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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Polarographic Studies on Aqueous Solutions of Poly-o-xylylviologen Dibromide

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**To cite this Article** Prasad, B. B.(1985) 'Polarographic Studies on Aqueous Solutions of Poly-o-xylylviologen Dibromide', *Journal of Macromolecular Science, Part A*, 22: 1, 1 – 12

**To link to this Article:** DOI: 10.1080/00222338508063292

**URL:** <http://dx.doi.org/10.1080/00222338508063292>

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## Polarographic Studies on Aqueous Solutions of Poly-o-xylylviologen Dibromide

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### ABSTRACT

Dropping mercury electrode polarography of the redox polymer poly-o-xylylviologen dibromide in water gave two well-defined irreversible diffusion controlled reduction waves over the pH range 1.70 to 6.40. The half-wave potentials for both waves ( $E_{1/2}$  (Wave I) = -0.404 V,  $E_{1/2}$  (Wave II) = -0.981 V vs SCE) are independent of pH and the total concentration of the solutions. However, the gross effect of pH on the relative wave heights suggests that an equilibrium of the type  $BH \rightleftharpoons H^+ + B$  (where B represents the compound studied) exists in solution where the reduction of the protonated as well as of unprotonated form of the polymer results in Waves I and II, respectively. A tentative mechanism for the reduction processes is proposed. The dissociation constant of the protonated species was found to be  $1.0 \times 10^{-3}$  ( $\mu = 0.1 \text{ M}$ ) on calculation from a pH-dependence study of the limiting currents for both waves at a particular concentration.

## INTRODUCTION

Dropping mercury electrode (DME) polarographic studies on aqueous solutions of the redox polymer poly-p-xylylviologen dibromide ( $p\text{-PXVBr}_2$ ) have recently been reported [1]. The present work deals with the polarographic behavior of an ortho-compound, poly-o-xylylviologen dibromide ( $o\text{-PXVBr}_2$ ), in water. The compound  $o\text{-PXVBr}_2$  represents a novel class of redox polyelectrolyte of the important "viologen" or "paraquat" family of biological interests [2, 3]. The presence of an o-xylylene moiety in between the two quaternary nitrogens of the compound introduces a structure distinct from  $p\text{-PXVBr}_2$  and therefore, at the DME, a different type of electron-transfer reaction might be expected in the present case. The redox activity of the compound was evident by the formation of a violet-colored cation radical on reduction with Zn dust (or  $\text{Na}_2\text{S}_2\text{O}_4$ ) and subsequent oxidation on exposure to atmosphere. Since such reductions are likely to be influenced by hydrogen ion concentration of the solution, the present study was carried out at different pH values (1.70, 2.20, 4.20, 5.00, and 6.40) and the overall ionic strength of the solutions was held constant at 0.1 M. The observed current-potential, the concentration, as well as the height-dependence behaviors of the limiting currents were analyzed on the assumption of a protonation equilibrium  $\text{B} + \text{H}^+ \rightleftharpoons \text{BH}^+$  (where  $\text{B} = o\text{-PXVBr}_2$ ) which has already been discussed in the case of  $p\text{-PXVBr}_2$  [1]. Although a rigorous interpretation would require knowledge of the rate constant ( $k$ ) which is not available in the present instance, it appears that a general assessment of the polarographic results is possible on the basis of the postulated protonation equilibrium.

## EXPERIMENTAL

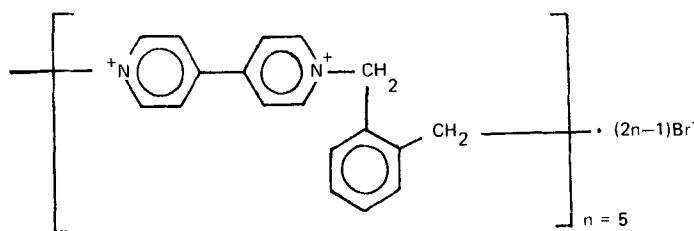
Materials and Methods

The conductivity grade water, obtained from the double distillation of deionized water, was used in the preparation of solutions. All other chemicals were of AnalaR or extrapure quality.

The reagent,  $\alpha, \alpha'$ -dibromo-o-xylene, used for the preparation of  $o\text{-PXVBr}_2$  was made according to an established procedure [4].

The compound  $o\text{-PXVBr}_2$  was prepared by a straightforward condensation of anhydrous 4,4'-bipyridine (Koch-Light) and  $\alpha, \alpha'$ -dibromo-o-xylene in acetonitrile according to an earlier recipe [3]. Analysis (%): C = 51.30, H = 3.75, N = 6.80. Infrared frequencies (KBr):  $\sim 2970 \text{ cm}^{-1}$  (C-H stretching),  $800 \text{ cm}^{-1}$  (C-H bending),  $1460 \text{ cm}^{-1}$  (C=C

stretching), and  $1630\text{ cm}^{-1}$  ( $>\text{C}=\text{N}-\text{C}$  substituted imine vibration) correspond to the terminal bipyridine ring; and  $3100\text{ cm}^{-1}$  (C-H stretching),  $1490\text{ cm}^{-1}$  (C-H bending), and  $590\text{ cm}^{-1}$  (C-Br stretching) are characteristic of the end  $-\text{CH}_2\text{Br}$  group in the system. Thermogravimetric analysis indicates that decomposition of the polymer starts above  $250^\circ\text{C}$ . Thin-layer chromatographic analysis of the compound in ethanol revealed only one spot after development in iodine chamber, and this was considered as verification of the purity of the polymer. Ionic bromine determination by conductometric titration in water showed 4.30 mol of  $\text{Br}^-$  per 1000 g of the sample. An analysis of the differential vapor pressure results of the compound with 13.88 and 24.29 mg/mL in water gave molarities of 0.06523 and 0.11613 M, respectively, as determined on the basis of a standard monomer (glucose). If one assumes a possible structure such as



these molarities can be accounted for if 10 ions (9  $\text{Br}^-$  ions and 1 cation) are produced from the molecule in question, and its average molecular weight is 2100. The latter is also consistent with the analysis of ionic bromine and the calculated value of 0.4619 mol/1000 g for non-ionic bromine. It should be noted that the much larger molecular weight obtained in the case of p-PXVBr<sub>2</sub> [1] may be attributed to its structure which favors a greater degree of polymerization.

Polarographic curves were recorded on a Leeds-Northrup Type E Electro-chemograph at room temperature ( $\sim 25^\circ\text{C}$ ) in the manner described earlier [1]. The capillary possessed the following characteristics in 0.1 M aqueous KCl (open circuit):  $m = 1.89\text{ mg/s}$  and  $t = 4.4\text{ s/drop}$  for  $h_{\text{Hg}} = 35\text{ cm}$ . The supporting electrolytes used were a HCl-KCl mixture and citrate buffers of known pH; the ionic strengths were adjusted to 0.1 M with the addition of requisite amounts of KCl. The currents and the potentials used in the final calculations have been corrected for the residual current and the  $iR$  drops involved.

## RESULTS AND DISCUSSION

Typical current-potential curves of o-PXVBr<sub>2</sub> at  $h_{\text{Hg}} = 35\text{ cm}$  in solutions of different pH values are shown in Fig. 1.

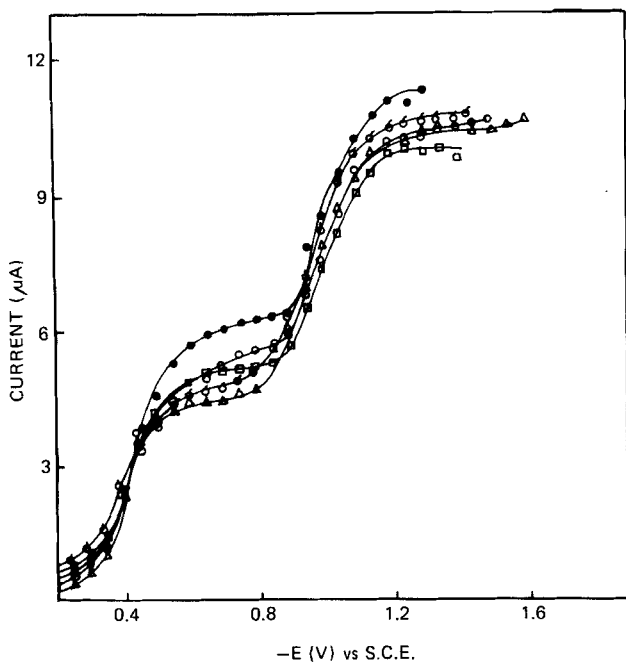


FIG. 1. Polarograms for aqueous solution of poly-*o*-xylylviologen dibromide at different pH values: (●) 1.70, (□) 2.20, (○) 4.20, (○) 5.00, and (△) 6.40 (concentration,  $\sim 1.10$  mg/mL;  $h_{\text{Hg}} = 35$  cm).

The results obtained from the analysis of all polarograms are summarized in Table 1. These results indicate that the relative heights of the two waves are effectively governed by the hydrogen ion concentration of the solution. With the exception of the pH = 1.7 results which might involve somewhat large uncertainty, the slopes of  $i_q$  vs  $C$  plots (Fig. 2) clearly demonstrate a decreasing trend for the height of the first wave and a corresponding increase in the second wave on raising the pH of the solution. This behavior is typical of certain acids (the keto acids; pyruvic acid, for example) whose undissociated (protonated) form reduces at a much smaller negative potential than the corresponding unprotonated anion [5]. Thus, it is reasonable to assume that two equilibrium forms of the substance are responsible for both waves: Wave I is due to reduction of the protonated form, while Wave II corresponds to the reduction of the unprotonated species.

The compound  $o\text{-PXVBr}_2$  seems to be unstable even in a mild basic medium as is evident from the light violet color visible in the cell. Therefore, further exploration at very high pH values had to be abandoned to avoid any possible complication due to betain formation [6] in

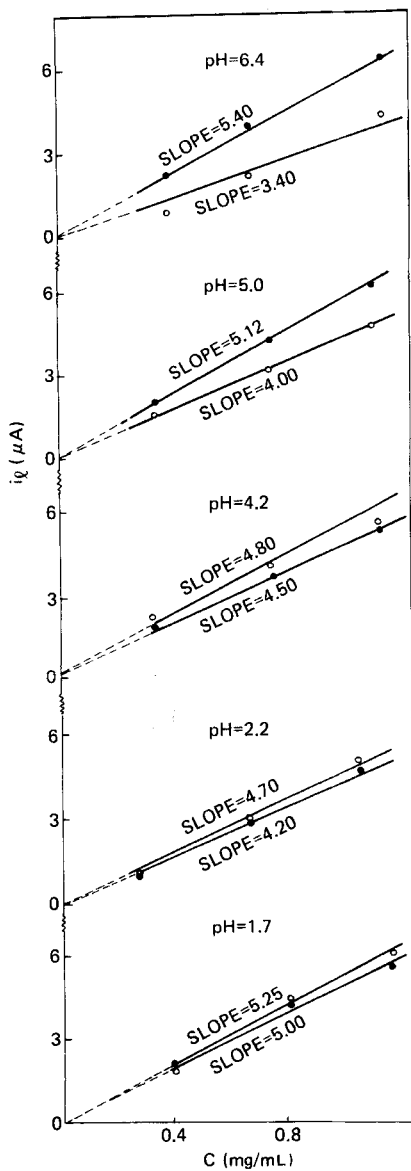


FIG. 2. Plots of limiting current vs concentration for different pH values at  $h_{\text{Hg}} = 35 \text{ cm}$ : (○) Wave I, (●) Wave II.

TABLE 1. Summary of Results on Polarographic Studies of Poly-o-xylylviologen Dibromide in Water at  $\sim 25^\circ\text{C}$ 

pH <sup>a</sup>	Concentration C, (g/L) $\times 10$	$h_{\text{Hg}}$ (cm)	Limiting current, $i_l$ ( $\mu\text{A}$ )	
			Wave I <sup>b</sup>	Wave II <sup>b</sup>
1.70 (HCl-KCl)	4.07	35	1.86	2.10
			(-0.373)	(-0.950)
	8.07	35	4.50	4.20
			(-0.412)	(-1.000)
	11.73 <sub>3</sub>	35	6.15	5.70
			(-0.420)	(-1.014)
50			7.35	6.90
		65	8.85	8.10
2.20 (HCl-KCl)	2.73 <sub>3</sub>	35	1.05	0.90
			(-0.395)	(-0.940)
	6.67	35	3.06	2.85
			(-0.405)	(-0.950)
	10.53 <sub>3</sub>	35	5.13	4.80
			(-0.415)	(-1.010)
			50	6.03
		65	6.93	6.90
		80	8.13	7.86
4.20 (citrate buffer)	3.33 <sub>3</sub>	35	2.10	1.80
			(-0.410)	(-1.015)
	7.53	35	3.90	3.60
			(-0.405)	(-0.990)
	11.40	35	5.40	5.10
			(-0.410)	(-1.010)
			50	6.60
		65	7.80	6.90
		80	8.40	7.50
5.00 (citrate buffer)	3.50	35	1.45	1.95
			(-0.405)	(-0.950)
	7.62	35	3.00	4.10
			(-0.410)	(-0.980)

(continued)

TABLE 1 (continued)

pH <sup>a</sup>	Concentration C, (g/L) × 10	h <sub>Hg</sub> (cm)	Limiting current, i <sub>l</sub> (μA)	
			Wave I <sup>b</sup>	Wave II <sup>b</sup>
6.40 (citrate buffer)	11.29	35	4.50 (-0.390)	6.00 (-0.970)
	4.13 <sub>3</sub>	35	0.96 (-0.400)	2.16 (-0.940)
	7.07	35	2.16 (-0.400)	3.90 (-0.970)
	11.73	35	4.32 (-0.400)	6.30 (-0.985)
		50	5.52	7.50
		65	6.72	8.85
		80	7.32	9.66

<sup>a</sup>Ionic strength adjusted to 0.1 M by adding calculated amount of KCl.

<sup>b</sup>Values in parentheses denote half-wave potential (E<sub>1/2</sub>) in volts vs SCE.

the present case. In this context, the E<sub>1/2</sub> values for both waves of *o*-PXVBr<sub>2</sub>, as measured polarographically in 0.1 F KCl buffer (pH = 9.00) by earlier workers [3], appear to be somewhat equivocal.

As no estimate of the value of the specific rate *k* for the protonation of *o*-PXVBr<sub>2</sub> was available, any direct quantitative verification [5] of the present result based on the magnitude of *k*[H<sup>+</sup>] did not seem feasible in the present study [1]. However, despite these limitations, in view of the gross effect of the pH on the wave heights and the reasonable assumption that the observed currents for Waves I and II are primarily determined by the protonated and nonprotonated forms of the *o*-PXVBr<sub>2</sub>, respectively, it appeared worthwhile to find the pH at which the two limiting currents would be equal for a given concentration. Figure 3 presents the pH dependence of the limiting currents for both waves at h<sub>Hg</sub> = 35 cm and concentration ~1.10 mg/mL. The pH at which the two curves intersect is found to be 3.0. The ratio of the equilibrium concentration of the two forms B and BH<sup>+</sup> may be taken as unity at the intersection point of the limiting currents. Thus, a tentative value for



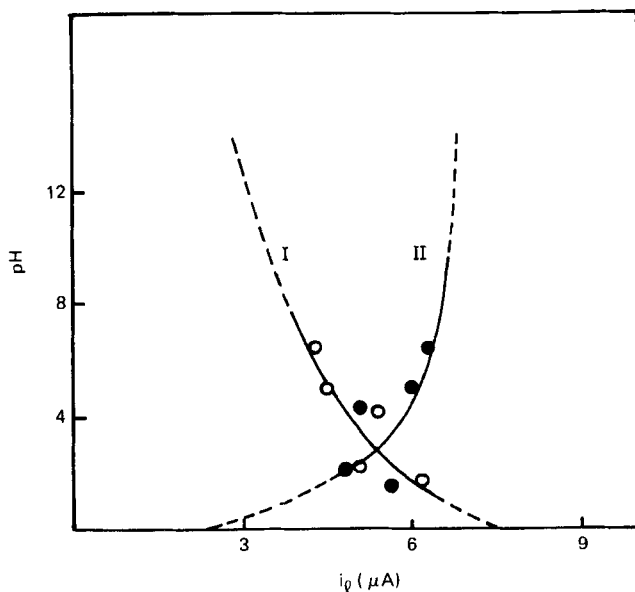


FIG. 3. Variation of limiting current with pH for Waves I and II at a concentration of  $\sim 1.10$  mg/mL.  $h_{\text{Hg}} = 35$  cm.

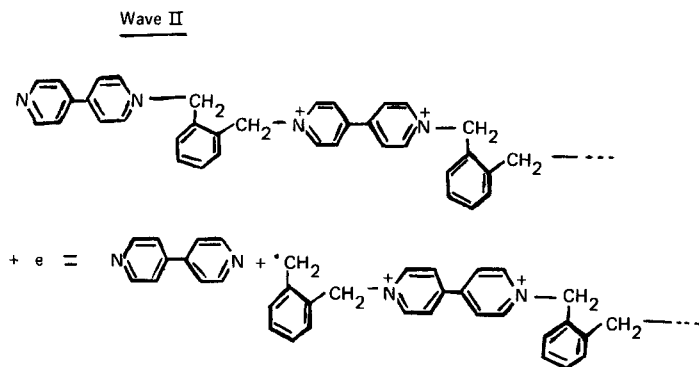
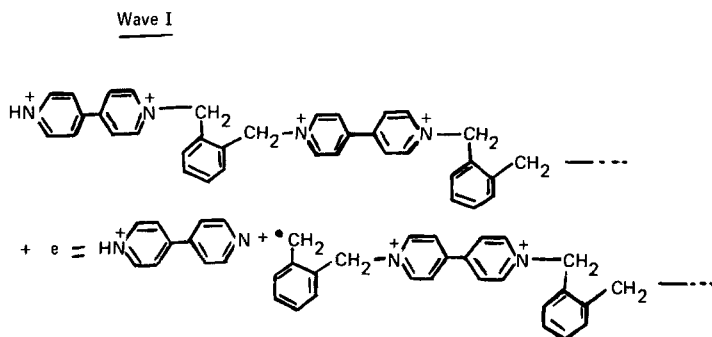
the acid dissociation constant  $K = \frac{[\text{H}^+][\text{B}]}{[\text{BH}^+]}$  (where  $\text{B} = o\text{-PXVBr}_2$ ) is found to be  $1.0 \times 10^{-3}$ . The acid dissociation constant values ( $\mu = 0.1$  M) for the protonated forms of 4,4'-bipyridine [7],  $p\text{-PXVBr}_2$  [1], and  $o\text{-PXVBr}_2$  follow a sequence [ $1.4 \times 10^{-5}$  (4,4'-bipyridine  $2\text{H}^+$ ; second acid dissociation constant)  $< 7.9 \times 10^{-5}$  ( $p\text{-PXVBr}_2\text{H}^+$ )  $< 1.0 \times 10^{-3}$  ( $o\text{-PXVBr}_2\text{H}^+$ )] which fairly indicate the less stable nature of the protonated form of  $o\text{-PXVBr}_2$  as compared to that of  $p\text{-PXVBr}_2$ . Although it may be of limited significance, it is to be pointed out that extrapolation of the individual curves (Fig. 3) approximates the following values of limiting current ( $\mu\text{A}$ ) at extreme pH values:

pH = 0	7.7 (Wave I);	2.5 (Wave II)
pH = 14	2.8 (Wave I);	7.0 (Wave II)

If these estimates are considered to be close to the diffusion currents, the proportionality constant  $i_d/C$  is obtained as 7.00 for Wave I at pH = 0, and 6.36 for Wave II at pH = 14, in comparison with the experimental

values of 4.88 (Wave I at pH = 2.2) and 5.38 (Wave II at pH = 6.4) (cf. Table 1).

In a molecule of *o*-PXVBr<sub>2</sub>, one of the two nitrogens of the terminal bipyridine moiety is not quaternized and may therefore serve as the proton acceptor. Further, an inspection of the plane-project model of a monomeric segment of this polymer reveals that the bond rotation about the  $\text{>N}^+$ -xylylene bond is hindered unlike its *p*-isomer. This steric compression in the *o*-PXVBr<sub>2</sub> seems to be responsible for a different mode of reduction at the DME as compared to *p*-PXVBr<sub>2</sub> [1] and other pyridinium compounds [8]. Thus, it is conceivable that the nearby  $\text{>N}^+$ -xylylene bond of the terminal would be the most vulnerable in order to relieve its strain, and the reduction for both the protonated and unprotonated forms of the system will occur with the involvement of a single-electron attack at this point [9]. The electron-transfer reaction in the respective cases may accordingly be represented as follows:



The half-wave potentials for both waves ( $E_{1/2}(\text{I}) = -0.404 \pm 0.011$  V and  $E_{1/2}(\text{II}) = -0.981 \pm 0.027$  V vs SCE) are found to be independent of pH as well as of concentration. A comparative study demonstrates that the half-wave potentials obtained in the present case are  $\sim 90$  mV less negative (Wave I) and  $\sim 45$  mV more negative (Wave II) than the corresponding waves of p-PXVBr<sub>2</sub> [1]. A plausible explanation of this behavior may easily be related to the structure of the two compounds. The reduction of the protonated o-PXVBr<sub>2</sub> in the present study is facilitated due to the presence of the quite vulnerable terminal  $\text{>N}^+$ -xylylene bond in the structure as compared to the protonated form of p-PXVBr<sub>2</sub>. Furthermore, the vulnerability of this bond is presumably minimized to some extent at lower acidities where the unprotonated form of the compound is considered to be more dominant. This may be attributed to the fact that quaternary centers, in the present instance, may experience a pool of interactions with active methylene groups of the adjacent o-xylylene moieties at higher pH. Under such circumstance, the relative proximity of an electron-rich bulky o-xylylene moiety to the terminal bipyridine ring of the unprotonated species appears to play an important part in shielding as well as blocking the positive charge of the quaternized nitrogen in question, and thereby making it somewhat less accessible to electron attack.

It was decided [1] that analysis of the results of height-dependence studies as well as the reversibility tests from  $E_{1/4}$  and  $E_{3/4}$  values would be more relevant if the data at pH = 2.2 (which can be considered more representative of the characteristics of the reduction of the protonated species) for Wave I and those at pH = 6.4 (which may possess less kinetic complications and represent all currents (diffusion) contributed by the nonprotonated form as such at higher pH) for Wave II were chosen for the purpose.

The electrode processes in the present case are found to be diffusion controlled because the slopes for the plots of  $\log i_\ell$  vs  $\log h_{\text{Hg}}$  (Fig. 4) are close to 0.5 for both Waves I (pH = 2.2) and II (pH = 6.4).

Assuming the following relationship to hold true at 25°C for Wave I (pH = 2.2) and Wave II (pH = 6.4),

$$E_{\text{DME}} = E^{\circ'} - \frac{0.05916}{\alpha n} \log \frac{i^2}{id - i} \quad (1)$$

where  $E^{\circ'}$  consists of the standard potential  $E^\circ$  and terms containing the activity coefficients of the oxidized and the reduced forms and the current-concentration proportionality constants which involve the properties of the capillary and the respective diffusion coefficients, one obtains

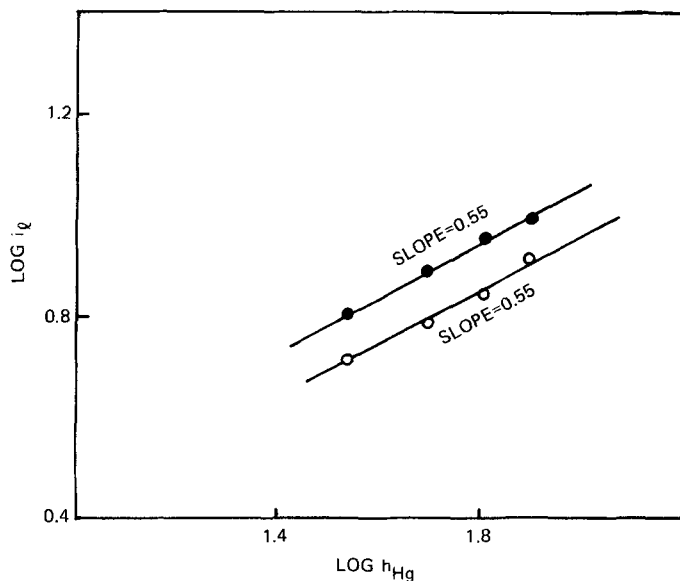


FIG. 4. Plots of  $\log i_l$  vs  $\log h_{\text{Hg}}$ : ( $\circ$ ) Wave I at pH = 2.20, ( $\bullet$ ) Wave II at pH = 6.40 (concentration  $\sim 1.10$  mg/mL).

$$E_{3/4} - E_{1/4} = \frac{-0.05916}{\alpha_n} \log 27 \quad (2)$$

Therefore

$$\alpha_n = \frac{-0.08465}{E_{3/4} - E_{1/4}} \quad (3)$$

Substituting the values of  $E_{1/4}$  and  $E_{3/4}$  as obtained from Wave I (pH = 2.2; 1.05 mg/mL total concentration) and Wave II (pH = 6.4; 1.17 mg/mL total concentration) in Eq. (3),  $\alpha_n$  is 0.65 (Wave I) and 0.53 (Wave II). Although practically no dependence of  $E_{1/2}$  values on concentration is observable in either case, the values of  $\alpha_n$  obtained above seem to be reasonable and indicate the irreversible nature of both waves.

#### ACKNOWLEDGMENTS

The author is indebted to Dr L. M. Mukherjee (Chemistry Department, Florida Atlantic University, Boca Raton, Florida) and to Dr P.

Dasgupta (Chemistry Department, Banaras Hindu University, Varanasi, India) for their generous advice and encouragement during this research.

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Accepted by editor July 11, 1983.

Received for publication August 14, 1983