JOURNAL OF APPLIED ELECTROCHEMISTRY **18** (1988) 333–338

Electrochemical behaviour of viologen–cyclodextrin inclusion complexes. The case of non-alkyl group substituted viologen

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Received 19 May 1987; revised 24 September 1987

The electrochemical behaviour of non-alkyl substituted viologens, 4,4′-dibenzyl bipyridinium (BzV), 4,4′-dicyanophenyl bipyridinium (CyV) and α-, β-, γ-cyclodextrin (α, β, γ-CD) was studied using cyclic voltammetry and a spectroelectrochemical method. It was found that BzV and $Fe(CN)_6^{4-}$ formed a charge-transfer (CT) complex with a ratio of 2 : 1 and the colour of the solution faded with the addition of an electrolyte. This behaviour is the same as in the *n*-heptyl viologen and ferrocyanide system [1]. BzV, α-CD and γ-CD formed an inclusion complex only in the reduced state, whilst BzV and β-CD formed an inclusion complex in both the oxidized and the reduced state. An EC scheme in which a chemical reaction follows an electrochemical reaction was considered to predominate in the BzV and α-, γ-CD systems, while a CE scheme in which a chemical reaction preceded an electrochemical reaction predominated in the BzV and β-CD system. On the other hand, CyV was found to form an inclusion complex with α-, β-, γ-CD in both the oxidized and the reduced states, therefore a CE scheme was considered to predominate in the CyV–α-, β-, γ-CD systems.

1. Introduction

Although the applications of the colour changes of the viologen redox reaction to electrochromic displays (ECDs) have been intensely studied, practical uses have not yet been found due to the appearance of ‘residues’ on the display electrode during repeated cycling [1]. The main reason for the residues is said to be the crystallization brought about by the strong intermolecular interaction between viologen monocation radicals. We showed that in the alkyl viologen systems the intermolecular interaction could be weakened by forming an inclusion complex between viologen and cyclodextrin, and that the residues could be completely eliminated. Furthermore, the blue colour ascribed to the viologen monomer could be obtained in addition to red-violet (the colour of the dimer) [2, 3].

We proposed the following scheme in a previous paper [3]. In alkyl viologen systems with short alkyl chains, viologen is not included in β-, γ-CD in the oxidized state of viologen, but is included in the reduced state. Therefore, an EC scheme in which an electrochemical reaction precedes a chemical reaction should predominate in these systems. An α-CD does not form an inclusion complex with methyl or ethyl viologen either in the oxidized or in the reduced state.

In the case of viologens with longer alkyl chains, viologens in the oxidized state can form inclusion complexes with α- and β-CD but not with γ-CD. However, in the reduced state, these viologens can form inclusion complexes with α-, β- and γ-CD. The reaction schemes are that a CE scheme should predominate in the α-, β-CD system, and that an EC scheme should predominate in the γ-CD system.

In this report, the reaction schemes of CDs and viologens with non-alkyl group substituents, dibenzyl and dicyanophenyl, are studied using the method previously described [3]. Furthermore, the reasons for the occurrence of different types of reaction schemes were considered from the standpoint of the electronic and the size effects.

2. Experimental details

2.1. *Reagents*

Benzyl viologen dibromide (4,4′-dibenzyl-bipyridinium dibromide) (denoted as BzV) (Nihon Kagaku Kogyo Co. Ltd) and cyanophenyl viologen dichloride (4,4′-dicyanophenyl-bipyridinium dichloride) (denoted as CyV) (Japanese Research Institute for Photosensitizing Dyes Co. Ltd) were used without further purification. Potassium ferrocyanide, sodium hypophosphite and α-, β-, γ-cyclodextrin were all commercially available.

2.2. *Instrumentation*

The potentiostat, function generator and spectrophotometer were described previously [1], as were the electrochemical cell for monitoring the cyclic voltammetry and absorption spectra [2].

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3. Results and discussion

3.1. *Formation of an inclusion complex between BzV and CD in the oxidized state of BzV*

It was reported by Kamiya *et al.* that the formation of an inclusion complex between BzV in the oxidized state and β-CD could be confirmed by ^{1}H NMR spectroscopy, because the phenyl groups have magnetic anisotropy [4]. But they reported that with α-CD, it was impossible to detect the spectral difference between the spectra with and without BzV. These authors considered that the size of the cavity in α-CD was too small to include the phenyl groups of BzV.

If an inclusion complex is formed, a change in the absorption spectra brought about by the change in interaction between the solvent molecules and the viologen molecules is expected [5].

The absorption spectra of the BzV–α, β-, γ-CD systems are shown in Fig. 1. Only in the β-CD system was the red shift of the BzV absorption maximum observed. This indicates the existence of the intermolecular interaction between BzV and β-CD (i.e. the formation of the inclusion complex). Therefore, the oxidized state of BzV can be included in the β-CD torus. This result coincides with the result obtained by ^{1}H NMR spectroscopy. BzV in the oxidized state did not form an inclusion complex with α-CD or γ-CD.

3.2. *Charge-transfer complex between BzV and ferrocyanide*

From the practical point of view, ferrocyanide is added to alkyl viologen systems as an auxiliary redox system to lessen the applied voltage and side reactions. The formation of a charge-transfer complex between an alkyl viologen and ferrocyanide has been previously reported [1, 6, 7]. For BzV and ferrocyanide, a charge-transfer complex was also found to be formed. The absorption maximum of the CT complex appeared at 560 nm. By monitoring the change of the absorbance with increasing ferrocyanide concentration, the composition of BzV and ferrocyanide could be determined. The result is shown in Fig. 2. In Fig. 2 the absorbance showed a constant value with the ratio of BzV to ferrocyanide less than 2 : 1. This indicates that the composition of a CT complex between BzV and ferrocyanide is 2 : 1. Kamiya also obtained the same result by monitoring the electroconductivity changes as the BzV solution was titrated with ferrocyanide solution [8].

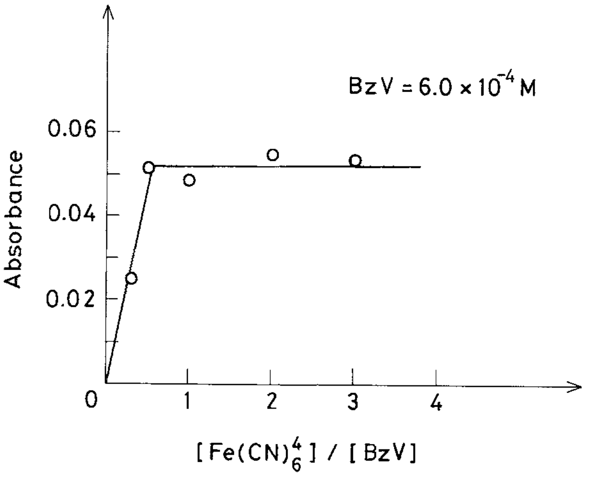

Fig. 2. Absorbance change of CT complex with increase of $Fe(CN)_6^{4-}$ concentration (at 560 nm).

A fading effect of the electrolyte, NaH_2PO_2, on the colour of the CT complex is shown in Fig. 3. The absorption spectrum without the electrolyte (1)

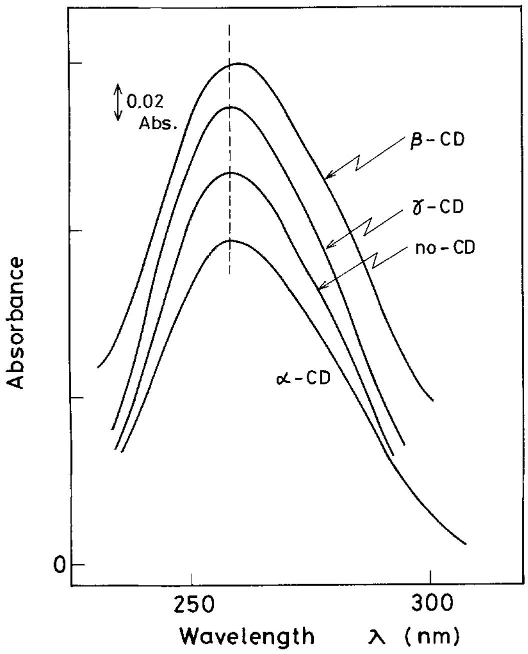

Fig. 1. The absorption spectra of the BzV–α-, β-, γ-CD systems (spectra of the solutions). BzV = 1.0 × 10^{-5} M, α-CD = 7.1 × 10^{-3} M, β-CD = 5.7 × 10^{-3} M, γ-CD = 5.8 × 10^{-3} M.

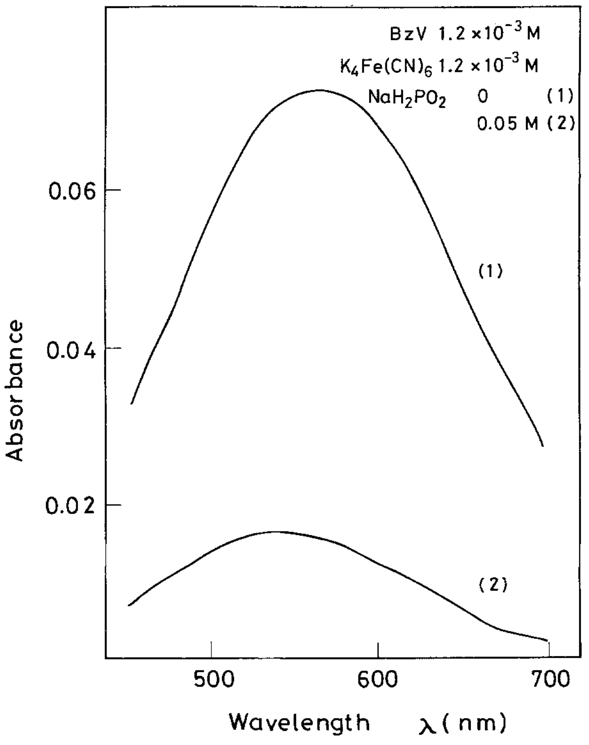

Fig. 3. Fading effect in the BzV–$Fe(CN)_6^{4-}$ charge-transfer complex system with the addition of NaH_2PO_2.

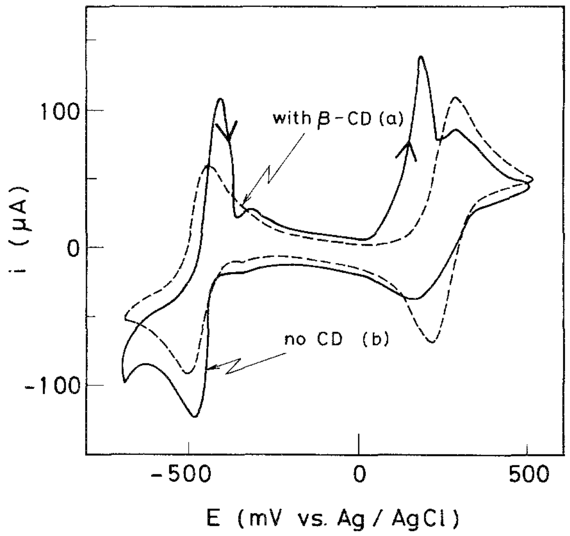

Fig. 4. Cyclic voltammograms of the BzV–$K_4Fe(CN)_6$–NaH_2PO_2 systems (a) with β-CD and (b) without β-CD. BzV = 0.01 M, $K_4Fe(CN)_6$ = 0.005 M, β-CD = 0.03 M, NaH_2PO_2 = 1.0 M. The working electrode was Pt. The scan rate was 30 mV sec^{-1}.

changed to (2) with the addition of 5.0×10^{-2} M NaH_2PO_2 to 1.2×10^{-3} M BzV. Further addition of NaH_2PO_2 did not cause any further change in the absorbance. It is considered that NaH_2PO_2 prevents the formation of a CT complex. Precipitates of a CT complex appeared with increasing BzV and ferrocyanide concentration. With the addition of an electrolyte such as NaH_2PO_2 or KBr, the precipitates disappeared and the solution became transparent [9]. This phenomenon is almost the same as in the case of *n*-heptyl viologen [1].

3.3. *Formation of an inclusion complex between BzV and β-CD*

Cyclic voltammograms of the BzV–$K_4Fe(CN)_6$–NaH_2PO_2 system with (a) and without (b) β-CD are shown in Fig. 4. In Fig. 4(a), a reoxidation wave of the strongly adsorbed reductant was observed, and in the less-negative potential region, the stripping wave of the reductant was observed. In the system with β-CD, the stripping wave caused by the strong adsorption disappeared and the shape of the voltammogram was similar to that of the electrochemically reversible system. This suggests a weakening of the adsorption, that is the viologen–electrode interaction.

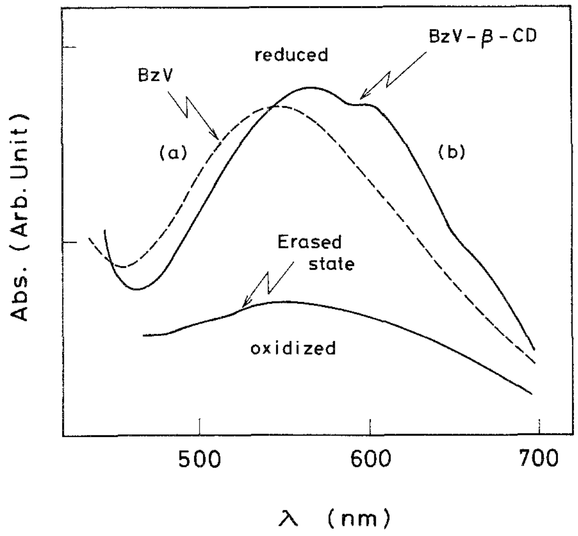

Fig. 5. The absorption spectra for the reduced state of the BzV–$K_4Fe(CN)_6$–NaH_2PO_2 systems (a) without β-CD and (b) with β-CD.

The reduction peak (E_p) of the BzV–β-CD inclusion complex shifted in the negative direction. This result is in agreement with a CE scheme in which a chemical reaction precedes an electrochemical reaction [3, 12].

The reason why NaH_2PO_2 was used for an electrolyte is the following. If KBr or KCl is used, Br^- or Cl^- could be included in the β-CD torus and prevent BzV from forming an inclusion complex.

The absorption spectra of the reduced state of the BzV systems are shown in Fig. 5, where (a) is without β-CD and (b) with β-CD. The absorption maximum at 540 nm in Fig. 5(a) is ascribed to the viologen dimer and the absorption maximum at 600 nm in Fig. 5(b) is ascribed to the monomer [10, 11]. This spectral behaviour is the same as in the case of the *n*-heptyl viologen system. The spectral change is explained as follows. By forming an inclusion complex between BzV and β-CD, the intermolecular interaction between viologen monocation radicals was weakened, and the absorption of the viologen monomer predominated.

3.4. *Effects of α- and γ-CD on the cyclic voltammetry of the BzV systems*

The change in the voltammograms with the addition of α-CD are shown in Fig. 6, where (a) is without and (b) with α-CD. In Fig. 6(a), the reoxidation wave of BzV^+ was observed at the negative side of the oxidation wave of $Fe(CN)_6^{4-}$ which was the same as in the *n*-heptyl viologen system [1]. With the addition of α-CD, the shape of the voltammogram became reversible and the stripping wave was completely

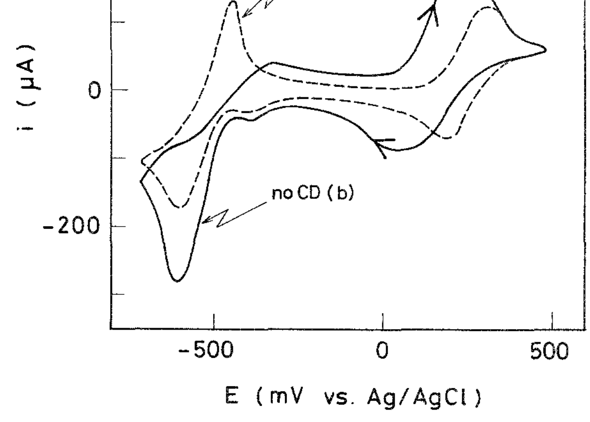

Fig. 6. Cyclic voltammograms of the BzV–$K_4Fe(CN)_6$–NaH_2PO_2 systems (a) with α-CD and (b) without α-CD. The working electrode was ITO. BzV = 0.01 M, $K_4Fe(CN)_6$ = 0.005 M, α-CD = 0.03 M, NaH_2PO_2 = 1.0 M. The scan rate was 10 mV sec^{-1}.

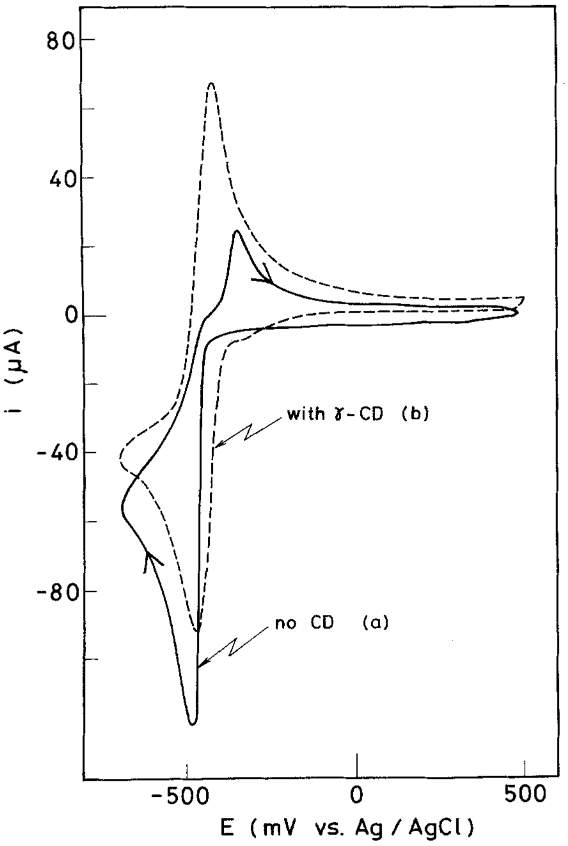

Fig. 7. Cyclic voltammograms of the BzV–NaH_2PO_2 systems (a) without γ-CD and (b) with γ-CD. BzV = 0.01 M, γ-CD = 0.03 M, NaH_2PO_2 = 0.5 M. The working electrode was Pt. The scan rate was 30 mV sec^{-1}.

eliminated. The peak potential of the reduction of BzV was shifted in the positive direction. This result supports the EC mechanism in which an electrochemical reaction precedes a chemical reaction [3, 12]. The EC mechanism indicates that an inclusion complex between BzV and α-CD is formed only with BzV in the reduced state, although the associated UV-visible absorption change was not observed.

Cyclic voltammograms of the BzV–NaH_2PO_2 system with and without γ-CD are shown in Fig. 7(a) and (b), respectively. In Fig. 7(a), because of the strong adsorption of the reductant on the electrode, the reduction wave was steep and the separation between the reduction and reoxidation peaks was large (ΔE = 160 mV) as is shown in Fig. 7(a), while in the system with γ-CD the shape of the voltammogram became reversible and the peak separation became 60 mV which is the value of the reversible redox system. Furthermore, E_p shifted to the positive direction by 25 mV. The α- and γ-CD systems showed the same behaviour as the β-CD system in Fig. 8, in which the formation of an inclusion complex was confirmed in both the oxidized and the reduced state. Therefore, the change in the cyclic voltammograms of the α- and γ-CD systems can be ascribed to the effect of forming an inclusion complex.

3.5. *Reaction scheme of the BzV–CD systems*

The formation of inclusion complexes between BzV and CDs is summarized in Table 1 together with the results of the alkyl viologen cases previously reported [3]. The conditions for forming an inclusion complex of BzV were found to be different from those for the methyl V and heptyl V types. In the oxidized state of BzV, the phenyl group is too large to be included in the α-CD cavity [4], but is included in the reduced state. This phenomenon is explained as follows. With the injection of an electron to the BzV from the electrode, the polarity of the pyridinium ring is changed from positive to neutral, which allows the apolar field of the α-CD cavity to draw in the BzV thus forming the inclusion complex.

In the β-CD system, since an inclusion complex was formed in both the oxidized and the reduced states of BzV, an inclusion site was considered to exist at the phenyl group in the oxidized state while in the reduced state the inclusion site moved to the bipyridine position.

In the γ-CD system an inclusion complex formed, not in the oxidized state, but in the reduced state of

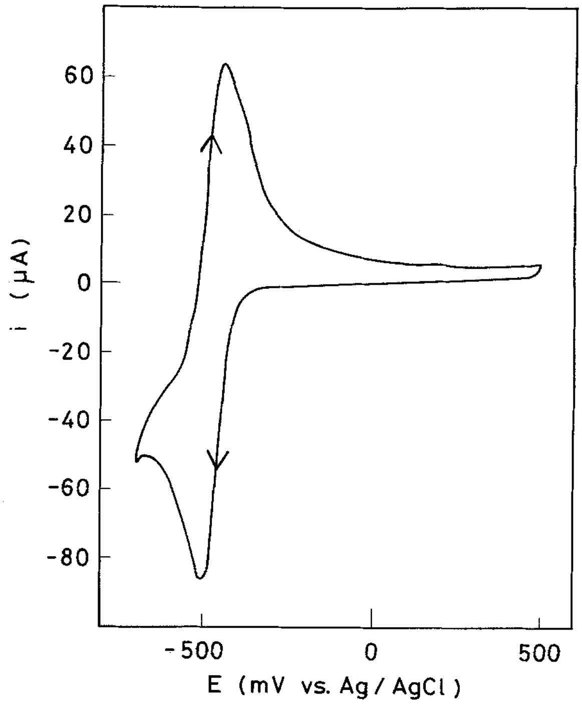

Fig. 8. Cyclic voltammogram of the BzV–β-CD–NaH_2PO_2 system. BzV = 0.01 M, β-CD = 0.03 M, NaH_2PO_2 = 0.5 M. The working electrode was Pt. The scan rate was 30 mV sec^{-1}.

Table 1. Inclusion complex and reaction schemes

V	*Methyl V Ethyl V*			*Hexyl V Heptyl V*			*BzV*		
CD	*Ox.*	*Red.*	*Scheme*	*Ox.*	*Red.*	*Scheme*	*Ox.*	*Red.*	*Scheme*
α-CD	x	x	III	o	o	I	x	o	II
β-CD	x	o	II	o	o	I	o	o	I
γ-CD	x	o	II	x	o	II	x	o	II

o: Forming inclusion complex.
x: Not forming inclusion complex.

Type I: $V^{2+} + CD \rightleftharpoons V^{2+}\text{-}CD$
$V^{2+}\text{-}CD + e \rightleftharpoons V^{+\cdot}\text{-}CD$

Type II: $V^{2+} + e \rightleftharpoons V^{+\cdot}$
$V^{+\cdot} + CD \rightleftharpoons V^{+\cdot}\text{-}CD$

Type III: $V^{2+} + e \rightleftharpoons V^{+\cdot}$

BzV. The reason why an inclusion complex is not formed between γ-CD and BzV in the oxidized state is considered to be that the size of BzV (6.5 Å) is small compared with the size of the γ-CD cavity (8.5 Å), so the interaction force is too weak to form an inclusion complex. But in the reduced state, the formation of the viologen dimer seems to occur because the colour is red-violet. The larger size of the dimer results in an interaction force large enough to allow the formation of the inclusion complex. Because of the repulsion between positive charges of BzV in the oxidized state it may be impossible to form the dimer.

A reaction scheme was determined according to whether or not BzV and CD formed an inclusion complex in each redox state. In the case of forming an inclusion complex in both the oxidized and the reduced states, a CE scheme in which chemical reaction precedes an electrochemical reaction is likely and in the case of forming an inclusion complex only in the reduced state, an EC scheme in which a chemical reaction follows an electrochemical reaction is probable.

3.6. *CyV–CD systems*

The effect of α-, β-, γ-CD on the cyclic voltammograms in the *p*-dicyanophenyl viologen (CyV) system was investigated. The change in the cyclic voltammogram with the addition of each CD was almost the same as for the β-CD system shown in Fig. 9, where (a) is without β-CD and (b) with β-CD. The change with the addition of β-CD was that both the reduction potential peak (E_p) of CyV and the reoxidation peak shifted in the negative direction. In the case of the negative shift of the reduction peak, it was considered that CyV increased its stability by forming an inclusion complex, on the other hand, the negative shift of the reoxidation peak could be ascribed to the weakening of the viologen–electrode interaction. The reduction potential peaks of each system are shown in Table 2.

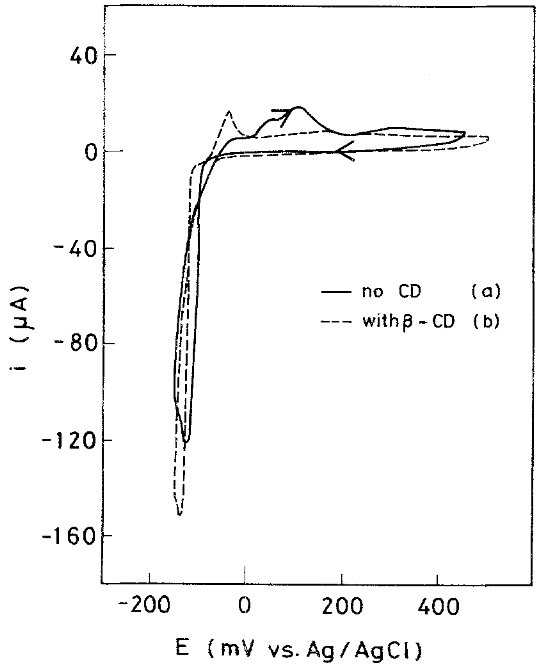

Fig. 9. Cyclic voltammograms of the CyV–β-CD–NaH_2PO_2 systems (a) without β-CD and (b) with β-CD. CyV = 0.005 M, β-CD = 0.02 M. Thw working electrode was Pt. The scan rate was 30 mV sec^{-1}.

Table 2. E_p *of CyV–CD systems and shift direction*

CD	E_p (*mV*)	*Shift direction*
No CD	−110	
α-CD	−140	Negative
β-CD	−130	Negative
γ-CD	−120	Negative

Scan rate = 10 mV s^{-1}.

Because E_p shifted in the negative direction with the addition of any CD it was considered that CyV formed an inclusion complex with CD already in the oxidized state, and that a CE scheme predominated in each system.

4. Conclusion

The electrochemical behaviour of non-alkyl substituted viologens, BzV and CyV, were studied.

In BzV, the formation of a CT complex with ferrocyanide was confirmed and the composition was BzV:$Fe(CN)_6^{4-}$ = 2 : 1. The fading effect produced by an electrolyte was found to be similar to that in the *n*-heptyl viologen–$Fe(CN)_6^{4-}$ system [1].

In the BzV-CD systems, an EC scheme was considered to predominate because BzV did not form an inclusion complex with α- and γ-CD in the oxidized state of BzV but formed an inclusion complex in the reduced state. However, with β-CD, since BzV forms an inclusion complex in both the oxidized and the reduced states, a CE scheme could predominate in the system.

Since CyV is considered to form an inclusion complex in both the oxidized and the reduced states a CE scheme predominates in the systems.

It was confirmed that cyclic voltammetry was an excellent method for studying the electrochemical behaviour of an inclusion complex.

Acknowledgements

The authors wish to express their sincere thanks to Prof. Ohta and Dr Kamiya of Yokohama National University for their helpful advice.

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