# Complex Formation between Heptylviologen and Cyclodextrin

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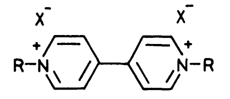
(Received January 24, 1986)

**Synopsis.** Complex formation between heptylviologen (**1**) and cyclodextrins (α and β) was confirmed indirectly. The absorption and circular dichroism (CD) spectra of *p*-nitrophenolate aqueous solution containing α- or β-cyclodextrin were changed, when **1** was added to the solution. Contrary to **1**, methylviologen (**3**) did not give the spectral changes.

Methylviologen (**3**) has been widely used as an electron mediator (a relay compound) for hydrogen formation[1-3] and fixation of carbon dioxide.[4,5] Recently attention has been directed to viologens possessing hydrophobic groups. For example, their inclusion complexes with cyclodextrin (CD$_x$) increase the stability of the pyridinium moiety of the viologens to hydrogenation,[6] and the viologens are promising for electrochromic display applications.[7] Okuno et al. have estimated the complex formation between hydrophobic viologen and CD$_x$ by the measurement of fluorescence quenching of excited $[Ru(bpy)_3]^{2+}$ by hydrophobic viologens.[6] In the case of viologens with aromatic groups, inclusion compounds can be detected by NMR and Raman spectroscopy, too.[6,7] For heptylviologen (**1**), however, the complex formation can not be detected by these spectroscopic analyses.[7]



**1** R = *n*-$C_7H_{15}$, X = Br
**2** R = $CH_2Ph$, X = Cl
**3** R = $CH_3$, X = Cl

As described above, the detection of the inclusion compounds for viologens having hydrophobic groups other than aromatic ones is not so easy. In the present study, we have indirectly confirmed the complex formation between **1** and CD$_x$ and estimated the dissociation constant.

## Experimental

Heptylviologen (**1**) (Aldrich Chemical Co.), benzylviologen (**2**) (Sigma Chemical Co.), methylviologen (**3**) (Nakarai Chemicals), α-CD$_x$ and β-CD$_x$ (Nakarai Chemicals), tri-*O*-methyl-β-CD$_x$(Funakoshi Chemicals), *p*-nitrophenol (p-NP) (Wako Pure Chemical Industries), and tris(2,2′-bipyridyl)-ruthenium(II) chloride (Strem Chemicals) were used as supplied.

Absorption, circular dichroism (CD) and fluorescence spectra were taken on a JASCO UVIDEC-1 spectrophotometer, a JASCO J-20 spectropolarimeter and a JASCO FP-4 fluorescence spectrophotometer, respectively, using 10 mm cells at room temperature. All measurements were carried out at pH 9.5 (0.1 mol dm$^{-3}$ $KHCO_3$–0.1 mol dm$^{-3}$ $Na_2CO_3$ buffer solution).

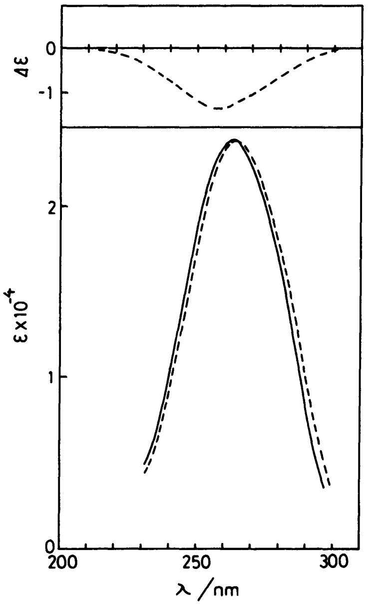


Fig. 1. Absorption and CD spectra of **1** (5×10$^{-5}$ mol dm$^{-3}$) at pH 9.5.
Absorption: α-CD$_x$ free (——); [α-CD$_x$]=4×10$^{-3}$ mol dm$^{-3}$ (---).
CD: [α-CD$_x$]=4×10$^{-3}$ mol dm$^{-3}$ (---).

## Results and Discussion

As shown in Fig. 1, the absorption band of **1** was slightly red-shifted upon addition of α-CD$_x$. Corresponding to the change in the absorption spectrum, small negative Cotton effect was also observed in the CD spectrum, while **3** did not give any spectral changes. These results give the possibility that the hydrophobic chains of **1** should be included in the cavity of α-CD$_x$. Similar tendency was seen when β-CD$_x$ was added into the solutions of **1** and **3** instead of α-CD$_x$. On the other hand, tri-*O*-methyl-β-CD$_x$ caused little spectral change for **1**, suggesting that tri-*O*-methyl-β-CD$_x$ has much smaller ability to form inclusion compounds.

To obtain more definitive evidence, we investigated the effect of **1** upon the absorption and CD spectra of p-NP in aqueous solution containing α-CD$_x$ (Fig. 2). It should be noted that the addition of **1** caused appreciable changes in the spectra, which indicates that **1** undergoes complex formation with α-CD$_x$ in competition with p-NP. On the other hand, **3** did not bring about the changes in the absorption and CD spectra. When β-CD$_x$ was added instead of α-CD$_x$, similar spectral changes were observed upon addition of **1**. These findings suggest that the hydrophobic chains of **1** are included in α- or β-CD$_x$. The influence of tri-*O*-methyl-β-CD$_x$ was not studied, for the spectral

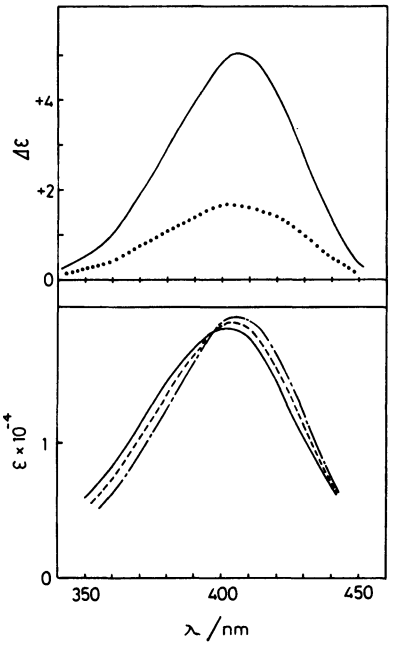


Fig. 2. Absorption and CD spectra of *p*-nitrophenol ($5\times10^{-5}$ mol dm$^{-3}$) at pH 9.5.
Absorption: $\alpha$-CD$_x$ free, **1** free (——); [$\alpha$-CD$_x$]= $5\times10^{-4}$ mol dm$^{-3}$, **1** free (– – –); [$\alpha$-CD$_x$]=$5\times10^{-4}$ mol dm$^{-3}$, [**1**]=$1\times10^{-3}$ mol dm$^{-3}$ (---).
CD: [$\alpha$-CD$_x$]=$2.5\times10^{-3}$ mol dm$^{-3}$, **1** free (——); [$\alpha$-CD$_x$]=$2.5\times10^{-3}$ mol dm$^{-3}$, [**1**]=$5\times10^{-3}$ mol dm$^{-3}$ (····).

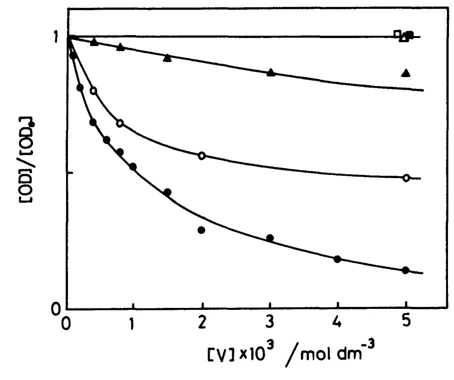


Fig. 3. Relation between relative absorbance ([OD]/[OD$_0$]) at 410 nm and concentration of various viologens ([V]) in *p*-nitrophenol/CD$_x$ solution (pH 9.5); [OD] and [OD$_0$] designate absorbance in the presence and absence of viologens, respectively. [p-NP]=$5\times10^{-5}$ mol dm$^{-3}$, [CD$_x$]=$5\times10^{-4}$ mol dm$^{-3}$; **1**/$\alpha$-CD$_x$ (●), **1**/$\beta$-CD$_x$ (O), **2**/$\alpha$-CD$_x$ (▲), **2**/$\beta$-CD$_x$ (△), **3**/$\alpha$-CD$_x$ (■); **3**/$\beta$-CD$_x$ (□).

changes of p-NP solution were small when it was added. Reasonable structure of **1**/CD$_x$ ($\alpha$ and $\beta$) complex is shown below.

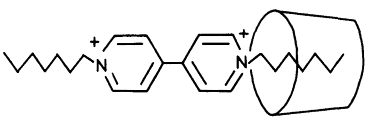


Figure 3 shows the changes in the relative absorbance of p-NP/CD$_x$ solution at 410 nm as a function of the concentration of the viologens. The results for benzylviologen (**2**) are also shown for comparison. It can be said from Fig. 3 that **1**/CD$_x$ complex is more stable than **2**/CD$_x$ one. From the relation in Fig. 3, we tried to estimate the dissociation constant of **1**/$\alpha$-CD$_x$ complex.

When the concentration of **1** is relatively higher than that of $\alpha$-CD$_x$, the following two equilibriums can be expected to hold.

$$\text{p-NP} + \alpha\text{-CD}_x \rightleftarrows \text{p-NP}\cdot\alpha\text{-CD}_x \qquad [\text{I}]$$

$$\mathbf{1} + \alpha\text{-CD}_x \rightleftarrows \mathbf{1}\cdot\alpha\text{-CD}_x \qquad [\text{II}]$$

As the concentration of $\alpha$-CD$_x$ ($5\times10^{-4}$ mol dm$^{-3}$) is much higher than that of p-NP ($5\times10^{-5}$ mol dm$^{-3}$), the dissociation constant of [I] ($K_1$) and that of [II] ($K_2$) are approximately described as follows.

$$K_1 = (p-x_1)(c-x_2)/x_1 \qquad (1)$$

$$K_2 = (V-x_2)(c-x_2)/x_2 \qquad (2)$$

$p$ : total concentration of p-NP($5\times10^{-5}$ mol dm$^{-3}$).
$c$ : total concentration of $\alpha$-CD$_x$($5\times10^{-4}$ mol dm$^{-3}$).
$V$: total concentration of **1**.
$x_1$: concentration of p-NP·$\alpha$-CD$_x$ complex.
$x_2$: concentration of **1**·$\alpha$-CD$_x$ complex.

Eqs. 1 and 2 yield

$$K_2 = \frac{\{(p-x_1)(V-c) + K_1x_1\}x_1K_1}{\{c(p-x_1) - K_1x_1\}(p-x_1)}. \qquad (3)$$

The $x_1$ value can be calculated from

$$x_1 = \Delta A/\Delta\varepsilon \qquad (4)$$

where $\Delta A$ is the increase in the absorbance at 410 nm upon addition of CD$_x$ and **1** and $\Delta\varepsilon$ is the difference in the molar absorption coefficient between p-NP·$\alpha$-CD$_x$ complex and p-NP. $K_1$ and $\Delta\varepsilon$ were obtained in a similar manner to that by Cramer et al.,[8] as to be $3.3\times10^{-4}$ mol dm$^{-3}$ and $3.4\times10^3$ mol$^{-1}$ dm$^3$ cm$^{-1}$, respectively. Therefore we could estimate $K_2$ from Eqs. 3 and 4 as a function of $V$ (Fig. 4). $K_2$ was found to be approximately constant (ca. $2\times10^{-4}$ mol dm$^{-3}$) under the conditions of $V>c$.

The complex formation between **1** and $\alpha$- or $\beta$-CD$_x$ was also demonstrated by the measurement of fluorescence quenching of excited [Ru(bpy)$_3$]$^{2+}$ by **1** as reported by Okuno et al.[6] That is to say, Stern-Volmer constant ($k_q\tau$) in the presence of **1** (Fig. 5(a)) decreased much more than those in the presence of **2** or **3** (Fig. 5(b), (c)), when $\alpha$- or $\beta$-CD$_x$ was added. However, tri-*O*-methyl-$\beta$-CD$_x$ did not essentially influence $k_q\tau$ values, probably due to the deficiency of ability to form inclusion complex.

As for the reduced form of **1** (cation radical), Yasuda et al. proposed an inclusion compound with $\beta$-CD$_x$, where it was more deeply situated in the cavity of $\beta$-CD$_x$.[7] Therefore we wish to mention some qualita-

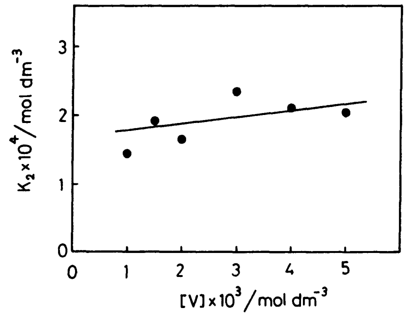


Fig. 4. Relation between dissociation constant ($K_2$) of **1**/$\alpha$-CD$_x$ complex and concentration of **1** ([V]).

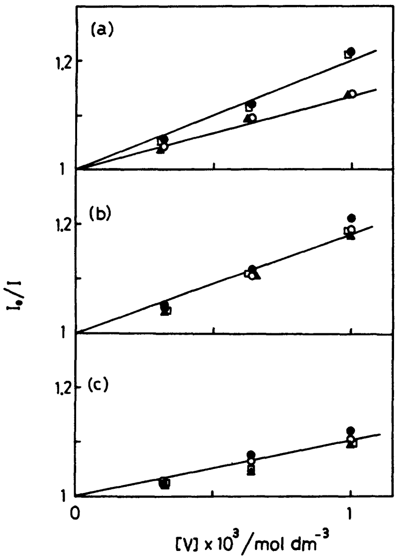


Fig. 5. Stern-Volmer plots for quenching of luminescence of [Ru(bpy)$_3$]$^{2+}$ (1×10$^{-4}$ mol dm$^{-3}$) by viologen in the presence and absence of CD$_x$; (a) **1**, (b) **2**, (c) **3**.

CD$_x$ free (●), [$\alpha$-CD$_x$]=2×10$^{-3}$ mol dm$^{-3}$ (○), [$\beta$-CD$_x$]=2×10$^{-3}$ mol dm$^{-3}$ (▲), [tri-*O*-methyl-$\beta$-CD$_x$]=2×10$^{-3}$ mol dm$^{-3}$ (□).

tive results about the reduced form of **1**. When **1** was reduced with sodium dithionite ($Na_2S_2O_4$), the reduced form of **1** (purple) was precipitated in aqueous solution. In the presence of $\alpha$- or $\beta$-CD$_x$, however, the aqueous solution of **1** turned blue by $Na_2S_2O_4$ without precipitation. Moreover, when p-NP was added to the above solution, the reduced form of **1** was again precipitated. On the other hand, when *o*-nitrophenol which is scarcely included in CD$_x$ was added to the solution instead of p-NP, the precipitate was not formed. The findings mentioned above suggest that the reduced form of **1** is also included in $\alpha$- or $\beta$-CD$_x$.

In the present study, the complex formation between **1** and $\alpha$- or $\beta$-CD$_x$ was definitely confirmed and the dissociation constant of the complex (**1**·$\alpha$-CD$_x$) was estimated by making use of the competitive binding of **1** and p-NP with CD$_x$. The indirect method as shown in the present study will be useful, when the spectroscopic analyses such as absorption, NMR and Raman spectroscopy do not give fruitful information about the complex formation.

## References

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