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Study of Electron Transfer Reactions Associated with Benzyl Viologen-β-Cyclodextrin Complexation in Buffer Solution of pH 7: Equilibrium and Kinetic Aspects

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In this study, complex formation of benzyl viologen dication (BzV^{2+}) with β-cyclodextrin (β-CD), in its different oxidation states, had been studied in buffer solution of pH 7, through cyclic voltammetry. In buffer solution of pH 7, extensive deposition of benzyl viologen neutral (BzV^{o}) has been found. Further to that first redox process of BzV^{2+} was found reversible in buffer solution of pH 7. Benzyl viologen mono-cation ($BzV^{+\bullet}$) was found to interact with β-CD reversibly according to EC mechanism. Equilibrium constant of $BzV^{+\bullet}$-nβ-CD complex in buffer solution of pH 7, has been calculated as 5.49 M^{-n}. The value of n was found to be 0.2. The bimolecular rate constant for the complex formation of $BzV^{+\bullet}$ with β-CD was found to be 6.44 $M^{-n}s^{-}$ in buffer solution of pH 7. This study is based upon an electrochemical approach to obtain the bonding equilibrium constant, the rate constants of formation and the association numbers of the complex formed between reduced forms of viologen and β-CD. This study explore the electron transfer reaction mechanism of benzyl viologen with β-CD to extend their applications at neutral pH.

Keywords: Benzyl viologen, β-Cyclodextrin, Cyclic voltammetry, Equilibrium constant, rate constant.

INTRODUCTION

Applications of viologen [1] (1,1′-disubstituted 4,4′-bipyridinium ion) are diversified. Viologen have gained considerable attention as redox catalyst [2-5], redox indicators in biological studies [6] and electron mediators [7-9]. Some of the members of viologen family (paraquat and benzyl homologue) possess herbicidal activity [10,11]. Viologen have versatile redox system with three oxidation states: V^{2+}, V^{+} and V^{o} and have tendency to change their colour reversibly many times upon reduction and oxidation. Owing to this property of viologen they have significant importance in electrochromic display systems [12].

Cyclodextrins (CD) are defined as the class of cyclic oligosaccharide having tendency to form inclusion complexes [13]. Electrochromic properties of viologen and that further reaction where viologen participates are affected by the dimer formation and precipitation of reduced forms of viologen [14,15]. That′s why practical use of viologen is limited due to the appearance of residues. Short alkyl group viologen deposits on the electrode and this problem has been resolved by the complexation of reduced form of viologen with β-cyclodextrin (β-CD) [16,17]. Most of the previous studies [14,15,18] are based on electrochromic properties of non-alkyl group substituted viologen, these reports however do not emphasize on quantitative determination of thermodynamic and kinetic parameters of that systems. Murugavel [19] have reported the biological applications of benzylic viologen dendrimers as an antiviral, antibacterial and antifungal agent. Benzyl viologen dication and β-CD, both have potential applications in the field of medicine for drug delivery, food, agriculture and textile, *etc*.

To extend the applications of viologen and cyclodextrins, thermodynamic and kinetics data on the reaction of stated viologen is necessary. This study is aimed to understand the equilibrium, kinetic and mechanistic aspects of benzyl viologen dication (BzV^{2+})-β-CD system in buffer solution of pH 7 by cyclic voltammetry. This report presents the quantitative determinations of equilibrium constant, rate constants for the BzV^{2+} and β-CD system.

EXPERIMENTAL

β-Cyclodextrin, benzyl viologen dichloride (1,1′-disubstituted 4,4′-bipyridinium) were purchased from Merck. Buffer solution of pH 7 (phosphate buffer, Merck) was used as solvent. Deionized water was used throughout the experiment. White spot nitrogen gas (99.9% pure) was provided by Pakistan Oxygen Company Ltd., Karachi, Pakistan.

Electrochemical experiments: Electrochemical measurements were carried out on the Electrochemical Analyzer (Model CHI600C Series). For cyclic voltammogram (CV), a glassy carbon electrode 3 mm in diameter, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE) were used. Before taking each run the glassy carbon electrode was polished with 0.05 μm alumina on a felt surface and rinsed with deionized water. Benzyl viologen solution (0.116 mM) was prepared by dissolving an appropriate amount in buffer solution of pH 7. This solution was purged with nitrogen for 15 min and then CVs of benzyl viologen solution were taken in the absence and presence of varied concentration of β-CD at different scan rates. For blank correction, CVs of buffer solution of pH 7 were taken at different scan rates. Cyclic voltammogram (CV) of blank buffer solution did not show presence of any electroactive species in the solution.

RESULTS AND DISCUSSION

Fig. 1 shows the cyclic voltammogram of benzyl viologen dication (BzV^{2+}) in buffer solution of pH 7 on a scan rate of 0.05 V/s. The second reduction peak was remarkably sharp due to extensive deposition of benzyl viologen neutral (BzV^{o}). This neutral deposition gets oxidized back to produce a large anodic peak which however, well removed from its cathodic partner. A small closely spaced anodic peak appeared with the large anodic peak. This peak may have emerged due to oxidation of the benzyl viologen mono-cation ($BzV^{+\bullet}$) in solution. Cyclic voltammograms (CVs) of BzV^{2+} in buffer solution of pH 7 were also recorded at different scan rates (Fig. 2). It was found that by varying the scan rate between 0.03 V/s to 0.8 V/s, the second reduction peak remained sharp even at higher scan rates. Against that both anodic peaks were found to get completely merged.

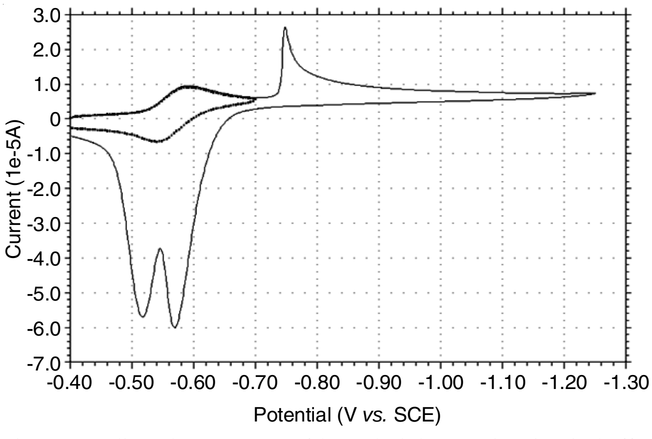


Fig. 1. Cyclic voltammogram of benzyl viologen Di-cation in buffer solution of pH 7 at 0.05 V/s scan rate

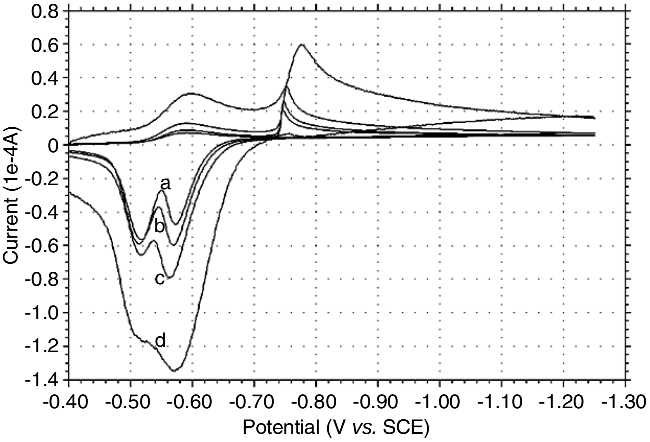


Fig. 2. Cyclic voltammograms of benzyl viologen Di-cation in buffer solution of pH 7 at different scan rates; (a-d) are different scan rates. a = 0.03 V/s, b = 0.05 V/s, c = 0.1 V/s, d = 0.8 V/s

The electrochemical parameters for the first reduction of BzV^{2+} in buffer solution of pH 7 are given in Table-1. For checking the reversibility of redox process ($BzV^{2+}/BzV^{+\bullet}$), ratio of peak currents and peak to peak separations were calcu-lated in the absence of β-CD host. The ratio of peak currents $|I_{pa}/I_{pc}|$ for $BzV^{2+}/BzV^{+\bullet}$ redox process was calculated as 1.02. On the other hand, cathodic to anodic peak separation for this redox process was found to be -0.049 V (Table-2). These calculated values were found close to the requirements of a reversible system. Half peak potentials ($E_{p/2}$) and half wave potentials ($E_{1/2}$) for the first redox process of benzyl viologen dication were also calculated in the absence of β-CD host. When diagnostic tests were applied to these electrochemical parameters of benzyl viologen dication, the values of $|E_p - E_{p/2}|$ and $|E_p - E_{1/2}|$ for the first redox process ($BzV^{2+}/BzV^{+\bullet}$) were also found close to the reversible system (Table-2). It suggests that first reduction process of BzV^{2+} is reversible.

$$BzV^{2+} + e \rightleftharpoons BzV^{+\bullet} \quad (1)$$

Inclusion complexation of benzyl viologen mono-cation with β-CD host in buffer solution of pH 7: Inclusion complexation of benzyl viologen with β-CD host in buffer solution of pH 7 was studied by recording cyclic voltammograms of BzV^{2+} in the presence of different concentrations of β-CD. In case of viologen with short alkyl chain the deposition problem of neutral

TABLE-1
ELECTROCHEMICAL PARAMETERS: REDUCTIONS OF BzV^{2+} IN THE ABSENCE AND PRESENCE OF β-CD AT 0.05 V/s SCAN RATE IN BUFFER SOLUTION OF pH 7

Substance/s (mM)	$Epc_1{}^c$ (V)	$Epa_1{}^d$ (V)	$Ipc_1{}^e \times E^{-6}$ (A)	$Ipa_1{}^f \times E^{-6}$ (A)
$0.116^a + 0.000^b$	-0.591	-0.542	6.683	-6.821
$0.116^a + 0.397^b$	-0.591	-0.539	7.458	-6.958
$0.116^a + 1.492^b$	-0.584	-0.531	7.374	-6.654
$0.116^a + 10.00^b$	-0.573	-0.516	6.517	-6.271

[a]Concentration of benzyl viologen solution; [b]Addition of β-CD host in 0.116 mM BzV^{2+} solution; [c]Peak potential for the first reduction step; [d]Peak potential for the first oxidation step; [e]Cathodic peak currents measured for the first redox process; [f]Anodic peak current measured for first redox process.

TABLE-2

ELECTROCHEMICAL PARAMETERS MEASURED FOR BzV^{2+} IN THE ABSENCE AND PRESENCE OF β-CD AT 0.05 V/s SCAN RATE

Substance/s (mM)	$\|Ipa_1/Ipc_1\|$	▲ $Ep_1=Epc_1-Epa_1$ (V)	$(E_{pc}-E_{pc/2})_1$ (V)	$(E_{pa}-E_{pa/2})_1$ (V)	$(E_p-E_{1/2})c_1$ (V)	$(E_p- E_{1/2})_{a1}$ (V)
$0.116^a + 0.000^b$	1.02	-0.049	-0.041	0.041	-0.021	0.021
$0.116^a + 0.397^b$	0.93	-0.052	-0.044	0.043	-0.022	0.022
$0.116^a + 1.492^b$	0.90	-0.053	-0.046	0.047	-0.023	0.024
$0.116^a + 10.00^b$	0.96	-0.057	-0.049	0.050	-0.025	0.025

Ipa_1/Ipc_1, is the anodic to cathodic peak current ratios measured for the first redox process. $Epc_1 – Epa_1$ is the cathodic to anodic peak separation measured for the first redox process. $(Ep_{C/2})_1$ and $(Ep_{a/2})_1$ are the first cathodic and anodic half peak potentials respectively. $(E1/2)c_1$ and $(E1/2)a_1$ are the first cathodic and anodic half wave potentials respectively.

[a]Concentration of benzyl viologen solution; [b]Addition of β-CD host in 0.116 mM BzV^{2+} solution.

viologen was removed by the use of β-CD [16]. For the case of benzyl viologen it was observed that even on the addition of 85 times concentrated β-CD host, the electrodeposition of BzV° couldn′t be removed and the peak of neutral benzyl viologen remained sharp at different scan rates (Figs. 3-6). On the other hand, first reduction peak of BzV^{2+} was shifted to positive direction by the successive addition of β-CD host. Electrochemical parameters for the first reduction of BzV^{2+} in the presence of β-CD are given in Table-1. The calculated values of $|I_{pa}/I_{pc}|$, ΔE_p, $E_p – E_{p/2}$ and $E_p – E_{1/2}$ for the first redox process were closed to the reversible system (Table-2). It means that the reaction of $BzV^{+\bullet}$ with β-CD is reversible.

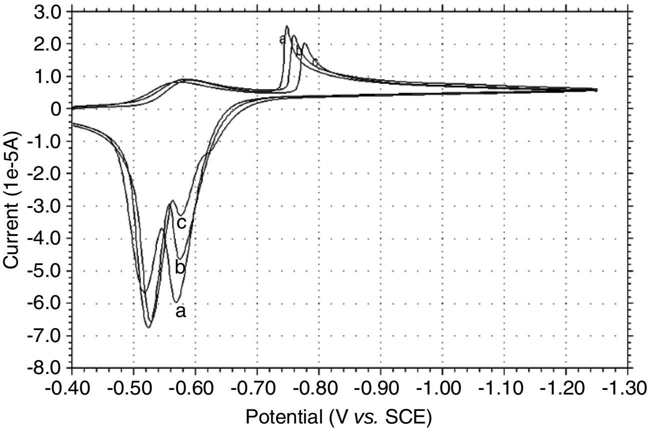


Fig. 3. Effect of the additions of β-CD on cyclic voltammogram of BzV^{2+} in buffer solution of pH 7 at 0.05 V/s scan rate; Cyclic voltammograms of BzV^{2+} in the absence (a = 0.116 mM BzV^{2+}) and the presence of different concentrations (b,c) of β-CD. Where b = 1.492 mM, c = 0.01 M

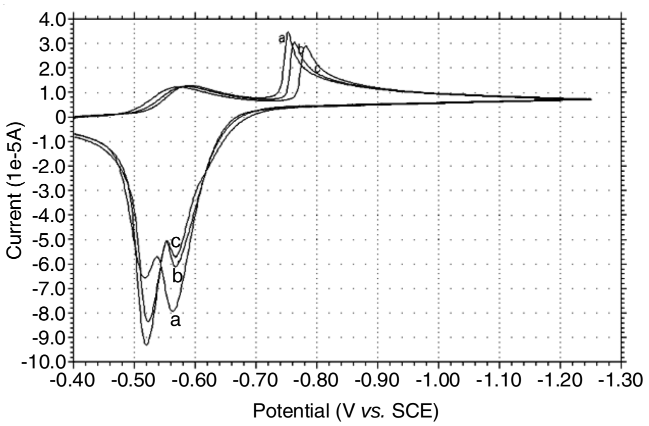


Fig. 4. Effect of the additions of β-CD on cyclic voltammogram of BzV^{2+} in buffer solution of pH 7 at 0.1 V/s scan rate; Cyclic voltammograms of BzV^{2+} in the absence (a = 0.116 mM BzV^{2+}) and the presence of different concentrations (b,c) of β-CD. Where b = 1.492 mM, c = 0.01 M

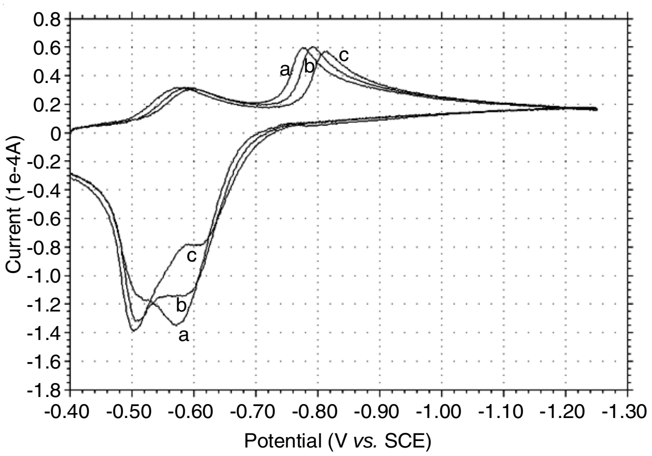


Fig. 5. Effect of the additions of β-CD on cyclic voltammogram of BzV^{2+} in buffer solution of pH 7 at 0.8 V/s scan rate; Cyclic voltammograms of BzV^{2+} in the absence (a = 0.116 mM BzV^{2+}) and the presence of different concentrations (b,c) of β-CD. Where b = 1.492 mM, c = 0.01 M

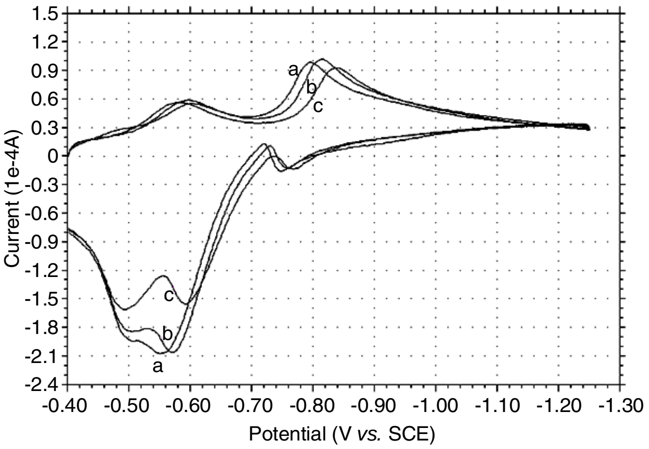


Fig. 6. Effect of the additions of β-CD on cyclic voltammogram of BzV^{2+} in buffer solution of pH 7 at 3 V/s scan rate; Cyclic voltammograms of BzV^{2+} in the absence (a = 0.116 mM BzV^{2+}) and the presence of different concentrations (b,c) of β-CD. Where b = 1.492 mM, c = 0.01 M

Quantitative determination of inclusion complex of benzyl viologen with β-cyclodextrin

Equilibrium constants: Fig. 7 simply demonstrates the positive shifting of first cathodic peak potential in the presence

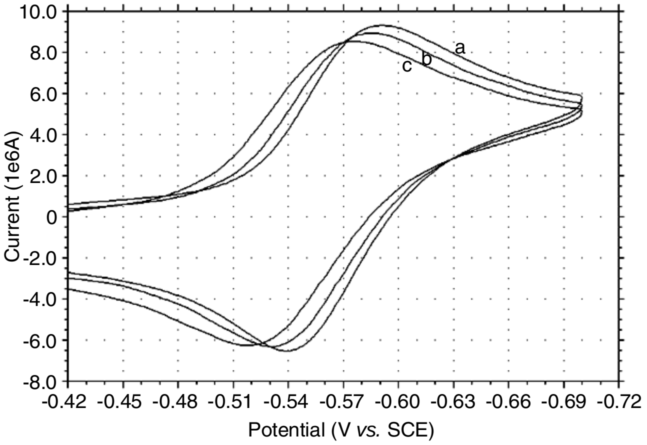
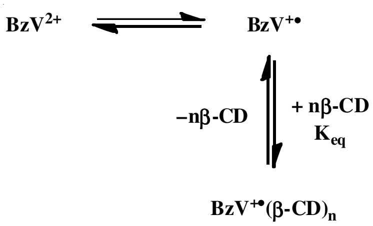


Fig. 7. Effect of the additions of β-CD on the first cathodic peak of BzV^{2+} in buffer solution of pH 7 at 0.05 V/s scan rate; Scan of the first cathodic peak of BzV^{2+} in the presence of different concentrations (a-c) of β-CD. Where a = 0.397 mM, b = 1.492 mM, c = 0.01 M of β-CD host. It was noted that as concentration of β-CD host was increased the peak current ratios for the first redox process of BzV^{2+} decreased (Table-2). It indicates the binding of $BzV^{+\bullet}$ with β-CD. The shift in the peak potential and change in the peak current ratios confirmed the coupling of chemical reaction and the electron transfer reaction [20,21]. Positive shifting of peak also confirms the presence of EC mechanism. On the basis of these observations, the reaction scheme is developed as given below:



Following eqn. 2 [22] was used for determination of equilibrium constant (K_{eq}) and n (number of β-CD associated with $BzV^{+\bullet}$).

$$E_P - E_P^o = \left(\frac{2.3RT}{F}\right)\log K_{eq} + (n)\left(\frac{2.3RT}{F}\right)\log[\beta CD] \quad (2)$$

In this equation, E_P^o is the cathodic peak potential of benzyl viologen obtained in the absence of β-CD and E_P is the potential of the same obtained in the presence of β-CD.

Different values of E_P were obtained by addition of increasing amounts of β-CD (Table-1). Experimentally determined values of $E_P - E_P^o$ for the first reduction peak were plotted against log β-CD (Fig. 8). Values of slope and intercept, as obtained from the graph, were 0.0129 and 0.0437, respectively. The 'n' can be obtained from the slope and K_{eq} from the intercept. Thus n, the fraction of β-CD associated with $BzV^{+\bullet}$ was found to be 0.2 and K_{eq} obtained for $BzV^{+\bullet}$-nβ-CD complex in buffer solution of pH 7 was 5.49 M^{-n}.

Rate constants: As the complex formation of $BzV^{+\bullet}$ with β-CD is the case of reversible chemical reaction following a reversible charge transfer, Nicholson-Shain theory [21] was used for the evaluation of rate constants.

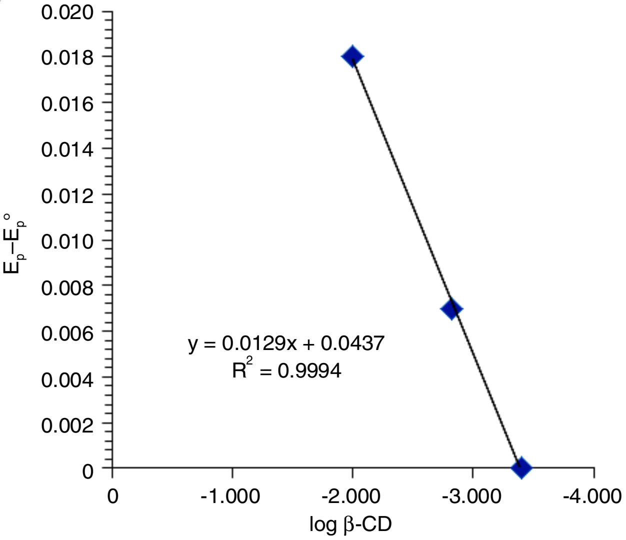


Fig. 8. Plot of first cathodic peak potentials against log β-CD

$$BzV^{2+} + e \rightleftharpoons BzV^{+\bullet} \quad \text{(re. 1)}$$

$$BzV^{+\bullet} + n[\beta\text{-CD}] \rightleftharpoons BzV^{+\bullet} - n\beta\text{-CD} \quad (3)$$

β-CD was in excess so reaction (eqn. 3) was assumed to be a pseudo-first order one. To this effect, following equation was used for determination of k_b, the first order reverse reaction, as determined for EV° – β-CD complex previously.

$$E_p = E_{1/2} - \left(\frac{RT}{nF}\right)\left[0.78 + \ln K_{N.S} + \frac{1}{2}\{\ln a - \ln k_b(1+K_{N.S})\} - \ln(1+K_{N.S})\right] \quad (4)$$

where E_p is the peak potential of benzyl viologen in the presence of β-CD, $E_{1/2}$ is the half wave potential of benzyl viologen in the absence of host E_p is the peak potential of benzyl viologen in the presence of β-CD, $E_{1/2}$ is the half wave potential of benzyl viologen in the absence of host, $K_{N.S} = K \times [\beta\text{-CD}]^n$ and $a = nF\nu/RT$ (ν is scan rate in V s^{-1}). By putting these values in above equation, k_b was calculated as 1.17 s^{-1}. From this value of k_b, k_f' (pseudo-first order rate constant) can be calculated using the following eqn. 5.

$$K_{N.S} = \frac{k_f}{k_b} \quad (5)$$

The value of $k_{f'}$ for the reaction of $BzV^{+\bullet}$ with β-CD (3) was obtained as 2.57 s^{-1}.

From this pseudo-first order rate constant, second order rate constant k_2 was calculated using eqn. 6.

$$k_2 = \frac{k_{f'}}{[\beta\text{-CD}]^n} \quad (6)$$

The value of k_2 was found to be 6.44 M^{-n} s^{-1}.

Conclusion

In this study, an interaction of non-alkyl group substituted viologen with β-cyclodextrin (β-CD) has been explored by means of cyclic voltammetry. This study is based upon a simple electrochemical approach, which is useful for evaluating the equilibrium constants and kinetic parameters, like the rate constants which have not been reported by earlier workers for non-alkyl group substituted viologen-CD systems in buffer of pH 7. This electrochemical study of benzyl viologen may extend its application for mediating/triggering electron transfer reaction in the field of biotechnology.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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