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Inclusion Complexation of Benzyl Viologen by β-Cyclodextrin in DMF-H_2O Mixed Solution

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Abstract

Complex formation between benzyl viologen and β-Cyclodextrin (βCD) in 9:1(v/v) DMF-H_2O mixed solution was studied by cyclic voltammetry. In order to examine the probable mechanism of the reaction of benzyl viologen dication (BzV^{2+}) and its reduced forms with βCD, cyclic voltammograms were digitally simulated. Detailed analysis of the mechanism by digital simulation revealed that in 9:1(v/v) DMF-H_2O mixed solution, benzyl viologen mono-cation ($BzV^{+\cdot}$) formed inclusion complex with βCD according to EC mechanism, while its fully reduced form (BzV°), could not form inclusion complex with βCD. Bonding equilibrium constant, K_{eq}, pertaining to the bonding of $BzV^{+\cdot}$ with βCD was estimated as 10.6 M^{-n}. The second order rate constant for the reaction of $BzV^{+\cdot}$ with βCD was determined as 4.93 $M^{-n}S^{-}$. By the use of this solvent system (9:1(v/v) DMF- H_2O mixed solution) the comprehensive study of non-alkyl group substituted viologens and long alkyl chain viologens with βCD is possible.

Keywords: Benzyl viologen, β-Cyclodextrin, EC mechanism, DMF- H_2O mixed solvent, cyclic voltammetry.

Introduction

Applications of viologens [1] cannot be limited to its short alkyl group substituents. The study of electrochromic properties of non-alkyl group / long alkyl group substituted viologens has also been a vital objective of researchers [2-4]. It has been found that benzyl homologue caused pulmonary toxicity which was at least five times as toxic to rats as paraquat and they have more pronounced ability to trigger redox cycling reaction than paraquat [5]. Benzyl homologue was also reported for phytotoxicity [6]. As viologens are electroactive specie and have the ability to show two consecutive reductions so their applications may be extended through the study of their electrochemical behaviors. Though electrochemical study of long alkyl / non alkyl group substituted viologens is restricted to its one electron reduced form because of the extensive deposition associated with its neutral form in aqueous media [3, 7].

The deposition problem of the short alkyl group substituted viologens was resolved either by designing such derivatives of viologens which were water soluble in all their oxidation states [8] or by the use of cyclodextrins (CDs) [9, 10]. There have been conflicting claims about the interaction of βCD with the neutral and cationic forms of the methyl viologen dication in aqueous solution. About a decade ago, Matsue and his coworkers reported that the fully reduced uncharged form of methyl viologen dication bind strongly by the host βCD [9]. On the other hand Usha and his coworkers [11] reported to have found ionic forms to be more reactive towards βCD than the neutral form. A. Mirzoian [8] reports otherwise and then our work [10] substantiates the work of Matsue. Thus we found the ionic forms of ethyl viologen to be less reactive and that Usha report is not seem to be plausible.

Recently our group has also revealed that this deposition problem associated with lower oxidized form of benzyl viologen, could not be resolved in aqueous media, even at the excess addition of CD host. Only few reports are published regarding to the inclusion of long alkyl / non alkyl group substituted viologens into CD cavity [7]. The reason of this is the extensive deposition of the lower oxidized form of these viologens in aqueous medium.

In order to study the benzyl viologen – βCD binding interactions in a more quantitative fashion we elected the 9:1 v/v DMF-Water mixed solvent in which this viologen exhibit solubility in all of its oxidation states. Extensive studies related to binding of different substrate with βCD are reported but has always involved aqueous solution [12, 13]. Present report also invoke the fact that the cavity of βCD can bind/interact viologen in non-aqueous media, also.

The complexation between the benzyl viologen and βCD was monitored by cyclic voltammetry in 9:1 v/v DMF-Water mixed solvent. In this report we determined the equilibrium constant and rate constants of reactions of benzyl viologen and its reduced forms with βCD. These results are confirmed by digital simulation technique. Based on these results we propose a mechanism for the reaction of BzV^{2+}, $BzV^{+\cdot}$ and BzV°.

Materials and Methods

β-cyclodextrin and benzyl viologen dichloride (1,1'-dibenzyl-4,4'bipyridinium) were purchased from Merck and used as received without any further purification. Dimethylformamide (DMF) was used as solvent and it was also provided by Merck. Tetra butyl ammonium perchlorate (TBAP) was used as an electrolyte and purchased from Aldrich. Double deionized water was used where it was required.

Electrochemical Experiments

Electrochemical measurements were carried out on the Electrochemical Analyzer (Model CHI600C Series). For cyclic voltammetery (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 the solvent. Unless otherwise specified, all solutions prepared using 9:1(v/v) DMF/H_2O mixed solvent contained 0.415 mM BzV^{2+}, 0.10M TBAP supporting electrolyte and appropriate amounts of βCD. Before recording cyclic voltammogram the solution was purged with nitrogen gas for 15 minutes in order to eliminate oxygen.

Results and Discussion

All viologens studied show two consecutive reductions.

$$V^{2+} + e \leftrightarrow V^{+\cdot}$$
$$V^{+\cdot} + e \leftrightarrow V°$$

Fig.1 shows the cyclic voltammogram of BzV^{2+} in buffer solution of pH 7. As shown in figure the second reduction peak is sharp due to extensive deposition of BzV° and this neutral deposit is oxidized back to large anodic peak which is well removed to its cathodic partner. In case of viologens with short alkyl chain, the deposition problem of neutral viologens can be removed by the use of CDs, but for non-alkyl group substituted viologens (like BzV^{2+}) this is not so easy, as discussed in previous section. Addition of βCD to aqueous solution of BzV^{2+} could not remove the electrodeposition of BzV°, even at the addition of 0.01M βCD Fig. 2.

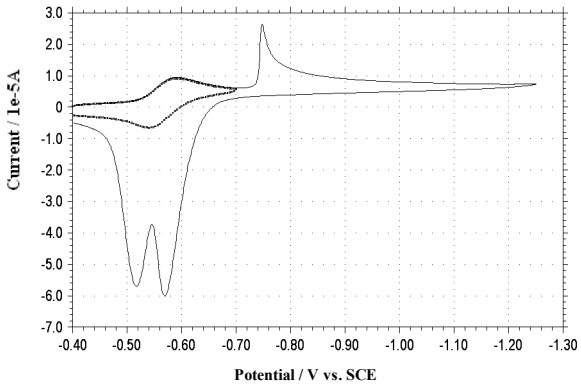


Figure 1. **Cyclic Voltammogram of benzyl viologen di-cation in buffer solution of pH 7 at 0.05V/s scan rate**

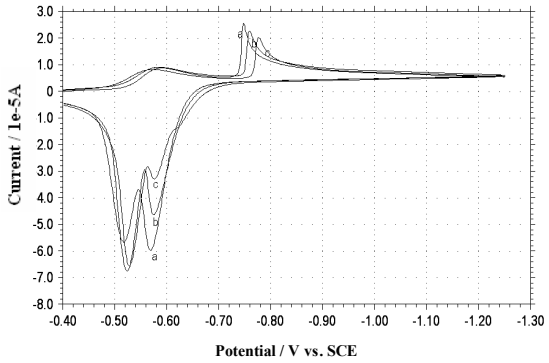


Figure 2. **Cyclic voltammograms of Bzv^{2+}in the absence (a = 0.116 mM Bzv^{2+}) and the presence of different concentrations (b,c) of βCD in buffer solution of pH 7 . Where b = 1.492mM, c = 0.01M. Scan rate: 0.05 V/s**

In order to study the interaction of $BzV^{2+}$and its reduced forms with βCD it was necessary to obtain a reversible cyclic voltammogram of BzV^{2+}. So by analogy with the treatment of Lee and his coworkers [14] we used 9:1(v/v) DMF/H_2O mixed solvent and we obtained a reversible cyclic voltammogram of BzV^{2+} as shown in Fig. 3. The reduction and oxidation peak potentials are quite similar to the values as reported earlier [14]. In this solvent the ratio of anodic to cathodic peak currents (Ipa/Ipc) and cathodic to anodic peak separation (ΔEp = Epc- Epa) for the second redox process ($BzV^{+\cdot}$/BzV°) was found to be 0.9 and 64 mV respectively. These values are quite close to the reversible system. In addition to that a graph was plotted between cathodic peak currents of benzyl viologen and square root of the scan rates Fig. 4, this graph was also resulted in a straight line.

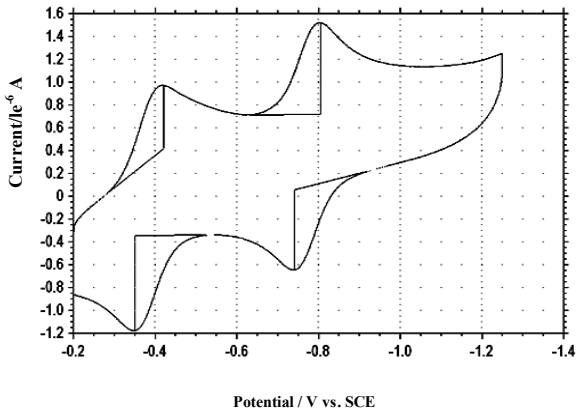


Figure 3. **Cyclic voltammogram of benzyl viologen di-cation in 9:1(v/v) DMF/H_2O mixed solvent at 0.05V/s scan rate**

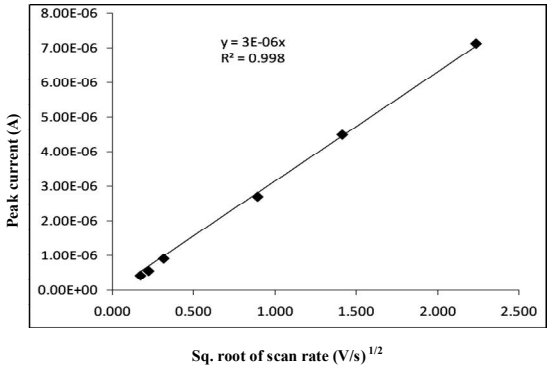


Figure 4. **Plot of cathodic peak current against square root of scan rates for determination of diffusion coefficient**

The Inclusion Complexation

Characterization of coupled chemical reaction

To study the inclusion complexation of benzyl viologen di-cation, cyclic voltammograms of BzV^{2+} were recorded in the presence of different concentrations of βCD at 0.05 V/s scan rate Table 1. It was found that the values of Ipa/Ipc (ratio of anodic to cathodic peak currents) and ΔEp (cathodic to anodic peak separation) for the first and second redox processes were close to the reversible system Table 2. It means that the reaction of $BzV^{+\cdot}$ and /or BzV° with βCD is reversible.

The coupling of chemical reaction to the electron transfer reaction can easily be detected with the help of the shifting of peak potentials as well as by the change in the ratio of peak currents. It was observed that when βCD was added to BzV^{2+} solution, position of first cathodic peak was shifted to positive direction but the second cathodic peak did not shift by the successive additions of βCD in 9:1 (v/v) DMF/H_2O mixed solvent Fig. 5. Similar effect was observed with the ratio of peak currents. With successive additions of βCD to the benzyl viologen solution (0.415 mM), the value of |Ipa/ Ipc| for the first redox process (BzV^{2+}/ $BzV^{+\cdot}$) decreased from 1.5 to 1.0 but for second redox process ($BzV^{+\cdot}$/BzV°) this ratio did not change Table 2. The change of peak position as well as peak currents of the first redox process confirms the presence of chemical reaction of βCD with $BzV^{+\cdot}$. For second redox process it may be concluded that βCD does not bind with BzV°. In fact along with the compatibility of size and shape between βCD host and guest molecule the

inclusion complexation also depends upon the substitution of included cavity water molecule by the less polar guest in aqueous medium. As a consequence of this substitution non polar guest interacts with non-polar β-CD cavity and polar cavity water interacts with polar bulk water. This scenario suggests that in aqueous medium, by this substitution, unfavorable interactions convert into favorable one. Contrary to that in case of 9:1(v/v) DMF/ water mixed solvent, there is minimum amount of water present in bulk solution. Thus the neutral form of benzyl viologen being more soluble in this solvent than its ionized counterpart ($BzV^{+\cdot}$), there may be no driving force for the substitution of included cavity water with benzyl viologen neutral.

Table 1. **Electrochemical parameters: Reduction of benzyl viologen in the presence of βCD at 0.05 V/s sweep rate in 9:1(v/v) DMF/H_2O mixed solvent.**

Conc. of solutions (mM)	Ep_1[c] (V)	Ep_2[d] (V)	$(E_{1/2})_1$[e] (V)	$(E_{1/2})_2$[f] (V)
0.415[a] + 0.000[b]	-0.421	-0.805	-0.388	-0.775
0.415 + 6.19	-0.410	-0.805	-0.381	-0.775
0.415+ 6.80	-0.409	-0.802	-0.377	-0.773
0.415 + 14.0	-0.402	-0.802	-0.370	-0.773

(a) Concentration of benzyl viologen solution, (b) addition of βCD host in 0.415 mM BzV^{2+} solution. (c) Peak potential for the first reduction step (d) same as (c) for the second reduction step. (e) Half wave potential for first redox process (f) same as (e)for second redox process.

Table 2. **Electrochemical parameters measured for benzyl viologen solution in the absence and presence of βCD at 0.05 V/s scan rate.**

Substance/s (mM)	$\lvert Ipa_1/Ipc_1\rvert$	$\lvert Ipa_2/Ipc_2\rvert$	$\blacktriangle Ep_1=Epc_1-Epa_1$ (V)	$\blacktriangle Ep_2=Epc_2-Epa_2$ (V)
0.415[a] +0.000[b]	1.5	0.9	-0.071	-0.064
0.415[a]+ 6.19[b]	1.3	0.9	-0.063	-0.068
0.415[a]+ 6.80[b]	1.2	0.9	-0.062	-0.065
0.415[a]+ 14.0[b]	1.0	0.9	-0.055	-0.068

Ipa1/ Ipc1, is the anodic to cathodic peak current ratios measured for the first redox process and Ipa2/Ipc2 is same for second redox process.Epc1 – Epa1 is the cathodic to anodic peak separation measured for the first redox process and Epc2 – Epa2 is same for second redox process. (a) Concentrationof benzyl viologen solution, (b) Addition of βCD host in 0.415 mM BzV^{2+} solution.

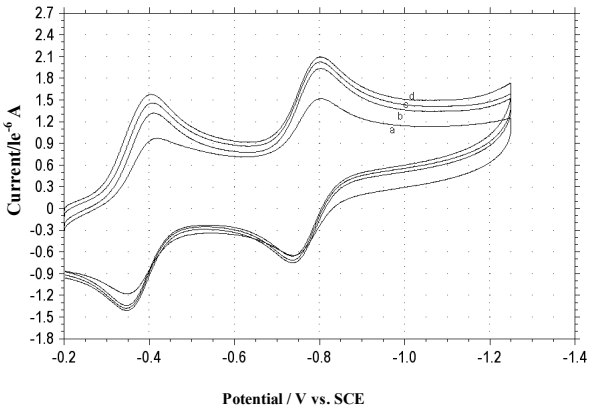
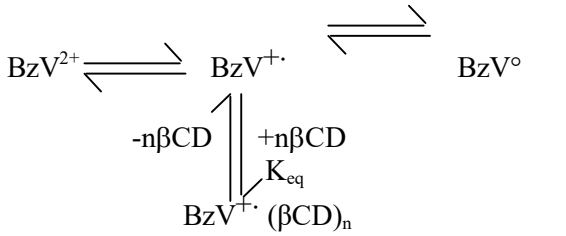


Figure 5. **Cyclic voltammograms of Bzv^{2+}in the absence (a = 0.415 mM Bzv^{2+}) and the presence of different concentrations (b-d) of βCD in 9:1(v/v) DMF/H_2O mixed solvent. Where b = 6.19mM, c = 6.8mM, d = 0.014M. Scan rate: 0.05 V/s**

Determination of the equilibrium constant for the formation of $BzV^{+\cdot}$-n βCD complex

The shifting of the first reduction peak of BzV^{2+} in positive direction with successive additions of βCD indicates the absence of CE mechanism [15]. It means that BzV^{2+}- βCD complex was not form. This result also confirms the presence of EC mechanism [15]. Second reduction peak of BzV^{2+} didn't shift by the additions of βCD so we can say that there may be no chemical reaction between BzV° and βCD in 9:1 (v/v) DMF/H_2O mixed solvent. It is concluded that neutral species (BzV°) oxidized back to $BzV^{+\cdot}$, without reacting with βCD. On the basis of these observations, a mechanism may be proposed which shows all relevant electron transfer reactions coupled to the chemical reactions. This mechanism is given below.



Mechanism1. **Electrochemical and chemical reactions of benzyl viologen guest with βCD host in 9:1(v/v) DMF/ water mixed solvent.**

For determination of equilibrium constant (K_{eq}) and number of βCD (n) associated with $BzV^{+\cdot}$, following equation was used.

$$E_P - E_P^o = \left(\frac{2.3RT}{F}\right)\log K_{eq} + (n)\left(\frac{2.3RT}{F}\right)\log[\beta CD] \text{-----}(i)\ [16]$$

Where E_P^o is the peak of the benzyl viologen obtained in the absence of βCD. E_P is the potential of the same benzyl viologen peak obtained in the presence of βCD. K_{eq} is the formation constant for $BzV^{+\cdot}$-βCD complexation. By plotting the experimentally determined values of E_P -E_P^o for the first reduction peak versus log βCD, one can obtain the values of n and K_{eq} from the slope and intercept respectively. This plot is shown in Fig. 6. Thus the value of n obtained is 0.4 and equilibrium constant, Keq, obtained for $BzV^{+\cdot}$-$(\beta CD)_n$ complex in 9:1(v/v) DMF/H_2O mixed solvent is 10.6 M^{-n}.

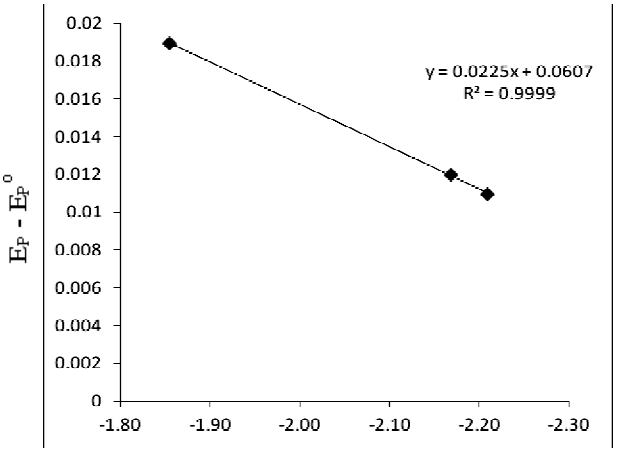


Figure 6. **Plot of the first cathodic peak potentials against log βCD**

Kinetics of the reaction of $BzV^{+\cdot}$ with βCD

Cyclic voltammograms of BzV^{2+} are recorded in the presence of βCD at slow and fast scan rates. It was observed that at 0.05 V/s scan rate, the first reduction peak of BzV^{2+} shifted in positive direction by the additions of βCD in 9:1 (v/v) DMF/H_2O mixed solvent Fig. 5. Whereas at fast scan rates the position of this peak remain unchanged. At fast scan rate (5 V/s) the peak potentials of BzV^{2+} in the presence and absence of βCD host were same Fig. 7. It means that at slow scan rate $BzV^{+\cdot}$ has more time to form complex with βCD and that corresponding reduction peak got shifted in positive direction but as scan rate increased $BzV^{+\cdot}$ was left uncomplexed. From these observations it is inferred that the rate of complex formation of $BzV^{+\cdot}$ with βCD could be quite slow in 9:1 (v/v) DMF/H_2O mixed solvent.

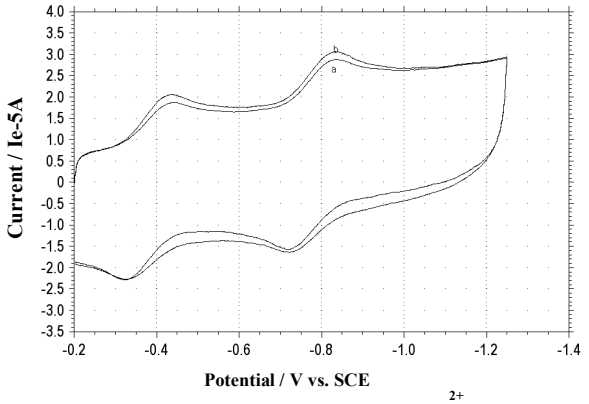


Figure 7. **Cyclic voltammograms of 0.415 mM Bzv^{2+} in absence (a) and the presence (b) of 0.014 M βCD in 9:1(v/v) DMF/H_2O mixed solvent. Scan rate: 5V/s.**

Complex formation of $BzV^{+\cdot}$ with βCD in 9:1(v/v) DMF/H_2O mixed solvent follows a reversible charge transfer.

$$BzV^{2+} + e \leftrightarrow BzV^{+\cdot} \quad \text{(ii)}$$

$$BzV^{+\cdot} + n[\beta CD] \leftrightarrow BzV^{+\cdot} - n\beta CD \quad \text{(iii)}$$

As βCD was in excess (0.014 M) so the value of k_b, the first order reverse reaction can be obtained by using the following equation [15].

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

Where

Ep is the peak potential of benzyl viologen in the presence of βCD, $E_{1/2}$ is the half wave potential of benzyl viologen in the absence of host, $K_{N.S} = K \times [\beta CD]^n$ and $a = nF\upsilon / RT$ (υ is scan rate in Vs^{-1}).

By putting these values in above equation, k_b was calculated as 0.465 s^{-1}. From this value of k_b, k_f (pseudo-first order rate constant) for the reaction of $BzV^{+\cdot}$ with βCD was obtained by using the following equation.

$$K_{N.S} = k_f / k_b \quad \text{(v)}$$

The value of k_f is found to be 0.893 s^{-1}.

From this pseudo-first order rate constant, second order rate constant k_2 can be calculated by using this equation.

$$k_2 = k_f / [\beta CD]^n \quad \text{(vi)}$$

The value of k_2 in 9:1(v/v) DMF/H_2O mixed solvent is found to be 4.93 $M^{-n}s^{-1}$. This proposed electrochemical method is superior to the peak current ratios method [10] for the kinetics study of viologens.

Digital simulation

In order to confirm our results we decided to simulate the experimental cyclic voltametric curves of BzV^{2+} in 9:1(v/v) DMF/H_2O mixed solvent. Mechanism1 that has been specified above was used for mechanistic probe. For simulation the values of electron transfer rate constant (ks) for first and second redox processes have been used as 0.01 and 0.001 cm/s, respectively. Diffusion coefficient has been taken as 1 x 10^{-7} cm^2/s. Experimentally determined values of rate constants (k_2, k_b) were used for simulation.

Simulated curve was found to be matched with the experimental curve Fig. 8 which confirm the proposed mechanism of the reaction of benzyl viologen in its reduced forms with βCD.

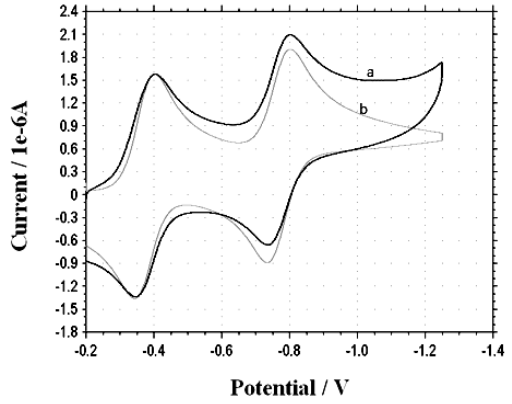


Figure 8. **Overlays of experimental (a) and simulated (b) curvesof Bzv^{2+} in the presence of βCD in 9:1(v/v) DMF/H_2O mixed solvent. Scan rate: 0.05V/s, [Bzv^{2+}] = 0.415 mM, [βCD] = 2mM. For other parameters see digital simulation section.**

Conclusion

Present study shows that BzV^{2+} doesn't form inclusion complex with βCD in 9:1 (v/v) DMF/H_2O mixed solvent. It was found that in 9:1(v/v) DMF/ H_2O mixed solvent benzyl viologen mono-cation radical ($BzV^{+\cdot}$) formed complex with βCD according to EC mechanism. The equilibrium constant and the second order rate constant of $BzV^{+\cdot}$-nβCD complex has been determined as 10.6 M^{-n} and 4.93 $M^{-n}s^{-}$ respectively.

The applications of βCD are limited to aqueous medium. Nevertheless, present study showed that the cavity of βCD can bind the viologen substituent in non-aqueous medium and permits thermodynamic and kinetics study. As to circumvent the complications associated with the dimerization of $V^{+\cdot}$ and electro deposition of $V^{+\cdot}$ and/ or V°, 9:1(v/v) DMF/H_2O mixed solvent has been used, it might become useful for the advance study of applications of non-alkyl group substituted and long alkyl chain substituted viologens and may provide a new avenue to study how these viologens trigger redox cycling reactions.

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