

Polarographic Reduction of Sulphophthalein Dyes & Studies on Their Co(II), Ni(II), Cu(II) & Zn(II) Complexes

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The polarographic reductions of methylthymol blue, xylene orange and pyrocatechol violet have been studied. All these dyes give diffusion-controlled reversible waves. A new empirical relationship between $E_{1/2}$ and pH , viz. $E_{1/2} = 0.068 - 0.31 pH \pm 0.003$ is proposed. The composition and stability constants of Co(II), Ni(II), Cu(II) and Zn(II) complexes of these dyes have also been determined.

SOME studies have been made on the polarographic behaviour of azo dyes¹⁻⁵ but very little is known about the polarographic reduction behaviour of sulphophthalein dyes⁶⁻⁸. However, complexes of these sulphophthalein dyes with some metal ions⁹⁻¹² are reported. In the present paper we report the results of our studies on the polarographic reduction of methyl thymol blue (MTB), xylene orange (XO) and pyrocatechol violet (PV) and their complexes with Co(II), Ni(II), Cu(II) and Zn(II).

Materials and Methods

A slightly modified method of Yoshino *et al.*¹³ was used for the purification of commercially available methyl thymol blue and xylene orange. They were dissolved in a small amount of deionized water, placed on a cellulose column and then eluted with *n*-butanol saturated with 0.1% acetic acid. The first zone contained mainly thymol blue and cresol red. The second zone contained semi-MTB and iminodiacetic acid in the case of MTB and semi-XO and iminodiacetic acid in the case of XO. The dyes in the purified form were extracted into a small volume of water from *n*-butanol, evaporated to dryness at <50°C and finally washed with ethyl ether. The purity of the dyes was tested by the well known molar ratio method. Purity was found to be 90 per cent against the standard copper sulphate solution.

All the other reagents used were of AR (BDH) grade and were used without purification, further all the solutions were prepared in doubly distilled water. The solutions of dyes were freshly prepared whenever used. Britton-Robinson buffers were prepared by a known method¹⁴.

An Elico pen recording polarograph was used for recording the polarograms. The polarographic cell was kept immersed in a thermostatic bath maintained at $35 \pm 1^\circ$. The solutions were deaerated by bubbling purified nitrogen. The capillary characteristics were measured in 1.0M KCl solution at 0.0 V (VS SCE) and at a mercury height

55.00 cm. The value of $m^{2/3} t^{1/6}$ was found to be 1.367.

The pH measurements were carried out on an Elico (India) pH-meter model LI-10.

Procedure — The polarograms for the solutions of several sets given below were recorded :

(i) Dye (1.0 ml, 0.01M) + KCl (1.0 ml, 1.0M) + 8.0 ml buffer. Different sets were prepared using the buffers of different pH values. In the case of PV, gelatin was used as the maxima suppressor.

(ii) Metal ion (1.0 ml, 0.001M) + KCl (1.0 ml, 1.0M) + 13.00 ml buffer

(iii) Metal ion (1.0 ml, 0.001M) + KCl (1.0 ml, 1.0M) + dye (*x*, ml, 0.01M; where *x* varies from 1.0 to 4.0 ml). The total volume was made up to 15 ml with buffer solution.

Results and Discussion

Polarograms for different dyes (I-III) were recorded at different pH and at different concentrations. A single wave was obtained at pH below 4.00, 5.40 and 4.20 and two waves in the pH ranges 4.20-11.00, 5.80-11.00 and 4.40-11.00 in the case of XO, MTB, and PV respectively. The limiting current of both the waves for each system was found to be diffusion-controlled as shown by linear plots of i_d vs $h_{eff}^{1/2}$. Further verification of diffusion-controlled nature of these waves was evident from the value of temperature coefficients ranging between 1.35 and 1.63 K⁻¹. The heights of the waves were also found to be independent of pH. The values of $E_{1/2}$ for the different dyes at different pH values are given in Table 1, from which the following empirical relationship was established :

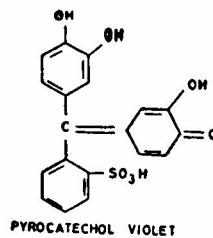
$$E_{1/2} = 0.068 - 0.31 pH \pm 0.003.$$

The first wave of the dyes was found to be reversible and the second was irreversible as indicated by the following observations :

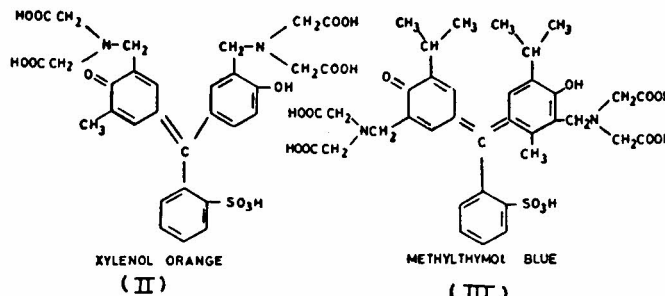
(a) Plot of $\log \frac{i}{i_d - i}$ vs $E_{d.e}$ is linear for the first

wave and its slope gives the value of *n* (No. of electrons) while in the second wave, a non-

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(I)


 TABLE 1 — $E_{1/2}$ VALUES IN B. R. BUFFER (pH range 2.20–11.0) AT CONC. = $1.0 \times 10^{-3}M$ and $h = 54$ cm.

pH	Xylenol orange		pH	Methyl thymol blue		pH	Pyrocatechol violet	
	$-E_{1/2}$ (1st)	$-E_{1/2}$ (IInd)		$-E_{1/2}$ (1st)	$-E_{1/2}$ (IInd)		$-E_{1/2}$ (1st)	$-E_{1/2}$ (IInd)
2.40	0.45	—	2.30	0.42	—	2.40	0.48	—
3.70	0.54	—	3.20	0.52	—	3.50	0.54	—
4.40	0.58	—	4.60	0.60	—	4.60	0.60	1.16
4.60	0.60	1.23	5.00	0.61	—	5.10	0.62	1.18
5.00	0.60	1.23	5.40	0.62	1.13	6.00	0.68	1.19
6.00	0.64	1.25	6.45	0.68	1.15	6.40	0.73	1.20
6.60	0.73	1.26	7.02	0.74	1.16	7.00	0.74	1.20
7.20	0.76	1.27	8.02	0.78	1.18	8.00	0.76	1.22
8.20	0.82	1.27	8.60	0.80	1.20	9.70	0.83	1.42
8.80	0.88	1.28	8.90	0.83	1.20	10.00	0.85	1.44
9.40	0.90	1.32	9.40	0.86	1.21	11.00	0.94	1.46
10.00	0.92	1.33	11.00	0.91	1.23			
11.00	0.95	1.36						

linear curve and fractional value of n is obtained. But the plot of $\log \frac{i}{i_d - i} - 0.546 \log t$ ($t = \text{drop time}$) vs $E_{d,e}$ gives a straight line and its slope gives the value of αn .

- (b) The equation $E_{3/4} - E_{1/4} = 0.0591/n$ was found to be valid for the first wave and $E_{3/4} - E_{1/4} = 0.0546/\alpha n$ for the second wave.
- (c) The value of n was verified by millicoulometry which gave $n = 1$ i.e. one electron process.
- (d) In A.C. polarograms, a peak was observed only in the case of first wave.

The polarograms of the dyes were recorded at various concentrations ($10^{-3}M - 10^{-5}M$) and it was found that limiting current increases with increase in concentration. The value of $E_{1/2}$ of the first wave remains unchanged with varying concentrations while that of the second wave shifts towards more negative potentials with increase in concentration. Diffusion coefficients of XO, MTB and PV were found to be 0.205×10^{-5} ($pH = 4.6$), 0.398×10^{-5} ($pH 5.0$) and 0.06×10^{-5} cm^2/sec ($pH 6.00$) respectively.

Metal complexes — On increasing the concentration of the dye, the value of $E_{1/2}$ shifts towards more negative potentials. The value of j (number of ligands bound per metal ion) was calculated from the slopes of the linear plots of $E_{1/2}$ vs. $\log Cx$.

In the case of Co(II) complexes of XO and MTB the curve is non-linear. Two straight lines were obtained indicating thereby the formation of two complexes over the particular ligand concentration range studied.

$$\frac{\Delta E_{1/2}}{\Delta \log Cx} = -j \frac{0.0591}{n} \quad (\text{For reversible process})$$

$$\frac{\Delta E_{1/2}}{\Delta \log Cx} = -j \frac{0.06015}{\alpha n} \quad (\text{For irreversible process})$$

$$\alpha n = 0.0564/(E_{3/4}) - E_{1/4}$$

The value of j was found to be approximately two in the case of Cu(II) complexes of XO and PV; Zn(II) complexes of XO, MTB and PV, Ni(II) complexes of MTB and PV; and nearly one in the case of Ni(II) complex of XO and Cu(II) complex of MTB. While

TABLE 2 — POLAROGRAPHIC DATA OF THE METAL-DYE COMPLEXES

Complexes	Conc. range of the ligand $\times (10^{-2}M)$	pH	an or n	$\log B$	$\Delta E_{1/2}/\Delta \log C$	j
Co(II)-XO	1.0-2.0	4.70	0.335	3.09	0.0730	0.88
	3.0-4.0	4.70	0.335	5.70	0.1119	1.86
Co(II)-MTB	1.0-2.0	5.00	0.423	3.22	0.0641	0.70
	3.0-4.0	5.00	0.423	5.82	0.3277	1.89
Ni(II)-XO	0.5-4.0	4.70	0.365	4.26	0.1617	0.98
Ni(II)-PV	1.5-4.0	7.00	0.734	7.46	0.1629	1.99
Ni(II)-MTB	1.0-4.0	4.85	0.515	7.19	0.2336	2.00
Cu(II)-XO	0.1-5.0	4.70	1.000	7.36	0.1000	1.80
Cu(II)-PV	1.5-4.0	6.00	1.000	6.93	0.1106	1.88
Cu(II)-MTB	1.0-5.0	4.65	1.000	4.52	0.0650	1.10
Zn(II)-XO	1.5-5.5	4.70	2.000	7.23	0.0530	2.12
Zn(II)-PV	1.0-4.0	6.80	2.000	7.01	0.0625	2.11
Zn(II)-MTB	1.5-5.5	5.00	2.000	7.09	0.0642	2.16

both the values (~ 1 and 2) were obtained in the case of Co(II) complexes of XO and MTB. No change in $E_{1/2}$ was observed in the case of Co(II) complexes of PV. The values of an or n , $\log B$, $\Delta E_{1/2}/\Delta \log C$ and j are given in Table 2.

The stability constants of metal complexes were calculated using the Lingane and modified Lingane methods for reversible and irreversible processes,

$$E_{1/2} = \frac{RT}{nF} \ln Kc + j \frac{RT}{nF} \ln Cx$$

(For reversible process)

$$E_{1/2} = (E_{1/2})_M - (E_{1/2})_C = \frac{RT}{anF} \ln Kc + j \frac{RT}{anF}$$

(For irreversible process)

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