

Electron transfer reactions associated with ethyl viologen- β -cyclodextrin complexation: equilibrium and kinetic aspects

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Received: 5 March 2013 / Accepted: 25 August 2013 / Published online: 19 November 2013
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Abstract Formation of the complex of ethyl viologen in its cationic ($\text{Ev}^{+\bullet}$) and neutral (Ev°) forms with β -cyclodextrin (β -CD) was investigated by means of voltammetric technique in buffer solution of pH 7.00. The number of β CD (n or m) per viologen species ($\text{Ev}^{+\bullet}$) or (Ev°), bonding equilibrium constants as well as bonding rate constants was calculated. The calculated values of $K_{\text{eq}}^{(1)}$ and $K_{\text{eq}}^{(2)}$ (pertaining to the bonding of $\text{Ev}^{+\bullet}$ and Ev° with β CD) are 13.6 M^{-n} and $2.1 \times 10^3 \text{ M}^{-m}$, respectively, whereas the calculated values of n and m are 0.54 and 1.25, respectively. The bimolecular rate constant for the $\text{Ev}^\circ - \beta$ CD inclusion complex formation is $3.03 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$. These results are supported by the simulation of the experimental cyclic voltammograms. This study also highlights the significance of the proposed electrochemical method as compared to earlier studies on viologen-Cyclodextrin systems.

Keywords Viologen · β CD system · Inclusion complex · Cyclic voltammetry · Digital simulation

Introduction

Complex formation between cyclodextrin, CD [1] (cyclic oligosaccharides composed of seven D-glucose units) and viologens [2] can be electrochemically influenced through bringing changes in the oxidation states of viologen. Viologens have received much attention owing to their versatile redox system having three oxidation states: V^{2+} , $\text{V}^{+\bullet}$ and V° .



Viologen cation radical may be soluble or can form a deposit on the electrode but the neutral form of viologen is almost insoluble in aqueous media. Complexation of reduced form of viologen with β CD resolves the problem of dimer formation and precipitation [3–5]. A number of studies [6–8] have been published exploring CD-viologen interactions, but these studies relied heavily on digital simulation and hardly any kinetics study has been explored.

Simulation, in general, is extensively used to obtain information about phenomena/processes studied. However, they may give ambiguous results in the case of chemically coupled electrochemical processes [9, 10]. At the same time, a most useful utilization of the cyclic voltammetry is in obtaining thermodynamic and kinetic parameters (such as equilibrium constant and rate constants, respectively) for chemically coupled electrochemical processes through the use of the theory of stationary electrode voltammetry. Once (thus) obtained, these parameters can be used in the simulation of experimentally recorded cyclic voltammograms for such chemically coupled electrochemical process as encountered in the

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present case. It may be noted that sound theoretical treatment and elegant equations are available in the literature for many chemically coupled electrochemical processes [11, 12].

So far, in the case of kinetics study on viologens, previous works [13, 14] relied on the measurement of peak current ratios—a method which becomes less reliable in aqueous medium due to dimerization and deposition problems associated with $V^{+\bullet}$ and/or V° .

Through such an electrochemical approach [11, 12] and simulation technique, as adopted in the present study, it is not only possible to obtain the formation constants and rate constants but also the number of β CD forming the complex with a $V^{+\bullet}$ and/or V° molecule.

Thus, the objective of this investigation is to obtain the formation constants, the rate constants of formation and the association numbers of the complex formed between reduced species of Ev^{2+} and β CD.

Experimental

Chemicals

β -Cyclodextrin (Merck) and Ethyl Viologen dibromide (Merck) were used as received without any further purification. Buffer solution of pH 7 (Merck) and double deionized water were used. None of the reagents was found to show any spurious electrochemical signal in the voltage window of interest.

Electrochemical experiments

Electrochemical measurements were carried out on the Electrochemical Analyzer (Model CHI600C Series). For Cyclic voltammograms (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 μ m alumina on a felt surface and rinsed with double deionized water.

The concentration of ethyl viologen dibromide solutions was typically in the range of 0.3–1.0 mM, to which varied concentration of β CD ranging from 0.31 to 12.0 mM was added. All solutions were prepared in buffer solution of pH 7 and before recording a cyclic voltammogram, were purged with nitrogen gas for 15 min to eliminate oxygen. Cyclic voltammograms were recorded for the buffer solution (pH 7). CV of blank buffer solution did not show presence of any electro-active species in the solution. The scan rates were 0.02, ... 0.4 V/s. Simulation was carried out with DigiSim software (BAS E'CHEM Electrochemical Products Group).

Results and discussions

All viologens studied by various workers are known to exhibit two (reversible) reduction peaks corresponding to two single electron reductions. The two reduction waves of ethyl viologen dication (Ev^{2+}) were observed by cyclic voltammetry in buffer of pH 7 versus the SCE (Fig. 1, solid line).

In the presence of a host (β CD), cathodic peak position of Ev^{2+} shifted in positive direction. The second reduction peak in particular shifted significantly, as shown in Fig. 1.

The complexation phenomena

Characterization of Electron transfer reaction coupled to chemical reaction

The coupling of chemical reactions to the electron transfer reactions can lead to changes in the peak potentials and peak currents. If the ratio of anodic to cathodic peak currents is unity and is not affected by switching potential, any coupled chemical reaction is ruled out [11]. It is a best diagnostic criterion for the investigation of the coupled chemical reactions. When β CD solutions of concentration between 0.3 and 12 mM are added to the ethyl viologen solution of concentration 0.60 mM, the I_{pa}/I_{pc} values for the corresponding $Ev^{2+}/Ev^{+\bullet}$ redox process, Eq. (1), remain close to unity even at 0.4 V/s scan rate (Table 1) indicating no significant effect of the addition of β CD on this electrochemical process.

It may thus be concluded that the reaction of β CD with $Ev^{+\bullet}$, if any, is slow and that $Ev^{+\bullet}$ does not significantly bind with β CD. When Ev^{2+} , in aqueous media, gets reduced to Ev° , the later having poor solubility in water gets deposited on the electrode surface, giving rise to a corresponding oxidation peak which is sharp, symmetrical and much bigger in size. On the addition of β CD to Ev^{2+}

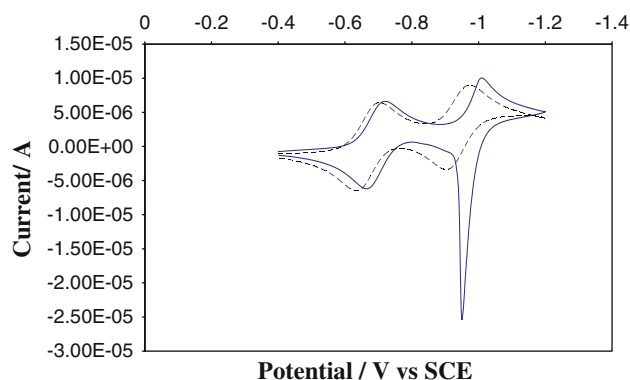


Fig. 1 CVs of 0.602 mM ethyl viologen in the absence (solid line) and the presence (dotted line) of 11.89 mM β CD. Scan rate: 0.05 V/s, Temperature: 25 °C

Table 1 Effect of the addition of β CD host on peak current ratios measured for ethyl viologen solution at different scan rates

S. No	Conc.(mM)/Scan rate	0.02 V/s		0.05 V/s		0.08 V/s		0.1 V/s		0.2 V/s		0.4 V/s	
		$ I_{pa_1}/I_{pc_1} $	$ I_{pa_2}/I_{pc_2} $	$ I_{pa_1}/I_{pc_1} $	$ I_{pa_2}/I_{pc_2} $	$ I_{pa_1}/I_{pc_1} $	$ I_{pa_2}/I_{pc_2} $	$ I_{pa_1}/I_{pc_1} $	$ I_{pa_2}/I_{pc_2} $	$ I_{pa_1}/I_{pc_1} $	$ I_{pa_2}/I_{pc_2} $	$ I_{pa_1}/I_{pc_1} $	$ I_{pa_2}/I_{pc_2} $
1	0.602 ^a + 0.000 ^b	0.9	2.7	1.1	4.1	1.1	4.6	1.1	4.7	1.1	4.8	1.1	4.5
2	0.602 + 0.313	1.1	3.0	1.0	3.7	1.0	4.0	1.0	4.1	1.1	4.1	1.1	3.8
3	0.602 + 0.626	0.9	2.2	1.1	3.6	1.0	4.0	1.0	4.1	1.0	4.1	1.1	3.8
4	0.602 + 0.938	1.0	2.6	1.0	4.0	1.0	4.1	1.0	4.1	1.1	3.9	1.1	3.5
5	0.602 + 1.25	1.0	2.0	1.0	2.8	1.0	3.2	1.0	3.2	1.0	3.1	1.0	2.8
6	0.602 + 3.13	1.0	1.2	0.9	1.4	0.9	1.5	0.9	1.5	0.9	1.5	1.0	1.7
7	0.602 + 6.26	0.9	1.3	0.9	1.4	0.9	1.5	0.9	1.5	0.9	1.6	0.9	1.6
8	0.602 + 9.07	0.9	1.4	0.9	1.4	0.9	1.4	0.9	1.5	0.9	1.5	0.9	1.7
9	0.602 + 11.89	1.0	1.4	0.9	1.4	0.9	1.4	0.9	1.4	0.9	1.5	0.9	1.6

I_{pa_1}/I_{pc_1} is the anodic to cathodic peak current ratios measured for the first redox process and I_{pa_2}/I_{pc_2} is same for second redox process

^a Concentration of ethyl viologen solution

^b Addition of β CD host in 0.602 mM Ev^{2+} solution

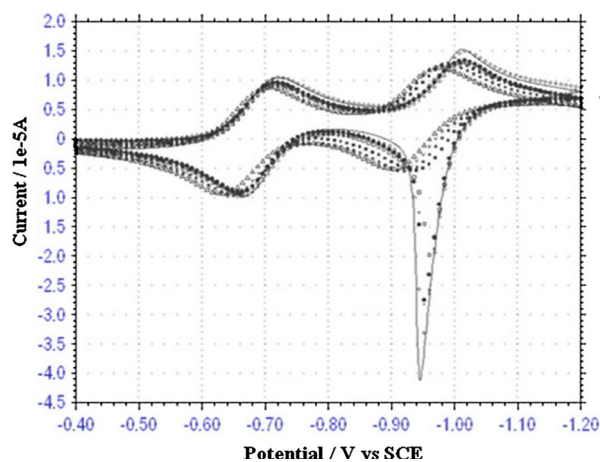


Fig. 2 CVs of 0.602 mM Ethyl viologen (0.1 V/s) in the absence (a), and in the presence of various concentration (b–i) of β CD host, in phosphate buffer of pH 7; (b) = 0.313 mM, (c) = 0.626 mM, (d) = 0.938 mM, (e) = 1.25 mM, (f) = 3.13 mM, (g) = 6.26 mM, (h) = 9.07 mM, (i) = 11.89 mM

solution, even when the ratio of β CD to Ev^{2+} is 2:1, no perceptible effect was found on either peak position or peak shape associated with the (two) reduction processes.

When the ratio (of β CD to Ev^{2+}) is increased to five (times) or higher, the shape as well as the position of the peak associated with the second reduction process ($Ev^{+\bullet}$ to Ev°) gets affected (Figs. 2, 3). The huge, sharp and symmetrical second anodic peak changed into a regular cyclic voltammetric anodic wave, characteristic of a reversible process. The ratio of anodic to cathodic peak currents approaches unity, indicating the reversibility of the process as well as possibility of coupled (reversible) chemical reaction.

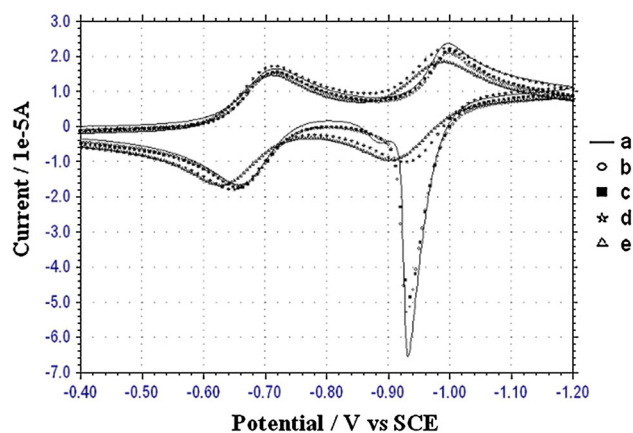


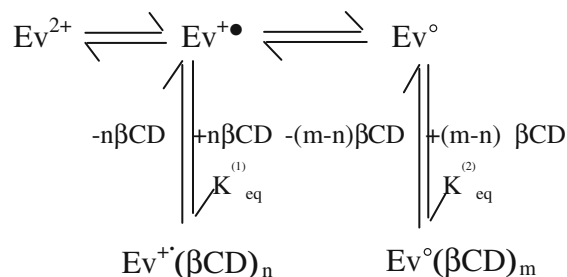
Fig. 3 CVs of 1.006 mM Ethyl viologen (0.1 V/s) in the absence (a) and in the presence of various concentration (b–e) of β CD host in phosphate buffer of pH 7: (b) = 0.5 mM, (c) = 1.01 mM, (d) = 5.03 mM, (e) = 10.06 mM

Evaluation of equilibrium constants for the formation of $Ev^{+\bullet}-n\beta$ CD and $Ev^\circ-m\beta$ CD complex

It has been found experimentally that the interaction between Ev^{2+} and β CD, if any, is very weak as evidenced by the absence of any CE (a chemical reaction followed by a reversible electron transfer) effect on the Cyclic voltammogram of Ev^{2+} (Fig. 2).

From the observation on the shape and position of the two peaks, on the addition of β CD, a scheme (Scheme 1) may be proposed for the interaction of β CD with $Ev^{2+}/Ev^{+\bullet}/Ev^\circ$.

The expression for the equilibrium constant for the complexation associated with the first reduction step can be written as Eq. (3) [15].



Scheme 1 Mechanism showing the electrochemical and chemical interactions of ethyl viologen guests in the presence of βCD

$$E_{P1} = E_{P1}^\circ + \frac{RT}{F} \ln \left(1 + K_{\text{eq}}^{(1)} [\beta\text{CD}]^n \right) \quad (3)$$

Where E_{P1}° and E_{P1} are the peak potentials of Ev^{2+} in the absence and in the presence of βCD , respectively. $K_{\text{eq}}^{(1)}$ is the formation constant for $\text{Ev}^{+\bullet} - \beta\text{CD}$ complexation, n is the number of βCD associated with one $\text{Ev}^{+\bullet}$. If $K_{\text{eq}}^{(1)} [\beta\text{CD}]^n \gg 1$, then Eq. (3) is reduced to

$$E_{P1} = E_{P1}^\circ + \left(\frac{RT}{F} \right) \ln K_{\text{eq}}^{(1)} + \frac{nRT}{F} \ln [\beta\text{CD}] \quad (4)$$

A value of n could be obtained from approximate $\ln[\beta\text{CD}] - E_{P1}$ relationship at higher concentration range of βCD which gave a value of 0.54 for n .

One can obtain the equilibrium constant for the first reduction step by plotting the right hand side (RHS) of Eq. (5) against $[\beta\text{CD}]^{0.54}$.

$$\exp[f(E_{P1} - E_{P1}^\circ)] = 1 + K_{\text{eq}}^{(1)} [\beta\text{CD}]^{0.54} \quad (5)$$

where $f = F/RT$. Such a plot is shown in Fig. (4).

The value of $K_{\text{eq}}^{(1)}$ thus obtained is 13.6 M^{-n} .

Gupta and Linshitz [16] have also reported $n = 0.5$ for the hydrogen bonding of the anion radical of dichlorobenzoquinone with tetrafluoroethanol. They neither elaborated

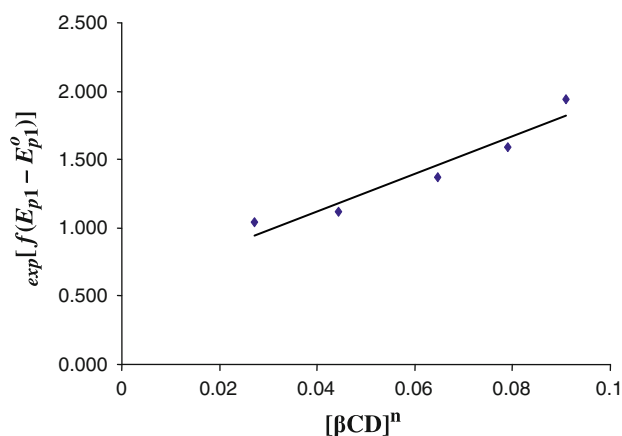


Fig. 4 Plot of the function $\exp[f(E_{P1} - E_{P1}^\circ)]$ for the first reduction step against βCD concentrations, $f = F/RT$

the significance of n nor commented upon the numerical value $n = 0.5$.

This value of $n = 0.54$ may be coming from the participation of dimer of $\text{Ev}^{+\bullet} - (\text{Ev}^{+\bullet})_2$ —in the association process with βCD . This dimerization of viologen cation radical is a known phenomenon [3–5, 17].

Second equilibrium constant $K_{\text{eq}}^{(2)}$ can be determined from Eq. (6) [15].

$$\exp \left[f(E_{P2} - E_{P2}^\circ) \right] = \frac{1 + K_{\text{eq}}^{(2)} [\beta\text{CD}]^m}{1 + K_{\text{eq}}^{(1)} [\beta\text{CD}]^n} \quad (6)$$

Where m is the number of βCD associated with one neutral ethyl viologen Ev° and $K_{\text{eq}}^{(2)}$ is the corresponding equilibrium constant. In case of strong association between host and guests, we may ignore 1 from numerator as well as denominator. The value of $m-n$ can be determined from the plot of second cathodic peak potential (E_{P2}) against $\ln[\beta\text{CD}]$. This plot is shown in Fig. (5). The value of $m-n$ thus obtained from slope is 0.71 which yields $m = 1.25$. However, if $1 \gg K_{\text{eq}}^{(1)} [\beta\text{CD}]^n$, then from Eq. (6) a plot of E_{P2} vs $\ln\beta\text{CD}$ will directly give the value of m . With n , m and $K_{\text{eq}}^{(1)}$ known, $K_{\text{eq}}^{(2)}$ can be obtained from Eqs. (6) or (7).

$$\left\{ \exp[f(E_{P2} - E_{P2}^\circ)] \right\} \left\{ 1 + K_{\text{eq}}^{(1)} [\beta\text{CD}]^n \right\} = 1 + K_{\text{eq}}^{(2)} [\beta\text{CD}]^m \quad (7)$$

A plot between the LHS of Eq. (7) against $[\beta\text{CD}]^m$ is shown in Fig. (6); a straight line is obtained. The slope of the plot yielded $K_{\text{eq}}^{(2)} = 2.1 \times 10^3 \text{ M}^{-m}$.

These values of $K_{\text{eq}}^{(1)}$ and $K_{\text{eq}}^{(2)}$ compare well with the values of formation constant reported for other CD-viologen inclusion complexes [6].

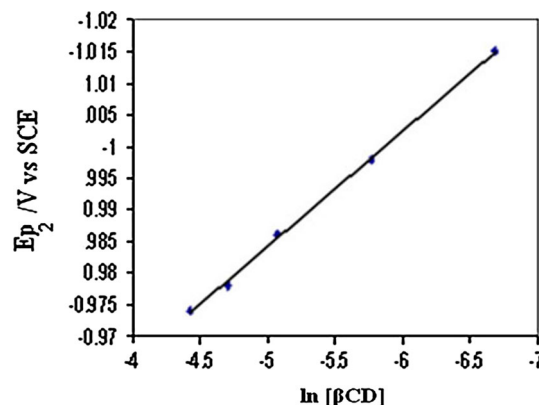


Fig. 5 Plot of the peak potential for the second reduction step against $\ln[\beta\text{CD}]$

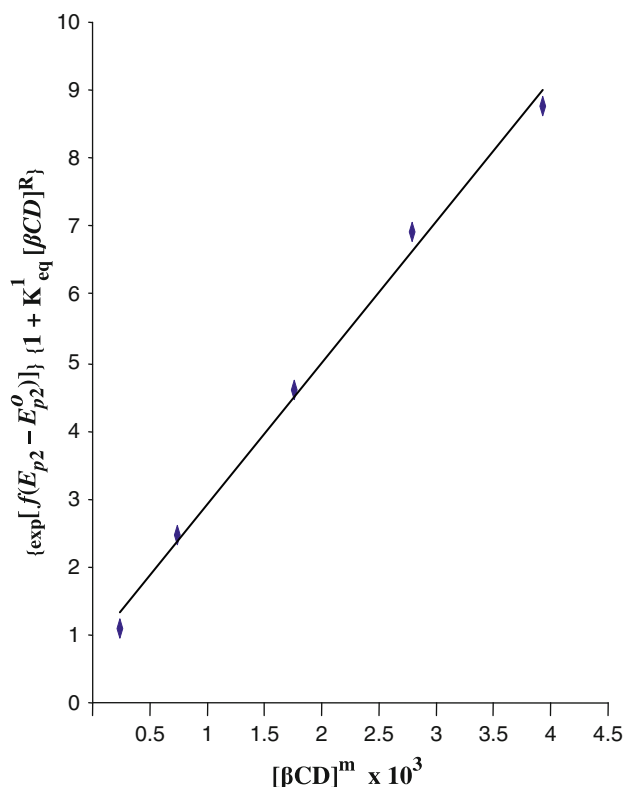


Fig. 6 Plot of the function $\left\{ \frac{\exp[f(E_{p2} - E_{p2}^0)]}{1 + K_{eq}^{(1)}[\beta CD]^n} \right\}$ for the second reduction step against βCD concentrations, $f = F/RT$

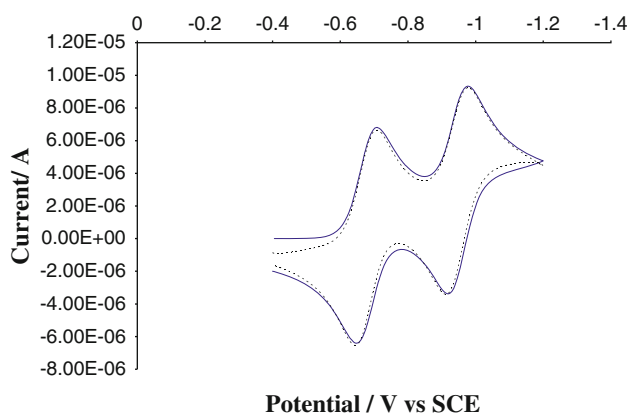


Fig. 7 Overlays of experimental (solid line) and simulated (dotted line) Cvs of 0.602 mM ethyl viologen with 9.07 mM βCD

The values of equilibrium constant thus obtained get further support from the simulation of CVs (Fig. 7) (see below).

The neutral ethyl viologen (Ev°) has a formation constant with βCD which is at least 100 times that of the oxidized form, $Ev^{+\bullet}$. βCD has empty cone-like shape with non-polar interior and polar exterior of the cavity.

Formation of the inclusion complex depends on the geometric compatibility between host cavity and the guest and also on the polarity and charge of the guest. Neutral molecules can easily be included in the βCD cavity as compared to its ionized counterpart $Ev^{+\bullet}$. This quantitative determination of equilibrium constant establishes that the neutral form of ethyl viologen dication forms much stronger complex with βCD as compared to its charged form ($Ev^{+\bullet}$).

Rate constants for the formation of viologen- βCD complex

When CVs of ethyl viologen dication were recorded in higher concentration range of βCD at various scan rates, it was observed that the ratio of peak currents corresponding to second reduction process ($Ev^{+\bullet}/Ev^\circ$) increased with the increasing scan rates (see Table 1). It showed that there was greater contribution of uncomplexed Ev° at higher scan rates. From this, it is inferred that at slow scan rate, more Ev° had complexed by the time the $(E_p)_a$ was reached. This indicates that the kinetics of formation of $Ev^\circ - \beta CD$ complex is not quite as fast. Peak current ratio related to first reduction process was not found to be significantly affected. It is noted that the charged form of ethyl viologen ($Ev^{+\bullet}$) has low formation constant with βCD which also indicates that the rate of complex formation for $Ev^{+\bullet}$ could be quite slow.

Rate constant for the reaction of Ev° with βCD could easily be obtained using the Nicholson-Shain theory [11] for the case in which a reversible chemical reaction follows a reversible charge transfer.



where $O = Ev^{+\bullet}$, $R = Ev^\circ$, $A = \beta CD$ (which is in “large” excess), $Z = Ev^\circ - \beta CD$ complex, $K_{NS} = k_f'/k_b$, where K_{NS} is equilibrium constant and k_f' is pseudo-first order rate constant for forward reaction, whereas k_b is first order reverse reaction. NS notates Nicholson-Shain.

By assuming a 1:1 interaction between Ev° and βCD and βCD is in large excess, a pseudo-first order rate constant (k_f') can be obtained from Eq. (10).

$$E_p = E_{1/2} - \left(\frac{RT}{nF} \right) [0.78 + \ln K_{NS}(a/l)^{1/2} - \ln(1 + K_{NS})] \quad (10)$$

where $l = k_f' + k_b$, $K_{NS} = K \times [\beta CD]$, E_p is the peak potential of viologen in the presence of βCD ; $E_{1/2}$ is the half wave potential of viologen in absence of host and

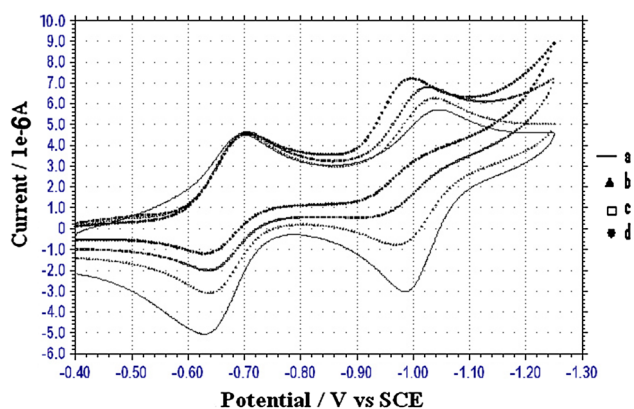


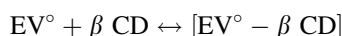
Fig. 8 Cvs of 0.396 mM ethyl viologen (0.05 V/s) in the absence (a) and in the presence (b = 1.24 mM), (c = 4.36 mM), (d = 25.5 mM) of β CD host in 1:9 (v/v) DMF/H₂O solvent; (Temperature: 25 °C; 0.1 M KCl used as an electrolyte)

$a = nFv/RT$ (v is scan rate, Vs^{-1}). From this pseudo-first order rate constant, second order rate constant k_2 could be obtained using Eq. (11).

$$k_2 = k_f' / [\beta CD] \quad (11)$$

The pseudo-first order condition was maintained using $[\beta CD]$ about 10–20 times $[Ev^{2+}]$.

k_2 for the reaction



was calculated to be $3.03 \times 10^3 M^{-1}s^{-1}$ and value of $k_b = 1.45 s^{-1}$.

These values of k_2 and k_b were used in the simulation of the experimental CVs.

In the course of the investigation on the kinetics of $Ev^\circ - \beta CD$ complex, it was found that in 1:9 (v/v) DMF/H₂O solvent system, the second electron transfer step of Ev^{2+} followed an irreversible chemical reaction as,



On the other hand, in the same 1:9 DMF/H₂O solvent system, no change was recorded in the peak current and/or in the peak position of first reduction step of Ev^{2+} on the addition of βCD as evident from Fig. 8.

If βCD is in large excess, a pseudo-first order rate constant (k_f') can be obtained from Eq. (14) [11].

$$E_p = E_{1/2} - \left(\frac{RT}{nF} \right) \left[0.78 - \ln \left(k_f' / a \right)^{1/2} \right] \quad (14)$$

From this pseudo-first order rate constant, the second order rate constant for the irreversible chemical reaction, (re Eq. (13))

Table 2 Electrochemical parameters: Reduction of ethyl viologen in the presence of βCD at 0.05 V/s sweep rate in phosphate buffer of pH 7

Conc. of solutions/(mM)	E_{P1}^c (V)	E_{P2}^d (V)	$E_1^{\circ,e}$ (V)	$E_2^{\circ,f}$ (V)
0.602 ^a + 0.000 ^b	-0.720	-1.009	-0.668	-0.9795
0.602 + 6.26	-0.712	-0.986	-0.682	-0.958
0.602 + 9.07	-0.708	-0.978	-0.677	-0.949
0.602 + 11.89	-0.703	-0.974	-0.673	-0.944

^a Concentration of ethyl viologen solution

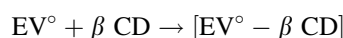
^b Addition of βCD host in 0.602 mM Ev^{2+} solution

^c Peak potential for the first reduction step

^d Peak potential for the second reduction step

^e Formal reduction potential for first redox process

^f Formal reduction potential for second redox process



was calculated as $1.44 \times 10^3 M^{-1}s^{-1}$.

Digital simulation

For simulating the experimental cyclic voltammetric curves of Ev^{2+} in buffer of pH 7, the reaction scheme (scheme 1) that has been mentioned above was used for mechanistic probe. The experimentally determined values of n , m , equilibrium constants ($K_{eq}^{(1)}, K_{eq}^{(2)}$) and rate constants (k_2, k_b) were used for simulation of cyclic voltammograms(s). Values of electron transfer rate constants (k_s) for first and second redox processes have been used as 0.05 and 0.1 cm/s, respectively, for simulation. α (electron transfer coefficient) was taken as 0.5 and D (diffusion coefficient) has been taken as $7.4 \times 10^{-6} cm^2/s$. Rate constant for the formation of $Ev^{+\bullet} - \beta CD$ has been taken as $1 M^{-1}s^{-1}$. For other parameters see Table 2.

Conclusion

Simulation, a powerful technique for investigating processes of interest, however, can be used as a good supporting technique in cases where there are chemically coupled electrochemical processes. Nevertheless, the present study presents a simple (electrochemical) approach for evaluating the equilibrium constant and rate constants for viologen- CD system which is based on sound stationary electrode voltammetric theory. This proposed simple electrochemical method gives equally reliable results. Furthermore, it is shown that through the use of the theory of stationary electrode voltammetry, the rate constants can also be evaluated for Viologen-CD system. This parameter—the rate constant—has not reported by earlier

workers. The present method is, thus, superior to the peak current ratios method for the determination of rate constants, in particular, for viologens in aqueous medium.

Acknowledgments Shaz Akber is thankful to Dr. M Tariq and Dr. Lubna Naz, ICCBS Karachi University for their useful suggestions and help in connection with the digital simulation.

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