoline compound is due to two-electron reduction of the quinoline moiety. A general mechanism for the reduction process is given.

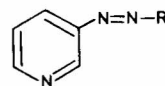
Florence *et al.*<sup>1</sup> while studying the reduction of heterocyclic hydroxyazo compounds at d.m.e observed that pyridylazo, thiazolylazo and quinolylazo phenols and naphthols yielded two-electron reduction waves in acid media and four-electron waves in alkaline media, in contrast to hydroxyazobenzenes which gave four-electron wave in acid medium. The stabilization of heterocyclic hydrazo compound formed in the first stage of the reduction was due to the electron attracting properties of the pyridyl, thiazolyl and quinolyl groups tending to cancel the electron donating effect of the hydroxy group. In the present investigation, the polarographic behaviour of some dyes containing the pyridylazo moiety has been studied in order to throw some light on the mechanism of the electrode process.

### Materials and Methods

Polarograms were recorded on a pen recording polarograph LP 60 (Laboratori Pristroje, Prague). The UV spectra were recorded on a UNICAM SP 1750 spectrophotometer. A specially designed cell was used<sup>2</sup> for polarographic measurements. The capillary used had the following characteristics in oxygen-free 0.1 M KCl in open circuit;  $m = 1.8$  mg/s;  $t = 3.7$  s at a mercury height (effective) of 60 cm. The cell used for coulometric studies was similar to that described by Zuman<sup>3</sup>. The pH values of the solutions were measured using a Prolabo pH-meter.

The azo dyes (I - IX) were prepared by coupling diazonium salt derived from 3-aminopyridine with phenol, *o*-, *m*- and *p*-cresols, 2-naphthol, Nevile and Winter's acid, Schaffer's acid, R-acid and 8-hydroxyquinoline in sodium hydroxide medium. The

resulting dyes were recrystallized from the appropriate solvent. The purity of the dyes was confirmed by elemental analyses. The stock solutions (0.001 M) of these dyes were prepared in DMF-ethanol (10:90, v/v). The Britton-Robinson buffers covering the pH range 3-12 were prepared as described before.



where R = *o*-cresol(I), *m*-cresol(II), *p*-cresol(III), phenol(IV), 2-naphthol(V), R-acid(VI), Nevile and Winter's acid(VII), Schaffer acid(VIII) and 8-hydroxyquinoline(IX)

Ethanol (4.5 ml), the appropriate buffer solution (7.8 ml), gelatin solution 0.5% (0.3 ml) and the dye solution (1 ml) were mixed in the polarographic cell, deoxygenated by passing purified nitrogen for 15 min, and the polarogram recorded.

### Results and Discussion

Typical current-potential curves at  $pH \approx 10.0$  are shown in Fig. 1. The half-wave potentials and limiting current for these compounds at different pH values are given in Table 1. Based on their polarographic behaviour, the compounds under investigation can be classified into two categories: (i) compounds (I-VIII) whose polarograms consist of one reduction wave, which splits into two daughter waves after certain pH for compounds containing sulphonic acid group, viz. VI-VIII; and (ii) compound (IX) whose polarogram consists of two waves in the range  $-0.1$  to  $-0.6$  V and  $-1.0$  to  $-1.6$  V (vs SCE) respectively.

Table 1—Polarographic Behaviour of the Azo Dyes Containing 3-Pyridyl Moiety

I			V			VI				
pH	$-E_{\frac{1}{2}}(A)$	$i_d(A)$	pH	$-E_{\frac{1}{2}}(A)$	$i_d(A)$	pH	$-E_{\frac{1}{2}}(A)$	$i_d(A)$	$-E_{\frac{1}{2}}(c)$	$i_d(c)$
3.9	0.21	1.06	3.9	0.24	0.85	5.55	0.33	1.50	—	—
4.65	0.23	1.23	4.55	0.31	0.92	6.95	0.45	1.45	—	—
5.40	0.32	1.03	5.35	0.37	0.87	7.45	0.53	1.40	—	—
6.65	0.41	0.97	6.65	0.44	0.86	8.20	0.59	1.40	D	0.07
7.70	0.49	0.87	7.80	0.52	0.90	8.85	0.63	1.35	D	0.09
8.65	0.59	0.82	8.70	0.58	0.91	9.55	0.67	1.18	1.10	0.19
9.85	0.60	0.84	9.55	0.65	0.97	9.95	0.70	1.13	1.10	0.19
10.00	0.67	0.77	10.00	0.67	1.01	10.30	0.74	0.99	1.10	0.27
10.60	0.86	0.96	10.60	0.70	0.96	10.90	0.81	0.78	1.14	0.57
11.25	0.94	1.03	11.20	0.71	0.94	11.10	0.80	0.70	1.14	0.57

VIII					IX				
pH	$-E_{\frac{1}{2}}(A)$	$i_d(A)$	$-E_{\frac{1}{2}}(c)$	$i_d(c)$	pH	$-E_{\frac{1}{2}}(A)$	$i_d(A)$	$-E_{\frac{1}{2}}(B)$	$i_d(B)$
3.95	0.18	1.06	—	—	3.95	0.15	0.90	—	—
4.65	0.34	1.03	—	—	4.65	0.22	0.98	—	—
5.50	0.32	1.17	—	—	5.35	0.29	0.87	—	—
6.15	0.34	1.15	—	—	5.95	0.33	0.78	—	—
7.45	0.45	1.14	—	—	7.25	0.43	0.78	—	—
8.05	0.48	1.13	—	—	8.70	0.56	1.02	—	—
9.40	0.55	1.10	—	—	10.00	0.66	1.39	1.45	0.70
10.10	0.60	1.09	—	—	10.35	0.67	1.40	1.58	0.60
10.95	0.66	1.05	1.27	0.12	10.65	0.68	1.40	1.57	0.58
11.50	0.73	0.86	1.30	0.17	11.30	0.79	1.43	1.57	0.54
11.70	0.72	0.77	1.25	0.27	11.70	0.83	1.45	1.64	0.44

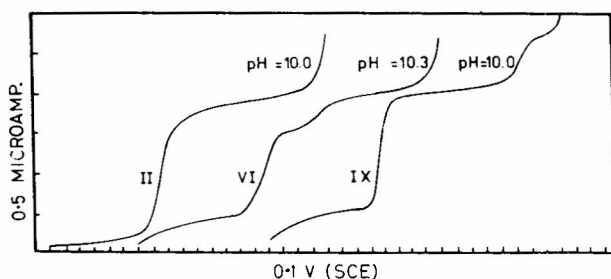


Fig. 1—Polarographic behaviour of II, VI and IX at pH 10

In the reduction waves of compounds (I-V) retardation of reduction is not operating at all pH values. The height of this wave is approximately constant and  $E_{\frac{1}{2}}$  is shifted to more negative potentials on increasing the pH. The single wave of compounds VI-VIII containing a sulphonic acid group suffers distortion of the plateau at pH ~ 9 as revealed by the appearance of a minimum covering the potential range 0.8-1.3V (vs SCE). The split in the wave is apparent from a hump followed by a minimum and then a rising portion. The height of the first part (A) decreases while that of the second part (A<sub>2</sub>) increases with increasing pH. The data in Table 1 show that the suppression of the current preceding the minimum is to an extent of 30-70% depending on the number of SO<sub>3</sub>Na groups in

the molecule. As the retarding effect starts at pH in the pK range of the dye and increases with increase in pH, it is apparently due to adsorption of the dye anion.

The  $E_{\frac{1}{2}}$  versus pH plots for the waves obtained denote that hydrogen ions are consumed in the electrode process. The logarithmic analyses of the polarographic waves are linear plots with slopes = 0.06 indicating that the electrode process proceeds irreversibly. The effect of mercury height on the limiting current for some compounds has been examined at different pH values; the plot of log  $i$  versus log  $h_{\text{eff}}$  is linear with a slope = 0.45 for the single wave indicating that the electrode process is mainly diffusion-controlled, whereas for the retarded part it is kinetically controlled as revealed by the slope = 0.25. Plots of the limiting current of the wave (A) versus molar concentration of the depolarisers are linear passing through origin indicating the validity of Ilkovic equation.

#### Mechanism of the electrode process

The polarograms of compounds (I-IX) reveal the following characteristics: (i) compounds (I-V) exhibit one reduction wave (A) only over the whole pH range; (ii) compounds VI-VIII show one wave, which suffers a minimum at the plateau and a decrease of the original

wave with the appearance of another wave ( $A_1$ ) at more negative potential; and (iii) compound (IX) gives a two-wave (A and B) polarogram.

For understanding the course of the electrode process corresponding to each of the waves, it is necessary to assign first the waves observed due to the electroactive groups in compound (IX) as representative. For this purpose controlled potential coulometry (CPC) has been carried out with IX. The absorption spectrum of IX before reduction exhibits two intense bands, one at 485 nm attributed to the  $\pi - \pi^*$  transition within the azo group influenced by charge transfer and second at 318 nm assigned to  $\pi - \pi^*$  transition of the quinoline moiety. In the absorption spectrum after CPC at potential corresponding to wave (A) the first band vanishes indicating the cleavage of the N=N group, while the second band is shifted to 294 nm. When CPC is carried out at  $-1.7$  V which is the potential corresponding to wave (B), the 294 nm band shifts to lower wavelength due to reduction of the quinoline moiety. The absorption spectrum of compound (VII) at  $pH$  5.5 exhibits three bands at 486, 354 and 292 nm, which can be assigned to  $\pi - \pi^*$  electronic transitions in the azo group, hydrogen chelate ring and naphthalene moiety respectively. After CPC at  $-0.55$  V the first two bands disappear and the third one appears with reduced intensity due to structural changes. At  $pH$  11.3 only two bands are observed at 498 and 322 nm. The band at 498 nm disappears on CPC and that at 322 nm shifts to lower wavelength due to lack of conjugation. 3-Aminopyridine has been detected among the products of CPC at potential corresponding to wave (A)<sup>6</sup>. The  $E_{1/2}$  of wave (A) shifts to more negative potential with increase in  $pH$  for all compounds suggesting the participation of  $H^+$  in the reduction of azo linkage, i.e. the reduction of the protonated form.

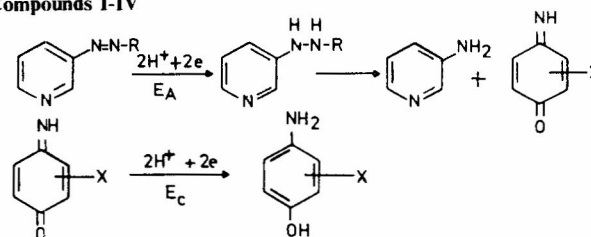
The results of CPC on wave (A) in acidic and slightly alkaline media show that the number of electrons transferred in the electrode process is approximately four and the reduction gives two molecules of amine.

In strong alkaline media, in the  $pK$  ranges, compounds VI-VIII containing sulphonic acid groups are reduced at d.m.e in different ways. Wave (A) is splitted into two waves (A and  $A_1$ ) which may be due to nonionized-ionized forms, or to separation of reduction stages, or due to retardation of reduction due to adsorption of certain species. It is found that the  $pH$  ranges within which the absorbance and limiting current decrease are quite different from each other. The number of electrons consumed as revealed by CPC for A and  $A_1$  are equal, this favouring adsorption of certain species as the possible reason for the separation of the waves. 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 it is unhindered on the bare portions. The suppression of the current preceding the minimum to an extent of 30-70% can be explained only by the incapability of the adsorbed negative ion to retard the reduction process due to competition for adsorption sites. The adsorbed species are the sulphonate anions probably associated with the buffer cations<sup>4,5</sup>, since the anion of compounds(I-V) and (IX) which do not have the sulphonic acid group have no adsorption effects.

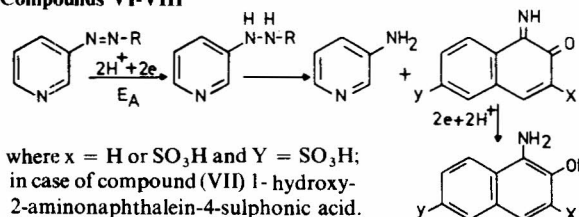
The half-wave potential of wave (B) in compound (IX), which is due to the quinoline moiety, is  $pH$  dependent. Therefore the reduction would involve the protonated form of the quinoline nucleus by the uptake of two hydrogen ions and two electrons to give the dihydrocompound in agreement with the previously reported investigations<sup>2,12</sup>. The change of structure from phenyl to naphthyl moiety in the dye shows more or less normal effect on  $E_{1/2}$  and  $i_d$  of wave (A), except in compounds (VI-VIII) where  $i_d$  increases

#### Compounds I-IV



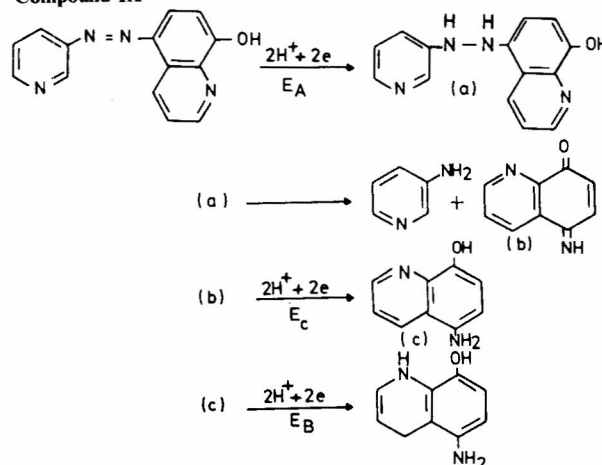
for compound (III) *o*-amino-*p*-cresol.

#### Compounds VI-VIII



where  $x = H$  or  $SO_3H$  and  $Y = SO_3H$ ; in case of compound (VII) 1-hydroxy-2-aminonaphthalen-4-sulphonic acid.

#### Compound IX



Scheme 1

with increase in the number of sulphonic groups in the dye molecule, indicating increase in the area of the mercury drop covered by the compound.

On the basis of the above results, the electrode mechanism for the reduction of the azo group corresponding to wave (A) in all compounds and  $A_1$  in (VI-VIII) can be represented as given in Scheme 1.

In the reduction process of these compounds the reactions are fast along the first wave and  $E_A \approx E_c$  and therefore one four-electron wave is obtained.

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