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γ-Cyclodextrin-Enhanced Dimerization of Viologen Radicals

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Abstract. The effects of cyclodextrins (CDs) on the monomer-dimer equilibria of 1,1′-dialkylviologen radical cations ($C_nC_nV^{\cdot+}$: n = 1–5) and one-electron reduced 1,1′-bis(3-sulfopropyl)viologen (SPV) were investigated spectroelectrochemically. The dimerization is enhanced upon addition of γ-CD, while the addition of α-CD and β-CD suppresses the dimerization. This is attributed to the stabilization of dimers by the inclusion of the dimer in the cavity of γ-CD. From the dependence of the apparent dimerization constants (K'_D) on the concentration of γ-CD, the association constants of the monomer (K_{C1}) and dimer (K_{C2}) with γ-CD were determined. The K_{C1} value increases slightly, from 5 M^{-1} for n = 1 to 35 M^{-1} for n = 5, as the length of the alkyl substituents of viologen increases. The K_{C2} value depends strongly on the alkyl substituents giving the smallest value of 85 M^{-1} for $(SPV^{\cdot-})_2$ and the largest one of 3500 M^{-1} for $(C_4C_4V^{\cdot+})_2$. These results, together with the difference in UV-vis absorption spectra obtained in the absence and in the presence of γ-CD, suggest that the alkyl substituents and part of the bipyridine ring of viologen radicals are included in the γ-CD cavity forming dimers in which the bipyridine rings are stacked at an oblique angle.

Key words: γ-Cyclodextrin, dimerization, viologen, inclusion complexes, association constants, spectroelectrochemistry.

1. Introduction

Cyclodextrins (CDs) have generated great interest because of their ability to form inclusion complexes with a variety of organic molecules by admitting the guests into their hydrophobic cavities [1, 2]. The cavity size of γ-CD is large enough to include two guest molecules [3, 4]. Because of this property, γ-CD can be used as a molecular vessel in which interactions and reactions between two guest molecules are facilitated [4–7].

1,1′-Disubstituted-4,4′-bipyridinium salts (viologens: V^{2+}) are very attractive materials as electron mediators in various types of redox reaction systems, herbicides and electrochromic displays [8]. Most of the reported applications of viologens have been focused on the blue viologen radical cations ($V^{\cdot+}$) which can be generated from the colorless viologen dication (V^{2+}) via one-electron reduction. $V^{\cdot+}$ is also known to dimerize in aqueous media as shown in the following equation [5, 9–24].

$$2V^{\cdot+} \rightleftharpoons (V^{\cdot+})_2 \quad K_D = [(V^{\cdot+})_2]/[V^{\cdot+}]^2 \tag{1}$$

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where K_D is the equilibrium constant for the monomer–dimer equilibrium. Absorption spectroscopy has frequently been used to study dimerization since the spectrum of the dimer can be distinguished from that of the monomer. However, quantitative study of the dimerization has been mainly confined to the dimethylviologen radical cation ($C_1C_1V^{\cdot+}$), where the reported K_D value is in the range of 380–840 M^{-1} [9, 11, 12, 20].

It was found that the addition of CDs shifts the position of the monomer–dimer equilibrium of viologen radical cations by formation of inclusion complexes with the radical monomer or dimer [5, 13, 15–17, 21, 23, 24]. The effects of CDs on the dimerization depend on the substituents of the viologens and the cavity size of the CD. It seems well established that α- and β-CD suppress the formation of the dimer by inclusion of the alkyl chains of viologens in the cavity of the CDs. Electrochemical and spectroelectrochemical studies indicated that γ-CD facilitates the dimerization of viologen radical cations presumably due to inclusion of the dimers into γ-CD [5]. However, little is known about the association constants between the dimer of the viologen radical cation and γ-CD as well as the structure of the inclusion complexes.

In previous papers we have reported the dependence of the dimerization constants of unsymmetric viologen radical cations on the length of the alkyl chains [24] and the effects of α and β-CD on the dimer formation [21, 24]. We also presented facile dimerization of the viologen radical cations covalently bonded to β-CD [23]. In the present study we have investigated the effects of γ-CD on the monomer–dimer equilibria of di-n-alkylviologen radical cations ($C_nC_nV^{\cdot+}$: n = 1–5) and one-electron reduced 1,1′-bis(3-sulfopropyl)viologen (SPV) using a spectroelectrochemical technique. The association constants of the monomer (K_{C1}) and dimer (K_{C2}) with γ-CD were obtained from plots of the apparent dimerization constants (K'_D) against the concentration of γ-CD. The γ-CD-enhanced dimer formation and the structural features of the dimer–γ-CD inclusion complexes are shown.

2. Experimental

2.1. MATERIALS

The viologens used are halides of 1,1′-di-n-alkyl-4,4′-bipyridinium cation ($C_nC_nVX_2$: n = 1–5) and the inner salt of 1,1′-bis-(3-sulfopropyl)-4,4′-bipyridinium (SPV). $C_1C_1VCl_2$ and $C_2C_2VBr_2$ were obtained from Aldrich and SPV was purchased from Molecular Probes. They were used as received. $C_3C_3VBr_2$, $C_4C_4VBr_2$ and $C_5C_5VCl_2$ were prepared by a literature procedure [8] starting from 4,4′-bipyridine (Aldrich) and an excess amount of the corresponding 1-bromoalkanes (Tokyo Kasei). CDs were obtained from Aldrich. Solutions were prepared from reverse osmosed water which was further purified by passage through a Millipore purification train.

2.2. Apparatus and Methods

The concentrations of viologens in solutions were calculated from absorption data using $\epsilon_{262\text{nm}} = 21\ 000\ \text{M}^{-1}\ \text{cm}^{-1}$ [25]. The concentrations of γ-CD solutions were calculated from optical rotation data using $[\alpha]_{\text{D}}^{25} = 177.4°$ [1]. All solutions contained 0.1 M KCl as supporting electrolyte. The spectroelectrochemical cell was assembled using a cover of a demountable rectangular cell (light path length: 100 μm, Uvonic Cuvettes) and a piece of indium tin oxide (ITO) coated glass (Delta Technologies). The assembled cell was clipped to maintain a reproducible light path length as described previously [24]. Electrolysis of viologen to produce viologen radicals was achieved by application of a potential to the ITO working electrode, which was controlled appropriately for $1 - e^-$ reduction of viologen with an AFRDE5 bipotentiostat (Pine Instruments) [24]. A Hewlett-Packard 8452A diode array spectrophotometer with a data acquisition time of 1 second was used to obtain absorption spectra of the reduced viologen. The solution prior to electrolysis was used as a blank.

3. Results and Discussion

3.1. Effects of CDs on UV-vis Absorption Spectral Behavior of One-Electron Reduction Products of Viologens

The shifts in the position of the monomer–dimer equilibria of viologen radicals by the addition of CDs cause changes in the UV-vis absorption spectrum because of a large difference in the spectra of the monomer and the dimer. The absorption spectrum of the monomer of $1 - e^-$ reduced viologen shows absorption maxima at 367, 385, 396, and 602 nm of which the absorbance ratio is 1.0 : 1.7 : 2.5 : 0.84 [15–24, 25, 26], whereas that of the dimer exhibits absorption maxima near 360 and 520 nm with the absorbance ratio of 2.4 : 1.0 [10, 18–24].

Electrolysis of viologen solutions at ca. −0.8 V vs. Ag/AgCl results in $1 - e^-$ reduction of viologens and exhaustive reduction is achieved after ca. 2 min [24]. Absorption spectra of the reduction products were taken after >3 min electrolysis. Figure 1 shows the effect of CDs on the absorption spectrum of $1 - e^-$ reduction products of $C_1C_1V^{2+}$. The spectrum taken in the absence of CDs (spectrum 1a) shows the presence of the $C_1C_1V^{\cdot+}$ monomer as well as its dimer. Addition of 15 mM α-CD (spectrum 1b) causes little spectral change confirming that α-CD is not effective in suppression of the dimer formation due to the poor binding affinities of $C_1C_1V^{\cdot+}$ monomer to α-CD [24]. A small but noticeable increase is observed in absorbances at 396 and 602 nm with 15 mM β-CD with concomitant decreases in absorbances near 360 and 520 nm (spectrum 1c). This is interpreted as suppression of the dimer formation by the inclusion of part of the bipyridine ring into the β-CD cavity [5, 21, 24]. A large decrease in monomer peaks (396 and 602 nm) and increase in dimer peaks (360 and 520 nm) are observed on addition of 18 mM γ-CD (spectrum 1d). This is attributed to the stabilization of the dimer

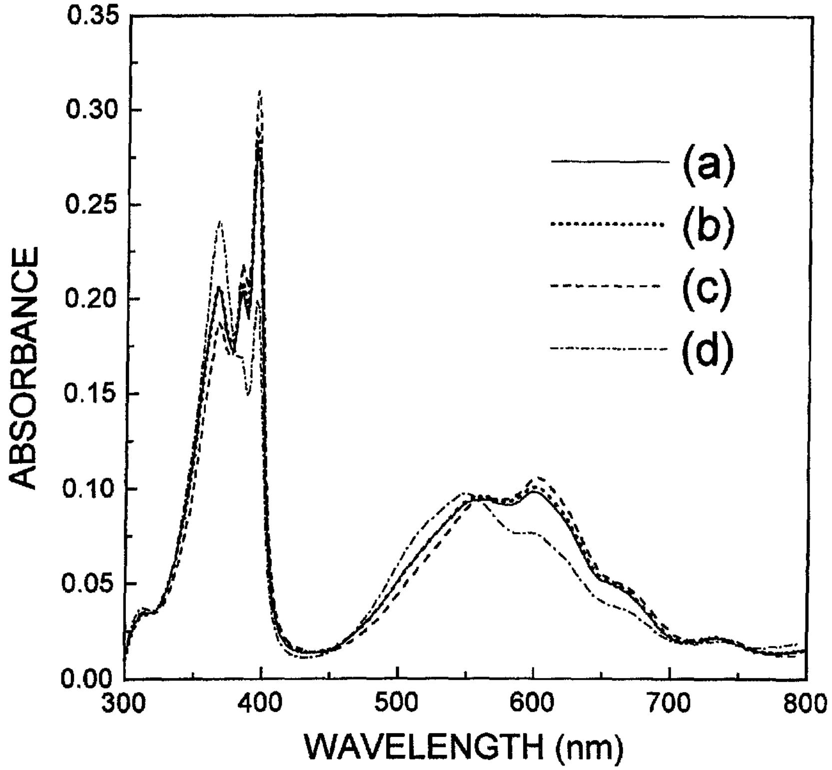


Figure 1. Absorption spectra of 1 − e^- reduced $C_1C_1V^{2+}$ using an ITO glass electrode taken at its potential of −0.8 V. In the absence of CDs (a, ——), and in the presence of 15 mM α-CD (b, · · ·), 15 mM β-CD (c, - - - - -), and 18 mM γ-CD (d, - · - · - ·). The light path length is 100 μm. Concentration of $C_1C_1V^{2+}$ is 1.0 mM in aqueous 0.1 M KCl.

by inclusion of the dimer in the cavity of γ-CD [5]. These results indicate that the dimer fits better into the γ-CD cavity than into the α- or β-CD cavity.

As the length of the alkyl substituents (C_n) increases, a more pronounced effect of CDs on the dimerization of $C_nC_nV^{\cdot +}$ is observed. Such alkyl chain dependence of the absorption spectra of 1−e^- reduction products of $C_nC_nV^{2+}$ is not observed in the absence of CDs. This is quite analogous to the observation of the insensitivity of the extent of dimerization of $C_1C_nV^{\cdot +}$ to the variation of the alkyl substituents when the alkyl substituent is shorter than nonyl [24]. Figure 2 shows the effects of α- and γ-CD on the absorption spectrum of $C_4C_4V^{\cdot +}$. In agreement with a previous report [24], the spectrum taken in the presence of 30 mM α-CD (spectrum 2b) is virtually that of the monomer. β-CD exhibited a similar effectiveness to α-CD for disruption of dimer formation. On the other hand, the spectrum obtained in the presence of 18 mM γ-CD (spectrum 2c) shows all the absorption characteristics of the dimer of the viologen radical cation [23] and only a hint of the presence of the monomer as a spike at 396 nm.

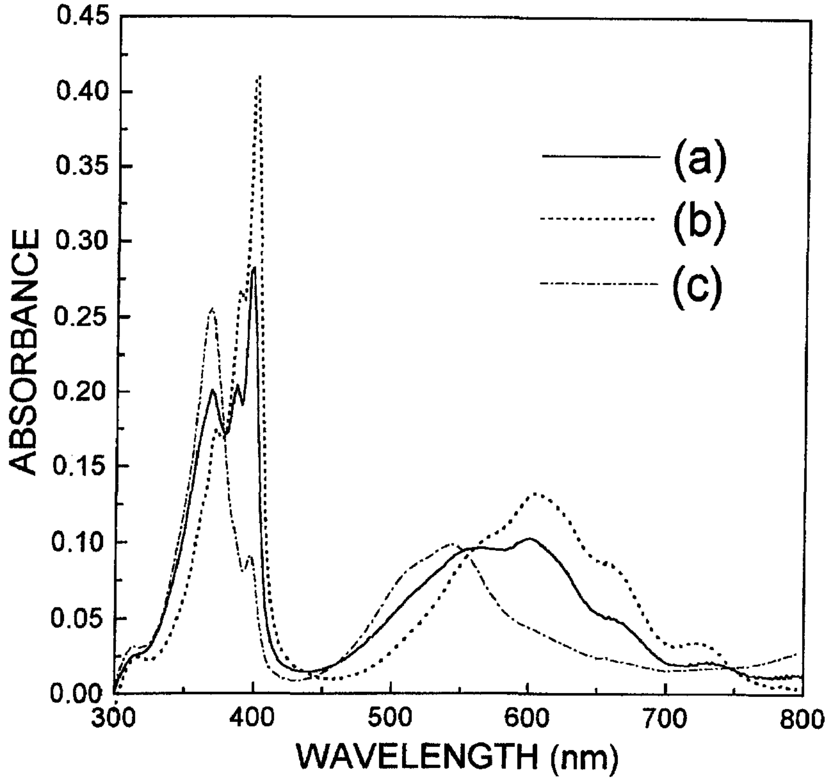


Figure 2. Absorption spectra of 1 − e^- reduced $C_4C_4V^{2+}$ in the absence of CDs (a, ——), and in the presence of 30 mM α-CD (b, · · ·) and 18 mM γ-CD (c, - · - · - ·). Other conditions are the same as in Figure 1.

Figure 3 compares the effect of γ-CD on the absorption spectra of $C_1C_1V^{\cdot+}$ and $C_4C_4V^{\cdot+}$. It is clearly seen that the addition of γ-CD enhances dimerization of viologen radical cations and the effect of γ-CD on the dimerization is much more pronounced for $C_4C_4V^{\cdot+}$ than for $C_1C_1V^{\cdot+}$.

3.2. ABSORPTION SPECTRA AND STRUCTURES OF DIMERS OF VIOLOGEN RADICALS

Each spectrum of the mixture of viologen radical monomer and dimer can be decomposed into monomer and dimer components by the linear combination of the respective spectra. For this we used absorption spectra taken at two different concentrations, e.g. 0.50 and 1.0 mM [27]. Since the spectrum taken at high viologen concentration contains a larger fraction of dimer than that taken at low concentration, the dimer spectrum of the viologen radical can be generated by subtracting the latter spectrum (multiplied by a factor) from the former spectrum. The multiplication factor is adjusted to make the 396 nm absorption disappear

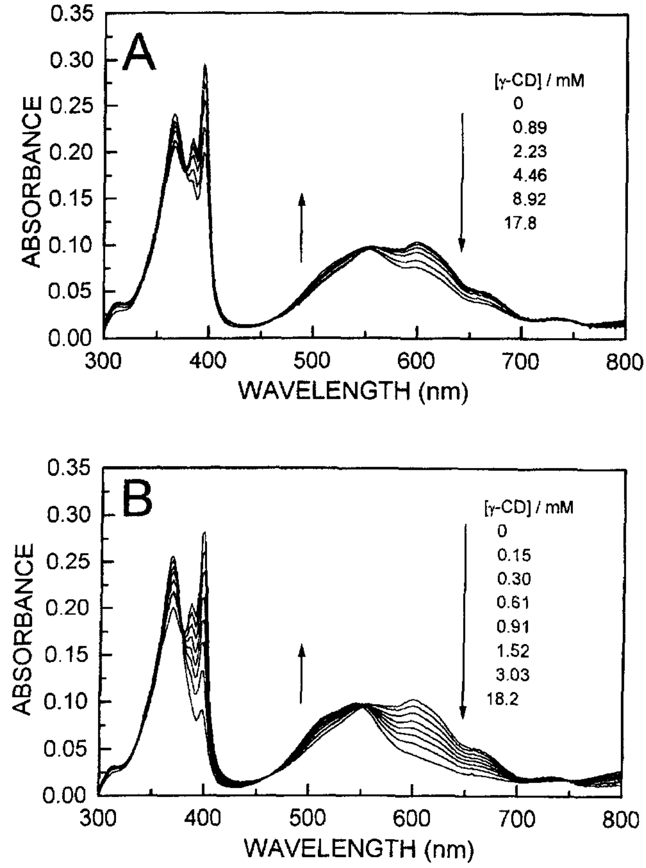


Figure 3. Effect of added γ-CD on the spectrum of $C_1C_1V^{\cdot+}$ (A) and $C_4C_4V^{\cdot+}$ (B). The concentrations of γ-CD are shown. Other conditions are the same as in Figure 1.

smoothly in the resulting spectrum. The resulting spectrum is that of the dimer in the mixture, but the absorbance scale is relative. The spectrum of monomer component in a mixture spectrum is obtained by subtracting the dimer spectrum (multiplied by a factor) from the mixture spectrum. Again, the multiplication factor is adjusted to make the resulting monomer spectrum indistinguishable from the reported monomer spectrum [23] in shape. An example of the result of spectral decomposition is shown in Figure 4 for $C_1C_1V^{\cdot+}$.

The monomer spectra of various viologen radical cations depend little on the nature of the alkyl substituents on the bipyridine ring and the presence of CDs. This agrees with our earlier findings that the absorption characteristics of viologen radical monomer do not vary significantly with the variation of the alkyl substituents and upon complexation with CDs [23, 24]. In the absence of γ-CD, the shape of the dimer spectrum does not depend on the alkyl substituents, either. However, the shape of the dimer spectrum obtained in the presence of γ-CD is noticeably

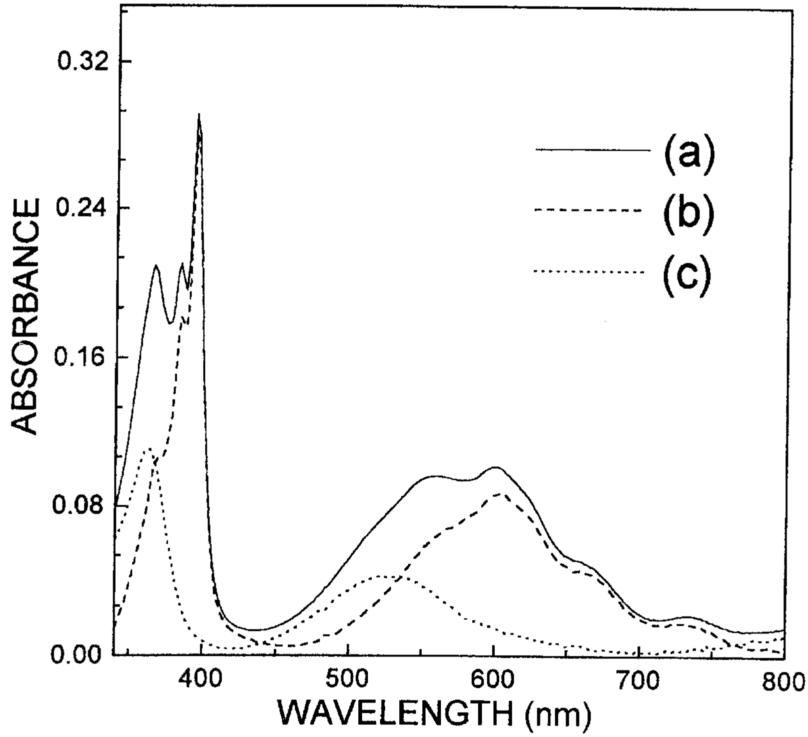


Figure 4. Separation of an absorption spectrum (a, ——) of $C_1C_1V^{\cdot +}$ into the monomer spectrum (b, - - - - -) and dimer spectrum (c, · · ·). The initial concentration of $C_1C_1V^{2+}$ was 1.07 mM. The concentrations of $C_1C_1V^{\cdot +}$ and $(C_1C_1V^{\cdot +})_2$ in the solutions were calculated to be 0.64 and 0.22 mM, respectively.

different from that obtained in the absence γ-CD. The largest alteration of the dimer spectrum was observed with $C_4C_4V^{\cdot +}$, which dimerizes nearly quantitatively in the presence of γ-CD. The comparison of the dimer spectra is shown in Figure 5.

Spectrum a in Figure 5 is the usual spectrum of dimers of viologen radicals. The same spectrum was observed for dimers of β-CD-appended viologen radical cations [23]. Spectra similar to spectrum b in Figure 5 were reported for radicals of bisviologens bridged by trimethylene or tetramethylene groups [26], or by *o*- or *m*-xylyl groups [28], which exhibit a strong tendency to intramolecular dimerization. However, bisviologens linked by longer polymethylene chains or a *p*-xylyl group form less stable dimers via intermolecular processes and the absorption spectrum of the dimers is similar to spectrum a [26, 28]. It is generally believed that the intermolecular dimer of viologen radicals exists in solution in a face-to face configuration involving overlap of the two π systems. CPK space filling models of the bisviologens which exhibit a strong tendency to intramolecular dimerization and give spectra similar to spectrum a indicate that the two viologen units in the dimers cannot stack in a completely cofacial configuration due to structural strain.

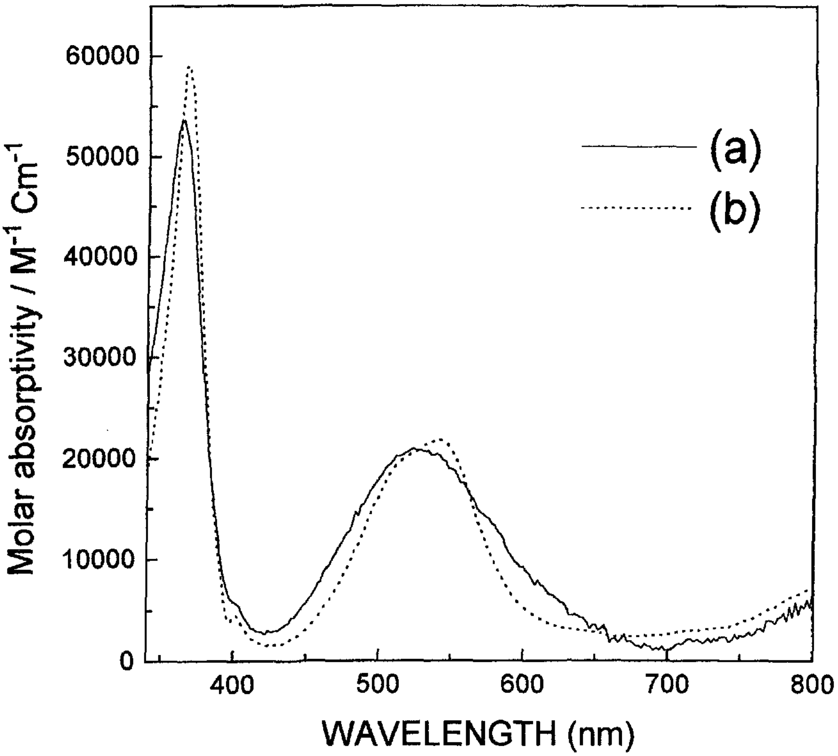
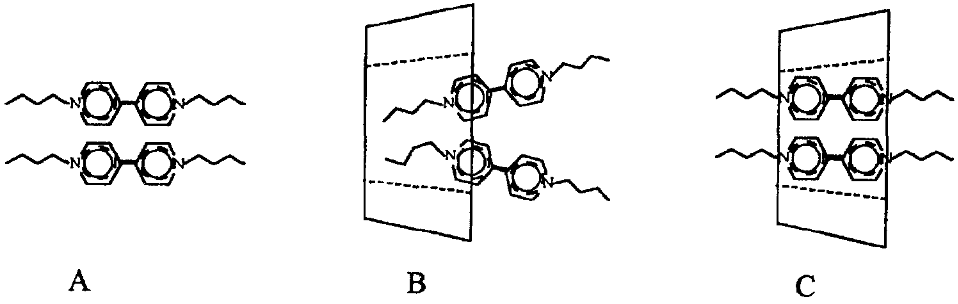


Figure 5. Comparison of the resolved dimer spectra of $C_4C_4V^{\cdot+}$ in the absence of γ-CD (a, ——) and in the presence of 18 mM γ-CD (b, - - - - - -).

This suggests a possibility that the viologen units in the dimers formed in the presence of γ-CD may not be completely cofacial.

Unlike the dialkyl viologens, little enhancement of dimerization by γ-CD is found for SPV radicals ($SPV^{\cdot-}$) (see below). Inclusion of propyl sulfonate groups of the viologen in cavities of CDs is highly disfavored by the large desolvation energy of the ionic groups [29]. Thus, γ-CD-enhanced dimerization of $SPV^{\cdot-}$ would be the result of inclusion of the two viologen units in the cavity of γ-CD and protrusion of the propyl sulfonate groups from the γ-CD cavity (see structure C in Scheme 1). The observation of a small effect of γ-CD on the dimerization of $SPV^{\cdot-}$ suggests that structure C is only weakly favored. This might be due to the hydrophilic character of the bipyridine moiety bearing a positive charge, though the charge is greatly delocalized. In connection with this, it is worthwhile mentioning that the full inclusion of $1 - e^-$ reduced bipyridine rings of the viologen radicals into the cavity of CD is not favorable, but a part of the bipyridine rings is inserted into the CD cavity in the viologen radical/β-CD complexes [5, 21, 24]. Based on these results, it can be reasonably assumed that the alkyl chains and only part of the bipyridine rings of dialkyl viologen radical cations are included in the γ-CD cavity



Scheme 1. Schematic representations of intermolecular dimers of viologen radicals in water (A) and in γ-CD cavities (B and C). Structure B is more favored than structure C. Charges are not shown.

to form a dimer with structure B in Scheme 1. The stacking of viologen units in a face-to-face configuration would be unfavorable due to steric hindrance and the positive charge of the bipyridine rings would be partially localized in the protruded portion of the rings. This view is supported by the absorption spectra.

3.3. DIMERIZATION CONSTANTS AND ASSOCIATION CONSTANTS OF THE DIMERS WITH γ-CD

The monomer–dimer equilibria of viologen radicals ($V^{\cdot+}$) in the presence of γ-CD can be represented by the following scheme: here, we do not consider formation of 2 : 2 complexes between γ-CD and viologen radicals since they would give a completely cofacial dimer whose presence is unlikely based on the spectral behavior described in Section 3.2.

$$\begin{tikzcd}[column sep=large] 2V^{\cdot+} \arrow[r, shift left, "K_D"] \arrow[d, shift left] & (V^{\cdot+})_2 \arrow[l, shift left] \arrow[r, shift left, "K_{C2,\gamma\text{-CD}}"] & (V^{\cdot+})_2\cdot\gamma\text{-CD} \arrow[l, shift left] \\ 2\quad V^{\cdot+}\cdot\gamma\text{-CD} \arrow[u, shift left, "K_{C1}\ \gamma\text{-CD}"] \arrow[r, shift left, "K'_{C1,2\gamma\text{-CD}}"] & V^{\cdot+}\cdot 2\gamma\text{-CD} \arrow[l, shift left] \end{tikzcd}$$

(2)

where K_D is the dimerization constants of viologen radicals defined in Equation (1). K_{C1} and K'_{C1} are the first and the second association constants of viologen monomer with γ-CD. K_{C2} is the association constant of viologen dimer with γ-CD.

$$K_{C1} = \frac{[V^{\cdot+}\cdot\gamma\text{-CD}]}{[V^{\cdot+}]\cdot[\gamma\text{-CD}]};\quad K'_{C1} = \frac{[V^{\cdot+}\cdot 2\gamma\text{-CD}]}{[V^{\cdot+}]\cdot[V^{\cdot+}\cdot\gamma\text{-CD}]} \tag{3}$$

$$K_{C2} = \frac{[(V^{\cdot+})_2\cdot\gamma\text{-CD}]}{[(V^{\cdot+})_2]\cdot[\gamma\text{-CD}]}. \tag{4}$$

The apparent dimerization constant (K'_D) in the presence of γ-CD is defined in Equation (5).

$$K'_D = \frac{[(V^{\cdot+})_2] + [(V^{\cdot+})_2 \cdot \gamma\text{-CD}]}{([V^{\cdot+}] + [V^{\cdot+} \cdot \gamma\text{-CD}] + [V^{\cdot+} \cdot 2\gamma\text{-CD}])^2}. \tag{5}$$

The K_D values are calculated from the monomer and dimer concentrations in their mixed solutions which do not contain CDs. For this, the concentration of monomer in a mixture was calculated from the decomposed absorption spectra (see Figure 4) by using $\epsilon_{M,602} = 1.4 \times 10^4\ M^{-1}\ cm^{-1}$ [23, 25, 30]. The concentrations of dimers were calculated from a relationship, [dimer] = $\{[\text{viologen}]_{\text{total}} - [\text{monomer}]\}/2$. The concentrations of dimer calculated by this method agree well with those determined from decomposed dimer spectra using a reported absorption coefficient of $2.1 \times 10^4\ M^{-1}\ cm^{-1}$ at 518 nm for the dimer [23] indicating that exhaustive electrolysis of viologens is achieved. The K_D values are summarized in Table I, which shows that the K_D values of dialkylviologen radicals depend little on the variation of the alkyl substituents of dialkyl viologen from methyl to pentyl. This is similar to our previous work [24] which showed that the K_D value of 1-methyl-1′-alkylviologen cation radical ($C_1C_nV^{\cdot+}$, $n < 8$) increases less than 30% when the alkyl substituents are varied from methyl to octyl. This confirms that the major driving force for the dimerization is π–π interaction between viologen units and the interaction between alkyl chains in the dimer contributes little to the stability of the dimer [24].

Since the UV-vis absorption spectra of uncomplexed and CD-complexed viologen radicals are the same [23, 24], the total concentration of viologen radical monomer, ($[V^{\cdot+}] + [V^{\cdot+} \cdot \gamma\text{-CD}] + [V^{\cdot+} \cdot 2\gamma\text{-CD}]$), is calculated from the decomposed monomer spectra obtained in the presence of γ-CD by using $\epsilon_{M,602} = 1.4 \times 10^4\ M^{-1}\ cm^{-1}$. The total concentration of dimer in the presence of γ-CD, ($[(V^{\cdot+})_2] + [(V^{\cdot+})_2 \cdot \gamma\text{-CD}]$) is then half of the value obtained by subtracting the total monomer concentration from the total viologen concentration. The K'_D values were determined using these concentrations at various concentrations of γ-CD and shown in Figure 6.

Rearrangement of Equation (5) using Equations (1), (3) and (4) gives Equation (6).

$$K'_D = K_D \frac{1 + K_{C2} \cdot [\gamma\text{-CD}]}{(1 + K_{C1} \cdot [\gamma\text{-CD}](1 + K'_{C1} \cdot [\gamma\text{-CD}]))^2}. \tag{6}$$

Since the alkyl chains of viologen monomer may bind independently with γ-CD, we can assume that K'_{C1} is $K_{C1}/2$. The K_{C1} and K_{C2} values were determined from the dependence of K'_D on [γ-CD] by nonlinear least-square regression analysis. In this analysis, we used K_D values (Table I) as a fixed parameter, and K_{C1} and K_{C2} values were used as fitting parameters. Initial K_{C1} and K_{C2} values were obtained by assuming that [γ-CD] is the same as the initial total concentration of γ-CD,

Table I. Monomer–dimer equilibrium constants (K_D) of viologen radicals and the association constants of the monomer (K_{C1}) and dimer (K_{C2}) with γ-CD in aqueous solutions containing 0.1 M KCl at 25 °C.[a,b]

Viologen radical	K_D/M^{-1}	K_{C1}/M^{-1}	K_{C2}/M^{-1}
$C_1C_1V^{\cdot+}$	530	5	210
$C_2C_2V^{\cdot+}$	560	16	880
$C_3C_3V^{\cdot+}$	530	25	2400
$C_4C_4V^{\cdot+}$	580	27	3500
$C_5C_5V^{\cdot+}$	560	35	1700
SPV	880	13	85

[a] The uncertainty of the K_D values is estimated to be ±15% based on the 5% uncertainty of the absorption coefficients of the viologen monomer and dimer [23] and 2% uncertainty of spectral deconvolution.

[b] The absolute uncertainty of the K_{C1} and K_{C2} values is about ±25%: ±15% from uncertainty of the K_D values and ±10% from parameter fitting. Thus we believe that the relative ratio of the equilibrium constants among viologens is correct within 20% uncertainty.

$[\gamma\text{-CD}]_{\text{initial}}$. The calculated K_{C1} and K_{C2} values were used to obtain improved concentrations of uncomplexed γ-CD, $[\gamma\text{-CD}]$, for each experimental point, and then the improved $[\gamma\text{-CD}]$ was used to obtain further improved K_{C1} and K_{C2} values. The fitted lines are shown in Figure 6. The smooth fitting of experimental data on Equation (6) indicates the validity of the complexation scheme given as Equation (2) and assumptions made to evaluate the equilibrium constants. The parameters obtained are given in Table I.

For $C_nC_nV^{\cdot+}$ (n = 1–5), K_{C2} values are 40–100 times larger than K_{C1} values. This reflects the large enhancement of dimerization upon addition of γ-CD. The K_{C1} values increase monotonically with the length of the alkyl chain, but the increment in K_{C1} values per methylene group is much less than the usual threefold increase, which was reported for association of surfactant molecules with β-CD [23, 31]. This might be due to the large cavity size of γ-CD so that the alkyl chains of viologens rattle around inside the cavity of γ-CD and contribute little to the stability of the inclusion complexes: the internal diameter and the depth of γ-CD are reported to be 0.85 and 0.70 nm, respectively [1]. The strong dependence of the K_{C2} values on the alkyl chain length of $C_nC_nV^{\cdot+}$ (n = 1–5), together with weak binding of $(SPV^{\cdot-})_2$ with γ-CD, can be taken as evidence that the alkyl chains are included in the cavity of γ-CD to form complexes depicted as structure B in Scheme 1. Interestingly, the K_{C2} value show maximum value with n-butyl substituents. The cavity volume of γ-CD is estimated to be 0.40 nm^3 from its dimension. This is large enough to accommodate two methyl and ten methylene

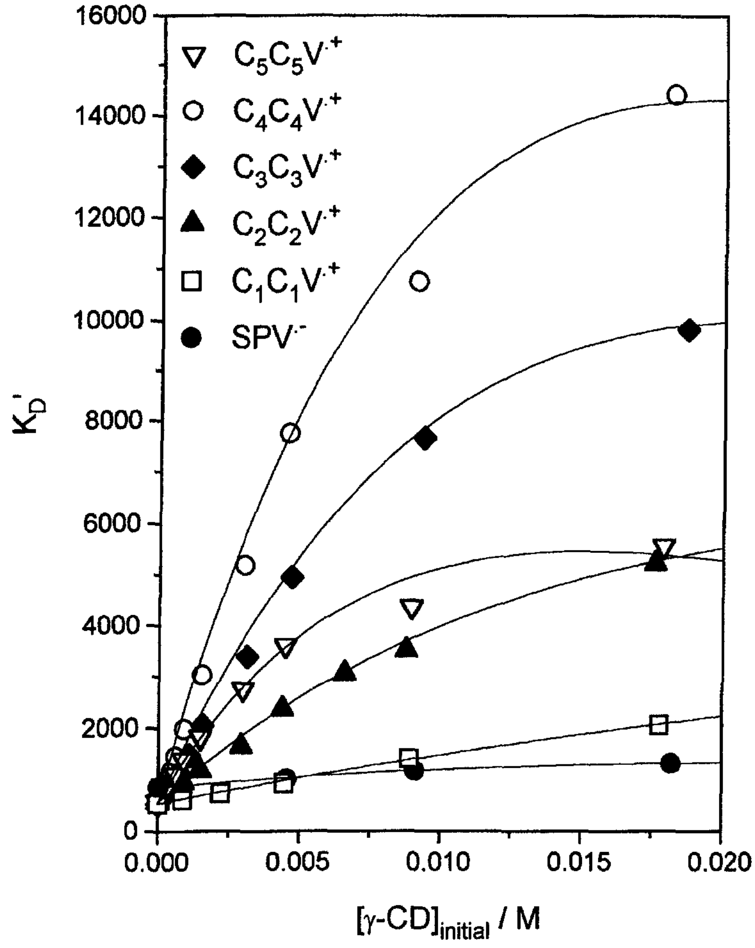


Figure 6. The plot of K_D' against initial concentrations of γ-CD, $[\gamma\text{-CD}]_{\text{initial}}$, for $C_nC_nV^{\cdot+}$ (n = 1–5) and $SPV^{\cdot-}$. Solid lines are the fitted lines according to Equation (6) using parameters in Table I.

groups, whose volume per group is 0.054 and 0.027 nm^3, respectively [29]. If only alkyl chains are included, we expect a higher binding affinity for $C_5C_5V^{\cdot+}$ than for $C_4C_4V^{\cdot+}$. Thus the observation of optimum affinity for $C_4C_4V^{\cdot+}$ can be attributed to inclusion of part of the bipyridine radical ring into the γ-CD cavity: a further increase in the length of the alkyl chain beyond butyl seems to result in steric hindrance between alkyl chains in the complexes and destabilization of the complexes. This agrees well with the conclusions derived from spectral properties of the dimer described in previous sections.

4. Conclusions

The monomer–dimer equilibria of viologen radical cations (($C_nC_nV^{\cdot+}$: n = 1–5) and one-electron reduced 1,1′-bis(3-sulfopropyl)viologen (SPV) were investigated spectro-electrochemically in the presence of CDs. In contrast to α-CD and β-CD, γ-CD enhances the dimerization of viologen radicals. The dimer spectrum obtained in the presence of γ-CD is different from that observed in the absence of γ-CD, but similar to those obtained with bisviologen radicals linked with short polymethylene chains or o- or m-xylyl groups. Analysis of the dependence of the apparent dimerization constants on the concentration of γ-CD gives the association constants of the monomer (K_{C1}) and dimer (K_{C2}) with γ-CD. The K_{C1} value increases slightly as the length of the alkyl substituents increases: 5 M^{-1} for n = 1 and 35 M^{-1} for n = 5. The K_{C2} values are 210, 880, 2300, 3500, and 1700 M^{-1} for $(C_nC_nV^{\cdot+})_2$ from n =1–5, respectively, and 85 M^{-1} for $(SPV^{\cdot-})_2$. The alkyl substituents and part of the bipyridine rings of the viologen radical dimers are included in the cavity of γ-CD and the bipyridine rings are stacked with an oblique angle in the dimer/γ-CD complexes.

Acknowledgments

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