Complexation of Naphthalene-Viologen Linked Compounds with α-Cyclodextrin: Effect of Linkage Length on Thermodynamic Parameters and Complex Structures

Hee Jung Hwang, Sanghyuk Lee,* and **Joon Woo Park**

Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea
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Inclusion complexation between α-CD and naphthalene-viologen compounds linked with a flexible polymethylene bridges [-$(CH_2)_n$-; n = 3, 5, 7, 9, 12] is examined by NMR spectroscopy. Thermodynamic parameters such as equilibrium constants, enthalpy changes, and entropy changes of complexation were obtained. The equilibrium constants increase dramatically as the chain becomes longer. It is shown that the chain-length dependence of the equilibrium constant is dominated mainly by the entropy factor due to the hydrophobic interaction. Effects of intramolecular complexation on the apparent complexation constants are discussed. Structural features of the complex are also examined from chemical shift change and ROESY experiment. The main inclusion site seems to be the aromatic moiety for short chain molecules, and it moves toward the alkyl chain part as the chain becomes longer.

Introduction

Covalently-linked donor-acceptor dyad molecules, D-L-A, where D is an electron donor, A is an electron acceptor, and L is linkage, have drawn a great amount of interest with respect to various applications such as electron-transfer process and photochemical molecular devices.[1-5] Since the electron-transfer process depends highly on the distance and orientation between D and A, rigid bridges are commonly used as L to obtain a well-defined structure.[2,3] The D-L-A molecules with flexible bridges, on the other hand, have potential to be used as molecular switches if the molecule changes its conformation according to the external environment. However, studies on these molecules are usually complicated since the molecule may adopt various conformations.[4,5] Also they form intramolecular charge transfer complexes in bent conformation when D and A are in ground-state.[5-8]

Cyclodextrins (CDs) are macrocyclic oligosaccharides with 6 (α), 7 (β), 8 (γ) D-glucose units. CD has a relatively hydrophobic cavity whose diameter depends on the number of glucose units: 0.57 nm for α-CD, 0.78 nm for β-CD, and 0.95 nm for γ-CD. They form pseudorotaxane type complexes with D-L-A molecules having long polymethylene linkage and inhibit the grounds-state charge-transfer interactions and photoinduced electron-transfer reactions between D and A.[5,6-10]

In a recent paper, we reported linkage length dependence of intramolecular photoinduced electron-transfer reactions between aromatic donors (1-naphthoxyl, 2-naphthoxyl, 2-dibenzofuranoyl) and viologen moieties linked by polymethylene bridges in the presence of β-CD.[5] Extension of the molecules is observed for all spacer length, which is due to the inclusion into the β-CD cavity. However, NMR signals from the pseudorotaxane molecule and free D-L-A molecule

are not separated since the exchange rate is fast compared to the NMR time scale. This is quite a contrast to the behavior of R-$(CH_2)_n$-viologen molecules when R is a bulky 'stopper' such as anthracene,[6] carbazole,[7] phenothiazine,[8] or Ru(bpy)$_3^{2+}$:[9] Formation of pseudorotaxanes with these dyad molecules is observed only when the linkage length is greater than the depth of CD cavity (0.78 nm), *i.e.* n > 7. This suggested little steric and energy barrier for penetration of the aromatic moieties through the β-CD ring in our system.

Rotaxanes and pseudorotaxanes that incorporate CDs as ring components have been investigated by many groups, and the researches in this area have been reviewed recently.[11] It is hoped that we may able to find application of rotaxanes in nanotechnology as molecular machines, controllable by various stimuli.[12] For this purpose, it is desirable to be able to vary the lifetimes of pseudorotaxanes by changing the size-match between the dumbbell and ring components. In this paper, we present the studies on the formation of pseudorotaxane between 2-naphthoxyl-$(CH_2)_n$-viologen (2NC$_n$V: n = 3, 5, 7, 9, 12) and α-CD by NMR measurements, and show that 2-naphthoxyl group can be used as a dumbbell with moderate potential energy barrier for α-CD-based pseudorotaxanes. We also investigate the linkage length dependence of structures and thermodynamic parameters for pseudorotaxane formation between α-CD and 2-naphthoxyl/viologen dyad molecules linked with a polymethylene chain.

Experimental Section

The synthesis of the dyad molecules 2NC$_n$V were described elsewhere.[5] NMR measurement was carried out at 25 °C on Bruker DPX-250 or Varian Unity 600 MHz NMR spectrometers in D$_2$O solutions with TMSP (sodium 3-trimethylsilyl[2,2,3,3-^{2}H$_4$ propionate] as an internal standard. Thermodynamic parameters for formation of the pseudorotaxane molecules are obtained by NMR titration method. To correct the change in magnetic susceptibility as guest or host

*To whom correspondence should be addressed. Phone: +82-2-3277-2888, Fax:+82-2-3277-2384, e-mail: sanghyuk@mm.ewha.ac.kr

molecules are being added, a minimal amount of methanol is used as an additional internal reference.[13] The concentration of guest molecule was varied at fixed α-CD concentration for our NMR measurements. The susceptibility change due to the concentration change of guest molecule was calibrated by the following procedure. The chemical shift change of methanol peak at a specific concentration of guest molecule was measured with respect to the external reference in the absence of α-CD, which was assumed to stem from the concentration change of guest molecule. It was measured to be approximately 0.04 ppm over the range of 1-10 mM for 2NC$_5$V, to give an example. This value was subtracted from the overall chemical shift change of α-CD protons.

Results and Discussion

Addition of 2NC$_n$V to a α-CD solution results in the spectral change in proton NMR spectra. However, details of the NMR change depend largely on the linkage length of the guest molecule (Figure 1). For the molecules with short linkage (n=3, 5, and 7), the overall spectral shape remains essentially unchanged, but progressive change in chemical shifts for α-CD protons is observed as the concentration of 2NC$_n$V increases. This indicates that complexes between α-CD and the guest molecules have been formed but their dissociation rates are fast relative to the NMR time scale.
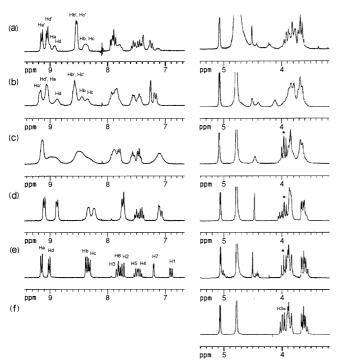

Figure 1. ^{1}H NMR spectra of 2NC$_n$V and α-CD mixture in D$_2$O at 25.0 ^{o}C. The chain length is (a) n=12, (b) n=9, (c) n=7, (d) n=5, and (e) n=3. The spectrum (f) is that of α-CD. The assignment of peaks was made with the aid of COSY and NOESY spectra. Prime denotes signals from the uncomplexed species. Concentrations of the host and guest molecules are as follows: (a) [2NC$_{12}$V] = 1 mM, [α-CD] = 0.8 mM, (b) [2NC$_9$V] = 2 mM, [α-CD] = 1.6 mM , (c) [2NC$_7$V] = 5 mM, [α-CD] = 5 mM, (d) [2NC$_5$V] = 5 mM, [α-CD] = 5 mM, (e) [2NC$_3$V] = 5 mM, [α-CD] = 5 mM.

For such fast exchange case, the observed chemical shift of a species is the population-weighted average of the chemical shifts in complex and free species. The observed chemical shift of protons in host molecule can be written as[14]

$$\delta_{obs}^H = \frac{\delta_c^H - \delta_f^H}{2[H]_t K}\Bigg\{ K([H]_t + [G]_t)+1$$
$$- \sqrt{K([H]_t + [G]_t)+1-4K^2[H]_t[G]_t} \Bigg\} + \delta_f^H \quad (1)$$

where δ_c^H and δ_f^H are the chemical shifts of protons in host molecule in complex and free species, respectively. [H]$_t$ and [G]$_t$ denote the total concentration of host and guest molecules, respectively. By fitting the observed chemical shifts at various [G]$_t$/[H]$_t$ ratios, one obtains the equilibrium constant (K) for complexation reaction and the chemical shift in complexed species (δ_c^H).

In principle, the chemical shift variation of protons in guest molecule can also be used. But the guest molecule itself is involved in the conformational equilibria between the intramolecular and intermolecular charge transfer complexation in the present system,[14] which complicates the analysis. Therefore, we chose to fit the signal from H$_{3\alpha}$ proton of α-CD since it showed the largest change among the host CD protons.[15] The chemical shift change due to complexation was calibrated according to the procedure described in experimental section, and the resulting shift fitted to Eq. (1) is shown in Figure 2. The equilibrium constant for complexation reaction and the chemical shift in complexed species at 25 ^{o}C are summarized in Table 1.

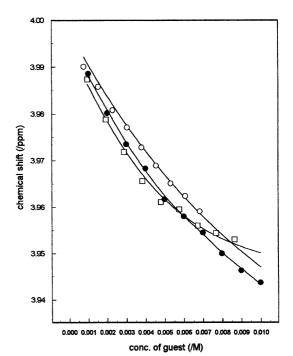The NMR titration was repeated at various temperatures to

Figure 2. Nonlinear least squares fitting of NMR shift of H$_3$ proton of α-CD caused by complexation with 2NC$_n$V in D$_2$O at 25 ^{o}C. n=3 ($\bigcirc$), n=5 ($\bullet$), n=9 ($\square$).

Table 1. Thermodynamic Parameters for Complexation of 2NC$_n$V with α-CD at 25 °C

n	K	$\Delta G°$	$\Delta H°$	$\Delta S°$	K_{in}	$K_{open, \alpha\text{-}CD}$	$K_{open, \beta\text{-}CD}$
3	92	11.2	19.8	28.9	0.16	110	450
5	210	13.2	19.6	21.5	0.23	260	1100
7	710	16.2	20.4	14.1	0.13	800	2220
9	3400	20.1	20.3	0.70	0.10	3700	3100
12	23000	24.8	20.4	14.8	0.14	26000	5700

*Units of K, $K_{open,\alpha\text{-}CD}$, $K_{open,\beta\text{-}CD}$ are M^{-1}, $\Delta G°$ and $\Delta H°$ are in kJ mol^{-1}, and $\Delta S°$ is given in J K^{-1} mol^{-1}. **K and the thermodynamic parameters are those of the apparent complexation (see text).

determine the temperature dependence of K values. The van't Hoff plot of ln$K$ versus 1/T gave a good straight line (not shown), and the standard enthalpies of complexation ($\Delta H°$) are calculated. Then, entropy changes of complexation ($\Delta S°$) are deduced from the relationship $\Delta G° = \Delta H° - T\Delta S°$, where $\Delta G°$ is related to K by $\Delta G° = -RT \ln K$. The thermodynamic parameters for the complexation are given in Table 1.

In contrast to the case of 2NC$_n$V molecules with short linkage, the mixture of α-CD and 2NC$_n$V with longer linkage (n = 9 and 12) shows distinct signals from α-CD-complexes and those from uncomplexed species at room temperature indicating the slower exchange rate (see Figure 1). For these slow exchange cases, the equilibrium constants of complex formation reaction were obtained directly from the integrated area of separated peaks. Peaks from viologen H$_b$ and H$_c$ protons are chosen to calculate the K values. The K values are obtained at three different concentration ratios for each guest molecule and the result is reported in Table 1. Thermodynamic parameters evaluated from the temperature dependence of the K values are also included in Table 1.

The driving forces for inclusion complexation have been attributed to hydrogen bonding, van der Waals forces, hydrophobic interactions, relaxation of the conformational strain in the CD, and release of hydrogen-bonded water molecules from the cavity. Enthalpy change of complexation was approximately −20 kJ/mol regardless of the chain length, which indicates a favorable van der Waals interaction. Entropy change, however, increases as the chain becomes longer. For short chain molecule, entropy decreases on complex formation mainly because the complex is more stable (so called, *enthalpy-entropy compensation*).

The fact that entropy change increases as the chain becomes longer can be explained in terms of hydrophobic interaction. Water molecules around the hydrophobic alkyl residue are rather well structured. These structured water molecules becomes loose when the guest molecule is incorporated inside the α-CD cavity, resulting in the increased entropy. More water molecules are located around the alkyl chain as the chain becomes longer, thereby entropy change increases. Therefore the chain-length dependence of the equilibrium constant is dominated mainly by the *entropy factor* due to the hydrophobic interaction in this case.

The Gibbs free energy change decreases by about 1.5 kJ/mol as the alkyl chain length increases by one carbon unit.

When a linear saturated fatty acids form a micellar structure, this Gibbs free energy change per one carbon unit is known to be approximately −3 kJ/mol. The reason for the decreased effect may be that the α-CD cavity is less hydrophobic than the alkyl chain.

The dyad molecules used in this work forms intramolecular charge transfer complexes adapting folded conformation.[5,14] Considering the size of the α-CD cavity, only the open form is considered to be in equilibrium with α-CD complex.

$$\text{Open} \rightleftharpoons \text{Folded} \qquad K_{in} = [\text{Folded}]/[\text{Open}] \qquad (2)$$

Open + α-CD $\rightleftharpoons$ α-CD complex
$$K_{open, CD} = [\alpha\text{-CD complex}]/[\alpha\text{-CD}][\text{Open}] \qquad (3)$$

The K values determined from NMR titration are the *apparent* complex formation constants as defined in Eq (4), and thus differ from $K_{open, CD}$ as given in Eq. (5).

$$K = [\alpha\text{-CD complex}]/[\alpha\text{-CD}]([\text{Open}] + [\text{Folded}]) \qquad (4)$$

$$K_{open, CD} = K(1 + K_{in}) \qquad (5)$$

The $K_{open, CD}$ values are evaluated from the K values and the reported K_{in} values,[5] and they are compared with those for β-CD in Table 1.

The CIS (complexation induced shift) values from NMR titration provide some structural information on complex. The pseudorotaxane complex between α-CD and 2NC$_n$V can exists as various conformers, and the chemical shift of H$_3$ proton in α-CD complexed with 2NC$_n$V is the weighted average of those conformers. The H$_3$ proton is located near the wider (secondary) rim of α-CD cavity, and most affected by the aromatic moiety when the guest is included from the secondary face. Table 2 shows that the upfield shift of H$_3$ proton becomes smaller as linkage length becomes longer. This implies that the mean position of α-CD moves toward the linkage as the spacer becomes longer. Several authors have reported formation of α-CD based pseudorotaxanes with R-(CH$_2$)$_n$-R´ type molecules, where R and R´ are bulky or ionic groups.[6-9,16-18] For those molecules, appreciable complex formation is observed only when n > 7, as inclusion of R or R´ inside the α-CD cavity is unfavorable energetically or sterically.[7,16,18] 2-Naphthoxyl group used in this work is small enough and energetically favorable enough to form a complex where α-CD extends over the aromatic moiety and polymethylene linkage.

For long chain guests (n = 9, 12), separate signals are

Table 2. Chemical Shifts ($\Delta\delta$) of H$_3$ proton of α-CD complexed with 2NC$_n$V dyad molecules at 25 °C

n	δ (ppm)	$\Delta\delta$ (ppm)^a
3	3.88	0.11
5	3.91	0.08
7	3.94	0.05

$^a\Delta\delta$ is complexation induced chemical shift change calculated by $\delta_{\text{free }\alpha\text{-CD}} - \delta_{\text{complex}}$ where $\delta_{\text{free }\alpha\text{-CD}}$ is 3.99 ppm.
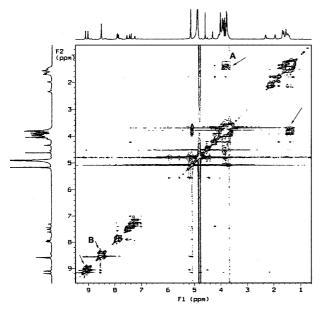
Figure 3. 600 MHz ROESY spectrum for α-CD/2NC$_{12}$V in D$_2$O at 25 $^{\circ}$C. NOE crosspeaks between spacer alkyl chain and α-CD are indicated by arrow A, and the exchange crosspeaks in viologen region are indicated by arrow B. [α-CD] = 1 mM, τ_{mix} = 100 ms were used.

Figure 4. Temperature dependence of NMR spectra in 5 : 3 mixture of 2NC$_{12}$V and α-CD. [2NC$_{12}$V] = 0.76 mM. See Figure 1 for peak assignment.

observed from complex and free species since the exchange process is slow (cf. Figure 1). NOE has been used to probe the molecular structure of the stable CD complexes. T$_1$ relaxation time is not appropriate to observe crosspeaks in NOESY experiment for molecules with molecular weight of around 1,000.[19] 2D-ROESY spectrum in Figure 3, however, clearly shows the crosspeaks between α-CD protons and the alkyl protons. The phase of NOE crosspeaks is opposite to the diagonal peaks. This indicates that CD is located along the alkyl chain for long chain molecules. We also observe the exchange crosspeaks between viologen protons in complex and free species whose phase is the same as the diagonal peaks. Therefore, we conclude that the primary inclusion site of CD is the polymethylene chain when the chain length
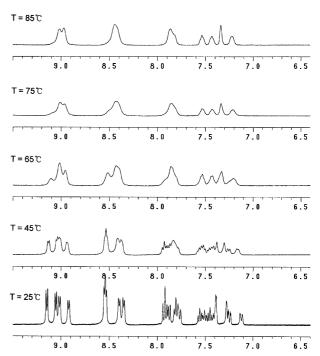
is longer than the depth of α-CD, *ca.* 0.7 nm.

Observation of the distinct signals from pseudorotaxane type complexes in the present systems is rather unusual as we observed the formation of α-CD complexes where α-CD extends over the naphthoxyl moiety and polymethylene linkage. This can be possible when the naphthalene moiety has a low potential energy barrier for the formation of the throughring complexes. To ascertain this, we measured temperature effects on the NMR spectra of α-CD/2NC$_{12}$V system in D$_2$O (Figure 4). The coalescence point is observed at 70 $^{\circ}$C. Yonemura *et al.*[7] showed no hint of NMR coalescence up to 90 $^{\circ}$C in α-CD/carbazole-C$_{12}$V system, where α-CD should be inserted from viologen side. This is a clear indication that
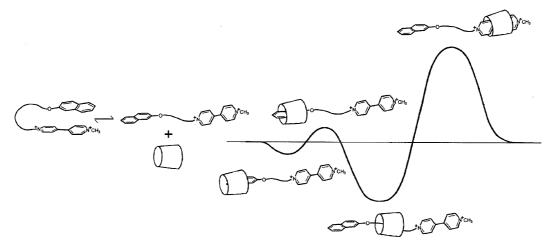

Figure 5. Schematic presentation of potential energy profile for formation of the pseudorotaxane between α-CD and 2-naphthoxyl/viologen dyad molecules linked with a long spacer chain.

α-CD is mainly exchanged through naphthoxyl side, where potential energy barrier is much lower than the viologen side.[20] The reaction profile for the pseudorotaxane can be depicted as Figure 5.

The complex formation constant of 2NC$_n$V with α-CD as well as β-CD increases as the chain becomes longer. However, the linkage length dependence of α-CD complex is quite different from that of β-CD complex. For the molecules with short chain, $K_{open, β-CD}$ is greater than $K_{open, α-CD}$ for the corresponding guest, while the opposite is observed for molecules with longer chain. This can be explained in terms of size fitness: 2-naphthoxyl groups fits snugly into β-CD but seems to fit too tightly to α-CD,[21] whereas the polymethylene linkage fits well into α-CD but rattles around inside the β-CD cavity.[24] This suggests a favorable van der Waals interaction between the guest and the host molecules when the naphthoxyl or the polymethylene group is in close proximity of CD without causing structural distortion.

The complex formation constants for the open form of 2NC$_n$V ($K_{open, α-CD}$) are considerably greater than those of α,ω-alkanedicarboxylate (determined at pOD=13)[16] and α,ω-bis(pyridinium)[18] compounds having the corresponding polymethylene linkage. This can be attributed to the enhanced stability of α-CD-2NC$_n$V by inclusion of naphthoxyl moiety into α-CD, while the carboxylate or pyridinium group of the latter compounds is energetically disfavored. Yonemura *et al.* reported thermodynamic parameters for complex formation between a-CD and carbazole-viologen dyad molecules (CAC$_n$V) linked with a polymethylene chain.[7] The apparent binding constants of CAC$_{12}$V with α-CD was found to be 4.9×10^4 M at 30 °C, which is about twice that of 2NC$_n$V, even though carbazole group is too bulky to be included inside the α-CD cavity. This difference is greater than that can be accounted for the intramolecular complexation by Eq. (5). A possible explanation for this behavior is interaction between the protruded carbazole moiety and the outer surface of α-CD.

The linkage length dependence of thermodynamic parameters for the complex formation between 2NC$_n$V and α-CD (Table 1) is very similar to that of CAC$_n$V/α-CD system.[7] The stability of the complexes becomes greater as the chain length increases, but enthalpy of complex formation is relatively insensitive to the chain length, making the entropy term as the dominant factor for the linkage length dependence of K.

It should be pointed out that the evaluation of thermodynamic parameters from the apparent K values using van't Hoff relationship is not free from logical flaw, as the complex formation reaction is coupled by two reactions, Eqs. (2) and (3). The enthalpy change of the complex formation between the open form and α-CD is derived as Eq. (6) by differentiating ln$K$ of Eq. (5) with respect to 1/T.

$$\Delta H^o_{open, CD} = \Delta H^o_{app} + \Delta H^o_{in} K_{in}/(1+K_{in}) \qquad (6)$$

When $K_{in} \ll 1$ as observed for 2NC$_n$V/α-CD systems, $\Delta S^o_{open, CD}$ is expressed as Eq. (7).

$$\Delta S^o_{open, CD} = \Delta S^o_{app} + [(\Delta H^o_{in}/T)K_{in}/(1+K_{in}) + RK_{in}] \qquad (7)$$

ΔH^o_{in} values are about 10 kJ mol^{-1}.[25] From this and K_{in} values in Table 1, the second term on the right hand side of Eq. (6) is estimated to be about 3 kJ mol^{-1} giving $\Delta H^o_{open, CD}$ as about 23 kJ mol^{-1}. Also the second term in right hand side of Eq. (7) is estimated to be about 10 J K^{-1} mol^{-1} resulting in $\Delta S^o_{open, CD}$ in the range of −30 (for n = 3) to 5 J K^{-1} mol^{-1} (for n = 12). However, the correction for the contribution of intramolecular charge transfer complexation to the thermodynamic parameters for complex formation does not change the trend of the chain length dependence of the parameters.

Thermodynamics of complexation with CDs has been investigated extensively and well documented.[26] These studies revealed that ΔH^o for complexation of guests with CDs decreases as the polymethylene chain of the guest molecule becomes longer, whereas ΔS^o shows little dependency on the chain length and is near zero. Taking this into account, we can conclude that the linkage length dependence of the thermodynamic parameters for complexation of 2NC$_n$V with α-CD arises from the change in inclusion or interaction parts of the guest molecule. Inclusion of 2-naphthoxyl group, which is the main inclusion part of molecules with short linkage, appears to results in a large decrease in enthalpy as well as entropy. The amount of enthalpy change would be similar to that associated with the inclusion of polymethylene linkage, whose inclusion results in little entropy change

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20. Determination of activation parameters is beyond the scope of this work. Studies are underway to evaluate the activation parameters for the present systems as well as other related systems. The results will be reported elsewhere.

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