



Thermodynamic and ^{13}C NMR Studies of the Inclusion Complexes of α - and β -Cyclodextrins with Cyano- and Nitrophenols in Aqueous Solution

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Abstract. Equilibrium constants for the formation of 1 : 1 inclusion complexes of α -cyclodextrin (α -CD) with neutral and anionic phenol derivatives (3- and 4-cyanophenols and 3- and 4-nitrophenols) have been evaluated at 5, 12, 25, and 35 °C by means of spectrophotometry. Similarly, the equilibrium constants have been determined for the inclusion complexes of β -cyclodextrin (β -CD) with the phenols. Enthalpy and entropy changes for the formation of the inclusion complexes have been estimated from the temperature dependences of the equilibrium constants. With α -CD, the enthalpy and entropy changes for the anionic species have been found to be more negative than those for the neutral ones, except for 4-cyanophenol, suggesting that the inclusion complexes of the anionic species are more rigid than those of the neutral species. From analyses of chemical shift differences in ^{13}C NMR spectra of 3- and 4-cyanophenols and 3- and 4-nitrophenols in aqueous solutions with and without CDs, a nitro or a cyano group has been found to be first bound to the α - and β -CD cavities.

Key words: cyclodextrins, phenols, inclusion complexes, spectrophotometry, thermodynamic quantities, ^{13}C NMR.

1. Introduction

Cyclodextrins (CDs) are cyclic oligomers composed of more than five D-glucopyranose residues [1]. CDs having six, seven, and eight D-glucopyranose residues are called α -, β -, and γ -CD, respectively. CDs are shaped like a truncated cone with a relatively hydrophobic cavity. Therefore, a wide variety of organic compounds can be incorporated into the CD cavity to form inclusion complexes. CDs have the potential to modify chemical reactions and achieve molecular recognition [2–8]. These characteristic abilities of CDs have thus been focused on and have been studied.

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In a previous paper we used spectrophotometry to investigate the acidities of 3-cyanophenol, 4-cyanophenol, 3-nitrophenol, 4-nitrophenol, 4-bromophenol, and 4-methoxyphenol included in the cavities of α - and β -CD [9]. These phenols, when inserted within the α -CD cavity, have been found to be stronger acids than the uncomplexed compounds, except for 4-methoxyphenol, which shows nearly the same acidity. However, 4-cyanophenol, 3-nitrophenol, and 4-methoxyphenol bound to the β -CD cavity are weaker acids than the uncomplexed compounds, although 3-cyanophenol, 4-nitrophenol, and 4-bromophenol bound to the β -CD cavity are stronger acids.

The dipole moments of CDs are estimated to be 10–20 D [10, 11]. The different effects of α - and β -CDs on the acidity are probably due to the difference in the magnitudes of the induced dipole moments of the guest caused by α - and β -CDs, because the distance between the wall of the α -CD cavity and the guest is shorter than that between the wall of the β -CD cavity and the guest. In the α -CD–4-cyanophenol and α -CD–4-nitrophenol inclusion complexes, a cyano and a nitro group are bound to the α -CD cavity, a hydroxyl and an oxido group extending into the aqueous phase [12–15]. On the other hand, the inclusion modes of β -CD–phenol inclusion complexes have not been investigated. There may be a difference in inclusion mode between α -CD and β -CD inclusion complexes. If so, the difference in inclusion mode may cause the difference in acidity of the phenols bound to the CD cavities.

Under these circumstances, we examined the inclusion complexation between α -CD (or β -CD) and several phenol derivatives, using thermodynamics and NMR spectroscopy.

2. Experimental

α -Cyclodextrin (α -CD) purchased from Nacalai Tesque was used as received. β -CD from Nacalai Tesque was recrystallized twice from water. Recrystallization from hexane and water was done twice for 3- and 4-cyanophenols, respectively, which were obtained from Tokyo Kasei Kogyo; and 3- and 4-nitrophenols from Tokyo Kasei Kogyo were twice recrystallized from ethanol.

Aqueous buffers of 0.02 mol dm⁻³ HCl–0.01 mol dm⁻³ potassium chloride (pH 2.58), 0.005 mol dm⁻³ boric acid–0.005 mol dm⁻³ potassium chloride–0.001 mol dm⁻³ NaOH (pH 8.52), and 0.0025 mol dm⁻³ NaHCO₃–0.0015 mol dm⁻³ NaOH (pH 10.3) were employed for the determination of equilibrium constants for the formation of an inclusion complex. Aqueous buffers of 0.01 mol dm⁻³ glycine–0.01 mol dm⁻³ NaCl–0.01 mol dm⁻³ NaOH (pH 10.5) were used for the ¹³C NMR measurements of anionic species of the phenol derivatives, while aqueous solutions without buffer were used for the measurement of the neutral phenol derivatives.

Absorption spectra were recorded on a Shimadzu UV-260 spectrophotometer. ¹³C NMR spectra were run on a Varian UNITY plus 400 spectrometer, operating at

100.6 MHz. At least 10 000 transients were collected for each spectrum. Chemical shifts were expressed in parts per million (ppm) relative to a standard of sodium 3-(trimethylsilyl)-1-propanesulfonate- d_4 in D_2O . ^{13}C NMR measurements were made at 35 ± 1 °C.

3. Results and Discussion

3.1. INCLUSION COMPLEXES OF α -CD (OR β -CD) WITH NEUTRAL 3-CYANOPHENOL OR NEUTRAL AND ANIONIC 4-CYANOPHENOLS AND 3- AND 4-NITROPHENOLS

The pK_a value of 4-cyanophenol has been reported to be 7.74 [9]. In pH 2.58 buffers, therefore, 4-cyanophenol exists as a neutral form. Figure 1 shows absorption spectra of neutral 4-cyanophenol (5.0×10^{-5} mol dm $^{-3}$) in buffers (pH 2.58) containing varying concentrations of α -CD at 5 °C. Upon the addition of α -CD, the absorption peak at 246 nm is shifted to longer wavelengths, accompanied by isosbestic points at 220 and 250 nm and a decrease in the peak absorbance. The spectral changes shown in Figure 1 indicate the formation of a 1 : 1 inclusion complex (α -CD·4CP) between α -CD and neutral 4-cyanophenol (4CP).



Here, K_1 is the equilibrium constant for the formation of the 1 : 1 α -CD–neutral 4-cyanophenol inclusion complex. The K_1 value can be estimated using the following equation [16, 17]:

$$1/(A - A_0) = 1/a + 1/(aK_1[\alpha\text{-CD}]_0), \quad (2)$$

where A , A_0 , a , and $[\alpha\text{-CD}]_0$ are the absorbance in the presence of α -CD, that in the absence of α -CD, a constant, and the initial concentration of α -CD, respectively. From double reciprocal plots based on Equation (2), the K_1 values for the α -CD–4-cyanophenol inclusion complex were evaluated at 5, 12, 25, and 35 °C, and are summarized in Table I. The K_1 values of 3-cyanophenol and 3- and 4-nitrophenols for α - and β -CDs as well as the K_1 values of 4-cyanophenol for β -CD were also evaluated (Table I). At pH 10.3, equilibrium constants, K_2 , of 4-cyanophenolate and 3- and 4-nitrophenolates have similarly been evaluated for α -CD and β -CD, and are summarized in Table I. The K_1 and K_2 values evaluated in this study are similar or comparable to those reported, although there are differences in some cases. The reason for the differences in K values is unclear at present.

Table I. Equilibrium constants, K_1 and K_2 , for the formation of the 1 : 1 inclusion complexes of neutral and anionic phenols with α - and β -CDs at various temperatures

Guest	Host		α -CD				β -CD			
	(n) ^a	Temp./°C	5	12	25	35	5	12	25	35
3-Cyanophenol	(n) ^a		130 ± 20	110 ± 30	94 ± 20 110 ± 30 ^b	76 ± 20	130 ± 20	120 ± 10	90 ± 10 36 ± 20 ^b	70 ± 10
	(a) ^c		1200	820	530 360 ^b	380	270	120	110 491 ^b	110
4-Cyanophenol	(n)		210 ± 20	180 ± 20	97 ± 20 120 ± 20 ^b 97 ^d	92 ± 10	580 ± 90	520 ± 30	400 ± 30 330 ± 30 ^b	280 ± 30
	(a)		1300 ± 160	1000 ± 120	640 ± 80 580 ± 50 ^b 630 ^d	570 ± 70	210 ± 30	200 ± 30	130 ± 30 230 ± 30 ^b	120 ± 30
3-Nitrophenol	(n)		220 ± 30	180 ± 30	120 ± 30 140 ± 60 ^b 124 ± 5 ^f	99 ± 40	630 ± 30	440 ± 30	240 ± 20 130 ± 10 ^e 274 ± 27 ^f	140 ± 40
	(a)		550 ± 40	440 ± 60	510 ± 30 300 ± 40 ^b 202 ± 3 ^f	420 ± 20	220 ± 20	170 ± 30	180 ± 30 75 ± 10 ^e 117 ± 19 ^f	160 ± 20
4-Nitrophenol	(n)		390 ± 20	270 ± 30	230 ± 10 170 ± 20 ^b 160 ^d 220 ± 20 ^f	190 ± 30	350 ± 50	330 ± 70	210 ± 60 220 ± 50 ^b 130 ± 15 ^e 350 ± 50 ^f	160 ± 60
	(a)		8000 ± 700	3700 ± 400	2000 ± 200 1910 ± 80 ^b 1590 ^d 1800 ± 300 ^f	1100 ± 100	1000 ± 70	930 ± 50	720 ± 50 320 ± 60 ^b 410 ± 40 ^e 570 ± 25 ^f	450 ± 40

^a Neutral species.

^b Ref. 9.

^c Anionic species.

^d M. R. Eftink and J. C. Harrison: *Bioorg. Chem.* **10**, 388 (1981).

^e A. Buvari and L. Barcza: *J. Chem. Soc., Perkin Trans. 2* 543 (1988).

^f G. L. Bertrand, J. R. Faulkner, Jr., S. M. Han, and D. W. Armstrong: *J. Phys. Chem.* **93**, 6863 (1989).

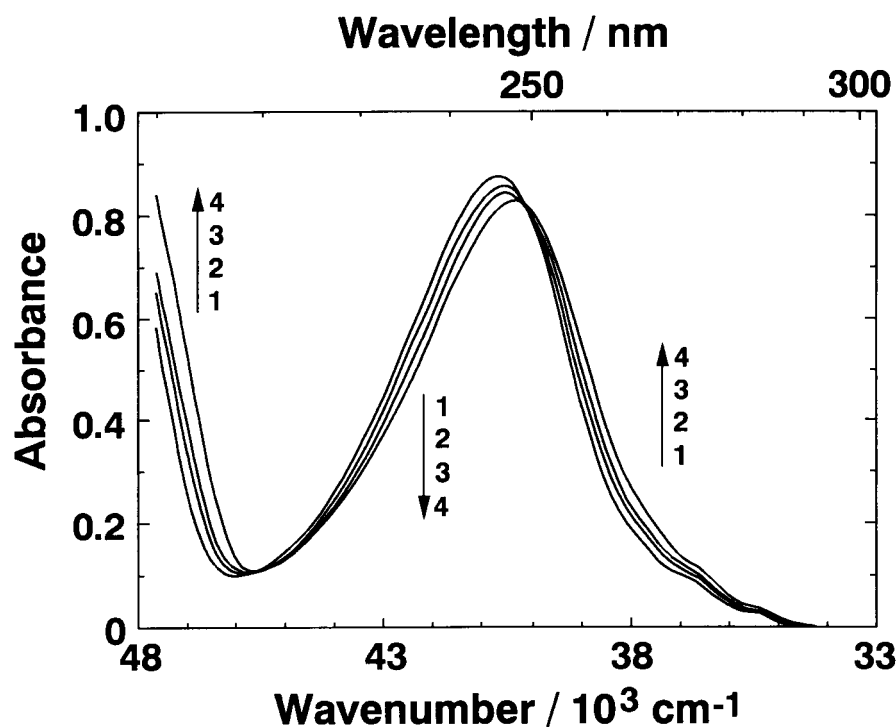


Figure 1. Absorption spectra of 4-cyanophenol ($5.0 \times 10^{-5} \text{ mol dm}^{-3}$) in pH 2.58 buffers containing varying concentrations of α -CD at 5°C . Concentration of α -CD: (1) 0, (2) 1.0×10^{-3} , (3) 2.0×10^{-3} , and (4) $5.0 \times 10^{-3} \text{ mol dm}^{-3}$.

3.2. INCLUSION COMPLEXES OF 3-CYANOPHENOL WITH α - AND β -CDS IN ALKALINE SOLUTIONS

The pK_a values of CDs are 12.1–12.3 [18–20]. On the other hand, the pK_a value of 3-cyanophenol is 8.66 [9]. The pH range at which all 3-cyanophenol molecules are deprotonated is above about 12 [9]. Because, at such a high pH, CDs are partly deprotonated, there is no pH range where 3-cyanophenol and CDs are predominantly present as an anion and a neutral species, respectively. Consequently, the K_2 value for the formation of the α -CD–3-cyanophenolate inclusion complex could not be estimated from a double reciprocal plot. Figure 2 shows absorption spectra of 3-cyanophenol ($2.7 \times 10^{-4} \text{ mol dm}^{-3}$) in pH 8.52 buffers at 5°C in the absence and presence of α -CD. As the α -CD concentration is increased, the intensity of the 295-nm band due to neutral 3-cyanophenol is reduced, whereas the intensity of the 322-nm band due to anionic 3-cyanophenol is enhanced.

To evaluate the K_2 values, we performed experiments in the pH range in which CD exists as a neutral form. At such pHs (e.g., 8.52), 3-cyanophenol exists partly as the neutral form. At a wavelength where only 3-cyanophenolate and its inclusion complex absorb light, the absorbance is expressed by the sum of the absorbances

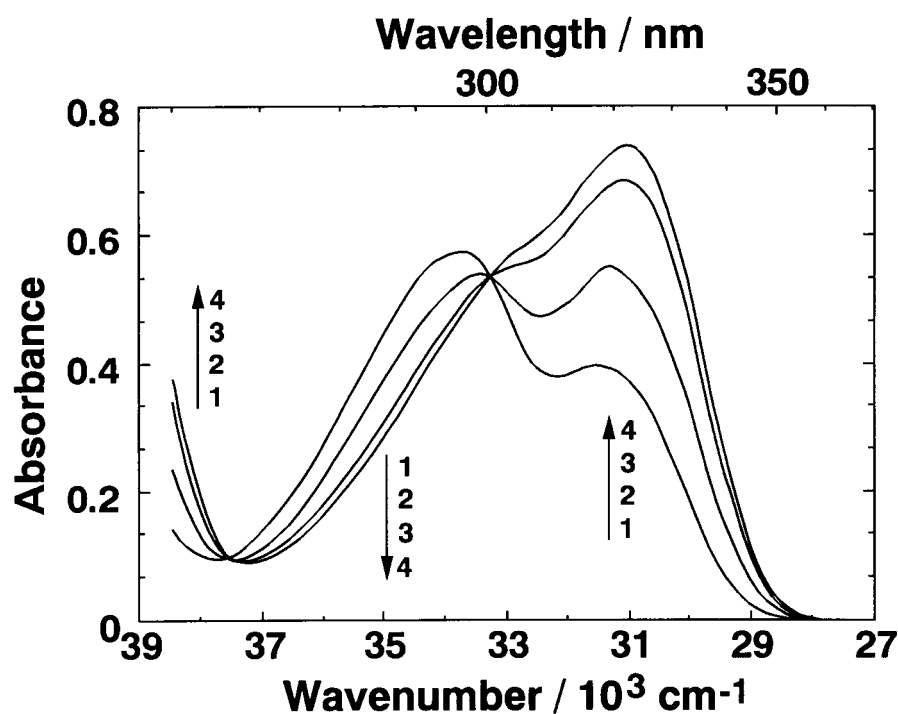


Figure 2. Absorption spectra of 3-cyanophenol ($2.7 \times 10^{-4} \text{ mol dm}^{-3}$) in pH 8.52 buffers containing varying concentrations of α -CD at 5°C . Concentration of α -CD: (1) 0, (2) 1.0×10^{-3} , (3) 5.0×10^{-3} , and (4) $1.0 \times 10^{-2} \text{ mol dm}^{-3}$.

of 3-cyanophenolate (3CP^-) and its inclusion complex. The concentration ratio, x , of $[3\text{CP}]$ to $[3\text{CP}^-]$ remains constant regardless of the presence of α -CD. Using the K_1 and K_2 values, the absorbance is represented as [9]

$$A = \frac{(\varepsilon_0^a + \varepsilon_1^a K_2 [\alpha\text{-CD}]_0) [3\text{CP}]_0}{((1 + K_1 [\alpha\text{-CD}]_0)x + (1 + K_2 [\alpha\text{-CD}]_0))} \quad (3)$$

where ε_0^a and ε_1^a are the molar absorption coefficient of uncomplexed 3-cyanophenolate and that of the α -CD–3-cyanophenolate inclusion complex, respectively. Since the K_1 and ε_0^a values are known, we can simulate the observed absorbances as a function of the initial concentration of α -CD by employing ε_0^a and K_2 as variables.

Figure 3 illustrates the best fit curve for the absorbances observed at 320 nm and 5°C , which has been calculated with $\varepsilon_0^a = 3420 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ and $x = 1.61$. From the simulation, $1200 \text{ mol}^{-1} \text{ dm}^3$ and $3360 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ are obtained as the K_2 and ε_1^a values, respectively. A K_2 value greater than the K_1 value is consistent with the spectral change shown in Figure 2. The K_2 values thus obtained for the α -CD– and β -CD–3-cyanophenol inclusion complexes are tabulated in Table I.

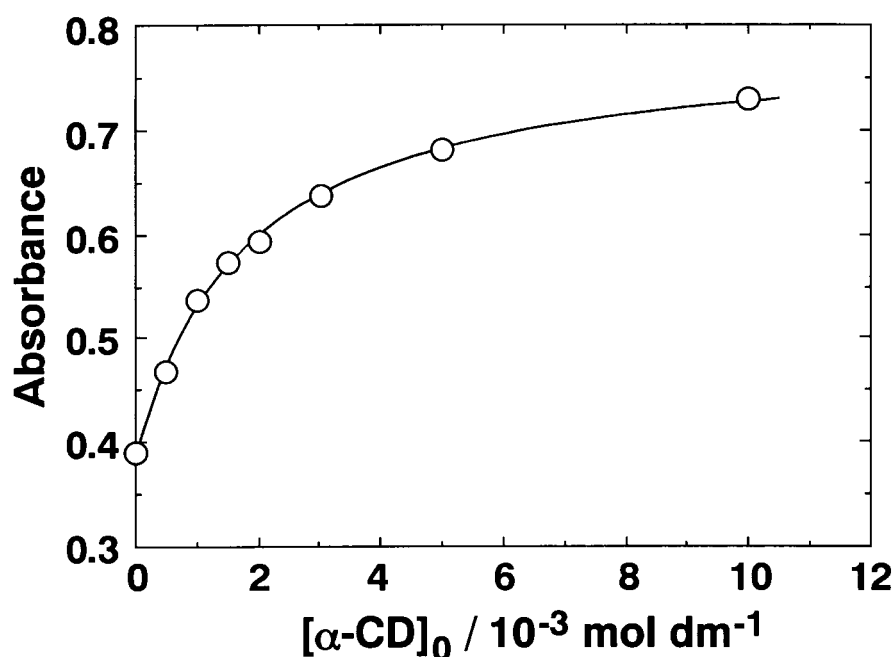


Figure 3. The best fit curve simulated for the absorbances (320 nm) of 3-cyanophenol (2.7×10^{-4} mol dm⁻³) in pH 8.52 buffers containing varying concentrations of α -CD. The simulation curve was calculated with the evaluated values of $K_1 = 130$ mol⁻¹ dm³ and $\epsilon_0^a = 3420$ mol⁻¹ dm³ cm⁻¹ and with the variables of $K_2 = 1200$ mol⁻¹ dm³ and $\epsilon_1^a = 3360$ mol⁻¹ dm³ cm⁻¹.

3.3. ENTHALPY AND ENTROPY CHANGES FOR THE FORMATION OF INCLUSION COMPLEXES OF THE PHENOLS WITH α - AND β -CDS

From the temperature dependences of the K_1 and K_2 values for the formation of the inclusion complexes of the phenols with α - and β -CDs, the values of the enthalpy and entropy changes (ΔH and ΔS) were estimated, and are summarized in Table II, together with several literature data.

Except for 4-cyanophenol, the $-\Delta H$ values for the α -CD–anionic species inclusion complexes are about double or much greater than those for the corresponding α -CD–neutral species inclusion complexes. Furthermore, the ΔS values for the α -CD–anionic species inclusion complexes are more negative than those for the corresponding α -CD–neutral species inclusion complexes. These results indicate that the interactions between α -CD and the anionic phenol are stronger than those between α -CD and the neutral phenol and that the α -CD–anionic phenol inclusion complexes have more rigid structures compared to the α -CD–neutral phenol inclusion complexes. These are due most likely to the stronger hydrogen bonding of the anionic species compared to the corresponding neutral species.

As in the case of α -CD, the absolute values of ΔS for the inclusion complexes of β -CD with 3- and 4-cyanophenolates are greater than those of β -CD with neutral

Table II. Enthalpy and entropy changes for the formation of the 1:1 inclusion complexes of neutral and anionic phenols with α - and β -CDs

Guest	Host	Host			
		α -CD		β -CD	
		$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{ mol}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J K}^{-1} \text{ mol}^{-1}$
3-Cyanophenol	(n) ^a	-13 ± 5	-4.7 ± 2	-13 ± 1	-7.4 ± 2
	(a) ^b	-27 ± 1	-38 ± 4	-21 ± 6	-30 ± 2
4-Cyanophenol	(n)	-21 ± 3	-32 ± 9	-15 ± 3	-1.7 ± 3
		-19^c	-27^c		
	(a)	-20 ± 2	-13 ± 5	-15 ± 2	-10 ± 7
		-25^c	-31^c		
3-Nitrophenol	(n)	-19 ± 1	-25 ± 2	-3.9 ± 3	38 ± 9
	(a)	-36 ± 1	-74 ± 4	-6.4 ± 2	21 ± 8
4-Nitrophenol	(n)	-15 ± 2	-4.7 ± 7	-20 ± 2	-22 ± 5
		-19^c	-23^c		
		-25.8 ± 0.4^d	-42 ± 2^d	-12.0 ± 0.6^d	8 ± 2^d
		-23.0^e	-38.6^e	-10.2^e	13^e
	(a)	-45 ± 3	-87 ± 10	-18 ± 3	-8.3 ± 10
		-39^c	-69^c		
		-40.9 ± 0.9^d	-75 ± 3^d	-15.5 ± 0.2^d	1 ± 1^d
	-42.8^e	-80.9^e	-16.1^e	-3.7^e	

^a Neutral species.

^b Anionic species.

^c Ref. d in Table I.

^d G. L. Bertrand, J. R. Faulkner, Jr., S. M. Han, and D. W. Armstrong: *J. Phys. Chem.* **93**, 6863 (1989).

^e V. Rudiger, A. Eliseev, S. Simova, H.-J. Schneider, M. J. Blandamer, P. M. Cullis, and A. J. Meyer: *J. Chem. Soc., Perkin Trans.* 2 2119 (1996).

3- and 4-cyanophenols, indicating that the inclusion complexes of the phenolates have rigid structures compared to those of the neutral phenols.

It should be noted that the positive ΔS values are obtained for only the β -CD-neutral and anionic 3-nitrophenol inclusion complexes. In addition, the $-\Delta H$ values for β -CD-neutral and anionic 3-nitrophenol inclusion complexes are remarkably less than those for the other phenols examined. These ΔH and ΔS values indicate the weak interactions between β -CD and 3-nitrophenol as well as the large degree of freedom of 3-nitrophenol within the β -CD cavity. These findings also suggest that the hydrophobic interaction between β -CD and 3-nitrophenol (3-nitrophenolate) may contribute to the complexation in spite of the negative ΔH value [21].

3.4. ^{13}C NMR INVESTIGATION OF THE INCLUSION COMPLEXES OF 3- AND 4-NITROPHENOLS AND 3- AND 4-CYANOPHENOLS

We further investigated the inclusion modes of the CD inclusion complexes by measuring ^{13}C NMR spectra of the neutral and anionic phenols in aqueous solutions in the absence and presence of α - and β -CDs. Chemical shift differences ($\Delta\delta$), which are given as a difference between the chemical shift in the presence of CD ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) and that in the absence of CD, have been obtained for the neutral and anionic species of 3- and 4-cyanophenols and 3- and 4-nitrophenols, and are summarized in Table III. In the cases of the α -CD-neutral and anionic 4-cyanophenol inclusion complexes, large negative $\Delta\delta$ values are observed for C-4 and C- α , indicating the inclusion of a cyano group. Our results concerning $\Delta\delta$ values for these inclusion complexes are in agreement with the results obtained by Gelb *et al.* [12]. The negative $\Delta\delta$ values of C- α in the β -CD-neutral and anionic 4-cyanophenol inclusion complexes indicate that the cyano group in 4-cyanophenol is bound first to the β -CD cavity as well as the α -CD cavity. For neutral and anionic 3-cyanophenol in α - and β -CD solutions, the negative $\Delta\delta$ values of C-3 and C- α suggest the incorporation of the cyano group into the CD cavity.

In the cases of the α -CD-neutral and anionic 4-nitrophenol inclusion complexes, a nitro group is buried within the α -CD cavity [12–15]. Because the $\Delta\delta$ values of C-1, C-3, C-4, C-5, and C-6 are negative for the β -CD-neutral and anionic 4-nitrophenol inclusion complexes, the nitro group is located within the β -CD cavity. On the basis of the negative $\Delta\delta$ value of C-3, the same conclusion was obtained for the α -CD- and β -CD-neutral and anionic 3-nitrophenol inclusion complexes.

In all the inclusion complexes examined, therefore, the cyano or nitro group of the phenols is inserted into the β -CD cavity as well as the α -CD cavity, the hydroxyl or oxido group of the phenols being exposed to the bulk water environment. Because the inclusion modes are the same for all the phenols examined, the differences in ΔH and ΔS would be ascribed to the differences in substituent, relative position of the substituents, and/or cavity size of CD.

In contrast to the α -CD-4-nitrophenol inclusion complexes, the $\Delta\delta$ values of the carbon atoms of 4-nitrophenol in the β -CD inclusion complexes are negative except for those of C-1, suggesting that neutral and anionic 4-nitrophenol is more deeply incorporated in the β -CD cavity than in the α -CD cavity. The same is true for neutral and anionic 3-nitrophenol; neutral and anionic 3-nitrophenol are most likely incorporated more deeply in the β -CD cavity than in the α -CD cavity. The ΔS values for the formation of the β -CD-3-nitrophenol inclusion complexes are positive, whereas those of the α -CD-3-nitrophenol inclusion complexes are negative. These findings imply that, in spite of the deep penetration of the guests, the degree of freedom of the guest in the β -CD-3-nitrophenol inclusion complexes is greater than that in the α -CD-3-nitrophenol inclusion complexes. This result suggests that there may be little specific interaction such as hydrogen bonding

Table III. The $\Delta\delta$ values for the neutral and anionic species of 3- and 4-cyanophenols and 3- and 4-nitrophenols in aqueous solution^a

	$\Delta\delta/\text{ppm}$						
	C-1	C-2	C-3	C-4	C-5	C-6	C- α
3-Cyanophenol							
α -CD							
Neutral species ^b	0.318	-0.053	-0.402	-0.098	0.023	0.356	-0.091
Anionic species ^c	0.152	0.371	-0.569	0.494	-0.076	-0.220	-0.144
β -CD							
Neutral species ^b	0.409	-0.243	-0.068	-0.493	-0.076	-0.091	-0.167
Anionic species ^c	0	-0.182	-0.212	0.069	0.007	-0.251	-0.182
4-Cyanophenol							
α -CD							
Neutral species ^b	0.356	0	-0.053	-0.485 (or -0.28) ^d	-0.053	0	-0.198
Anionic species ^c	0.283	-0.066	0.064	-0.559	0.064	-0.066	-0.293
β -CD							
Neutral species ^b	0.409	0	-0.265	-0.121 (or 0.091) ^d	-0.265	0	-0.258
Anionic species ^c	0.159	0.045	-0.326	-0.417	-0.326	0.045	-0.227
3-Nitrophenol							
α -CD							
Neutral species ^b	0.318	0.205	-0.266	0.038	-0.106	0.395	
Anionic species ^c	0.053	0.003	-0.243	0.220	-0.091	0.341	
β -CD							
Neutral species ^b	0.470	-0.114	-0.016	-0.531	-0.106	-0.212	
Anionic species ^c	0.015	-0.098	-0.069	-0.205	-0.046	-0.008	
4-Nitrophenol							
α -CD							
Neutral species ^b	0.357	0.054	0.152	-0.243	0.152	0.054	
Anionic species ^c	0.220	-0.106	0.341	-0.295	0.341	-0.106	
β -CD							
Neutral species ^b	0.341	-0.006	-0.136	-0.137	-0.136	-0.006	
Anionic species ^c	0.114	-0.015	-0.228	-0.295	-0.228	-0.015	

^a The $\delta\Delta$ values calculated as the difference between the chemical shift in the presence of CD (1.0×10^{-2} mol dm⁻³) and that in the absence of CD.

^b In aqueous solution.

^c In pH 10.5 buffer (Glycine–NaCl–NaOH).

^d The C-4 signal of neutral 4-cyanophenol could not be assigned because the C-1 signal of CD was overlapped.

between β -CD and neutral 3-nitrophenol (anionic 3-nitrophenol). As seen in Table II, the $-\Delta H$ values for 3-nitrophenol in the β -CD inclusion complexes are, indeed, considerably less than those for the other phenols examined.

4. Conclusions

For the α -CD inclusion complexes, except for the 4-cyanophenol inclusion complex, ΔH and ΔS values for anionic species are more negative than those for neutral species. This result indicates that the interactions between the anionic phenols and CD are stronger than the neutral phenols and that the inclusion complexes of anionic species have more rigid structures than those of neutral species. Positive ΔS values have been obtained only for β -CD-3-nitrophenol inclusion complexes, suggesting the large degree of freedom of the guest within the β -CD cavity. From ^{13}C NMR measurements of the guests, the binding modes of all the phenols examined have been found to be the same; a cyano or a nitro group is first bound to the α - and β -CD cavity.

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