

# Electrochromic properties of alkyviologen-cyclodextrin systems

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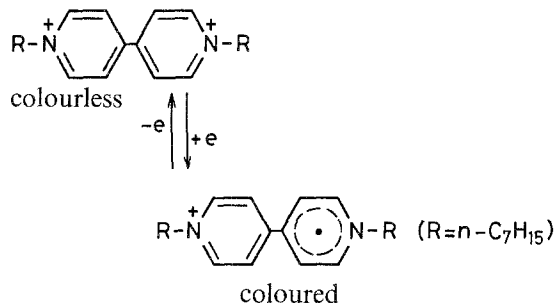
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Electrochromic properties of methyl, ethyl, n-hexyl and n-heptyl viologens, and  $\alpha$ -,  $\beta$ -,  $\gamma$ -cyclodextrin systems were studied using cyclic voltammetry and absorption spectroscopy. Colourations of red-violet ( $\lambda_{\max} = 530$  or  $560$  nm), blue ( $\lambda_{\max} = 600$  nm) and light purple ( $\lambda_{\max} = 560$  and  $600$  nm) could be obtained by changing the length of the alkyl chain of viologens or the radius of cyclodextrin. The intermolecular interaction between viologen radicals is weakened when the radicals form inclusion complexes so the blue colour inherent in the monomer of viologen radical appears. The red-violet colour is ascribed to the dimer of the reduced viologen. With the addition of  $\gamma$ -cyclodextrin, viologens were found to be included as dimer. The light purple colour is ascribed to the mixed colour of the monomer and the dimer. Furthermore, since the ratio of monomer and dimer depends upon the concentration of cyclodextrin, any colour between the red-violet of the dimer and the blue of the monomer can be obtained by adjusting the concentration of cyclodextrin. The redox reaction of an inclusion complex was found to depend upon the length of the alkyl viologen and the size of the cavity in cyclodextrin.

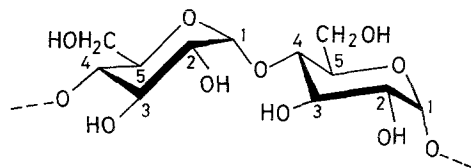
## 1. Introduction

Although various in-depth studies of the application of n-heptyl viologen, Heptyl V (see below), to an electrochromic display (ECD) have been made,



Heptyl V is not yet available for practical use because a 'residue' is produced on the electrode during repeated redox reactions [1]. The formation of the residue is caused by the crystallization brought about by the strong intermolecular interaction between viologen mono-cation radicals. To weaken the intermolecular interaction it is necessary for viologen molecules to be

separated from each other by some distance. For this purpose it may be possible to form an inclusion complex between viologen and cyclodextrin (CD). As is well known, cyclodextrin is a host molecule which has its own cavity and can form various kinds of inclusion complexes [2]. The nomenclature of CD is based on the number of 1,4-glucopyranose rings (see structure below): six for  $\alpha$ , seven for  $\beta$ , eight for  $\gamma$ , etc. The cavity is known to be hydrophobic.



With the addition of CD it was found that colours varied depending upon the size of the CD cavity and the length of the alkyl viologen. In addition to red-violet, blue is now available. Furthermore, the number of repeated colouring-erasing cycles increased by more than ten times.

In this report a spectroelectrochemical study of the relationship between the length of the

alkyl chain of the viologen and the size of the cavity in cyclodextrin in alkyl viologen-cyclodextrin systems, and the mechanisms of the redox reactions of inclusion complexes are reported.

## 2. Experimental details

### 2.1. Reagents

Methyl, ethyl, n-hexyl and n-heptyl viologens (abbreviated as Methyl V, Ethyl V, Hexyl V and Heptyl V, respectively) were supplied by the Japanese Research Institute for Photosensitizing Dyes Co. Ltd and were used without further purification. All viologens were dibromide salts. Cyclodextrins were GR grade supplied by Tokyo Kasei Co. Ltd. Distilled water was used as the solvent and the aqueous solutions were deoxygenated by having nitrogen passed through them.

### 2.2. Instrumentation

The instruments for monitoring cyclic voltammetry were described in a previous report [1]. The cell system for monitoring absorption spectra is shown in Fig. 1. The counter electrode was a platinum plate, 2.5 times larger than the indium-tin oxide working electrode, and the reference electrode was Ag/AgCl. In order to obtain the precise spectra of the reduced state, repeated redox reactions were made according to the potential diagram shown in Fig. 2, and the

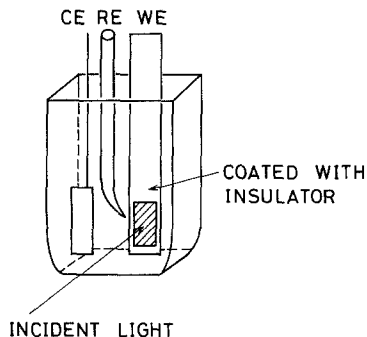


Fig. 1. Monitoring cell system. The shaded portion of the electrode is indium-tin oxide and other parts are coated with an insulator such as  $\text{SiO}_2$ . This cell was set in the sample beam position of the double-beam monochrometer. CE, Counter electrode, RE, reference electrode; WE, working electrode.

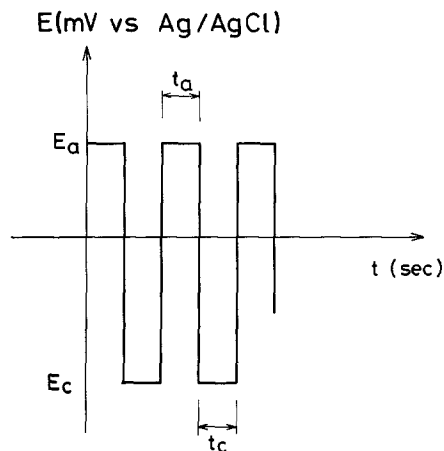


Fig. 2. Potential diagram for monitoring the absorption spectra of the reduction states of the viologens. For Methyl V and Ethyl V:  $E_a = +500$  mV;  $E_c = -850$  mV. For Hexyl V and Heptyl V:  $E_a = +500$  mV;  $E_c = -750$  mV vs Ag/AgCl;  $t_a = t_c = 2$  s.

absorption spectra of the redox state were obtained by tracing the envelope of the spectra.

## 3. Results and discussion

### 3.1. Effect of length of alkyl chain of viologen and radius of cyclodextrin on spectroscopic characteristics

The colours brought about by variations in the length of the alkyl viologen and the size of the cavity in cyclodextrins are shown in Table 1. In these systems, the ratio of viologen to CD was 1 to 3. The colours in Table 1 can also be obtained with a ratio of 1 to 2, but this appears to be the approximate minimum ratio. Potassium ferrocyanide was added as an auxiliary redox system and sodium hypophosphite as an electrolyte [1]. With the addition of  $\alpha$ -CD to Methyl V and Ethyl V, which have shorter alkyl chains, no colour change was observed, but with the addi-

Table 1. Colour changes of viologen-cyclodextrin systems

	Methyl V	Ethyl V	Hexyl V	Heptyl V
No CD	LP	LP	RV	RV
$\alpha$ -CD	LP	LP	B	B
$\beta$ -CD	B	B	B	B
$\gamma$ -CD	RV	RV	RV	RV

LP, Light purple; B, blue; RV, red-violet.

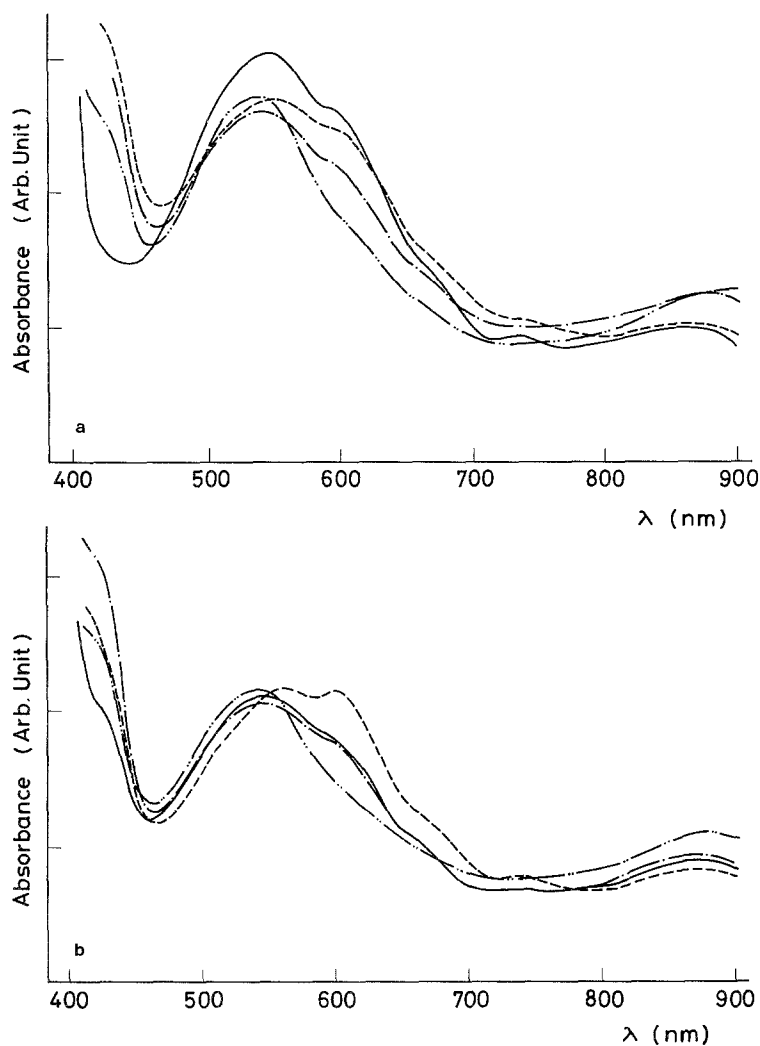


Fig. 3. (a) Absorption spectra of the reduced states of Methyl V (—), Methyl V/ $\alpha$ -CD (---), Methyl V/ $\beta$ -CD (···) and Methyl V/ $\gamma$ -CD (-·-·) systems. (b) Absorption spectra of the reduced states of Ethyl V (—), Ethyl V/ $\alpha$ -CD (---), Ethyl V/ $\beta$ -CD (···) and Ethyl V/ $\gamma$ -CD (-·-·) systems. Methyl V and Ethyl V,  $0.01 \text{ mol dm}^{-3}$ ;  $\alpha$ ,  $\beta$ ,  $\gamma$ -CD,  $0.03 \text{ mol dm}^{-3}$ ;  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $0.01 \text{ mol dm}^{-3}$ ;  $\text{NaH}_2\text{PO}_2$ ,  $0.25 \text{ mol dm}^{-3}$ .

ion of  $\beta$ -CD the colour changed to blue, and red-violet appeared when  $\gamma$ -CD was added.

These colour changes were investigated spectroscopically. The absorption spectra of Methyl V and Ethyl V are shown in Fig. 3a and 3b, respectively. In Fig. 3a, when the system was without CD, because the band at  $600 \text{ nm}$  ascribed to the viologen monomer and the band at  $560 \text{ nm}$  ascribed to dimer appeared [3, 4], the monomers and the dimers are in equilibrium. Light purple, which is a mixture of the blue of the monomer and the red-violet of the dimer, appeared. With the addition of  $\alpha$ -CD, the spectrum was exactly the same as the spectrum without CD. With the addition of  $\beta$ -CD, however, the ratio of the monomer to the dimer increased. With the addition of  $\gamma$ -CD the band of the

monomer disappeared completely and only the band of the dimer remained. In Ethyl V in Fig. 3b the above changes in the spectra appeared more clearly. In the Methyl V and the Ethyl V systems  $\alpha$ -CD does not seem to form an inclusion complex with Methyl V and Ethyl V, while  $\beta$ -CD may include the monomer and  $\gamma$ -CD may include the dimer.

In the case of Hexyl V and Heptyl V, which have longer alkyl chains, red-violet appeared in the reduced state without CD, as is shown in Table I. With the addition of  $\alpha$ -CD, blue appeared. The absorption spectra of the Hexyl V and the Heptyl V systems are shown in Fig. 4a and 4b, respectively. In the Hexyl V system the spectrum without CD coincides with the spectrum with  $\gamma$ -CD except the intensity of the band

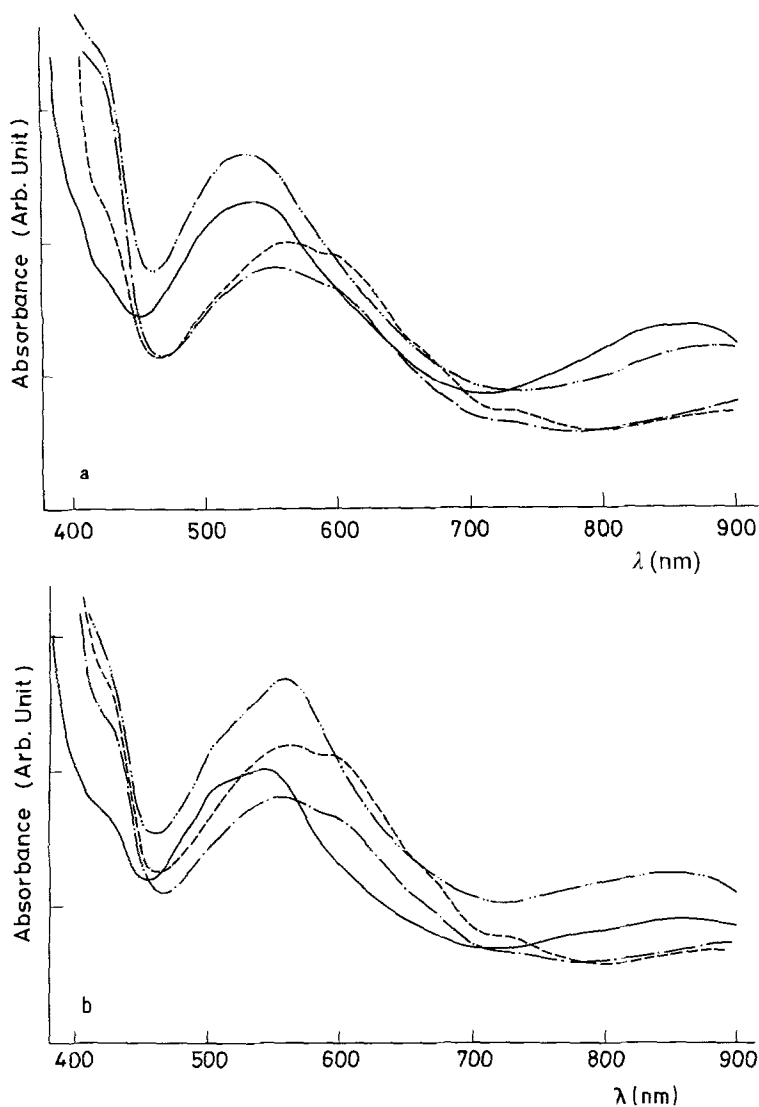


Fig 4. (a) Absorption spectra of the reduced states of Hexyl V (—), Hexyl V/ $\alpha$ -CD (---), Hexyl V/ $\beta$ -CD (-·-·-) and Hexyl V/ $\gamma$ -CD (····) systems. (b) Absorption spectra of the reduced states of Heptyl V (—), Heptyl V/ $\alpha$ -CD (---), Heptyl V/ $\beta$ -CD (-·-·-) and Heptyl V/ $\gamma$ -CD (····) systems. Hexyl V and Heptyl V,  $0.01 \text{ mol dm}^{-3}$ . Other concentrations are the same as in Fig. 3.

at 510 nm. The band at 600 nm indicates that blue colouration occurs with the addition of  $\alpha$ -CD. The intensity of the band at 600 nm is stronger with the addition of  $\beta$ -CD than with the addition of  $\alpha$ -CD. In the Heptyl V system shown in Fig. 4b, without CD, the absorption maximum shifted toward the shorter wavelength with the addition of ferrocyanide. The absorption maximum is 560 nm when ferrocyanide is eliminated. This seems to be caused by the forming of a charge-transfer complex between Heptyl V and ferrocyanide, even on the electrode [5, 6]. With the addition of  $\alpha$ -CD or  $\beta$ -CD the same changes as in the Hexyl V system were observed. The intensity of the band at 600 nm is stronger

with the addition of  $\beta$ -CD than with the addition of  $\alpha$ -CD. In order to obtain a high-contrast blue,  $\beta$ -CD was found to be superior to  $\alpha$ -CD.

To confirm that the cavity of CD was responsible for the above changes in the absorption spectra, methyl- $\alpha$ -glucoside was introduced as a model of 1,4-glucopyranose which was a unit of CD ring. The concentration of methyl- $\alpha$ -glucoside was adjusted to that of 1,4-glucopyranose, after which blue appeared; that is, the ratio of Hexyl V:methyl- $\alpha$ -glucoside was equal to 1:14, which corresponded to a ratio of Hexyl V: $\beta$ -CD of 1:2. In these conditions the colour of the Hexyl V/methyl- $\alpha$ -glucoside system was red-violet and the contrast of the display was

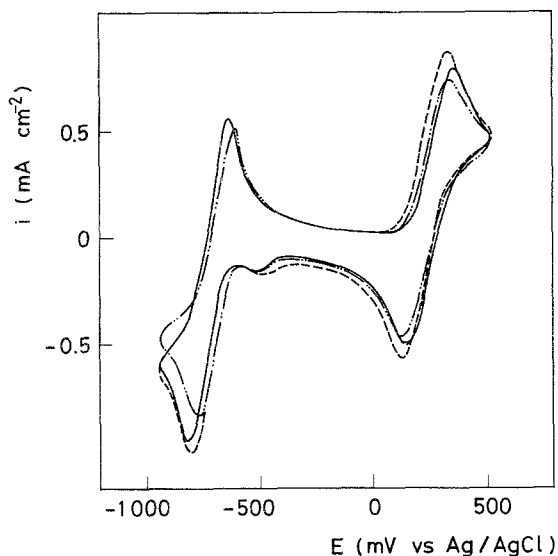


Fig. 5. Cyclic voltammograms of the Ethyl V systems, without CD (—), with  $\beta$ -CD (---) or with  $\gamma$ -CD (-.-.). The conditions are the same as in Fig. 3. Scan rate, 30 mV s<sup>-1</sup>.

extremely low. This suggests that the cavity in CD is responsible for the spectral changes.

### 3.2. Cyclic voltammetry of viologen and cyclodextrin systems

Cyclic voltammograms of the Ethyl V systems are shown in Fig. 5. The redox wave in the negative potential region is ascribed to Ethyl V<sup>2+</sup> → Ethyl V<sup>+</sup>, while the redox wave in the positive region is ascribed to Fe(CN)<sub>6</sub><sup>4-/3-</sup>. The voltammograms change with the addition of CD as follows. With the addition of  $\alpha$ -CD no change was observed; with the addition of  $\beta$ -CD the peak potential of the reduction ( $E_{pc}$ ) of Ethyl V<sup>2+</sup> shifted in the positive direction; with the addition of  $\gamma$ -CD the peak potential of the reduction also shifted in the positive direction. These shifts suggest an EC mechanism in which a chemical reaction follows after an electrochemical reaction [7]. In the Methyl V systems the changes in the voltammograms are the same as in the Ethyl V systems except for the positive shift of  $E_{pc}$  with the addition of  $\beta$ -CD. In the Methyl V/ $\beta$ -CD system only a small positive shift of the rising point of the potential of the reduction was observed. With the addition of  $\alpha$ -CD no changes were observed in the voltammograms as well as in the absorption spectra

for the Methyl V and the Ethyl V systems. This supports the hypothesis that an inclusion complex is not formed when  $\alpha$ -CD is added. Furthermore, the lack of change in the voltammograms indicates that there is no change in viscosity when CD is added [8].

To determine whether or not Methyl V and  $\beta$ -CD form an inclusion complex in the oxidized state, <sup>1</sup>HNMR spectra of  $\beta$ -CD and  $\beta$ -CD/Methyl V systems were investigated. <sup>1</sup>HNMR is known to be an excellent method of determining the existence of an inclusion complex in CD [9]. The result was that no change in the <sup>1</sup>HNMR spectrum of  $\beta$ -CD with the addition of Methyl V was observed. The same result was also obtained by Kamiya *et al.* [10]. Since a methyl substituent is a short chain, <sup>1</sup>HNMR must be changed by the interaction between the bipyridine ring and  $\beta$ -CD if an inclusion complex is to be formed [9]. We consider that Ethyl V<sup>2+</sup> (or Methyl V<sup>2+</sup>) accepts an electron on the electrode, after which the hydrophobicity of the bipyridine ring is increased and finally Ethyl V<sup>+</sup> is included in the hydrophobic cavity of  $\beta$ -CD.

Fig. 6 shows the cyclic voltammograms of the Heptyl V systems. With the addition of  $\alpha$ -CD

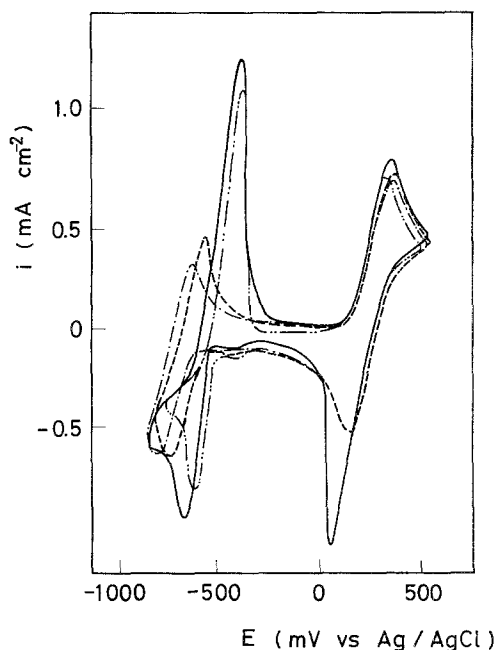


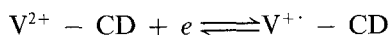
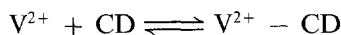
Fig. 6. Cyclic voltammograms of the Heptyl V systems, without CD (—), with  $\alpha$ -CD (---), with  $\beta$ -CD (-.-.) or with  $\gamma$ -CD (-.-.-). The conditions are the same as in Fig. 4. Scan rate, 30 mV s<sup>-1</sup>.

and  $\beta$ -CD, the peak potential of the reduction ( $E_{pc}$ ) of Heptyl  $V^{2+}$  shifted in the negative direction and the peak current of the reduction ( $i_{pc}$ ) decreased. The negative shift of  $E_{pc}$  indicates that a CE mechanism has occurred; that is, a mechanism in which a chemical reaction has preceded an electrochemical reaction [7]. The decrease in  $i_{pc}$  is considered to be caused by the decrease in the diffusion constant in the oxidation state. This suggests the formation of an inclusion complex in the oxidation state of Heptyl V. With the addition of  $\gamma$ -CD,  $E_{pc}$  shifted toward the positive potential. This suggests that there is a EC mechanism in the Heptyl V/ $\gamma$ -CD system. The same changes were observed in Hexyl V/CD systems.

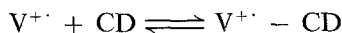
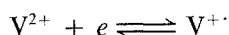
### 3.3. Types of redox reactions in alkyl viologen-cyclodextrin systems

The following three types of redox reactions can be seen in alkyl viologen and cyclodextrin systems:

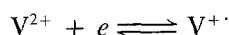
Type I



Type II



Type III



Type I is a CE mechanism, Type II is an EC mechanism and Type III involves only an elec-

trochemical reaction. In cyclic voltammograms a positive shift of the reduction peak indicates an EC mechanism, while a negative shift indicates a CE mechanism [7]. The changes in the absorption spectra previously described indicate the formation of an inclusion complex in the reduced state of the viologen. Table 2 shows the reaction types and whether or not they form an inclusion complex.

In the case of Methyl V and Ethyl V, which have short alkyl chains, no changes were observed in the cyclic voltammogram or in the absorption spectrum with the addition of  $\alpha$ -CD. Methyl V (or Ethyl V) does not seem to form an inclusion complex in either the reduced or oxidized state; therefore it is type III. In  $\beta$ -CD or  $\gamma$ -CD systems the positive shift of  $E_{pc}$  indicates an EC mechanism, and changes in the absorption spectra suggest the formation of an inclusion complex in the reduced state. Furthermore, in the  $\gamma$ -CD system, the fact that only the band from the dimer appeared indicates an inclusion of viologen dimer in the reduced state. In Hexyl V or Heptyl V the negative shift of  $E_{pc}$  on the cyclic voltammogram indicates a CE mechanism, in which an inclusion complex forms in the oxidized state and then accepts an electron. Therefore, Type I should predominate in the system with the addition of  $\alpha$ -CD or  $\beta$ -CD. In the  $\gamma$ -CD system the positive shift of  $E_{pc}$  indicates an EC mechanism and the appearance of the band of the dimer and the disappearance of the band of the monomer indicate the inclusion of a dimer of viologen. Therefore, Type II should predominate.

Using Raman and NMR spectroscopy, it was established that an inclusion complex was formed in the Heptyl V/ $\beta$ -CD system: the inclusion site was at the alkyl chain in the oxidized state, while in the reduced state the inclusion site moved to

Table 2. Inclusion complex and reaction types

	Methyl V, Ethyl V			Hexyl V, Heptyl V		
	Oxidation	Reduction	Type	Oxidation	Reduction	Type
$\alpha$ -CD	×	×	III	○	○	I
$\beta$ -CD	×	○	II	○	○	I
$\gamma$ -CD	×	○	II	×	○	II

○, Forming inclusion complex; × not forming inclusion complex.

the bipyridine ring position [11]. It has been reported that some length of alkyl chain is needed in order to form an inclusion complex [12]. It follows that the Ethyl V (or Methyl V)/ $\alpha$ -CD system does not form an inclusion complex. That  $\beta$ -CD includes the alkyl chain of Heptyl V in the oxidation state and that Ethyl V (or Methyl V) does not form an inclusion complex even in the reduced state suggests that in the Heptyl V (or Hexyl V)/ $\alpha$ -CD system, the inclusion site is confined to the alkyl chain even in the reduced state; that is, the cavity in  $\alpha$ -CD is not big enough to include the bipyridine ring.

#### 4. Conclusions

The colouration and number of redox cycles of alkyl viologen systems were found to be greatly improved with the addition of  $\alpha$ -,  $\beta$ - or  $\gamma$ -CD. In the alkyl viologen and cyclodextrin system, the formation of an inclusion complex was found to depend upon the length of the alkyl chain, the size of the cavity, and the redox state of the viologen. The existence of an inclusion complex in the reduced state was confirmed by absorption spectroscopy. An  $E_{pc}$  shift in the cyclic voltammetry was used to determine whether the chemical reaction occurs before or after the electrochemical reaction. Three types of mech-

anisms are proposed. The type of redox reaction of the viologen-CD system depends upon whether an inclusion complex is formed in the oxidized state (CE mechanism) or in the reduced state (EC mechanism).

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