Bull. Chem. Soc. Jpn., 74, 2031–2035 (2001)

Thermodynamic Parameters for the Complexation of the Pyridinio Derivatives of Cyclodextrins with Some Inorganic Anions in D_2O Solution

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(Received May 25, 2001)

Substitution of the pyridinio groups for the C(6)-OH's of cyclodextrins (CD's) brought about a remarkable increase in the binding constants (K_a) for 1 : 1 complexes of CD's with inorganic anions, such as I^-, SCN^-, and ClO_4^-. The thermodynamic parameters for the complexation of native α-CD and its pyridinio derivatives showed that the increase in K_a is mainly driven by an enthalpy term (ΔH), and that the contribution of an entropy term ($T\Delta S$) is minor. In contrast, the increase in K_a is mainly driven by $T\Delta S$, and the contribution of ΔH is minor, for the systems of β- and γ-CD's with the larger interior cavities. These results were explained in terms of the combined action of van der Waals and electrostatic interactions between the CD's and anions, together with desolvation upon complexation.

Native cyclodextrins (CD's) form 1 : 1 inclusion complexes with chaotropic inorganic anions, such as Br^-, I^-, SCN^-, ClO_4^-, and NO_3^- in D_2O, though the binding constants (K_a) for the complexes at 298 K are not so large as to exceed 33 $mol^{-1}\ dm^3$ for an α-CD–ClO_4^- complex.[1] In this connection, it was previously reported that the K_a values for 1 : 1 complexation of α-CD with I^-, SCN^-, and Br^- in H_2O increase by one order of magnitude with substitution of the pyridinio group for one of the α-CD C(6)-OH's and by two orders of magnitude with pyridinio substitution for two of the α-CD C(6)-OH's.[2,3] The K_a values remarkably decreased with increasing cavity size of CD's, indicating that van der Waals interactions contribute to the complexation.[1a,2] Antichaotropic anions, such as F^-, $H_2PO_4^-$, and SO_4^{2-}, showed virtually no interaction with the CD's and their pyridinio derivatives, suggesting that hydrophobic interactions also play an important role for complexation.[1a,4] For complexation of the pyridinio derivatives of CD's, electrostatic and charge-transfer interactions are also responsible.[2]

The present study was undertaken to reveal the major driving forces contributing to the remarkable increase in K_a for 1 : 1 complexes of the pyridinio derivatives of CD's with chaotropic anions from a thermodynamic point of view. The thermodynamic parameters for CD complexation give much information on inclusion phenomena.[5–7] The pyridinio derivatives of CD's examined in the present study are mono- and bis[6-(1-pyridinio)-6-deoxy]-α-, β-, and γ-CD's (**1–8**), as shown in Fig. 1. It has been shown by the continuous-variation method that even the dipyridinio derivatives of α-CD form 1 : 1 complexes with chaotropic anions.[2]

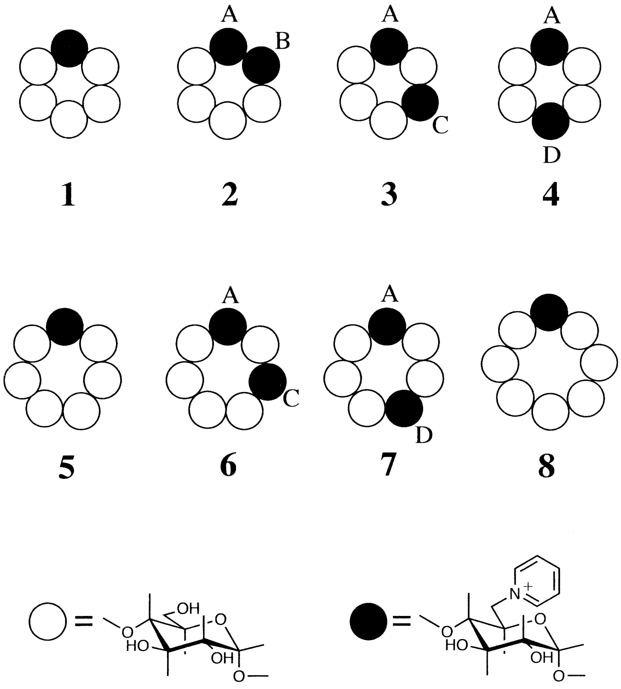

Fig. 1. The pyridinio derivatives of cyclodextrins examined.

Experimental

Materials. The α-CD was supplied by Nihon Shokuhin Kako Co., Ltd. The β- and γ-CD's were supplied by Bio Research Corporation of Yokohama, Ltd. They were dried overnight in vacuo at 110 °C. Reagent-grade pyridine was dried over CaH_2 and distilled in the presence of CaH_2 before use. Inorganic salts, such as NH_4HCO_3, KF, KBr, KI, KSCN, KNO_3, and $NaClO_4$, were of reagent grade and commercially available. The HCO_3^- salts of **1–8** were prepared by refluxing solutions of the corresponding 6-*O*-arylsulfonylated CD's in dry pyridine, followed by elution of the products from a column of CM-cellulose (50 × 550 mm, Serva) with aqueous NH_4HCO_3, as described previously.[8] The used D_2O

(Isotec) contained 99.9 atm% D. Reagent-grade methanol was used as an internal reference for a ^{1}H NMR measurement.

Apparatus. The ^{1}H NMR spectra were recorded using a JEOL Model JNM-A400 FT NMR spectrometer (400 MHz) with a sample tube of 5.0 mm diameter at 298, 308, 318, and 328 ± 0.1 K. Sample solutions contained 2.0 mmol dm^{-3} **1**–**8** in D_2O. The maximum concentrations of the inorganic salts added to the sample solutions were 10 mmol dm^{-3} for host-guest systems with large K_a values and 100 mmol dm^{-3} for those with small K_a values. The ionic strength of the solutions was adjusted to be 100 mmol dm^{-3} by the addition of KF, which shows virtually no interaction with CD's.[1a,4] A trace amount of methanol (0.4 mmol dm^{-3}) was added to the sample solution as an internal reference ($\delta = 3.343^9$) of ^{1}H NMR measurements.

Determination of Binding Constants and Thermodynamic Parameters. The pyridinio derivatives **1**–**4** of α-CD in D_2O containing 100 mmol dm^{-3} KF gave ^{1}H NMR signals similar to those previously reported.[8] The pyridinio derivatives, **5**–**8**, of β- and γ-CD's also gave ^{1}H NMR signals similar to the α-CD analogs. The addition of inorganic salts, such as KBr, KI, KSCN, KNO_3, and $NaClO_4$, in place of KF caused significant changes in the chemical shifts (δ) of some well-resolved signals of **1**–**8**, as previously described in detail with regard to **1**, **5**, and **8**.[4] For example, the (6^A, 6^C)-disubstituted isomer **3** gave a double doublet signal at $\delta = 2.74$ due to one of the C(6)-H of the unsubstituted D glucopyranose moiety [GP(D)] adjacent to the substituted glucopyranose GP(C) in a KF/D_2O solution at 298 K.[8] The signal was markedly shifted to an upper field with the addition of KSCN in place of KF (Fig. 2). Based on an assumption that **3** forms a 1:1 complex with SCN^-, the data were analyzed by a nonlinear least-squares curve-fitting method to give a K_a value for the complex. The thus-calculated curves (solid lines) were well-fitted to the observed data, indicating that the assumption of 1:1 complexation is valid. Similar measurements were carried out at 308, 318, and 328 K, and the obtained data were similarly analyzed to give K_a values at different temperatures. The enthalpy change (ΔH) and entropy change (ΔS) for the complexation were calculated from the slope and intercept, respectively, of a straight line obtained by a least-squares analysis of a relationship between ln K_a and $1/T$.

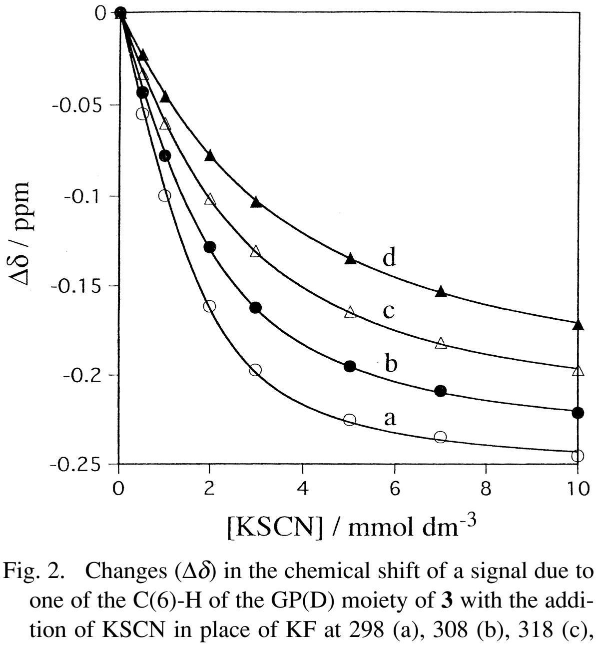

Fig. 2. Changes ($\Delta\delta$) in the chemical shift of a signal due to one of the C(6)-H of the GP(D) moiety of **3** with the addition of KSCN in place of KF at 298 (a), 308 (b), 318 (c), and 328 K (d).

Results

Table 1 shows the K_a values and thermodynamic parameters, ΔH and $T\Delta S$, at 298 K determined by ^{1}H NMR chemical shift titration for complexation of the pyridinio derivatives **1**–**4** of α-CD with some chaotropic anions, such as I^-, SCN^-, ClO_4^-, NO_3^-, and Br^-, in D_2O. The addition of Na^+ or K^+ salts of these anions to solutions of **1**–**4** caused significant changes in the chemical shifts of some host protons, sufficient for determining the K_a values. On the other hand, the effects of K^+ salts of NO_3^-, and Br^- on the ^{1}H chemical shifts of β- and γ-CD analogs **5**–**8** were too small to determine the K_a values. Thus, the K_a values and the thermodynamic parameters were determined only for complexes of **5**–**8** with I^-, SCN^-, and ClO_4^- (Tables 2 and 3). For a comparison, the previously reported values for native CD's[1a] are also given in these tables. The obtained K_a values for the complexation of **1**–**4** with I^-, SCN^-, and Br^- at 298 K in D_2O were in fair agreement with those determined in H_2O by UV/visible spectrophotometry, as

Table 1. Binding Constants (K_a) and Thermodynamic Parameters for Complexation of α-CD and Its Pyridinio Derivatives **1**–**4** with Chaotropic Anions in D_2O

Guest	Host	K_a/mol^{-1} dm^3 [a)]	$-\Delta H$/kJ mol^{-1}	$-T\Delta S$/ kJ mol^{-1} [a)]
I^-	α-CD[b)]	18.6 ± 0.1	31.6	24.3
	1	158 ± 10	36.6	24.2
	2	973 ± 37	39.3	22.4
	3	1380 ± 27	43.5	25.6
	4	1330 ± 40	38.4	20.8
SCN^-	α-CD[b)]	28.4 ± 0.1	32.2	23.9
	1	420 ± 8	37.5	22.7
	2	1280 ± 140	43.2	25.5
	3	2580 ± 140	48.3	28.9
	4	3010 ± 260	44.3	24.5
ClO_4^-	α-CD[b)]	33.0 ± 0.1	33.7	25.1
	1	234 ± 5	40.3	26.8
	2	1308 ± 80	40.4	22.6
	3	2070 ± 210	44.3	25.3
	4	6900 ± 30	48.5	26.6
NO_3^-	α-CD[b)]	1.4 ± 0.1	16.9	16.2
	1	17.1 ± 0.6	23.7	16.7
	2	62.2 ± 3.2	26.0	15.8
	3	65.0 ± 1.9	26.7	16.4
	4	70.2 ± 1.5	24.2	13.6
Br^-	α-CD[b)]	1.6 ± 0.1	15.7	14.5
	1	7.7 ± 0.6	15.3	10.2
	2	36.1 ± 2.9	20.0	11.1
	3	31.0 ± 0.5	21.9	13.4
	4	31.9 ± 0.4	17.7	9.1

a) Values at 298 K. b) Ref. 1a.

previously reported.[3] The obtained K_a values at 298 K in D_2O for the complexation of **1** with I^-, SCN^-, ClO_4^-, Br^-, and NO_3^- and for the complexation of **5** and **8** with I^- were also in fair agreement with those previously reported.[4]

Table 2. Binding Constants (K_a) and Thermodynamic Parameters for Complexation of β-CD and Its Pyridinio Derivatives **5**–**7** with Chaotropic Anions in D_2O

Guest	Host	K_a/mol^{-1} dm^3 a)	$-\Delta H$/kJ mol^{-1}	$-T\Delta S$/kJ mol^{-1} a)
I^-	β-CD[b)]	8.5 ± 0.4	22.7	17.6
	5	30.5 ± 0.7	21.3	12.8
	6	105 ± 3	19.4	7.8
	7	112 ± 6	21.0	9.3
SCN^-	β-CD[b)]	9.2 ± 0.5	19.7	14.3
	5	40.2 ± 0.7	17.8	8.7
	6	123 ± 6	19.2	7.2
	7	139 ± 7	20.5	8.3
ClO_4^-	β-CD[b)]	13.6 ± 0.7	17.6	10.9
	5	120 ± 11	22.4	10.4
	6	755 ± 29	28.9	12.6
	7	794 ± 67	29.2	12.6

a) Values at 298 K. b) Ref. 1a.

Table 3. Binding Constants (K_a) and Thermodynamic Parameters for Complexation of γ-CD and Its Pyridinio Derivatives **8** with Chaotropic Anions

Guest	Host	K_a/mol^{-1} dm^3 a)	$-\Delta H$/kJ mol^{-1}	$-T\Delta S$/kJ mol^{-1} a)
I^-	γ-CD[b)]	4.9 ± 0.3	16.5	12.5
	8	16.0 ± 0.3	15.5	8.7
SCN^-	γCD[b)]	4.1 ± 0.2	11.8	8.4
	8	18.8 ± 3.0	10.8	3.5

a) Values at 298 K. b) Ref. 1a.

The substitution of the pyridinio groups for the C(6)-OH's of α-CD resulted in remarkable increases in K_a for complexation with I^-, SCN^-, and ClO_4^- in D_2O. The maximum increase in K_a with pyridinio substitution was found for a **4**-ClO_4^- system, the K_a value of which was 210 times that of a α-CD–ClO_4^- system. To I^- and SCN^-, the hosts **3** and **4** showed the strongest binding, respectively. Pyridinio substitution also brought about an increase in K_a for complexation with NO_3^- and Br^-, though the increments were less than those for I^-, SCN^-, and ClO_4^-. More noticeable are the thermodynamic parameters in Table 1, which show that increases in K_a are mainly brought about by an enthalpy term (ΔH), and that the contribution of an entropy term ($T\Delta S$) to the increases is minor. For example, the difference ($\Delta\Delta H$) in ΔH between ClO_4^- complexes with a pyridinio derivative **4** and α-CD was -14.8 kJ mol^{-1}, whereas that [$\Delta(T\Delta S)$] in $T\Delta S$ was only -1.5 kJ mol^{-1}. Similarly, the $\Delta\Delta H$ values for complexes of **3** with I^- and **4** with SCN^- were -11.9 and -12.1 kJ mol^{-1}, respectively, whereas the corresponding $\Delta(T\Delta S)$ values were only -1.3 and -0.6 kJ mol^{-1}, respectively. The $T\Delta S$ values for complexes of α-CD and its pyridinio derivatives **1**–**4** with I^-, SCN^-, and ClO_4^- were roughly held constant (-24.6 ± 2.0 kJ mol^{-1}). Exceptional are complexes of **1** and **4** with Br^-, where increases in K_a with the pyridinio substitution are mainly brought about by $T\Delta S$, rather than ΔH. Thus, the $\Delta\Delta H$ values for Br^- complexes with **1** and **4** were 0.4 and -2.0 kJ mol^{-1}, respectively, whereas the corresponding $\Delta(T\Delta S)$ values were 4.3 and 5.4 kJ mol^{-1}, respectively.

Substitution of the pyridinio groups for the C(6)-OH's of β- and γ-CD's also resulted in significant increases in K_a for complexation with I^-, SCN^-, and ClO_4^- in D_2O, though the increments were less than those for the α-CD analogs (Tables 2 and 3). It is noteworthy that the increases in K_a with the pyridinio substitution of β- and γ-CD are mainly brought about by $\Delta(T\Delta S)$, rather than $\Delta\Delta H$, for complexes with I^- and SCN^-. For example, the $\Delta\Delta H$ values for complexes of **7** with I^- and SCN^- were only 1.7 and -0.8 kJ mol^{-1}, respectively, whereas the corresponding $\Delta(T\Delta S)$ values were as large as 8.3 and 6.0 kJ mol^{-1}, respectively. Exceptional is a complex of **7** with ClO_4^-, where $\Delta\Delta H$ (-11.6 kJ mol^{-1}) was much larger than $\Delta(T\Delta S)$ (-1.7 kJ mol^{-1}).

The above results can be generalized by saying that the magnitudes of $\Delta\Delta H$ and $\Delta(T\Delta S)$ are closely related to the cavity sizes of the CD's and the ionic sizes of the guest anions. Thus, when the ionic diameters of the anions are close to the cavity sizes of the CD's, the magnitudes of $-\Delta\Delta H$ are large and those of $-\Delta(T\Delta S)$ are small. A typical case is a complex of **4** with ClO_4^-. The ionic diameter (0.48 nm[10]) of ClO_4^- is very close to the cavity size of α-CD (0.47–0.52 nm[11]). On the other hand, the magnitudes of $-\Delta\Delta H$ are small and those of $-\Delta(T\Delta S)$ are large when the ionic diameters of the anions are significantly smaller than the cavity sizes of CD's. A typical case is a complexe of **4** with Br^- or **7** with I^-. The ionic diameters of Br^- (0.38 nm[10]) and I^- (0.42 nm[10]) are significantly smaller than the cavity sizes of α-CD and β-CD (0.60–0.64 nm[11]), respectively.

Discussion

It was previously[1a] suggested that complexation of native CD's with chaotropic anions is mainly brought about by van der Waals and hydrophobic interactions, together with free-energy changes with the conformational changes of CD macrocycles and the desolvation of the CD's and anions upon complexation. Thus, the total free-energy change (ΔG_0) for the complexation of a CD host with an anion can be represented by

$$\Delta G_0 = \Delta G_0(\mathrm{vdw}) + \Delta G_0(\mathrm{hyp}) + \Delta G_0(\mathrm{cnf}) + \Delta G_0(\mathrm{des}), \quad (1)$$

where ΔG_0(vdw), ΔG_0(hyp), ΔG_0(cnf), and ΔG_0(des) are free-energy changes due to van der Waals and hydrophobic interactions, conformational changes, and desolvation, respectively. The pyridinio substitution of CD would give rise to additional interactions, such as electrostatic and charge-transfer interactions, between a host and a guest anion.[2] Thus, the total free-energy change (ΔG) for the complexation of a pyridinio derivative of CD with an anion can be represented by

$$\Delta G = \Delta G(\mathrm{vdw}) + \Delta \mathrm{G}(\mathrm{hyp}) + \Delta G(\mathrm{cnf}) + \Delta G(\mathrm{des}) + \Delta G(\mathrm{elc}) + \Delta G(\mathrm{ct}), \tag{2}$$

where $\Delta G(\mathrm{elc})$ and $\Delta G(\mathrm{ct})$ are the free-energy changes due to electrostatic and charge-transfer interactions, respectively. Then, the difference ($\Delta\Delta G$) between ΔG for a complex of the pyridinio derivative of CD and ΔG_0 for a complex of the corresponding native CD is

$$\Delta\Delta G = \Delta\Delta G(\mathrm{vdw}) + \Delta\Delta G(\mathrm{hyp}) + \Delta\Delta G(\mathrm{cnf}) + \Delta\Delta G(\mathrm{des}) + \Delta G(\mathrm{elc}) + \Delta G(\mathrm{ct}), \tag{3}$$

where the $\Delta\Delta G$ values on the right-hand side of the equation are the $\Delta G - \Delta G0$ values for the interactions shown in parenthesis.

In order to estimate the $\Delta\Delta G(\mathrm{cnf})$ and $\Delta\Delta G(\mathrm{des})$ values, we plotted $T\Delta S$ *vs* ΔH for the complexation of α-CD and **1**–**4** with the examined anions (Fig. 3).[7] The plots gave good straight lines, as expressed for native α-CD systems by

$$T\Delta S = 0.56\,\Delta H - 6.18,\ n = 5, r = 0.9960, \tag{4}$$

for the systems of a α-CD monopyridinio derivative **1** by

$$T\Delta S = 0.62\,\Delta H - 1.12,\ n = 5, r = 0.9887, \tag{5}$$

and for the systems of α-CD dipyridinio derivatives **2**–**4** by

$$T\Delta S = 0.57\,\Delta H - 0.11,\ n = 15, r = 0.9905, \tag{6}$$

where n and r denote the number of sample and correlation coefficient, respectively. According to Inoue et al.,[7] the slope and intercept of a compensatory relationship between $T\Delta S$ and ΔH are quantitative measures of the conformational change of CD macrocycles and the extent of desolvation upon complexation, respectively. The slopes were virtually constant through native α-CD and its pyridinio derivatives, so that the $\Delta\Delta G(\mathrm{cnf})$ value for these systems is regarded as being negligibly small. On the other hand, the intercepts significantly increased with pyridinio substitution, indicating that desolvation around the pyridinio groups and anions plays an important role in complexation.

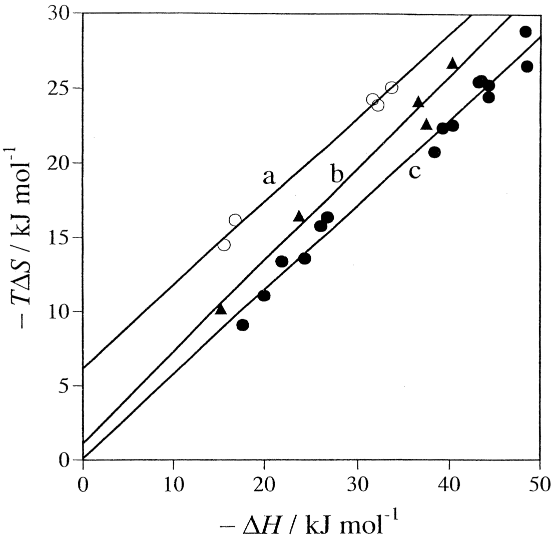

Fig. 3. Plots of $-T\Delta S$ vs $-\Delta H$ determined for the complexation of examined chaotropic anions with native α-CD (a), and the mono- (b) and dipyridinio (c) derivatives of α-CD.

Since the cavity sizes of **1**–**4** are the same as that of native α-CD, the van der Waals interactions between the host cavity and an anion would not be largely changed by pyridinio substitution. We can thus regard the $\Delta\Delta G(\mathrm{vdw})$ value as being negligibly small. The hydrophobicity of the α-CD cavity will not change with pyridinio substitution, since the pyridinio groups are located at the outer rim of the cavity. Then, the $\Delta\Delta G(\mathrm{hyp})$ value will also be negligibly small. Charge-transfer interactions have been observed for complexes of **1**–**4** with I^- and SCN^-, but not for those with $\mathrm{ClO_4}^-$.[2] Since changes in the thermodynamic parameters for $\mathrm{ClO_4}^-$ complexes with the pyridinio substitution are virtually the same as those for I^- and SCN^- complexes, we also regarded $\Delta G(\mathrm{ct})$ as being negligibly small. On the other hand, substitution of the positively charged pyridinio group(s) for the neutral OH group(s) of CD's must bring about electrostatic interactions between the hosts and guest anions, resulting in $\Delta G(\mathrm{elc}) < 0$.

The above discussion leads us to an assumption that the significant increase in K_a for CD-anion systems with the pyridinio substitution is mainly due to desolvation upon complexation and electrostatic interactions. Thus,

$$\Delta\Delta G \fallingdotseq \Delta\Delta G(\mathrm{des}) + \Delta G(\mathrm{elc}) \tag{7}$$

or

$$\Delta\Delta H - \Delta(T\Delta S) \fallingdotseq [\Delta\Delta H(\mathrm{des}) + \Delta H(\mathrm{elc})] - \{\Delta[T\Delta S(\mathrm{des})] + T\Delta S(\mathrm{elc})\}. \tag{8}$$

Substitution of the positively charged pyridinio group(s) for the neutral OH group(s) of CD's would enhance the electrostatic interactions between the hosts and the guest anions, resulting in $\Delta H(\mathrm{elc}) < 0$. An increase in the electrostatic interactions would also bring about a restriction of the molecular motion and a decrease in the entropy [$T\Delta S(\mathrm{elc}) < 0$]. On the other hand, complexation of a host with a guest anion is accompanied by desolvation of the host and guest. In the case of complexation of native CD with an anion, desolvation would occur around the surface of the anion and the interior cavity of the CD. In the case of complexation of the pyridinio derivative of CD with an anion, additional desolvation would occur in the vicinity of the pyridinio group, and the extent of the desolvation would be greater than that in the case of native CD. Since desolvation is generally endothermic and releases the restriction of molecular motion, we can state $\Delta\Delta H(\mathrm{des}) > 0$ and $\Delta[T\Delta S(\mathrm{des})] > 0$.

Our experimental results described above showed that the magnitudes of $-\Delta\Delta H$ are large, and that those of $-\Delta(T\Delta S)$ are small when the ionic diameters of anions are close to the cavity sizes of the CD's. In these cases, the close van der Waals contact of the anions with the CD cavity would restrict the motion of anions within the CD cavity to reinforce the electrostatic interactions between the anions and the pyridinio groups. Then, the contribution of $\Delta H(\mathrm{elc})$ to $\Delta\Delta H$ would exceed that of

$\Delta\Delta H$(des), and $\Delta\Delta H < 0$. At the same time, an increase in entropy, $\Delta[T\Delta S$(des)], due to desolvation would compensate a decrease in entropy, $T\Delta S$(elc), due to electrostatic interactions, and thus $\Delta(T\Delta S) \fallingdotseq 0$. The above results also showed that the magnitudes of $-\Delta\Delta H$ are small and those of $-\Delta(T\Delta S)$ are large when the ionic diameters of the anions are significantly smaller than the cavity sizes of the CD's. In these cases, the van der Waals contact of the anions with the CD cavity will be too loose to restrict the motion of the anions within the CD cavity and will not strongly reinforce the electrostatic interactions between the anions and the pyridinio groups. Then, the contribution of ΔH(elc) to $\Delta\Delta H$ is roughly equal to that of $\Delta\Delta H$(des), and $\Delta\Delta H \fallingdotseq 0$. At the same time, an increase in entropy, $\Delta[T\Delta S$(des)], due to desolvation is more than enough to compensate for a decrease in the entropy, $T\Delta S$(elc), due to electrostatic interactions, and thus $\Delta[T\Delta S] > 0$.

In conclusion, the remarkable increase in K_a with pyridinio substitution is mainly brought about by the combined action of the van der Waals and electrostatic interactions. Desolvation of the host molecule and the guest anion also play an important role in complexation. Although hydrophobic interactions, charge-transfer interactions, and the conformational change of the CD macrocycle will also take part in complexation, their contribution to the remarkable K_a increase would be regarded as negligible.

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