Polarographic Study of the Redox Polymer Poly-p-xylylviologen Dibromide in Water

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ABSTRACT

The polarographic behavior of the redox polymer poly-p-xylylviologen dibromide has been examined over the pH range 2.00-8.00. Two irreversible waves with half-wave potentials of -0.496 and -0.936 V vs SCE were observed. The pH dependence of the relative wave heights appears to suggest that the system conforms to a protonation equilibrium where the protonated form reduces, at the DME, at the lower negative potential and the second wave is due to the unprotonated species. Analysis of the limiting current-pH relationship for a given concentration of the compound yielded a value of 7.94×10^{-5} ($\mu = 0.1$ $\underline{M}$) for the dissociation constant of the protonated form.

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INTRODUCTION

Some interesting studies on the redox behavior of polymeric systems have recently been reported [1, 2]. Factor and Heinsohn [1], for instance, found that the compound poly-p-xylylviologen dibromide (PXVBr$_2$)–a condensation product of 4,4'-bipyridine and α,α'-dibromo-p-xylene– responded to Zn dust (or Na$_2$S$_2$O$_4$) reduction, presumably giving rise to a cation radical. Also, from DME polarography of the compound at pH = 9.00, these authors observed two irreversible waves ($E_{1/2}$(I) = -0.436 V, $E_{1/2}$(II) = -0.854 V vs SCE) although other details were not given. The object of the present work was to further explore the DME polarography in an effort to understand the mode of reduction of PXVBr$_2$ and the electron-transfer mechanism involved.

In a molecule of PXVBr$_2$, one of the two nitrogens of the terminal bipyridine moiety is not quaternized and may therefore serve as the proton-acceptor, allowing the system to exist in equilibrium between its protonated and unprotonated forms in the following manner:

$$PXVBr_2 + H^+ \rightleftharpoons PXVBr_2H^+$$

(unprotonated form, A)   (protonated form, B)   (1)

If both forms A and B are electroactive, one may expect two polarographic waves, and for very slow rates of attainment of the equilibrium (cf., Eq. 1), the observed limiting currents at any pH should represent the diffusion currents of the two possible forms in direct proportion to their equilibrium concentrations in the bulk of the solution. Thus one would observe a systematic reduction of the height of the wave due to B and a corresponding enhancement in that of the unprotonated form A as the pH is increased. On the other hand, if the rate of attainment of equilibrium between the unprotonated and the protonated forms is appreciable, the limiting current exhibited by the protonated form will include some additional kinetic contribution(s) at the cost of A due to A + H$^+$ → B. Quantitative treatment [3] suggests that the magnitude of this kinetic current is governed by the rate constant, k, of the protonation reaction and the hydrogen ion concentration of the solution, and it can be represented as a fraction of the diffusion current due to the unprotonated form. For very large values of k[H$^+$], which represents one of the limiting cases, the kinetic current assumes the full magnitude of the diffusion current of the unprotonated species, and only one wave due to the protonated form is to be expected under such conditions. The treatment also predicts that if k[H$^+$] is negligible, there will be virtually no kinetic current and so the limiting currents for either forms will be observed, and these should correspond to the respective diffusion currents.

The present study was carried out at several pH values (2.00, 2.40, 4.40, 6.00, and 8.00), and the overall ionic strength of the solutions was held constant at 0.1 $\underline{M}$. An attempt has been made to correlate

the observed current-potential behavior and the results of concentra-
tion and height-dependence studies of the limiting currents in terms
of the protonation equilibrium (cf., Eq. 1) mentioned above.

EXPERIMENTAL

Solvent and Chemicals

Demineralized water was distilled twice from a Pyrex glass still
before use in the preparation of solutions. The specific conductivity
of the water ranged between 1×10^{-6} and 5×10^{-6} mhos.

The compound PXVBr$_2$ was prepared essentially according to an
earlier recipe [1]. (Analysis (%): C = 50.72, H = 3.69, N = 7.01.)
The final bright yellow product was found to be infusible and decom-
posed above $240°$ as indicated by thermogravimetric analysis. The
terminal group of the polymer was characterized through its infrared
spectrum ($3034 \, \mathrm{cm}^{-1}$ (C–H stretching), $790 \, \mathrm{cm}^{-1}$ (C–H bending), 1400
cm^{-1} (C=C stretching), and $1630 \, \mathrm{cm}^{-1}$ (>C=N–C substituted imine
vibration) for the end pyridine ring system; $3100 \, \mathrm{cm}^{-1}$ (C–H stretch-
ing), $1500 \, \mathrm{cm}^{-1}$ (C–H bending), and $620 \, \mathrm{cm}^{-1}$ (C–Br stretching) for the
end –CH$_2$Br group). Differential vapor pressure measurements with
aqueous solutions at concentrations of 10.19 and 17.52 mg/mL corre-
sponded to total concentrations of 0.0479_2 and 0.0824_5 $\underline{M}$, respectively,
on the basis of glucose as a monomer. These molarities, together
with the analysis of ionic bromine, were reconciled with an average
molecular weight of 11,000 for the compound and the presence of 52
ions (51 bromide ions plus 1 cation) per molecule as indicated by the
structural formulation
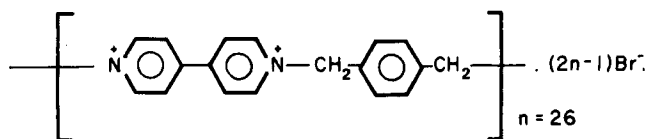
The intrinsic viscosity ($[\eta]$ = 0.045 dL/g at $25°$) of the substance in
0.5 M KBr solution was found to be almost identical with that ($[\eta]$ =
$0.04\overline{4}$ dL/g) of the original preparation reported [1] to have a molecu-
lar weight of 11,000.

All other chemicals were reagent-grade products.

Polarographic Measurements

All polarograms were recorded at room temperature ($\sim 25°$) with
the help of a Leeds-Northrup Type E Electro-chemograph, using a

simple set-up consisting of a tall beaker with a rubber stopper having openings for the dropping mercury electrode, a gas dispersion tube, and the agar bridge of the saturated calomel electrode. A known volume (15 mL) of the supporting electrolyte was introduced into the beaker and purged with nitrogen gas, and the residual current was obtained. Then the desired amounts of solid PXVBr$_2$ were added to the solution in the beaker. After the addition of each increment the nitrogen gas was allowed to pass through the mixture until the solid completely dissolved. The polarograms were subsequently run under a blanket of nitrogen in the usual manner.

The supporting electrolytes used consisted of a HCl-KCl mixture and citrate and phosphate buffers of the desired pH. The ionic strengths were adjusted to 0.1 $\underline{M}$ with the addition of requisite amounts of KCl.

All currents and potentials reported in this work were corrected for the residual current as well as the iR drops involved.

RESULTS AND DISCUSSIONS

Typical polarograms of PXVBr$_2$ at h$_{Hg}$ = 35 cm in solutions of the various pH values studied are shown in Fig. 1.
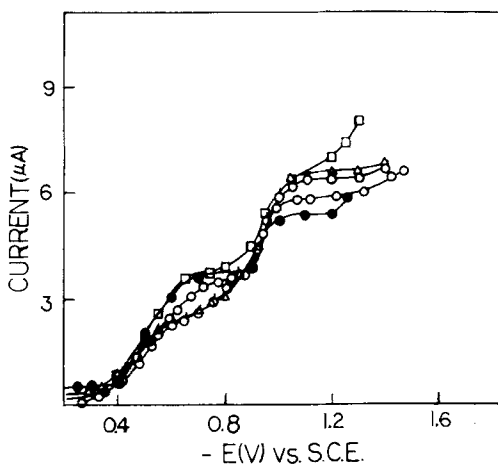

FIG. 1. Current-potential curves of poly-p-xylylviologen dibromide at different pH values: (●) 2.00, (□) 2.40, (○) 4.40, (◐) 6.00, (△) 8.00 (concentration: ~ 0.8 mg/mL; h$_{Hg}$ = 35 cm).

TABLE 1. Summary of Results on Polarographic Studies of Aqueous
Solutions of Poly-p-xylylviologen Dibromide

pH[a]	Concentration C (mg/mL) × 10	h_{Hg} (cm)	Limiting current, i_ℓ (μA)	
			Wave I[b]	Wave II[b]
2.00 (HCl-KCl)	3.73	35	1.28 (-0.510)	0.75 (-0.945)
	8.00	35	3.00 (-0.510)	1.65 (-0.940)
	11.33	35	4.50 (-0.510)	2.55 (-0.950)
		50	5.40	3.45
		65	6.00	4.50
		80	6.45	5.40
2.40 (HCl-KCl)	3.60	35	1.43 (-0.500)	1.50 (-0.930)
	7.80	35	3.83 (-0.500)	2.70 (-0.940)
	10.87	35	4.28 (-0.500)	3.00 (-0.935)
		50	5.18	3.60
		65	5.78	4.50
		80	6.90	4.28
4.40 (citrate buffer)	3.47	35	1.43 (-0.500)	1.20 (-0.940)
	8.00	35	3.45 (-0.500)	2.25 (-0.935)
		50	4.20	3.00
		65	4.95	3.60
		80	5.70	4.20
6.00 (citrate buffer)	3.47	35	0.75 (-0.495)	1.65 (-0.930)
	8.13_3	35	2.25 (-0.480)	3.90 (-0.925)
		50	2.70	4.80

TABLE 1 (continued)

pH[a]	Concentration C (mg/mL) × 10	h_{Hg} (cm)	Limiting current, i_ℓ (μA)	
			Wave I[b]	Wave II[b]
		65	3.23	5.33
		80	3.60	5.85
	11.13	35	2.85 (-0.500)	5.93 (-0.935)
8.00 (phosphate buffer)	3.53₃	35	0.83 (-0.480)	1.73 (-0.930)
	8.33₃	35	2.03 (-0.475)	4.20 (-0.930)
	11.13	35	2.70 (-0.490)	5.70 (-0.945)
		50	3.30	6.83
		65	3.75	7.73
		80	4.28	8.85

[a]Ionic strength adjusted to 0.1 $\underline{M}$ by adding calculated amount of KCl.
[b]Values in parentheses denote half-wave potential ($E_{1/2}$) in volts vs SCE.

The results of all current-potential measurements at different heights of mercury are summarized in Table 1. As is evident, two waves are obtained with half-wave potentials of -0.496 ± 0.011 V (Wave I) and -0.936 ± 0.007 V (Wave II) vs SCE, showing almost no variation with changes in pH and the total concentration of the solutions. It should be pointed out in this connection that the actual values of the half-wave potentials realized in the present study are ~ 70 mV more negative than those reported earlier [1]. It is considered that this discrepancy might be due to the difference in the junction potentials associated with the SCE reference electrodes used in the two investigations.

The observed pH-independence of the half-wave potentials is interesting, and it possibly implies that the H⁺ ions as such do not enter into the electron-transfer reactions in either of the two reduction steps. The only outstanding effect of pH variation appears to be in controlling the relative heights of the two waves. The individual plots of i_ℓ vs C at different values of pH are shown in Fig. 2. It is
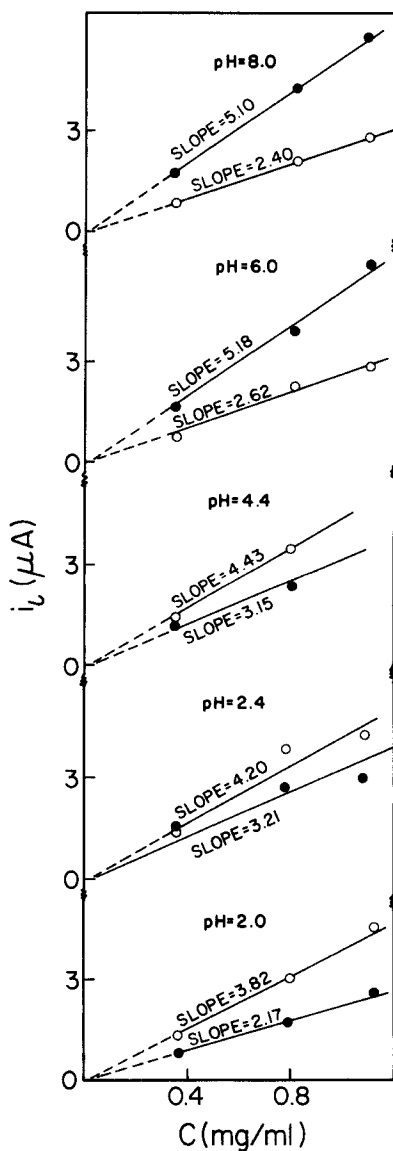
FIG. 2. Plots of limiting currents vs concentration for different pH values at h_{Hg} = 35 cm: (o) wave I, (•) wave II.

found that, between pH 2.00 and 4.40, the slopes for Wave I are some-what larger than those for Wave II and do not show any substantial variation, the average of the values being 4.1 ● 0.25. On the other hand, the slope for Wave II exhibits nearly a 50% rise as the pH is increased from 2.00 to 2.40, but a further increase of pH by two units does not indicate any significant change. It is remarkable, however, that a drastic change in the values of the slopes for both waves occurs as the pH is raised to 6.00. At this pH there seems to be a distinct reversal in the relative magnitudes of the slopes: the slope for Wave I reduces to 2.62 while the slope for Wave II is now found to assume a value almost twice as large. The results obtained at pH = 8.0 appear to exhibit a similar trend. Besides, it is interest-ing to note in this connection that regardless of the pH of the solution sum of the slopes for the individual waves, and hence the combined height of the two waves at any concentration, remains practically constant within the limits of experimental uncertainty. Also, one finds that the pH variation affects the distribution of the total current in a characteristic manner such that Wave I predominates at low pH (2.00-4.40) and, at high pH (6.00, 8.00), Wave II accounts for the major portion of the total current. Thus it is strongly suggested that two equilibrium forms of PXVBr$_2$ are involved in the present case, the current for Wave I being primarily determined by a protonated form of the substance and that of Wave II by the unprotonated molecules as such.

Unfortunately, an exact quantitative verification of the conclusions based on the magnitudes of $k[H^+]$ did not seem feasible in the present studies: two distinct waves were still noticeable even in the low pH solutions, and exploration of very high pH had to be abandoned in order to avoid any possible complications that may arise due to betain formation [4]. Moreover, no estimate of the value of the specific rate, k, for the protonation of PXVBr$_2$ was available. How-ever, it appeared from the overall behavior that a mechanism for the electron-transfer could be suggested by assuming that the $>N^+=C$ bond of the first regularly quaternized center at the same terminal where the protonation occurs would be the most vulnerable, and re-duction for both the protonated and the unprotonated form will take place with the involvement of a one-electron attack at this point [5]. Accordingly, the reactions at the DME for the respective waves may be represented as shown on the following page.

Due to the anticipated predominance of the nonprotonated form and lessening of kinetic complications at lower acidities, the observed heights of Wave II at higher pH values were assumed to be more re-liable in estimating the (diffusion) currents contributed by this form. Likewise, the low pH data for Wave I were considered more repre-sentative of the characteristics of the reduction of the protonated species. Thus analysis of the results of height-dependence studies as well as the reversibility tests from $E_{3/4}$ and $E_{1/4}$ potentials were carried out using the data at pH = 2.00 for Wave I and those at pH = 8.00 for Wave II.
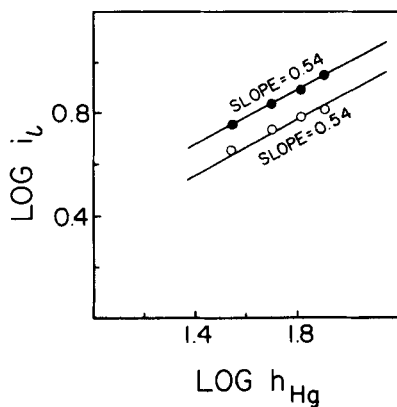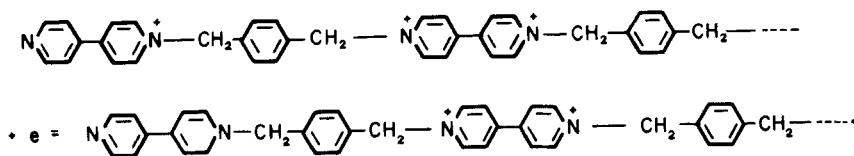
WAVE I
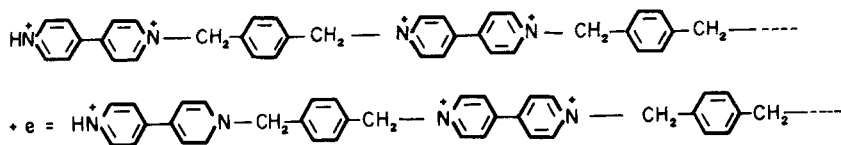
WAVE II

FIG. 3. Plots of log i_ℓ vs log h_{Hg}: ($\circ$) wave I at pH = 2.00, ($\bullet$) wave II at pH = 8.00 (concentration: $\sim$ 1.10 mg/mL).

The plots of log i_ℓ vs log h_{Hg} as given in Fig. 3 indicate that the values of the slopes are close to 0.5 for both Waves I (pH = 2.00) and II (pH = 8.00). This would suggest that the electron-transfer process in either case is diffusion-controlled. Now, assuming that both waves
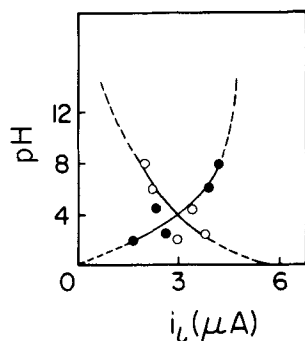
FIG. 4. Plots of pH vs limiting currents: (o) wave I, (•) wave II (concentration: ~0.80 mg/mL; h_{Hg} = 35 cm).

are irreversible and the following relationship holds true [6] at 25°,

$$E_{3/4} - E_{1/4} = -0.05172/\alpha n \tag{2}$$

substitution of the values of $E_{1/4}$ and $E_{3/4}$, as obtained for Wave I at pH = 2.00 (at 1.13 mg/mL total concentration) and for Wave II at pH = 8.00 (at 1.11 mg/mL total concentration), leads to the values 0.41 and 0.43 for αn, respectively. Similar calculations on the basis of the relationship for a reversible wave ($E_{3/4} - E_{1/4} = -0.0564/n$) also yield fractional values, viz., 0.45 (Wave I) and 0.47 (Wave II) for the number of electrons involved. Under the circumstances, it seemed reasonable to consider both waves to be irreversible in nature.

In this connection, it appeared interesting to find the pH at which the limiting currents for the two waves will be equal for a given concentration. Figure 4 presents the plots of these limiting currents at h_{Hg} = 35 cm as functions of pH for the concentration ~ 0.80 mg/mL. The pH at which the two curves intersect is determined to be 4.1. Considering that, at this point of equal limiting currents, the ratio of the equilibrium concentrations of the two forms is equal to unity, a tentative value for the dissociation constant $K = [H^+][B]/[BH^+]$ (where B represents $PXVBr_2$) is calculated to be 7.94×10^{-5}. (It may be of interest to note in this connection that the second acid dissociation constant of monomeric 4,4'-bipyridine is estimated to be 1.4×10^{-5} [7] at 0.1 M ionic strength.) Also, extrapolation of the individual curves (Fig. 4) provides the following values of limiting currents (μA) at extreme pH values:

pH = 0	5.55 (Wave I)	0 (Wave II)
pH = 14	0.75 (Wave I)	4.65 (Wave II)

Assuming that these estimates are close to the diffusion currents, the proportionality constants id/C approximates to 6.94 for Wave I at pH = 0, and 5.81 for Wave II at pH = 14.

ACKNOWLEDGMENTS

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Note Added in Proof. The flow rate and drop time for the capillary used were 2.01 mg/s and 4.3 s, respectively, at h_{Hg} = 35 cm.