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The Effect of Cadmium Ions on the Polarographic Reduction of Poly[(*p*-methylbenzyl)viologen] Dibromide in Water

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The d.c. polarographic reduction of a redox polyelectrolyte, poly[(*p*-methylbenzyl)viologen] dibromide, in the presence of cadmium sulfate salt demonstrated two well-defined, irreversible diffusion-controlled cathodic waves corresponding to the reduction of protonated form as well as the cadmium complex of the polyelectrolyte in aqueous buffers (pH 2.00—6.00). No wave was observed due to the reduction of the unprotonated form of the polymer in the present instance, however, another ill-defined wave of irreversible nature was emerged at relatively higher negative potential presumably because of the catalytic evolution of hydrogen, at the dropping mercury electrode. An attempt has been made to correlate these results in terms of cadmium ion interaction with the polyelectrolyte during the course of electrode processes.

A comprehensive study on the polarography of the redox polymers, viz., poly[(*p*-methylbenzyl)viologen] dibromides (*o, m, p*-PMVBr$_2$) has recently been made to understand their reduction mode as well as electron-transfer mechanism involved.[1] The present paper deals with the effect of cadmium ions on the polarographic reduction of poly[(*p*-methylbenzyl)viologen] dibromide (*p*-PMVBı$_2$) in the aqueous solutions of pH 2.00—6.00 range.

Polyelectrolytes have been found to demonstrate a significant impact over their conformational alterations with the addition of simple salts.[2] As a consequence of such salt-induced conformational transition, i.e., the coiling or contraction of cationic polyelectrolyte in interaction with the anions of the added salt in dilute solution and sometimes the possibility of a chemical reaction of polyelectrolyte with the added salt, the reduction behavior of these systems would likely to differ than those of the salt-free polymeric materials. As is evident from the structural formulation of *p*-PMVBr$_2$ [represented by the structure **1**], one of the two nitrogens of the terminal bipyridine is not quaternized and may therefore serve as the proton acceptor allowing the system to exhibit an equilibrium between its protonated and unprotonated form as $p\text{-PMVBr}_2 + \text{H}^+ \rightleftarrows p\text{-PMVBr}_2\text{H}^+$. However, in the presence of Cd^{2+} ions, this uncharged nitrogen of the compound would act as a potential site for the complexation as well. It seems to be feasible that both the protonation and complexation may occur simultaneously and/or compete with each other on the time scale involved for the electroreduction. Thus, a different type of electrode process as compared to that of the polymer alone could be expected, in the presence of cadmium sulfate in this investigation.

Experimental

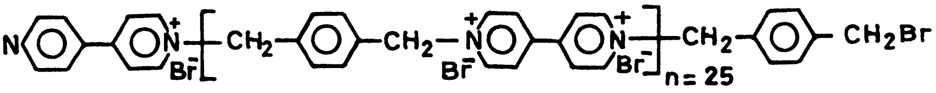
Materials. Demineralized water, distilled twice from a Pyrex glass still, with specific conductivity ranging between 1×10^{-6} to 2.5×10^{-6} S cm^{-1} was used in the preparation of solutions.

The preparation and characterization of the polymer *p*-PMVBr$_2$ (MW=11000) was followed according to the earlier recipes.[1c,3] All other chemicals were of analytical grade.

Methods. All the polarograms were recorded in the usual manner[1c] at room temperature (ca. 25 °C) with the help of Leeds Northrup Type E Electrochemograph using a dropping mercury electrode (DME) and a saturated calomel electrode (SCE) as working and reference electrodes, respectively. First, a known volume (15 ml) of the supporting electrolyte was introduced into the cell and purged with nitrogen gas, and the residual current was obtained. Then, desired amounts of solid depolarizer(s) were added to the solution in the cell; after each addition, the nitrogen gas was allowed to pass through the mixture until the solid completely dissolved and then the final polarogram was run under the blanket of this gas.

The DME used had following characteristics in the open circuit: m=1.90 mg s^{-1} and t=4.3 s (h_{Hg}=35 cm; 0.1 M aqueous KCl, M=mol dm^{-3}). The supporting electrolytes used were a KCl-HCl mixture (pH= 2.00) and citrate buffers (pH=4.40 and 6.00); the ionic strength was maintained at 0.1 M with the addition of requisite amounts of KCl. In each case of these buffers, polarograms were run in two ways: (i) keeping the concentration of *p*-PMVBr$_2$ in the buffer fixed and recording the current-voltage curves with subsequent addition of different known amount of cadmium sulfate, (ii) varying the concentration of polymer by introducing the weighed amount of *p*-PMVBr$_2$ into the buffer containing fixed concentration of cadmium ions.

It must be mentioned that any investigation in an alkaline medium may arise some complications of dequaternization[4] or ylide formation[5] in the system. Therefore all investiga-



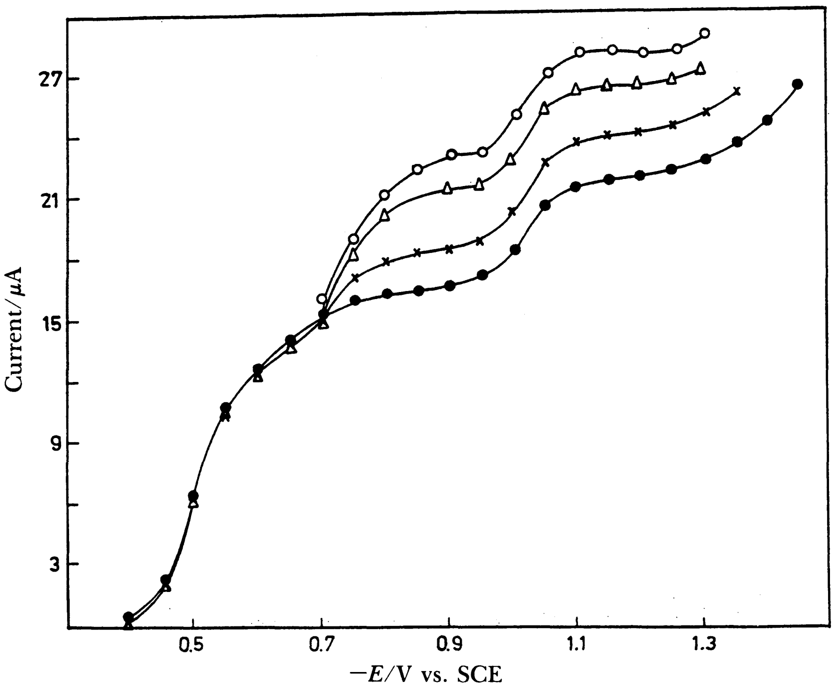


Fig. 1. Polarograms for aqueous solutions of poly[p-methylbenzyl)viologen] dibromide at 25 °C in the presence of various concentration of Cd^{2+} ions (in mg cm^{-3}): 0.215 (X); 0.420 (Δ); 0.640 (O) ([PMVBr$_2$]=4.65 mg cm^{-3} (●), pH=2.00, h_{Hg}=35 cm).

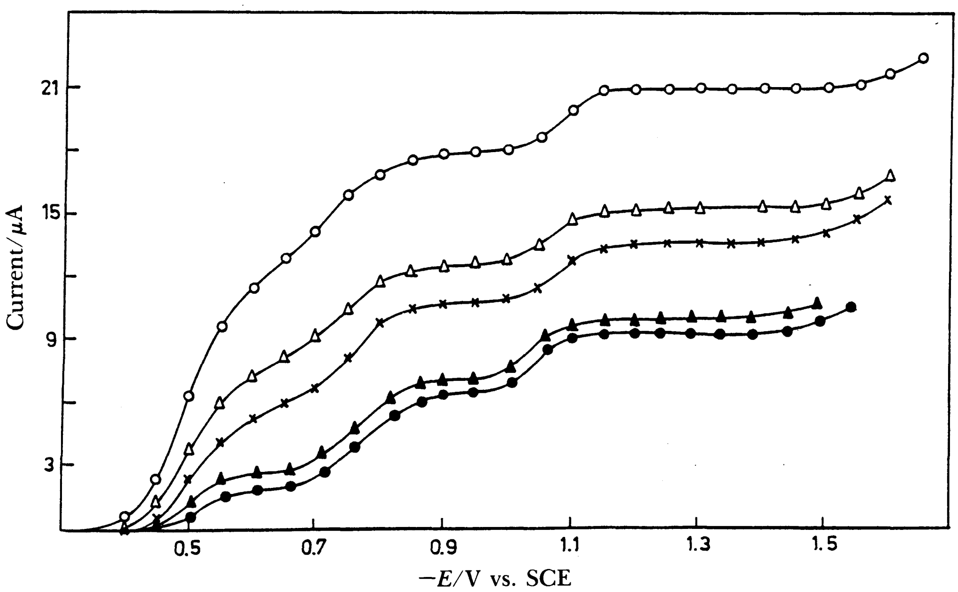


Fig. 2. Polarograms for aqueous solution of poly[(p-methylbenzyl)viologen] dibromide having varying concentrations (in mg cm^{-3}) of 0.410 (●), 0.800 (▲), 1.812 (X), 2.340 (Δ), and 3.962 (O) at 25 °C. ([Cd^{2+}]=0.40 mg cm^{-3} (fixed), pH=2.00, h_{Hg}=35 cm).

tions made in this case had to be confined to only acidic buffers.

The currents and potentials used in the final calculations have been corrected for the residual currents as well as the iR drops involved.

Results and Discussion

The representative polarograms of (i) p-PMVBr$_2$ with varying amount of Cd^{2+} ions and (ii) Cd^{2+} solution with increasing concentration of p-PMVBr$_2$ in a KCl-HCl mixture (pH=2.00) are illustrated in Figs. 1 and 2, respectively. All results obtained with different buffers from analysis of both kinds of polarograms are summarized in Tables 1 and 2.

As is evident from Fig. 1 , two irreversible waves ($E_{1/2}$(I)=−0.520 V and $E_{1/2}$ (II)=−1.00 V vs. SCE) were

Table 1. Summary of Results of Polarographic Measurements on Aqueous Solutions of Poly[(*p*-methylbenzyl)viologen] Dibromide (4.65 mg cm^{-3}) in the Presence of Varying Concentration of Cadmium Sulfate at ca. 25 °C (h_{Hg}=35 cm)

pH[a]	[CdSO$_4$]/mg cm^{-3}	Limiting current, $i_l/\mu A$		
		Wave I[b]	Wave II[b]	Wave III[b]
2.00	0	16.50	6.00	—
(KCl-HCl)		(−0.510)	(−1.00)	
	0.215	16.20	2.70	5.10
		(−0.515)	(−0.770)	(−1.02)
	0.420	16.15	5.40	5.00
	0.640	16.20	6.95	4.95
4.40	0	14.20	10.10	—
(citrate buffer)	0.225	13.94	3.80	4.35
		(0.510)	(−0.775)	(−1.20)
	0.418	14.00	6.10	4.50
	0.635	14.45	6.78	4.50
6.00	0	12.10	13.30	—
(citrate buffer)	0.200	12.45	3.75	2.15
		(−0.510)	(−0.770)	(−1.50)
	0.425	12.65	6.00	2.20
	0.645	12.40	6.95	2.28

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 V vs. SCE.

Table 2. Results of Polarographic Studies on Solutions of Varying Concentrations of Poly[(*p*-methylbenzyl)viologen] Dibromide (*p*-PMVBr$_2$) Contsining Fixed Amount of Cadmium Sulfate (0.40 mg cm^{-3}) in Water at ca. 25 °C

pH[a]	[*p*-PMVBr$_2$]×10^2 mg cm^{-3}	h_{Hg}/cm	Limiting current, $i_l/\mu A$		
			Wave I[b]	Wave II[b]	Wave III[b]
2.00	0	35	—	15.00	—
(KCl-HCl)				(−0.700)	
	41.0	35	2.10	4.60	2.68
			(−0.515)	(−0.790)	(−1.30)
	80.0	35	2.80	4.50	2.79
			(−0.505)	(−0.775)	(−1.25)
	181.2	35	6.00	4.50	2.70
			(−0.510)	(−0.770)	(−1.08)
	234.0	35	7.80	4.80	2.60
			(−0.500)	(−0.750)	(−1.07)
	396.2	35	13.20	4.80	2.85
			(−0.510)	(−0.740)	(−1.08)
		50	15.84	5.52	3.60
		65	17.20	6.20	4.50
4.40	0	35	—	15.10	—
(citrate buffer)	37.5	35	1.50	4.70	2.48
	85.0	35	2.60	4.65	2.45
	179.4	35	5.40	4.65	2.50
	236.5	35	6.27	4.90	2.45
	401.5	35	12.95	5.00	2.60
			(−0.510)	(−0.760)	(−1.35)
6.60	0	35	—	14.95	—
(citrate buffer)	35.0	35	0.75	4.90	1.55
	90.0	35	1.80	5.00	1.50
	180.0	35	3.40	4.70	1.55
	241.3	35	4.98	4.85	1.60
	403.3	35	10.95	5.10	1.65
			(−0.510)	(−0.760)	(−1.50)

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

obtained for pure p-PMVBr$_2$ (concentration: 4.65 mg cm^{-3}; pH=2.00). The cathodic currents for these waves (which are also obtained with other buffers studied; Table 1) have been previously correlated in terms of a protonation equilibrium $p\text{-PMVBr}_2+\text{H}^+ \rightleftarrows p\text{-PMVBr}_2\text{H}^+$.[1c] Keeping in view of the gross effect of pH variation on the wave height which decreases for first wave and increases for the second one with decreasing acidity of the medium, both waves have been attributed to the reduction of protonated and unprotonated form of the polymer, respectively. However, more interesting results are obtained in the presence of CdSO$_4$ which still demonstrated two well-defined waves with their pH-independent half-wave potentials approximately at −0.51 V and −0.75 V vs. SCE, and a third ill-defined wave emerging beyond −1.00 V depending upon the pH of the solution (Table 1). Similar results are also observed with the solution having fixed amounts of Cd^{2+} ions and varying concentration of p-PMVBr$_2$ (Fig. 2). In this case, the wave height for wave I increases while the limiting currents of waves II and III are practically constant at a certain pH with the successive increment in the polymer concentration (Table 2). It may be noted that the variation of Cd^{2+} ions concentration only affects the height of second wave which is found to be increasing; others remaining constant as before for a certain solution (Table 1). All three waves are, however, found to be increasing with the height of the mercury pressure.

The appearance of the first wave of the polymer in the presence of cadmium ions seems to be similar in every respect with the wave obtained for the reduction of the protonated form of p-PMVBr$_2$ alone.[1c] The wave II, whose wave height remains uneffected by the pH variation, may be assigned to a cadmium–PMVBr$_2$ complex. The negative shift in half-wave potential as compared to that of free Cd^{2+} ions and moreover the gradual decrease in $E_{1/2}$ values of wave II with the increase of p-PMVBr$_2$ concentration conforms the existance of a pH-independent complexation process in the solution (Table 2). It is of interest to note that the acidity of the medium is not effective at all in controlling the limiting current for wave II (Tables 1 and 2) since even smallest amount of unprotonated polymer (PMVBr$_2$) at any pH, is found to be sufficient enough to cause complete complexation with Cd^{2+} ions taken in the present instance. The increasing trend of the height of the wave II with the increase of Cd^{2+} ions concentration (Table 1) may reflect the spontaneous complexation process with high molecular weight unprotonated compound (PMVBr$_2$) obtained after the protonation equilibrium. However, a constant limiting current of wave II, irrespective of the variation of polymer concentration (Table 2), interestingly indicates the limiting magnitude of complexation between Cd^{2+} (fixed) and minimum concentration of unprotonated polymeric species available, at any pH.

The rates of electron-transfer processes and hence the limiting currents for the reduction of p-PMVBr$_2$H$^+$ (wave I) and Cd^{2+}-PMVBr$_2$ complex (wave II) are diffusion-controlled as slopes for the plots of $\log i_1$ vs. $\log h_{\text{Hg}}$ (Table 2; pH=2.00; [PMVBr$_2$]=3.962 mg cm^{-3}) are found to be close to 0.5 for both waves. However, a slope value of 0.8 in the case of wave III indicates that the electroreduction is not governed by a diffusion process. Further, on substitution of $E_{1/4}$ and $E_{3/4}$ values of waves I and II (Fig. 1, [Cd^{2+}]=0.215 mg cm^{-3}, pH=2.00) in the following relationships of an irreversible (Eq. 1) and a reversible wave (Eq. 2) at 25 °C

$$E_{3/4}-E_{1/4}=-0.0517/\alpha n \tag{1}$$

$$E_{3/4}-E_{1/4}=-0.0564/n \tag{2}$$

the fractional values of αn and n obtained for first and second waves [wave I (αn=0.47, n=0.51); wave II (αn=0.35, n=0.37)] reveal the irreversible nature of the reduction in either case. Moreover, the negative shift in half-wave potentials with the increase of ionic strength (>0.1 M) of the supporting electrolyte in the respective buffer is typically suggestive of the irreversibility of all the three waves appeared in the present case.[6a]

It is interesting to emphasis that wave I is still noticeable even at higher pH (in the presence of Cd^{2+} ions) whose wave height decreases with the pH of the solution conforming the reduction of p-PMVBr$_2$H$^+$ and therefore, one may conclude that the prospect of a protonation equilibrium is not at all hampered by the addition of Cd^{2+} ions. It appears that as and when protonation equilibrium exhibits in the solution, the Cd^{2+} ions subsequently start complexing to a maximum extent as discussed earlier with the unprotonated species (p-PMVBr$_2$) of the compound available, irrespective of the pH of the medium concerned. The complete omission of waves owing to the reductions of free unprotonated polymer and Cd^{2+} ions, surplus if any, in the solution after complexation is quite surprising and seems to reflect the nonavailability of the these species in the vicinity of the electrode for the reduction as such. One may speculate the existance of a somesort of interaction or binding between metal ion and ligand (not complexation) which probably restricts the process of reduction of these species individually on the time scale involved. Although D(complex)<D(Cd^{2+}), the relatively large decrease in the magnitude of free cadmium current (Table 2) when complexed with the polymeric material, might also corroborate the fact that all Cd^{2+} ions are not consumed in complexation with the unprotonated polymer; however some of these ions would presumably behave like electroinactive substance as a consequence of their possible interactions with p-PMVBr$_2$ and/or the cationic radical species[1c] obtained after the first reduction.

The nature of third wave is rather more interesting. The height of this wave, which is irreversible in nature, remains practically constant irrespective of the amount of p-PMVBr$_2$ added in the solution. The half-wave potentials realised in the case of p-PMVBr$_2$ (without Cd^{2+} ions) are pH-independent[1c)] whereas the same for wave III, in the present instance, shifts towards more negative potential with the increase of pH of the solution. Furthermore, the height of this wave in the presence of cadmium salt decreases with the pH in contrast to the wave obtained for the polymer alone which increases with increase of the pH of the medium concerned. As is apparent from the above experimental facts, the wave III in the present study, thus, might be considered due to the reduction of some different species other than unprotonated p-PMVBr$_2$. Further, this wave does not appear in shape as a polarographic maximum; however, an attempt to suppress the wave by the use of several maximum suppressors (e.g., gelatine, Triton X-100, soap etc.) was failed. On the basis of these observations, the wave III could reasonably be assigned to only a catalytic hydrogen current, appearing in the shape of a wave, before the normal evolution of hydrogen.[6b)] It should be mentioned in this connection that Brdička[7)] has discovered somewhat similar kind of catalysis and polarographic behavior during an investigation of proteins in the presence of cobalt salts. The interpretation of catalytic wave in the present investigation might be correlated with the first reduction of p-PMVBr$_2$. The catalytic effect corresponds to the first reduction product i.e., a cation radical p-PMVBr$_2$H†; from which, under the influence of cadmium, hydrogen is irreversibly reduced at the DME with decreased overvoltage.[8)] Thus, the following overall scheme for wave III can be tentatively suggested.

$$p\text{-PMVBr}_2\text{H}^{\dagger} + \text{Cd}^{2+} + e^- \rightarrow (p\text{-PMVBr}_2\text{Cd}^{2+})^- + 1/2\ \text{H}_2$$

The interaction of p-PMVBr$_2$H† with cadmium ions must be considered as further conditions necessary for the formation of a catalytic wave[7)] in the present case. As no catalytic wave was observed in the absence of Cd^{2+} ions in the case of the reduction of p-PMVBr$_2$ compound alone[1c)] in the similar concentration ranges (cf., Table 2), it seemed reasonable to consider some sort of intercoulombic bond between p-PMVBr$_2$H† and Cd^{2+} ion on the electrode surface which essentially facilitates the reduction of hydrogen with decreased overvoltage. The cation radical protons consumed in the electrode process are replaced by a reaction with proton of the medium. Normally, the height of the catalytic wave should increase with the concentration of p-PMVBr$_2$ (and hence p-PMVBr$_2$H†) and Cd^{2+} ions[8)] but it was found to be practically unaltered at a certain pH. This supports the fact that the surface of mercury electrode becomes fully covered, mainly at higher negative potential under the force of electrostatic attraction, by the adsorption of even small amount of high-molecular-weight catalytically-active cationic reduction product [a cation radical p-PMVBr$_2$H† under the interaction of Cd^{2+} ions in the present instance] which eventually limits the height of the catalytic wave to a constant magnitude.[9)] The anticipated decrease in current of this wave at lower acidities is quite interesting which reflects somewhat implicit behavior in context to the adsorption phenomenon as proposed above. However, the remarkable decrease in the catalytic wave height at pH=6.00 might be attributed to the scavenging of the electrode by the hydroxide ions of the medium.[1b)] It should be further noted that the possibility of partial adsorption of cationic cluster of p-PMVBr$_2$H† and Cd^{2+} ion [i.e., p-PMVBr$_2$H†-Cd^{2+}] even in the lower potential range of wave II cannot be fully ignored. This eventually appears to impede the reduction current of wave II to some extent, supporting as one of the possible reasons for the drastic decrease in the magnitude of free cadmium current after complexation (Table 2).

The catalytic wave height was observed to be decreasing with the increase of ionic strength (>0.1 M) by addition of KCl.[8),9)] This probably suggests the significant desorption of catalytic active cluster of cation radical reduction product with Cd^{2+} ions [p-PMVBr$_2$H†-Cd^{2+}] from the surface of the mercury electrode by the large amount of KCl added in the solution. The process of adsorption of "cationic cluster" at higher negative potential under the electrostatic influences might be apparently mitigated by the large excess of KCl present in the solution. Furthermore, a higher concentration of KCl may also induce curling or the contraction[2)] of the polyelectrolyte envelop around the electrode surface which, in turn, may cause desorption phenomenon. It should be pointed out in this connection that the cadmium salt or supporting electrolyte present in the solution might have also similar impact over the conformation of the polymeric film but not showed up effectively at the DME. On the other hand, the p-PMVBr$_2$H†-Cd^{2+} interaction appears to be instigating the catalytic reduction of hydrogen at ionic strength <0.1 M in the present study.

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