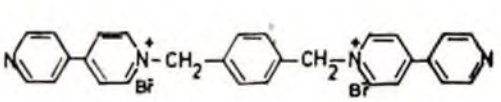
POLAROGRAPHIC BEHAVIOUR OF THE BOLAFORM ELECTROLYTE $\alpha\alpha$-BIS(4,4—BIPYRIDINIUM)—P—XYLENE DIBROMIDE IN WATER

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Cathodic reduction of a bolaform electrolyte α,α'-bis(4-4'-bipyridinium)-p-xylene dibromide) was carried out at dme in aqueous solutions of different pH ranging between 1.90-7.90, at constant ionic strength (μ = 0.1 M). Two well defined diffusion-controlled polarographic waves were observed in all solution studied. Although the half-wave potentials of these waves [$E_{1/2}$ (Wave I) = -0.586 V and $E_{1/2}$ (Wave II) = -0.968 V vs SCE] are practically independent of pH and depolarizer concentration, the electrode processes for both waves have been found to be irreversible in nature. Concepts based on the specific characteristics of the divalent bipyridinium bolaform salt regarding its "intramolecular coulombic interactions" and a typical "monoprotonation equilibrium" in aqueous solutions of varying pH have been invoked to explain the outstanding effect of pH variation on the relative wave heights including the mode of reduction as well as electron-transfer mechanism involved.

Electron-transfer behaviour of paraquat dimers, for instance, PQ^{2+}-R-PQ^{2+} (PQ^{2+} = mono, N-methyl 4,4'-bipyridinium salt and R= $-(CH_2)_{n=2,3,4}$ or o,m,p-xylylene moiety) and diethylene viologen dibromide ($DEVBr_2$, a condensation dimer of 4,4'-bipyridine and 1,2-dibromoethane) has recently assumed much attraction because of their distinctive structres <1,2>. The polarographic studies of other related polymeric system, viz, polyxylylviologen dibromides (o,m, & p-$PXVBr_2$) have also been undertaken in our laboratory (3a-c). Although, PQ^{2+}-R-PQ^{2+} has all its bipridyl nitrogens quaternized and the systems $DEVBr_2$ and $PXVBr_2$ possess an unshared bipyridine ring nitrogen at one of their terminals, the study related to the electroreduction of divalent system having only two quaternary centres, connected with an unshared ring nitrogen at both of its terminals seems to be so far unexplored and is expected to be different from others. It was, therefore, considered worthwhile to study the polarographic reduction of a dicationic bolaform type system (bolion) <4> possessing two unchanrged and heterocyclic ring nitrogens in addition to its both cationic rings seperated by an aromatic moiety in the structure. An aromatic bolaform salt α,α'-bis(4,4'-bipyridinium)-p-xylene dibromide, $(Bipy)_2XBr_2$, [represented by structure I] appears to be particularly relevant in this respect



The compound $(Bipy)_2XBr_2$ is a typical redox system belonging to an important "paraquat" or "viologen" family and is of much interest because of its expected herbicidal and pharmacological activities <5,6>. It is noteworthy that the present system is a divalent and cross-section (segement) of its polymeric analogue poly-p-xylylviologen dibromide (p-$PXVBr_2$) <3c>.

EXPERIMENTAL

The bolaform salt $(Bipy)_2XBr_2$ was prepared by a straight forward condensation of α,α'-dibromo-p-xylene (prepared in the lab, <11>) and 4,4'-bipyridine (Koch-Light) taken in the mole ratio of 1:2 in acetonitrile. Normally α-α'-dibromo-p-xylene (2.00 g/60 mL dry acetonitrile) solution was added gradually with continuous stirring to a solution of anhydrous 4,4'-bipyridine (2.37 g/60 mL dry acetonitrile) and the mixture was refluxed at ~ 80 C on a water bath for 1 h. The resulting yellowish crystalline product (yield is 85%) was washed several times with hot acetonitrile and then vacuum desiccated at 40° C for about 4 h. Analysis (%) : C = 57.86, H = 4.55, N = 9.83; Calc. ($C_{28}H_{24}N_4Br_2$): C = 58.33, H =4.16, N =9.72. Conductometric titration in water indicated 3.5 mol of Br- per 1000 g of the sample. The product decomposed above 300° C without melting. The terminal bipyridine rings of the salt were characterized through its infrared spectrum (nujol): 3034 cm^{-1} (C-H stretching), 800 cm^{-1} (C-H bending), 1400 cm^{-1} (C=C stretching), and 1624 cm^{-1} (>C=N-C

0013 466 x (35) 39 215-220

substituted imine vibration). Differential vapour pressure measurement in water at the concentration 2.83 mg/mL corresponded to the total concentration of 0,00864 M as determined on the basis of standard compound (glucose) Considering that the compound can dissociate to a dication and 2 anions, this molarity, together with an analysis of ionic bromine, was reconciled with an average molecular weight of 555. for the compound. (This is in agreement within 4% of the theoretical molecular weight of 576). The compound was further characterized through NMR spectrum (D_2O) which accounts for methylene (84.1), phenyl-(7.5-7.8, M) and hetero aromatic (8.2,S) protons in the molecule. TLC analysis in ethanol and development in iodine chamber -revealed only one spot.

All other reagents used were of anaytical grade. Deionized water, distilled twice from a pyrex glass still and having a specific conductance of 1.2-2.6 micro mho/cm was used to prepare the solutions.

Polarograms were taken in solutions of different pH values by employing HCl-KCl mixtures (pH = 1.9, 2.4) and citrate (pH 4.5, 5.9) and phosphate buffers (pH 7.4 & 7.9) as supporting electrolytes. The ionic strength of all solutions were held constant at 0.1 M with KCl. Leeds-Northrup Type E Electro-chemograph was used for recording the polargraphic curves at room temperature (~25°C) while a Beckman Zeromatic pH meter was used for measuring the pH values. The capillary characteristics at mercury height of 35 cm (open circuit) was $m^{2/3} t^{1/6} = 2.029\ mg^{2/3} Sec^{-1/2}$ in 0.1 M aqueous KCl. All currents and potentials reported in this work were corrected for the residual current and the iR drops, respectively.

RESULTS AND DISCUSSION

Two distinct cathodic waves were observed for $(Bipy)_2\ XBr_2$ in the polarogram. A typical set of polarograms in different media are shown in fig 1. A summary of the results of analysis of the polarograms are given in Table 1

The half wave potentials of the two waves are found to be practically independent of concentration and pH. However the individual wave height of the two waves vary with pH. The first wave decrease in height but the second increases with increase of pH. The height of the combined wave however is nearly independent of pH.

TABLE 1
RESULTS OF POLAROGRAPHIC MEASUREMENTS ON THE DROPPING MERCURY ELECTRODE FOR AQUEOUS SOLTIONS OF α,α'-BIS-(4,4'-BIYRIDINIUM)-p-XYLENE DIBROMIDE AT 25°C

(mg/mL)	h_{Hg} (cm)	Wave 1 iμA	Wave 1 -E/mv	Wave 2 iμA	Wave 2 -E/mv
		pH 1.90 HCl-KCl			
0.340	35	1.80	585	1.50	970
0.680	35	3.90	585	3.00	950
1.013	35	6.40	590	3.90	960
	50	8.10		6.90	
	65	9.60		8.85	
	80	10.80		10.50	
		pH 2.40 HCl-KCl			
0.350	35	1.75	585	1.65	970
0.700	35	3.83	585	3.10	965
1.034	35	6.00	580	4.50	960
	50	8.00		7.25	
	65	9.25		9.45	
	80	10.20		10.65	
		pH 4.50 Citrate buffer			
0.353	35	1.50	590	1.80	960
0.680	35	3.43	580	2.75	950
1.020	35	5.50	605	3.70	970
	50	7.95		6.90	
	65	8.80		10.00	
	80	11.45		10.85	
		pH 5.90 Citrate buffer			
0.347	35	1.00	570	2.00	970
0.693	35	2.28	595	4.10	975
1.000	35	3.51	600	6.00	970
	50	5.25		9.80	
	65	6.10		11.85	
	80	9.25		13.25	
		pH 7.40 Phosphate buffer			
0.380	35	1.10	580	3.25	975
0.712	35	1.85	590	5.80	970
1.050	35	2.00	600	8.20	990
	50	2.60		9.50	
	65	3.15		10.70	
	80	3.70		12.30	
		pH 7.90 Phosphate buffer			
0.360	35	0.60	585	4.10	970
0.693	35	0.85	570	7.20	970
1.047	35	0.90	575	9.80	980
	50	1.40		11.80	
	65	1.90		13.75	
	80	2.45		13.80	

Ionic strength maintained at 0.1 M with the requiste amounts of KCl in all cases.

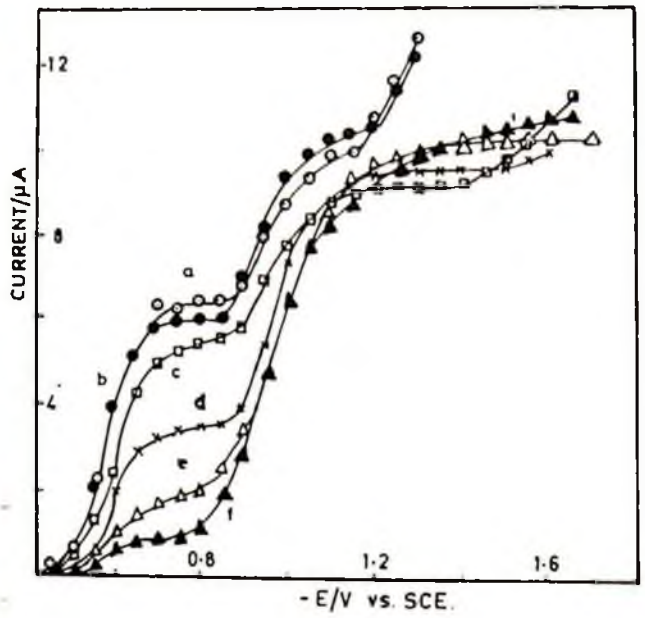


Fig. 1 Polarograms for 1.0 mg/ml $\alpha\alpha'$-, '-bis (4,4'-bipyridinium)-p-xylene dibromide in different aqueous solutions of pH values: 1.90,(a) 2.40,(b) 4.50, (c) 5.90, (d) 7.40,(e) 7.90 (f) at h = 35 cm

Similar behaviour is reported for certain keto acids such as pyruvic acid <12> and polyviologens <3a, 3c, 2>. These participate in protonation equilibrium and the two waves are reported to be due to the reduction of protonated and unprotonated species.

It is evident from the molecular structure of $(BiPy)_2\ XBr_2$ that it can act as 2:1 electrolyte <7,8> and at least one of the two bromids is dissociated leaving the triple ion species[BiPy N^+ $CH_2C_6H_4$-CH_2-N_2-N^+ ByPy. Br^-] <9>. It is likely that the bromide engages one of the terminal nitrogens. Under such circumstances it appears that only one unshared bipyridyl terminal nitrogen can act as proton acceptor. The protonation equilibrium can be written as:

$$(BiPy)_2\ XBr_2 + H^+ \longrightarrow (BiPy)_2\ XBr_2\ H^+ \quad \ldots.(1)$$

unprotonated B — Protonated BH^+

The two steps of reduction of $(BiPy)_2\ XBr_2$ have been closely analysed. The slope of the linear plot of i_l vs for the first step decrease from 0.60 to 0.11 as the pH increases; concurrently the slope of the second step incrreases from 0.41 to 1.01. The sum of the two slopes however is nearly independent of pH.

In view of these, it is reasonable to assume that the observed currents for step 1 and step 2 can be taken as due to the reduction of protonated and unprotonated forms of the compound. The corresponding wave heights are related to the equilibrium concentrations of the two species at any pH. However if protonation is very fast, as BH^+ is reduced at the electrode, it is formed from B and H^+ and the observed i_l includes a contribution of kinetic current (i_k). If the rate of proton associatioon is appreciably high, the limiting current due to unprotonated species would become vanishingly small. On the other hand, if the rate of attainment of the equilibrium between B and BH^+ at the electrode surface is very small, the limiting currents would only represent the diffusion curent of the two possible forms. Since the protonation reaction in the present instance is expected to be somewhat moderate enough to occur within the time scale of polarography because of the possible intramolecular electrostatic interaction of the concerned quaternized center with terminal lone pair of electrons of the triple ion, and interstingly two distinct waves are still noticeable even at the low pH values, it seems to be more reasonable to belive that any kinetic current contribution to the limiting current of BH^+ due to the kinetics of $B + H^+ \longrightarrow BH^+$ is marginal and thus both waves are apparently diffusion controlled <3c>. Under such circumstances a general analysis of the electron-transfer processes at various pH can be made more accurately if the data obtained at lower pH (1.90) for wave I and at higher pH (7.90) for wave II are chosen to be most reliable represntatives for the reductions of the protonated and unprotonated species of the system, respetively.

The effect of pH on the magnitude of limiting currents of the two waves at mercury head of 35 cm for a known concentration (1.0 mg/mL) of $(Bipy)_2\ XBr_2$ shows that as the first wave height decreases, the second increases and the two curves intersect approximately at pH 4.40.

At this point of equal limiting current, the ratio of the equilibrium concentration of the two forms B and BH^+ is taken as unity. The pK of the acid is taken as 4.4 and the dissociation constant $K = [B]\ [H^+] / [BH^+]$ is calculated to be 3.98×10^{-5} (u=0.1 M). This value for $(Bipy)_2\ XBr_2\ H^+$ is less than those of p-$PXVBr_2\ H^+$ ($K = 7.9 \times 10^{-5}$) <3c> and $DEVBr_2\ H^+$ ($K = 31.6 \times 10^{-2}$) <2>, at 0.1 M ionic strength. This suggests somewhat

more stable nature of the protonated form of $(Bipy)_2XBr_2$ and this may in turn lead to a conclusion that at least one of the terminal nitrogens is relatively more basic for the nono-protonation <13>. This may be because of the larger intramolecular attraction with the qaternary centers of the molecule in the present case. It may be noted further that monomeric quaternized 4'4'-bipyridine with second acid dissociation constant of 1.4×10^{-5} (μ = 0.1 M) comes into the stability sequence as 4'4' bipyridine $2H^+$ > (Bipy) XBr_2H^+ > P-PXVBr_2H^+ > DEVBr_2H^+. The stability order of these protonated molecules, i.e., basicity strength of the terminal nitrogen(s) of unprotonated system seems to be mainly controlled by its relative proximity with the electron-deficient cationic sites and other electron-withdrawing group ($-CH_2Br$) present in their respective structure.

The $E_{1/2}$ of $(Bipy)_2XBr_2$ [-0.586 ± 0.0098 V and -0.968 + 0.0097 V] is more negative than the $E_{1/2}$ of the anologous p PXVBr_2 (-0.496 ± 0.011 V and -0.936 ± 0.007 V) <3c>. This may be because of the reduced positive charge at the quanternized centre in $(Bipy)_2XBr_2$ due to its possible electrostatic interaction with (i) an associated Br^-, (ii) the proximate electron rich xylylene moiety and (iii) unshared lone pain of electrons on the terminal nitrogen in the molecule. However methyl viologen (1,1'-dimethyl, 4,4'-bipyridinium dibromide) has a half wave potential (-0.680 V) more negative than that of $(Bipy)_2XBr_2$. This may be due to the shielding of the positive charge on the quaternary ring nitrogen by the attached electron donating methyl group.

The conductance measurement of $(Bipy)_2XBr_2$ at 25° C was also undertaken to get an insight into the nature of electrolyte, in aqueous solution. A distinct inflection in the curve of Λ_f vs. $\sqrt{C}$ plot (Fig. 2) suggests some possible association of bromide ion with the positive nitrogen of the compound, despite low molecular weight of the system and the high dielectric constant of the solvent, and the system may be considered to behave as 1:1 electrolyte (triple ion) in water <7,9>. The limiting equivalent conductance (Λ° = 49.7) of this triple ion as obtained in the present instance is used to estimate its diffusion co-efficient (D) at infinite dilution <14>. By applying the value of D (0.66×10^{-5} cm^2 s^{-1}) in the Ilkovic equation, the total number of electrons involved in the complete reduction of the system at either pH 1.90 (concentration :

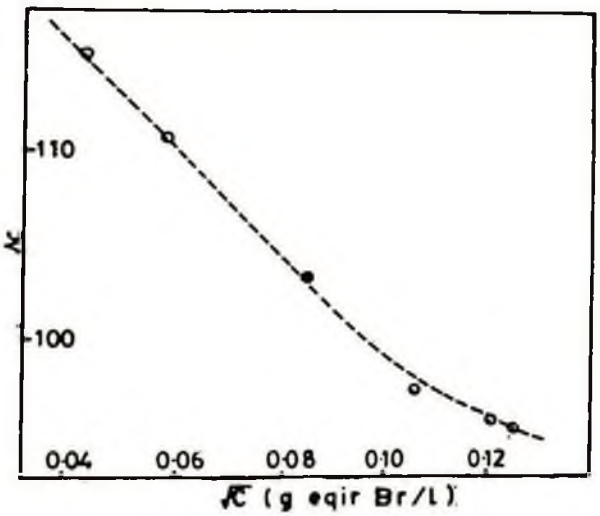


Fig. 2 Conductance behaviour of $(Bipy)_2XBr_2$ in water at 25 C

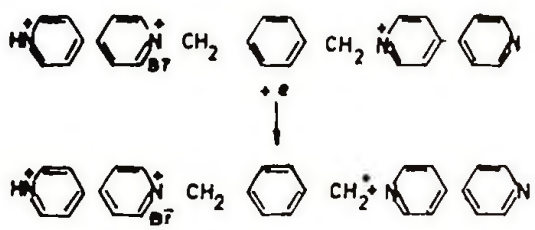
1.76 mM, total current : 10.3 μA) or pH 7.90 (concentration : 1.82 mM, total current : 10.7 μA) approximates to 2.0. This would apparently correspond to the one electron uptake in either of the two reduction processes.

The site of reduction however is not indicated in these studies. A complete electrolysis of $(Bipy)_2XBr_2$ has been carried out in deaerated aqueous solutions at -1.2V and the reduction is followed by recording the decay in current with time. This resulted in an insoluble residue identified as 4,4'-biyridine from elemental analysis and also iR spectra. There is another soluble violet product which readily undergoes aerial oxidation. Because of limited stability of this product <2,3,6>, this has not been characterized. It may be noted that similar unstable deep violet product is formed during the chemical reduction of $(Bipy)_2XBr_2$ with zinc dust or $Na_2S_2O_4$ and is presumed to be due to cation radical.

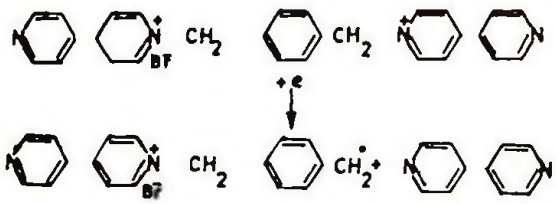
On the assumption of the formation of an ion-pair on one of the cationic sites of bis quaternary salt, it is reasonable to assume, as stated earlier, that the other site seemingly tries to interact with the anion of the ion-pair in an effort to induce an "intramolecular bending" <7,15> in the triple ion, inspite of its apparent rigidity and expected hydrophobic hydration around the molecule <16> in water. Under such condition, this unpaired

cationic site, i.e., the terminal >N⁺xylylene bond (without Br^- ion) would be somewhat strained and in order to relieve the steric compression arising in the solution this site becomes electrolytically more vulnerable. The vulnerability of this bond is apparently determined by its extent of intramolecular attraction which is perhaps less in alkaline media. On the basis of these results and discussion, a different type of electron-transfer mechanism as compared to that of p-PXVBr₂ <3c> and other pyridinium systems <17> could be tentatively proposed, by cleaving particularly this electron-deficient >N-xylylene bond of the compound involving a single-electron attack <18> in either of the two reduction process.

WAVE I



WAVE II



The electron-transfer reaction are diffusion-controlled as indicated by slope (≃ 0.5) of linear log i vs. log h_{Hg} plots for waves I (pH = 1.90) and II (pH = 7.90). If equation 2 is assumed to be valid for the proposed electron-transfer reactions at 25°C <3a>.

$$E_{dme} = E^{0'} + (0.05916/\alpha n) \log [i^2/(id - i)] \quad ...(2)$$

Then, one may obtain

$$E_{3/4} - E'_{1/4} = -(0.05916/\alpha n) \log 27. \quad ...(3)$$

$$\text{or} = -0.08465/\alpha n \quad ...(4)$$

Introducing the values of $E_{3/4}$ and $E_{1/4}$ for wave I (pH = 1.90, total concentration : 1.01 mg/mL) and wave II (pH = 7.90, total concentration : 1.04 mg/mL) into equation (4), the α n values were obtained as 0.76 and 0.58 respectively for the two waves. In spite of the fact that E value is practically independent of concentration in either of the two reductions, it seemed reasonable from the fractional values of n, to consider both waves to be irreversible in nature.

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