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Studies on the Polarographic Reduction of Poly-m-xylylviologen Dibromide in Water

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ABSTRACT

Polarographic studies on aqueous solutions of the redox polyelectrolyte poly-m-xylylviologen dibromide were carried out in the 1.70-7.90 pH range. The compound revealed two well-defined, diffusion-controlled cathodic waves with half-wave potentials of -0.482 and -0.906 V vs SCE. The electrode processes were found to be irreversible and independent of pH. The system did not conform to the protonation equilibrium ($PXVBr_2 + H^+ \rightleftharpoons PXVBr_2H^+$), in contrast to its ortho and para isomeric compounds. A suitable mechanism for the reduction processes is suggested.

INTRODUCTION

Some interesting polarographic investigations on the electron-transfer behavior of redox polyelectrolytes poly-o-xylylviologen dibromide (o-$PXVBr_2$) and poly-p-xylylviologen dibromide (p-$PXVBr_2$) have recently been undertaken in our laboratory [1, 2]. The analogous meta-compound, poly-m-xylylviologen dibromide (m-$PXVBr_2$), how-

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ever, has received limited attention. Factor and Heinsohn [3], for instance, merely reported two irreversible waves [$E_{1/2}(I) = -0.445$ V, $E_{1/2}(II) = -0.854$ V vs SCE] in 0.1 M aqueous KCl buffer (pH = 9.00) for m-PXVBr_2, but other related studies were not carried out. Therefore, it was considered worthwhile to explore further the DME polarography of m-PXVBr_2 to understand its reduction mode as well as the nature of the electron-transfer reactions involved.

The compound m-PXVBr_2, like its ortho and para isomeric polyviologens, represents a novel class of redox polyelectrolyte whose redox property was confirmed by Zn dust (or $Na_2S_2O_4$) reduction followed with subsequent air-oxidation to the original leuco salt [3]. The introduction of a m-xylylene moiety between the two charged centers of the polymer appears to be promising for DME polarography because these quaternaries, located meta to the xylylene ring, are expected to behave in a manner different from the compound which possesses an o- or p-xylylene moiety in its repeating unit.

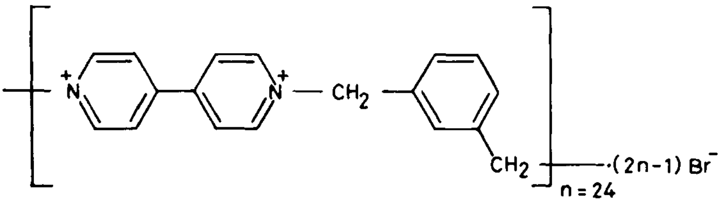
The present study was performed in various aqueous solutions of different pH values (1.70, 2.20, 4.20, 6.40, 7.40, and 7.90) and constant ionic strength ($\mu = 0.1$ M). It should be pointed out that further investigations in more alkaline solutions had to be abandoned to avoid any complications that might arise due to dequaternization [4] or ylide formation [5] in the system. An attempt has been made to propose a tentative mechanism for the reduction processes at the DME in the present case.

EXPERIMENTAL

Chemicals and Procedures

Deionized water, distilled twice from a Pyrex glass still, was used to make all solutions. The specific conductivity of the water varied between 1.5×10^{-6} and 2.5×10^{-6} mho/cm. All other reagents were of analytical grade.

m-PXVBr_2 was prepared according to an earlier procedure [3]. [Analysis (%): $\geq$C = 50.90, H = 3.85, N = 6.70.] The terminal group of the polymer was characterized through its infrared (KBr) analysis. The C–H stretching (2980 cm^{-1}), C–H bending (810 cm^{-1}), C=C stretching (1420 cm^{-1}), and $>$C=N–C substituted imine vibration (1625 cm^{-1}) are characteristics of the end pyridine ring systems while absorptions at 3110 cm^{-1} (C–H stretching), 1500 cm^{-1} (C–H bending), and 600 cm^{-1} (C–Br stretching) are considered due to the terminal –CH_2Br group in the system. The purity of the polymer was checked through its thin-layer chromatographic analysis in ethanol. The thermogravimetric curve revealed that the compound started decomposing above 250°. The elemental analysis and the ionic bromine (4.66 mol/1000 g; conductometrically) seem to suggest a possible structure:



The theoretical percentage of C, H, and N is 51.46, 3.83, 6.67, respectively, and the nonionic bromine is calculated to be 0.102 mol per 1000 g of the sample. Moreover, the differential vapor pressure measurement with 16.23 mg/mL of the compound in water corresponded to the total concentration of 0.07701 M as determined on the basis of glucose as a monomer. This agrees with an average molecular weight of 10,080 for the compound on consideration that 48 ions (47 Br^- ions plus 1 cation) per molecule would become available as suggested by the proposed structure. It is interesting to note that the intrinsic viscosity at 25°C in 0.5 M KBr solution has been determined to be 0.04 dL/g; a value almost equal to that ($[\eta]$ = 0.045 dL/g) of p-$PXVBr_2$ [2]. This may be taken as indicative of a similar order of magnitude for the molecular weight of the present system as for p-$PXVBr_2$.

All polarograms were recorded against an aqueous saturated calomel electrode (SCE) reference on a Leeds-Northrup Type E Electrochemograph at room temperature (~25°C) in the manner mentioned earlier [2]. The dropping mercury electrode had the characteristics $m = 1.89$ mg/s and $t = 4.4$ s at $h_{Hg} = 35$ cm in 0.1 M aqueous KCl (open circuit). The supporting electrolytes employed in this study were a HCl-KCl mixture and citrate and phosphate buffers of the desired pH. The ionic strength of all solutions was maintained at 0.1 M by adding calculated amounts of KCl. Residual current and IR drop corrections were made in all current and potential data reported in this work.

RESULTS AND DISCUSSIONS

The representative polarographic current-voltage curves of m-$PXVBr_2$ at various pH values are illustrated in Fig. 1.

A summary of the results of all current potential measurements at different heights of mercury is given in Table 1. The half-wave potentials for both cathodic waves as obtained in the present study are listed in Table 2 along with those of o-$PXVBr_2$ [1] and p-$PXVBr_2$ [2]. The compound m-$PXVBr_2$ may be regarded as somewhat structurally

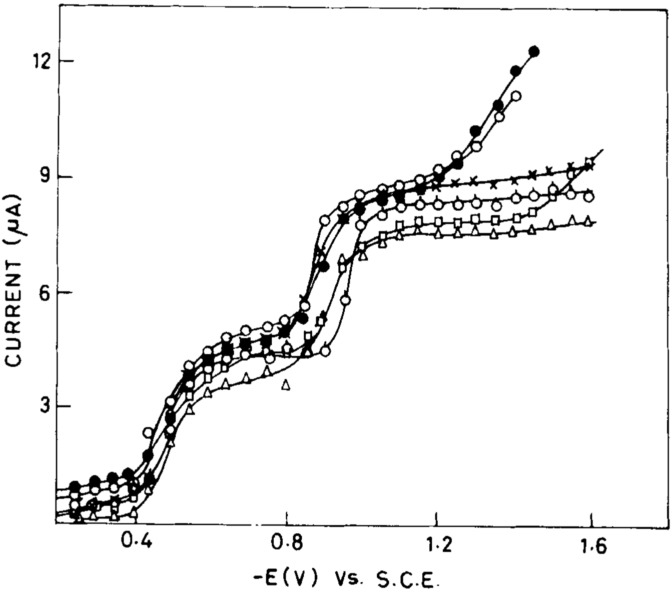


FIG. 1. Polarographic curves for ~1.1 mg/mL poly-m-xylylviologen dibromide in solutions of various pH values: (●) 1.70, (○) 2.20, (□) 4.20, (△) 6.40, (×) 7.40, (ό) 7.90, at h_{Hg} = 35 cm.

equivalent to the system p-PXVBr$_2$ on the basis of their respective plane-projection models. The slightly less negative $E_{1/2}$ values for both waves of m-PXVBr$_2$ than those of p-PXVBr$_2$ are, however, interesting and possibly indicate a little easier but similar mode of reduction as for the p-isomer. This may be ascribed to the presence of a m-xylylene ring in its monomeric unit which might induce some sort of electron-attracting resonating tendency (cf., "hyperconjugation") contrary to the ortho and para analogs and thus promotes a relatively more electron-deficient site for reduction. However, the major shifts in $E_{1/2}$ values of o-PXVBr$_2$ from those of para and meta isomeric polyviologens can be easily correlated in terms of structural conformations of individual systems as discussed earlier [1]. Further, the observed discrepancies between the results of present and earlier studies [3] for $E_{1/2}$ values of m-PXVBr$_2$ might be due to the differences in the junction potentials associated with the reference electrodes (SCE) used in the two investigations.

The individual plots of limiting current vs concentration for different pH values at h_{Hg} = 35 cm are shown in Fig. 2. Evidently, no sub-

TABLE 1. Results of Polarographic Studies on Aqueous Solutions of Poly-m-xylylviologen Dibromide at ~25°C

pH^a	Concentration C (mg/mL) × 10	h_{Hg} (cm)	Limiting current, il (μA)	
			Wave I^b	Wave II^b
1.70 (HCl-KCl)	3.87	35	1.74 (-0.500)	1.50 (-0.920)
	7.07	35	3.24 (-0.490)	3.00 (-0.915)
	11.20	35	4.90 (-0.490)	4.30 (-0.910)
		50	5.64	5.10
		65	6.48	5.40
		80	7.29	6.36
2.20 (HCl-KCl)	4.00	35	1.95 (-0.455)	1.56 (-0.890)
	9.33_3	35	4.05 (-0.455)	2.70 (-0.895)
	11.47	35	5.30 (-0.475)	3.90 (-0.900)
		50	6.00	4.80
		65	7.05	5.25
		80	7.95	6.15

(continued)

TABLE 1 (continued)

pH^a	Concentration C (mg/mL) × 10	h_{Hg} (cm)	Limiting current, il (μA)	
			Wave I^b	Wave II^b
4.20 (citrate buffer)	4.00	35	1.35 (-0.495)	1.05 (-0.925)
	7.00	35	2.40 (-0.495)	1.95 (-0.925)
	11.06_6	35	4.50 (-0.498)	3.30 (-0.935)
		50	5.40	4.05
		65	6.30	4.65
		80	7.20	5.01
6.40 (citrate buffer)	3.53_3	35	1.56 (-0.495)	1.50 (-0.910)
	6.53_3	35	2.70 (-0.475)	2.54 (-0.905)
	10.40	35	4.00 (-0.500)	3.75 (-0.915)
		50	4.86	5.10
		65	5.76	5.70
		80	6.96	6.36

7.40 (phosphate buffer)	3.60	35	1.65 (-0.490)	1.50 (-0.890)
	6.93_3	35	3.30 (-0.480)	2.70 (-0.900)
	11.40	35	4.80 (-0.480)	4.20 (-0.900)
		50	5.25	5.70
		65	6.30	6.00
		80	7.20	6.60
7.90 (phosphate buffer)	4.27	35	1.86 (-0.470)	1.46 (-0.870)
	7.53_3	35	3.15 (-0.460)	3.00 (-0.905)
	10.87	35	4.40 (-0.475)	4.20 (-0.905)
		50	5.16	5.10
		65	5.76	5.70
		80	6.66	6.60

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

TABLE 2

	$E_{1/2}$ (V) vs SCE	
	Wave I	Wave II
o-PXVBr$_2$	-0.404 ± 0.011	-0.981 ± 0.27
m-PXVBr$_2$	-0.482 ± 0.014$_5$	-0.906 ± 0.015
p-PXVBr$_2$	-0.496 ± 0.011	-0.936 ± 0.007

stantial variations in the values of the slopes for both waves could be observed with changes in pH of the solutions except in a few cases at higher acidities which might involve some uncertainty in slopes because of marked curvature in their respective il vs C plots. Moreover, as is obvious from Table 1, the relative heights of the two waves appear to be independent of any variation in the pH of the solution. This suggests that m-PXVBr$_2$ is surprisingly not competent enough to establish an equilibrium between its protonated and unprotonated species (cf., o-PXVBr$_2$ [1] and p-PXVBr$_2$ [2]), and thus any treatment based on the assumption of a protonation equilibrium ($PXVBr_2 + H^+ \rightleftharpoons PXVBr_2H^+$), as discussed in the cases of o- and p-PXVBr$_2$, seems to be no longer feasible in the present study. This may be attributed to the fact that the lone pair of electrons on the nitrogen of one of the pyridines in the bipyridine ring at the terminal is being drawn closer to the adjacent electron-deficient quaternized center, probably under the influence of an "electron-withdrawing inductive effect" exerted by m-xylylene moiety and thereby becoming less available for forming a bond with a proton in the present instance. Such an interaction of an unshared electron pair with the terminal quaternary nitrogen is marginal in o- and p-isomers owing to the proximity of an electron-rich o-xylylene moiety to the end bipyridine ring and a negligible dipole moment of the p-xylylene entity ($\geqslant N^+{-}CH_2C_6H_4CH_2{-}N^+\leqslant$), respectively.

The half-wave potentials for both waves were found to be practically constant with variations in pH and the total concentration of the solution. This apparently rules out any type of proton participation during the course of reductions at the DME. However, a probable mechanism for the electron-transfer reactions can be suggested by keeping in view that the $>N^+{=}C$ bond of the first regularly quaternized center of the terminal bipyridine ring is less accessible to electron attack since the positive charge density of the concerned quaternary center is presumably shielded by the terminal unshared nitrogen's electron pair interacting toward it. Under such circumstances, both reductions are believed to occur with a one-electron

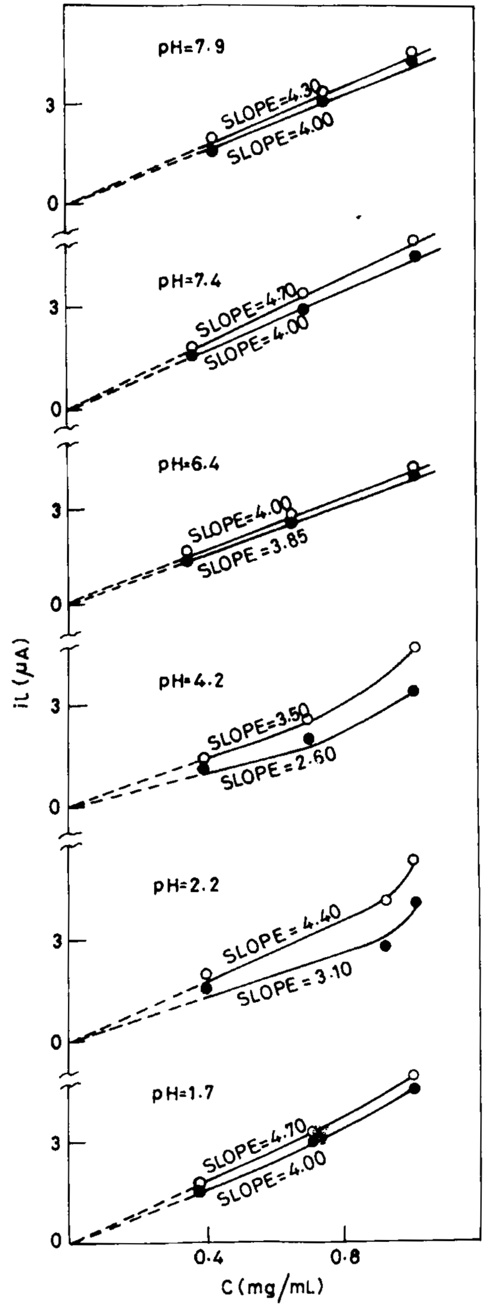
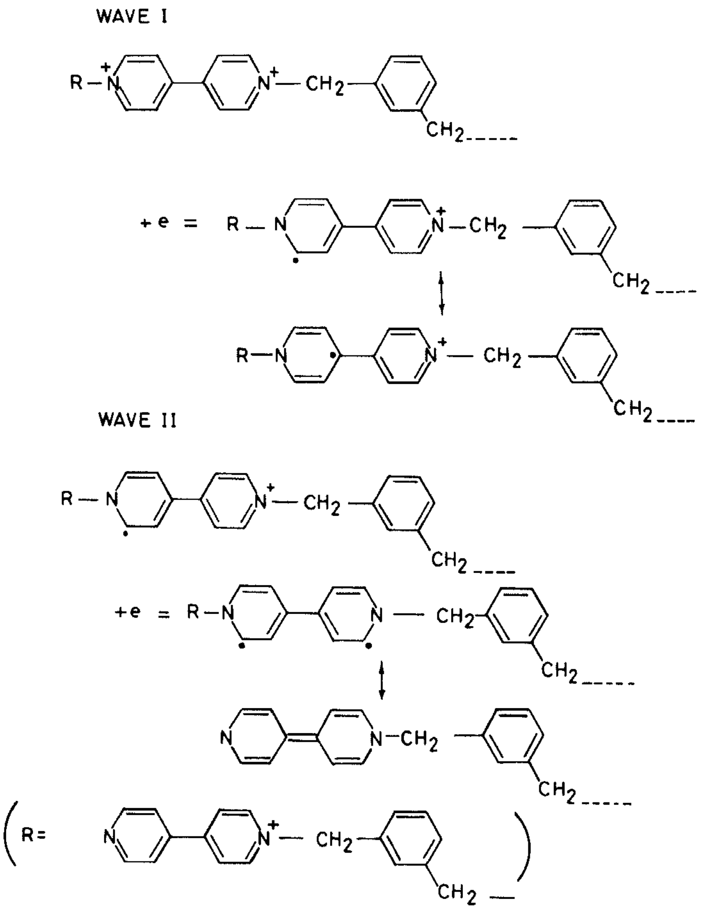


FIG. 2. Plots of limiting currents vs concentration for different pH values at h_{Hg} = 35 cm: (○) Wave I, (●) Wave II.

involvement in the vicinity of the next quaternary center [2, 6] other than the terminal positive nitrogen of the molecule. Thus, the system may undergo two successive reduction steps [4, 7]:



producing cationic mono- and diradicals [8] for Waves I and II, respectively, over the potential range 0 to ~-1.6 V studied. Although the diradical produced in the second reduction is considered reasonably stable [9], its further stabilization into a quinonoid form through electron pairing [5, 10] may not be ignored in the present case.

The electron-transfer processes are diffusion controlled as shown by slopes for the plots of log il vs log h_{Hg} (Fig. 3) which are close to 0.5 for both waves (pH = 4.20) in the present case. Also, the limiting currents are proportional to the concentration of the depolarizer as

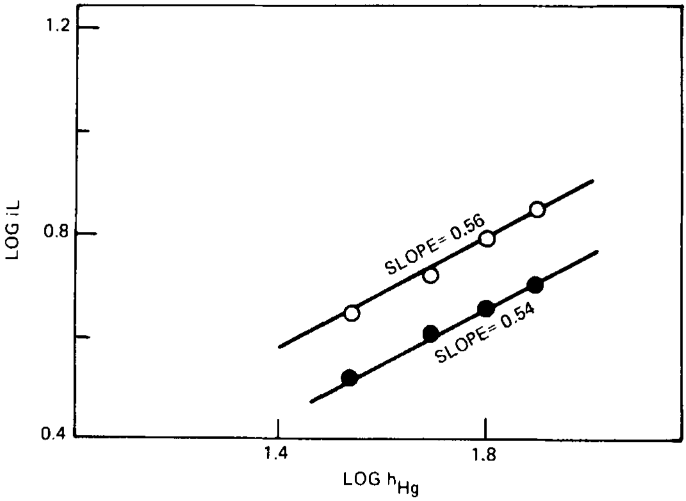


FIG. 3. Plots of log il vs log h_{Hg} at pH = 4.20: (○) Wave I, (●) Wave II, Concentration: ~1.10 mg/mL.

predicted by the Ilkovič equation; the upward trends visible at lower pH (< 4.20) and higher concentrations (> ~0.80 mg/mL) for both waves in il vs C plots seemingly reflect the contribution of additional adsorption current facilitated by the film of reduced species, alone or aggregated, adsorbed on the surface of the electrode [4, 7, 11]. It is remarkable, however, that such a phenomenon becomes ineffective at lower acidities because hydroxyl ions might act as "scavengers" to such films, resulting in linear plots for both waves.

On substitution of $E_{1/4}$ and $E_{3/4}$ values as obtained for waves I and II (at ~1.14 mg/mL total concentration for two different solutions with pH = 2.2 and 7.4) in the following relationships of an irreversible wave (Eq. 1) [12] and a reversible wave (Eq. 2) at 25°C,

$$E_{3/4} - E_{1/4} = -0.05172/\alpha n \qquad (1)$$

$$E_{3/4} - E_{1/4} = -0.0564/n \qquad (2)$$

the values of αn and n could be calculated as shown in Table 3. The fractional values for the number of electrons consumed in electron-transfer reactions in both acidic and moderate alkaline media appear to be reasonably significant enough to support the irreversibility of electrode processes at the DME, despite the fact that the half-wave

TABLE 3

	αn		n	
	Wave I	Wave II	Wave I	Wave II
pH = 2.2	0.43	0.74	0.47	0.80
pH = 7.4	0.52	0.58	0.56	0.63

potential realized for both waves is found to be almost independent of the concentration of the compound.

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