Electrochemical Studies on Sulphonaphthaleins: I. Polarographic Reduction of Pyrocatechol Violet.

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The polarographic reduction mechanism at a dropping mercury electrode of pyrocatechol violet has been studied in aqueous Britton-Robinson buffer solutions (pH 2.59-10.02). The dye is reduced in a single two-electron step in solutions of pH 6.7 or two one-electron steps at higher pH's. The mechanism of the electrode reaction is proposed and discussed.

The electrochemical reduction of sulphonphthaleins has been investigated by several authors[1-8]. The aim of the present paper is to study the polarographic behaviour of pyrocatechol violet in aqueous buffered media at dropping mercury electrode.

EXPERIMENTAL

Polarograms were recorded with three-electrode TACUSSEL Type EPL1 polarograph. The pH measurements were made on an ORION Research model 601A/ digital IONANALYZER. The pH meter was calibrated with standard Beckman buffer over the pH range investigated.

All measurements have been carried out in a thermostated cell (25±0.1°C) of 25 ml capacity. The dme has the following characteristics m = 2.34 ± 0.05 mg/sec and t= 3.73±0.05 sec/drop at 60 cm in deoxygenated 0.1M KCl solution at open circuit. The reference electrode was a SCE and the counter electrode was a platinum wire.

Analytical grade (BDH) reagents were further purified by recrystallization. Stock solutions of pyrocatechol violet, 10^{-2} M, was prepared in bidistilled water. Universal Britton-Robinson buffer solutions were used as supporting electrolyte. Solutions were deoxygenated by passing purified nitrogen. All experiments were performed in the presence of 8×10^{-4}% Triton X-100.

RESULTS AND DISCUSSION

POLAROGRAPHIC STUDY

Polarograms of pyrocatechol violet in Britton Robinson buffers were recorded over the pH interval of 2.59-10.02. Using a 0.5 mM dye concentration, reproducible data were obtained. Typical polarograms of pyrocatechol violet are shown in Fig.1.

Pyrocatechol violet exhibits a single polarographic reduction wave in acidic pHs (2.59 - 4.31) corresponding apparantly to two electrons. Over this pH range the observed limiting current is

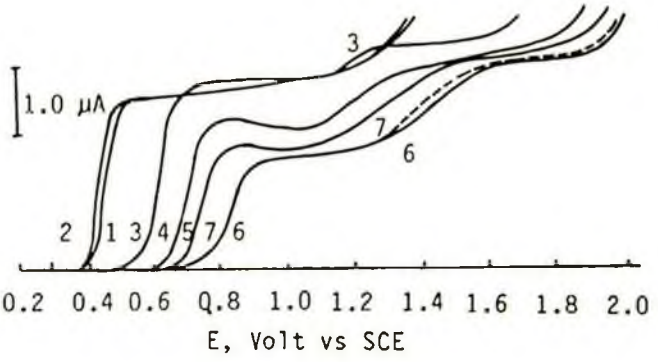


Fig 1. Polarograms of 0.5 mM Pyrocatechol Violet in Aqueous Britton-Robinson buffer solutions at different pHs, pH values for different curves 1-2.59 , 2-3.18 , 3-5.85, 4-7.08, 5-7.59 , 7-10.02 Temp 25°C.

more or less pH independent. The dependence of the limiting current on the height of the mercury column ($h^{\frac{1}{2}}$) at pH 4.31 shows a linear dependence for log i-log h plot with a slope of 0.493±0.011 (correlation coefficient r= 0.999). This proves that the limiting current is diffusion controlled. The limiting current is proportional to the concentration of the dye in the range of 2.5×10^{-4} to 1.25×10^{-3} M at pH 3.18. The diffusion coefficient of pyrocatechol violet is calculated from the Ilkovic equation using the limiting current at three pHs assuming a two-electron transfer. A value of $(4.63\pm0.30) \times 10^{-6}$ cm^2/sec is obtained. This is close to the value obtained for phenol red[1]. A linear least square plot of E against log $i/(i_{lim}-i)$ gives a straight line for each pH with slopes recorded in Table 1. The mean value of the slopes in that pH range is 34.0 ± 1.0 mV/ decade which is near the theoretical value of 29.5 mV/decade for a reversible two-electron transfer. The plot of half-wave potential vs pH is in accordance with the equation.

$$E_{\frac{1}{2}} = -0.351 - 0.0307\ pH \quad (r = 0.940) \qquad ..1$$

On increasing the pH of the solution, the single wave observed at pHs ≤ 4.31 splits to two daughter waves of unequal heights. The height of

TABLE 1

POLAROGRAPHIC DATA OBTAINED FOR PYROCATECHOL VIOLET AQUEOUS BUFFER BRITTON-ROBINSON SOLUTIONS AT 25°C.

pH	i_{lim} μA ±2%	$-E_{\frac{1}{2}}$ V ±1.5%	S* mV/decade	$E_{\frac{1}{4}} - E_{\frac{3}{4}}$ mV ±1%	i_{lim} μA ±1.5%	$-E_{\frac{1}{2}}$ V ±2%	S* mV/decade	$E_{\frac{1}{4}} - E_{\frac{3}{4}}$ mV ±3%
2.59	2.8	0.440	36	35	--	--	--	--
3.18	2.8	0.433	36	35	--	--	--	--
4.31	3.0	0.488	32	33	--	--	--	--
5.85	3.0	0.605	59	52	0.80	--	--	--
7.08	2.4	0.700	56	55	1.20	1.254	113	120
7.59	1.9	0.715	52	56	1.40	1.329	125	118
9.26	1.8	0.998	64	60	1.45	1.392	120	115
10.02	1.85	0.800	60	58	1.48	1.390	119	117

* Slope of the logarithmic analysis,

the second wave gradually increases at the expense of the first one with increasing pH. They attain equal heights at pH values ≥ 9.26. Polarograms of this type are aften observed in the reduction of organic acids where the equilibrium between the acid and its conjugate base is established slowly and the two species are reduced at different potentials. The plot of limiting current for the first wave as a function of pH has a shape of a dissociation curve with the point of inflection at pH = pK. Slope of log $[(\bar{i} - \bar{i}\,min)/(\bar{i}_d - \bar{i})]$ Vs pH plots, obtained by the regression analysis for the first wave close to the value of 1.0 and fits the following equation[9]

$$\log [(\bar{i} - \bar{i}_{min})/(\bar{i}_d - \bar{i})] = pH + \log 0.886(t\, k_{OH} K_1 K_W)^{\frac{1}{2}} \quad ...2$$

where $\bar{i}$ is the mean limiting current at a given pH,

$\bar{i}_d$ is the mean limiting current under conditions where it is diffusion controlled,

t is the drop time of the electrode,

K_W is the water dissociation constant,

K_1 is the dissociation constant of the acid,

k_{OH} is the rate constant of the hydrolythic dissociation reaction of the following type:

$$H_2A + OH^- \underset{-k_{OH}}{\overset{k_{OH}}{\rightleftharpoons}} HA^- + H_2O \quad ...3$$

This seems to indicate that in these instances a hydrolytic dissociation of a type as in equation 3 predominates. Thus, it is possible to consider equation 3 as describing the decrease of the current with pH at pH 6-8.

The K_1 value for pyrocatechol violet as calculated from a spectrophotometric experiment is 6.7 ± 0.1. Values for pK_{est} of 7.15 (estimated graphically at pH where $\bar{i}/\bar{i}_d = 0.5$), $p\bar{K}_{H_2A}$ of 7.13 (obtained by regression analysis of equation 2; $p\bar{K}_{H2A}$ = - intercept/ slope)[9], k_{OH} of 8.57×10^5 L per mole/sec (using equation 4) are obtained.

$$2p\bar{K} = pK_{H2A} - 2 \log 0.886\,(t\, K_W)^{\frac{1}{2}} - \log k_{OH} \quad ...4$$

Analysis of the waves applying the fundamental equation for polarographic waves indicated that the reduction process proceeds in a reversible one - electron manner (mean slope = 56.7 ± 3.0 mV/decade). Moreover, the increase of pH serves to shift the half-wave potential. The change of $E_{\frac{1}{2}}$ with pH fits the following equation:

$$E_{\frac{1}{2}} = - 0.292 - 0.0553\ pH \quad (r = 0.988) \quad ...5$$

The number of protons (p) participating in this step is determined as mentioned before and is found to be one (p = 0.975).

On the other hand, the $E_{\frac{1}{2}}$ of the second polaro-

graphic wave is pH - dependent according to the following equation:

$$E_{\frac{1}{2}} = - 0.472 - 0.111\ pH \quad (r = 0.993) \qquad ...6$$

This wave is irreversible one-electron wave as shown by the high slope of a linear least square plot of E against log $[i/(i_d - i)]$ (Table 1). The calculated number of protons (p) involved in this step is one (p = 0.941).

At higher pHs ($\geq$9.26), two one-electron reduction waves of equal heights are obtained. The $E_{\frac{1}{2}}$ and i_{IIm} of both waves are pH-independent (Fig.1). A logarithimic analysis for each wave at different pH values indicates that the first wave is reversible while the second one irreversible. The variation of i_{IIm} with increased concentration (0.25 - 1.25 mM) and with the variation of mercury height at different pH indicates that both waves are controlled by diffusion within that range of pH.

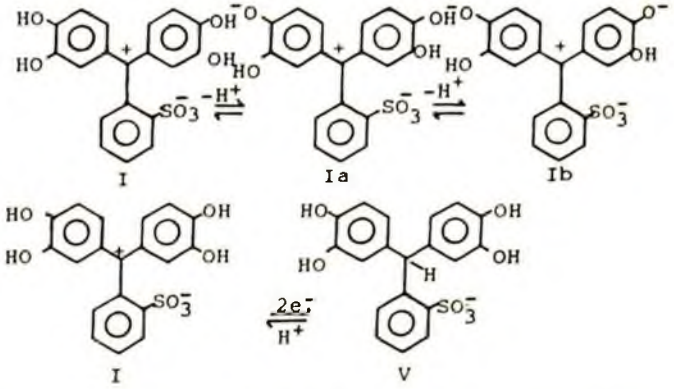
Spectral Study

Spectra of pyrocatechol violet in solutions of low pHs exhibit one visible band located at 440 nm, mainly due to the absorption by species with non-ionised OH-group. With increase in pH of the solution, its intensity decreases and at the same time another band appears at 500 nm, its intensity increases with pH. The second band is due to the absorption of single ionised OH-group. With further increase in pH, the intensity of the second band decreases and a third band develops at 590 nm, its intensity increasing with pH. The third band is due to the absorption of a doubly ionised OH-group. The spectra in the whole pH range display clear two isosbestic points, reveaing the existence of equilibrium between three forms of pyrocatechol violet. The dissociation constants pK_1 and pK_2 of the dye are determined from the variation of absorbance with pH. The values obtained at pK_1 = 6.7 and pK_2 = 9.2.

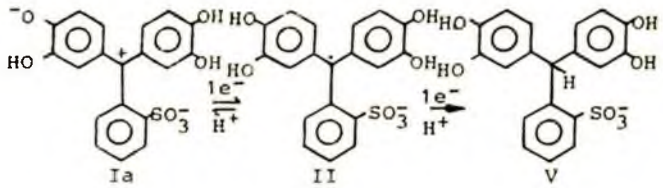
According to Bates [10] and the spectrophotometric results pyrocatechol violet is represented structurally as hybrid ions as follows:

According to the foregoing results, the mechanism can be explained as follows:

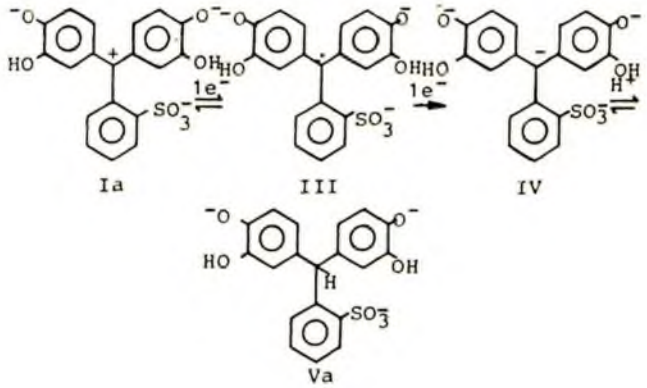
a) In solutions of pH $<$6.7 form I is predominant species and reduced directly through a two-electron step:



b) In solutions of pH 6.7 - 9.2 , form Ia is the predominant species and reduced through two one-electron steps.



c) In solutions of pH$>$9.2 , form Ib is the predominant species and reduced through the following two one-electron steps and the anion abstracts a proton rapidly from the medium.



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