Host-Guest Complexation of Mono[6-(1-pyridinio)-6-deoxy]-α-cyclodextrin with Several Inorganic Anions

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(Received November 16, 1988)

Mono[6-(1-pyridinio)-6-deoxy]-α-cyclodextrin (**1**) formed 1:1 charge-transfer complexes with such inorganic anions as I^-, SCN^-, and Br^- in an aqueous solution to afford characteristic UV absorption bands. The binding constant (K_a) for a I^- complex with **1** was ca. 45 times as large as that with a nonmacrocyclic analog of **1**, ca. 10 times that with native α-cyclodextrin, and 4.4 times that with a β-cyclodextrin analog. The I^- ion was bound to a dipyridinio analog of **1** more strongly than to **1** by a factor of 10. The K_a values decreased with an increase in the ionic strength of the medium. The complexation was competitively inhibited by ClO_4^-. Hydrophobic, van der Waals, electrostatic, and charge-transfer interactions were supposed to take part in the complexation co-operatively.

Cyclodextrin (CD) forms host–guest complexes with a variety of molecules or ions in aqueous solutions. Several intermolecular interactions have been proposed as being responsible for the complexation:[1-4] Hydrophobic interactions, van der Waals interactions including dipole–dipole interactions and London dispersion forces, hydrogen-bonding, interactions due to the relief of high-energy water from the CD cavity upon guest complexation, and interactions due to the relief of conformational strain in a CD–water complex upon guest inclusion. Recently, the modification or functionalization of CD has attracted much attention to enhancing the binding force and/or the selectivity of a host. For example, a CD derivative in which the OH groups of CD are displaced by the apolar OCH_3 groups forms a host–guest complex with an apolar guest more stable than the native CD does.[5] In this case, the modification enhances hydrophobic and van der Waals interactions between a host and a guest. The replacement of the OH group(s) of CD with positively or negatively charged group(s) results in an increase in the affinity of the host for the oppositely charged guests.[6-9] Electrostatic interactions between the host and guests are responsible for the binding.

In the course of an investigation of charged CD,[8-10] we recently found that a positively charged CD, mono[6-(1-pyridinio)-6-deoxy]-α-CD (**1**), forms stable 1:1 charge-transfer (CT) complexes with such inorganic anions as I^- and SCN^- to give characteristic absorption bands in the UV spectra. It has been known that the 1-alkylpyridinium ions form CT complexes with a few inorganic anions.[11-13] However, the interactions between them are very weak in an aqueous solution.[12] In contrast, the binding constant (K_a) for a complex of I^- with **1** is considerably larger than that for a complex of I^- with either the native α-CD or the 1-alkylpyridinium ion. This finding seems interesting in view of the development of host compounds to which inorganic anions are bound strongly and/or selectively. Only a few host compounds with such ability have hitherto been reported.[14-17] The present article deals with the binding properties of **1** and related compounds in aqueous solutions, together with the effects of environmental factors, such as the ionic strength (I_c) and polarity of the medium, on the complexation of **1** with the I^- and SCN^- ions.

Experimental

Materials. The α- and β-CD's were kindly supplied by the Nihon Shokuhin Kako Co., Ltd., and were dried overnight in vacuo at 110 °C. Reagent-grade pyridine and dimethyl sulfoxide (DMSO) were dried over calcium hydride and distilled in the presence of fresh calcium hydride before use. The hydrogencarbonate salts of **1** and A,D-bis[6-(1-pyridinio)-6-deoxy]-α-CD (**2**) were prepared by refluxing solutions of the corresponding C(6)-*O*-sulfonylated α-CD's in dry pyridine, followed by the column chromatography of the products on a CM-cellulose column with the elution of aqueous ammonium hydrogencarbonate solutions.[10] The hydrogencarbonate salts of mono[6-(1-pyridinio)-6-deoxy]-β-CD (**3**)[9] and methyl 6-(1-pyridinio)-6-deoxy-α-D-glucopyranoside (**4**)[10] were also prepared in a similar manner. Reagent-grade methanol was used after distillation. The inorganic salts, such as KI, KSCN, KBr, KCl, $KClO_4$, K_2SO_4, and NH_4HCO_3, were reagent grade and were used without further purification. The ionic strengths of aqueous solutions were adjusted, if necessary, using K_2SO_4 or KCl. The deuterium oxide (Merck, 99.75%) and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) were available for ^1H NMR use.

Apparatus. The absorption spectra were measured with a Hitachi Model 220 spectrophotometer. The quartz cells (1.0 cm) were maintained at a constant temperature (25 °C) by means of a jacket through which water was circulated from a constant-temperature bath. The ^1H NMR spectra were recorded using a JEOL Model JNM-GX270 FT NMR spectrometer (270 MHz).

Results

Formation of CT Complexes of 1—4 with I^-. Aqueous solutions of 0.4—0.8 mmol dm^{-3} **1**—**3** (pH 8.1—8.5[18]) or 5 mmol dm^{-3} **4** (pH 8.8[18]) exhibited virtually nothing of either UV or visible absorption in the region of wavelengths longer than 280 nm. When KI was added to the solutions, characteristic absorp-

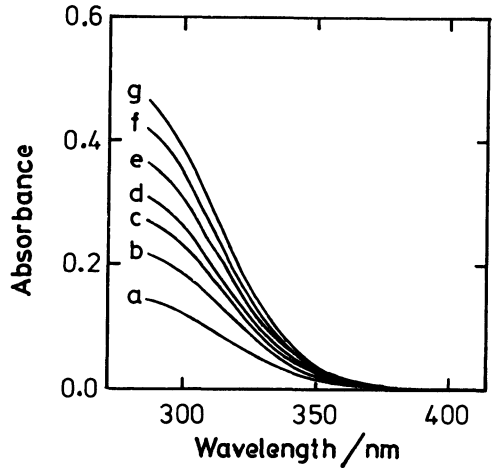

Fig. 1. Absorption spectra of 0.80 mmol dm^{-3} **3** in aqueous solutions containing various amounts of KI at 25 °C. [KI]/mmol dm^{-3}: (a) 10, (b) 20, (c) 29, (d) 39, (e) 57, (f) 83, and (g) 115.

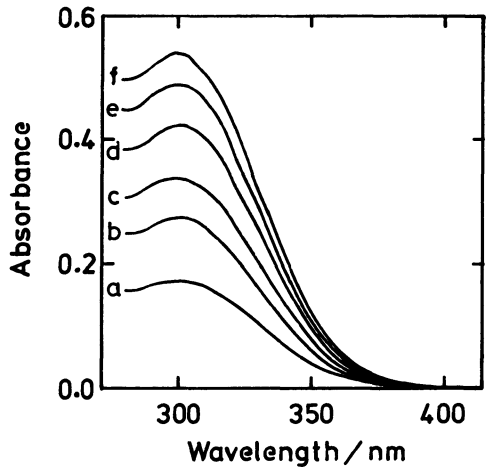

Fig. 2. Absorption spectra of 0.80 mmol dm^{-3} **1** in aqueous solutions containing various amounts of KI at 25 °C. [KI]/mmol dm^{-3}: (a) 2.5, (b) 4.9, (c) 7.1, (d) 11.3, (e) 17.0, and (f) 23.5.

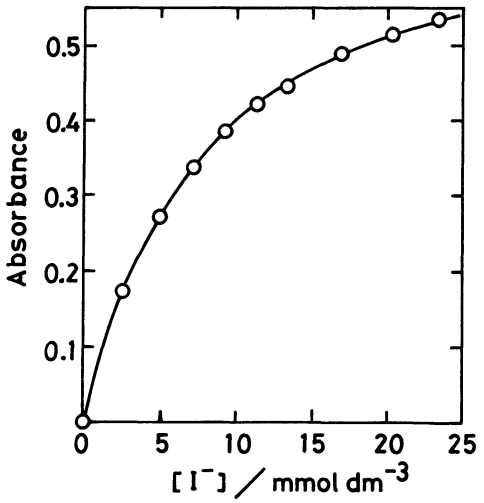

Fig. 3. Changes in absorbance at λ=300 nm of an aqueous **1** solution with increasing [I$^-$] at 25 °C. The solid line was obtained by the curve-fitting analysis upon an assumption of 1:1 complexation between **1** and I$^-$.

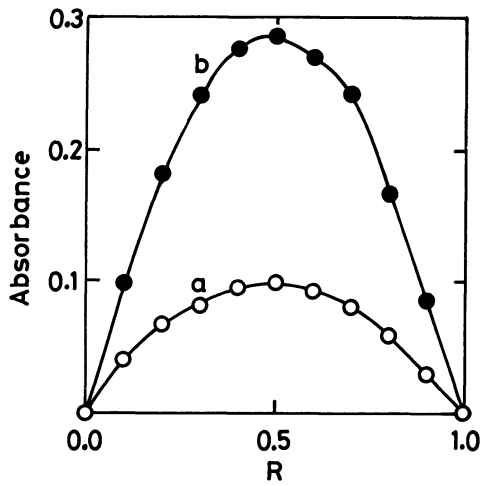

Fig. 4. Plots of absorbance at 300 nm against the ratio R=[host]/([host]+[guest]) for a **1**-KI system (a) at [host]+[guest]=2.0 mmol dm^{-3} and a **2**-KI system (b) at [host]+[guest]=1.0 mmol dm^{-3}.

tion bands appeared in the wavelength region from 280 to 350 nm. In a **3**-KI system (Fig. 1), the absorbance gradually increased with a decrease in the wavelength. No absorption maximum was observed in this wavelength region, similarly to the case of a CT complex of the 1-methylpyridinium ion (**5**) with I$^-$.[11] On the other hand, a **1**-KI system (Fig. 2) gave an apparent absorption maximum (λ_{max}) at 300 nm, indicating that a CT complex between **1** and I$^-$ is more stable than one between **3** and I$^-$.[13] The addition of KI to an aqueous solution of the dipyridinium derivative **2** also resulted in the appearance of a CT absorption band (λ_{max}=297 nm) very similar to that for a **1**-KI system. A CT band observed for an aqueous mixture of a nonmacrocyclic analog **4** with KI resembled that for a **3**-KI system.

The binding constants, K_a, for CT complexes of **1**—**4** with I$^-$ were determined by the curve-fitting analysis, by means of a microcomputer, of the changes in the absorbance at a given wavelength with the KI concentration, upon an assumption of a 1:1 complexation. The curves thus calculated were well fitted to the observed data (Fig. 3), indicating that the assumption of a 1:1 complexation is valid. The 1:1 stoichiometry was also confirmed by the continuous-variation method for complexes of **1** and **2** with I$^-$. Figure 4 shows the plots of the absorbance at 300 nm against the R=[host]/([host]+[guest]) ratio. The plots for both **1**-I$^-$ and **2**-I$^-$ systems gave maximum absorbances at R=0.5, indicating the 1:1 complexation. No indication of 1:2 complexation was

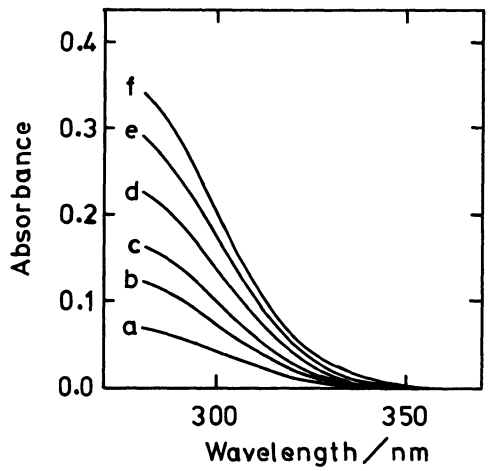

Fig. 5. Absorption spectra of 0.80 mmol dm^{-3} **1** in aqueous solutions containing various amounts of KSCN at 25 °C. [KSCN]/mmol dm^{-3}: (a) 0.6, (b) 1.2, (c) 1.8, (d) 3.0, (e) 4.8, and (f) 7.2.

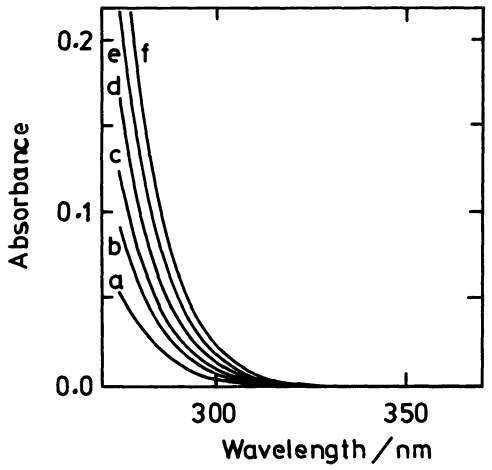

Fig. 6. Absorption spectra of 0.50 mmol dm^{-3} **1** in aqueous solutions containing various amounts of KBr at 25 °C. [KBr]/mmol dm^{-3}: (a) 14, (b) 28, (c) 41, (d) 63, (e) 103, and (f) 173.

recognized, even for a dipyridinio derivative **2**. The K_a values thus determined are shown in Table 1. The K_a value (3.0 mol^{-1} dm^3) for a nonmacrocyclic compound **4** was close to that (2.3 mol^{-1} dm^3) for **5**.[12] Interestingly, the K_a value (136 mol^{-1} dm^3) for **1** was remarkably larger than those for **4** and native α-CD by factors of about 45 and 10 respectively. It is evident that the hydrophobic cavity of **1** contributes to the stabilization of a CT complex of **1** with I^-. The K_a value (31 mol^{-1} dm^3) for a β-CD analog **3** was significantly smaller than that for **1**, though it was larger than those for **4** and native β-CD. Since the cavity size of **3** is larger than that of **1**, the van der Waals interactions between **3** and I^- may be weaker than that between **1** and I^-. The K_a value (1320 mol^{-1} dm^3) for a dipyridinio derivative **2** was about 10 times as large as that for the monopyridinio derivative **1**. It is also noteworthy that the molar absorption coefficient (ε) for a **2**–I^- CT complex was about twice that for a **1**–I^- complex. The two pyridinio groups in **2** may participate cooperatively in the stabilization of a CT complex with I^-.

Formation of CT Complexes of 1 and 2 with Inorganic Anions Other than I^-. According to Kosower and Klinedinst,[11] 1-alkylpyridinium ions form CT complexes not only with I^-, but also with SCN^- and Br^-. Hence, the complexation of **1** and **2** with inorganic anions other than I^- was examined by means of absorption spectrophotometry. The addition of KSCN or KBr to an aqueous solution of **1** resulted in the appearance of UV absorption in the wavelength region from 280 to 350 nm; such absorption is characteristic of a CT complex (Figs. 5 and 6). An aqueous mixture of **2** with KSCN or KBr also gave a similar CT band. The spectral data were analyzed by the curve-fitting method described in the preceding paragraph. The results indicated that **1** and **2** form 1 : 1 complexes with SCN^- and Br^-. The K_a values thus determined are summarized in Table 1. The K_a values for the **1**- and **2**–SCN^- systems were, respectively, about 12 and 80 times as large as that for a native α-CD–SCN^- system. The K_a values for the **1**- and **2**–Br^- systems were also larger than that for a native α-CD–Br^- system by factors of ca. 10 and 42 respectively. No CT absorption band was observed for aqueous mixtures of **1** and **2** with such inorganic salts as KCl, $KClO_4$, and K_2SO_4. Kosower and Klinedinst[11] also reported that the ClO_4^- ion forms no CT complex with **5**.

Effect of the Ionic Strength on the Binding Constants for CT Complexes of 1—3 with I^- and SCN^-. Kosower and Burbach[12] suggested that the K_a value for a CT complex of **5** with I^- is sensitive to the ionic strength, I_c, of the medium. Hence, the effect of I_c on the K_a values was examined for CT complexes of **1** and **2** with I^- and SCN^-. The I_c of the medium was adjusted by K_2SO_4. It is known that the sulfate ion forms no inclusion complex with α- and β-CD.[19–22] The K_a values were spectrophotometrically determined at I_c=1.0; they are summarized in Table 2. An increase in I_c caused a marked decrease in K_a values for the systems examined. Thus, the K_a values for the **1**–I^- and **1**–SCN^- systems at I_c=1.0 were 0.54—0.58 times those determined at I_c<0.024. The effect of I_c on K_a was more remarkable in divalent **2** systems than in monovalent **1** systems. In the **2**–I^- and **2**–SCN^- systems, the K_a values were only 0.25—0.28 times those at I_c<0.007. The addition of K_2SO_4 causes a decrease in the ionic activities of the host and guest ions, thus weakening the complexation between them. Thus, it is evident that electrostatic interactions are also responsible for the complexation of **1** and **2** with I^- and SCN^- and that the contribution of the electrostatic interactions to the complexation is larger in divalent **2**

Table 1. Binding Constants, K_a, for CT Complexes of **1** and the Related Compounds with a Few Inorganic Anions in an Aqueous Solution at 25 °C

Anion	Host	K_a / mol^{-1} dm^3	$\varepsilon\times10^{-3}$[a] / mol^{-1} dm^3 cm^{-1}	I_c / mol dm^{-3}
I^-	**1**	136 ± 2	0.88	<0.024[b]
	2	1320 ±20	1.86	<0.004[b]
	3	31 ± 2	0.60	<0.095[b]
	4	3.0 ± 0.1	0.45	<0.15[b]
	5[c]	2.3 ± 0.3	0.34[d]	0.01
	α-CD[e]	13.2		0.02
	β-CD[e]	3.9		0.02
SCN^-	**1**	286 ± 7	0.39	<0.008[b]
	2	1850 ±20	0.77	<0.006[b]
	3	14 ± 1	0.33	1.00
	α-CD[e]	22.8		0.02
	β-CD[e]	4.5		0.02
Br^-	**1**	8.4 ± 0.2	0.57[f]	<0.18[b]
	2	36 ± 1	0.16	<0.32[b]
	α-CD[g]	0.87± 0.02		0.50

a) Molar absorption coefficients at λ=300 nm, unless otherwise noted. b) The I_c was not kept constant. c) The 1-methylpyridinium ion; Ref. 12. d) λ=308 nm. e) Ref. 21. f) λ=280 nm. g) Ref. 25.

Table 2. The K_a/mol^{-1} dm^3 Values for Complexes of **1**—**3** with Inorganic Anions at 25 °C and I_c=1.0 as Adjusted by the Use of K_2SO_4 and KCl

Guest	Host	K_2SO_4	Ratio[a]	KCl	Ratio[a]
I^-	**1**	79 ± 1	0.58	45 ±1	0.33
	2	364 ± 7	0.28		
	3	10.2± 0.3	0.33	5.5±0.2	0.18
SCN^-	**1**	155 ± 5	0.54	83 ±2	0.29
	2	470 ±10	0.25		
	3	14 ± 1			

a) The ratio of K_a at I_c=1.0 to K_a in Table 1.

systems than in monovalent **1** systems.

Table 2 also includes the K_a values for CT complexes of **1** and **3** with I^- and SCN^- at I_c=1.0, as adjusted by the use of KCl. It is known that Cl^- forms inclusion complexes with α-CD, though the K_a value is very small.[19,23,24] The K_a values at I_c=1.0 (KCl) were always smaller than those at I_c=1.0 (K_2SO_4) by a factor of ca. 0.55. It is reasonable to consider that Cl^- retards the complexation of **1** or **3** with I^- or SCN^- not only electrostatically but also by competitive binding to the host cavity. The competitive binding of an inorganic anion to the host cavity was distinctly demonstrated by an examination of the effect of $KClO_4$ on the complexation of **1** with I^-. The perchlorate ion is known to form a relatively stable inclusion complex with α-CD.[22-26] The addition of $KClO_4$ to an aqueous solution of 0.792 mmol dm^{-3} **1** containing 19.8 mmol dm^{-3} KI caused an apparent decrease in the absorbance in the wavelength region from 280 to 350 nm due to a CT complex (Fig. 7). The I_c value of the medium was maintained at 1.0 by the use of K_2SO_4. Since the I_c of the medium was kept constant, the retarding effect of $KClO_4$ on the complexation of **1** with I^- is attributable to the competitive binding of ClO_4^- to the host cavity. In other words, the inclusion of I^- within the host

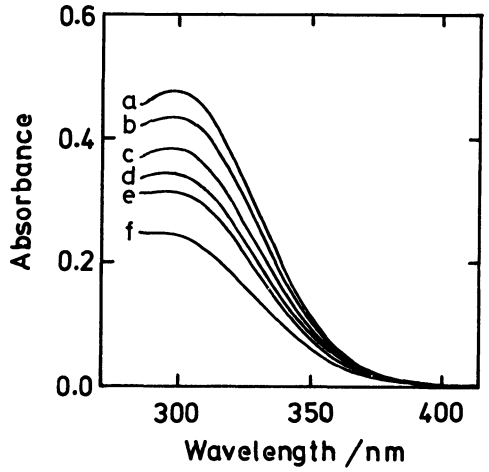

Fig. 7. Absorption spectra of a CT complex of **1** with I^- in aqueous solutions containing various amounts of $KClO_4$ at I_c=1.00 (K_2SO_4) and 25 °C. [**1**]=0.792 mmol dm^{-3}, and [KI]=19.8 mmol dm^{-3}. [$KClO_4$]/ mmol dm^{-3}: (a) 0.0, (b) 2.5, (c) 6.4, (d) 10.4, (e) 13.8, and (f) 27.8.

cavity is essential for the formation of a stable CT complex of **1** with I^-. The K_a value for a **1**-ClO_4^- system was determined to be 110 mol^{-1} dm^3 by the analysis of the inhibitory effect of ClO_4^- on the

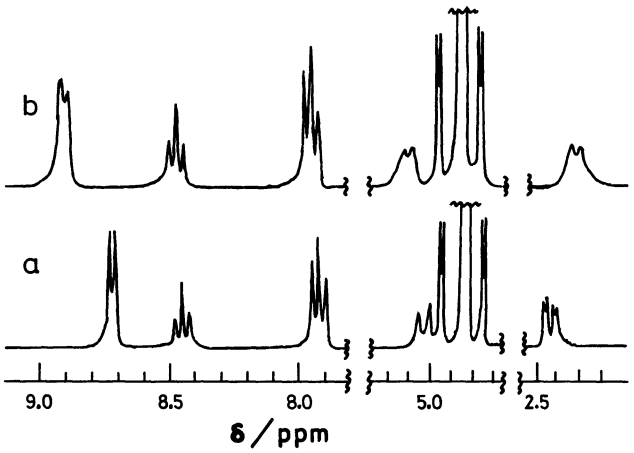

Fig. 8. Partial ^{1}H NMR spectra (270 MHz, D_2O, ref. DSS, 30 °C) of 20 mmol dm^{-3} **1** in the absence (a) and in the presence (b) of 92 mmol dm^{-3} KI.

complexation of **1** with I^-.[27] The K_a value is 3.7 times as large as that for a native α-CD-ClO_4^- system (K_a=30.6 mol^{-1} dm^3).[22]

^{1}H NMR Spectrometry of a CT Complex of 1 with I^-. The complexation of **1** with I^- was also examined by means of ^{1}H NMR spectrometry. Figure 8-a illustrates parts of the ^{1}H NMR spectrum of **1** in the absence of KI. The ortho-, meta-, and para-protons of the pyridinio group of **1** gave a doublet at δ=8.72 (2H, J=5.9 Hz), a triplet at δ=7.92 (2H, J=7.1 Hz), and a triplet at δ=8.45 (1H, J=8.1 Hz) respectively. An apparently doublet signal at δ=5.04 (1H, J=13.2 Hz) was assigned to one of the diastereotopic geminal C(6)-H's involved in the substituted glucopyranose ring [GP(A)], and a doublet-doublet signal at δ=2.43 (1H, J=3.3, 12.1 Hz), to one of geminal C(6)-H's involved in the unsubstituted glucopyranose ring [GP(B)] adjacent to GP(A).[10] The doublets at δ=4.76—4.96 (6H, J=ca. 3.2 Hz) were due to the anomeric C(1)-H's. Figure 8-b shows parts of the ^{1}H NMR spectrum of **1** in the presence of KI. The addition of KI caused a marked lower-field shift of the doublet signal due to the ortho-H's of the pyridinio group from δ=8.72 to 8.93. Furthermore, the doublet signal was significantly broadened by the addition of KI. In contrast to the signal of the ortho-H's, the triplet signals due to the meta- and para-H's of the pyridinio group showed only slight lower-field shifts and virtually no broadening of the signals upon the addition of KI. On the other hand, the apparent doublet signal and the dd-signal, due to the C(6)-H's of GP(A) and GP(B) respectively, showed a significant lower- or higher-field shift and signal broadening, whereas virtually no change was observed for the doublet signals due to the C(1)-H's. These facts indicate that the complexed I^- ion is located in the vicinity of the ortho- and C(6)-H's of **1**. The protons other than those described above gave ^{1}H NMR signals at δ=2.7—4.7; those signals were too complex to be completely assigned at the present stage of investigation. However, we also found that the complexation of **1** with I^- causes some changes in the pattern of the signals in this region.

Table 3. Effects of Organic Solvents on the λ_{max} and K_a Values of a CT Complex of **1** with I^- at 25 °C

Solvent	λ_{max}/nm	K_a/mol^{-1} dm^3
H_2O only	300	136 ±2
25% (v/v) MeOH	303	68.1±0.3
50% (v/v) MeOH	303	39.9±0.4
80% (v/v) MeOH	308	33.0±0.2
10% (v/v) DMSO	306	165 ±4
20% (v/v) DMSO	308	141 ±2
30% (v/v) DMSO	310	90.7±2.2
40% (v/v) DMSO	312	61.1±0.3
50% (v/v) DMSO	314	34.7±0.9
60% (v/v) DMSO	317	20.9±0.6
70% (v/v) DMSO	320	9.5±0.2
80% (v/v) DMSO	321	6.9±0.6

The Effect of Organic Solvents on the Complexation of 1 with I^-. Kosower showed that the CT absorption bands of 1-alkylpyridinium iodides are very sensitive to the polarity of the medium.[13] In the present work, we examined the effect of such organic solvents as methanol and DMSO on the CT absorption band and the K_a value of a **1**-I^- system (Table 3). The absorption maximum of the CT complex shifted to the direction of longer wavelengths. The effect was larger in DMSO than in methanol. These results are in agreement with those observed for 1-alkyl-4-(methoxycarbonyl)pyridinium iodides by Kosower.[13] The K_a value of a CT complex of **1** with I^- increased slightly with an increase in the DMSO concentration from 0 to 10% (v/v). A further increase in the DMSO concentration resulted in a significant decrease in the K_a value. The K_a value also decreased with the addition of methanol. DMSO and methanol are less polar than water. A decrease in the polarity of the medium with an increase in the concentration of the organic solvents is favorable for both electrostatic and CT interactions between **1** and I^-. However, it is unfavorable for hydrophobic interactions between them. Moreover, both DMSO and methanol are included within the α-CD cavity,[27,28] so they competitively inhibit the complexation of **1** with I^-. These unfavorable effects of the organic solvents may surpass the favorable effects in the systems examined, except for the cases of 10 and 20% DMSO.

Discussion

Judging from the results described in the preceding section, it seems that at least four kinds of intermolecular interactions are responsible for the complexation

of **1** with I^-: (1) Hydrophobic interactions, (2) van der Waals interactions, (3) electrostatic interactions, and (4) CT interactions. The host, **1**, forms relatively stable complexes with I^-, SCN^-, and ClO_4^-, which are known to be chaotropic or lipophilic anions.[29] On the other hand, **1** binds very weakly, if at all, to SO_4^{2-} and Cl^-, which are known to be antichaotropic or hydrophilic.[29] This fact indicates that hydrophobic interactions are involved in the complexation. The binding constant (K_a) for a I^- complex with **1** was ca. 45 times that with a nonmacrocyclic analog **4** and ca. 4.4 times that with a β-CD analog **3**. This suggests that the macrocyclic cavity of α-CD is essential for the formation of a stable complex of **1** with I^-. The I^- ion may be in close van der Waals contact with the α-CD cavity. The β-CD cavity in **3** may be too large to be in close contact with I^-. The host **1** is positively charged, and the guest, negatively charged. Thus, electrostatic interactions must also take part in the complexation. In fact, the K_a value for a **1**–I^- system decreases significantly with an increase in the I_c value of the medium. CT interactions may also contribute to the stabilization of the complex. This postulate is supported by the following observations. A mixture of **1** with I^-, SCN^-, or Br^- affords an distinct absorption band characteristic of a CT complex. The I^- and SCN^- ions are bound to **1** more strongly than to the native α-CD by factors of 6—7 at I_c=1.0. On the other hand, the K_a value for a **1**–ClO_4^- system at I_c=1.0 is only 3.7 times that for a native α-CD–ClO_4^- system. The ClO_4^- ion forms no CT complex with **1**. In conclusion, the four kinds of intermolecular interactions described above may take part cooperatively in the complexation of **1** with such inorganic anions as I^-, SCN^-, and Br^-.

Kosower and Burbach[12] suggested that, in a complex of **5** with I^-, the I^- ion is located over the center of the pyridine ring, although it is undeniable that the complexed I^- ion is located near the nitrogen of the pyridinio group. In the present **1**–I^- system, we found that ^1H NMR signals due to the ortho-H's of the pyridinio group and C(6)–H's of GP(A) and GP(B) are significantly influenced by the complexation, whereas only small changes, if any, in the signals are observable for the meta- and para-H's of the pyridinio group and the C(1)–H's of the GP's. This suggests that the complexed I^- ion is located in the vicinity of the nitrogen of the pyridinio group. The nitrogen is positively charged, so that the location of the complexed I^- ion near the nitrogen is advantageous for electrostatic interactions.

We have showed that I^- forms more stable complexes with the C(6)-mono- and C(6)-dipyridinio derivatives, **1** and **2**, than with the native α-CD by factors of ca. 10 and 100 respectively at I_c<0.024. This finding directed our attention to the development of a host compound to which inorganic anions are bound strongly and/or selectively. Very recently, we have found that the I^- is bound to the C(6)-tri- and C(6)-hexapyridinio derivatives of α-CD more strongly than to the native α-CD by factors of ca. 10^3 and 10^5 respectively at I_c<0.01. Thus, the effect of the number of the pyridinio groups on the stability is extremely large. The C(6)-di- and C(6)-tripyridinio derivatives of α-CD involve three and four regioisomers respectively. The effects of the positions of the pyridinio groups on the stability may also be interesting. The experimental results on these subjects will be presented elsewhere in detail.

It is anticipated that electrostatic and CT interactions between **1** and I^- will be strengthened by lowering the polarity of the medium. However, the addition of an organic solvent to the medium caused virtually no such favorable effect on the complexation as had been anticipated; this was because of the competitive binding of the organic molecule to the host cavity. It may be advantageous, for strengthening the electrostatic and CT interactions, to make the microenvironment around the pyridinio group less polar. In fact, we recently found that I^- is bound to the peracetylated derivative of **1** more strongly than to **1** by a factor of ca. 4 at I_c<0.024. Further details will be reported elsewhere.

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