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FT-Raman Spectra of *o*-, *m*-, and *p*-Nitrophenol Included in Cyclodextrins

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Abstract

FT-Raman spectra of *o*-, *m*-, and *p*-nitrophenol included in α-cyclodextrin (CD), β-CD, hydroxypropyl (HP) β-CD, and sulfated β-CD were recorded. The phenyl ν(C=C) band of *o*- and *p*-nitrophenol in the CD inclusion complexes was shifted to higher wavenumber than that of pure *o*- and *p*-nitrophenol, whereas the phenyl ν(C=C) band of *m*-nitrophenol in the CD inclusion complexes was shifted to lower wavenumber than that of pure *m*-nitrophenol. The ring νCH peak of *o*-nitrophenol in the CD complexes was shifted to higher wavenumber than that of pure *o*-nitrophenol, whereas the ring νCH peak of *m*- and *p*-nitrophenol in the CD complexes was shifted to lower wavenumber than that of pure *m*- and *p*-nitrophenol.

Introduction

Cyclodextrins (CDs) are macrocycles formed by six or more glucose units connected by α-1,4-linkages. The best known, with six to nine glucose units, are named α-(6), β-(7), γ-(8), and δ-(9) CD. CDs form inclusion complexes with various compounds of low molecular weights [1–3]. CDs also have several advantages in other areas, such as the food and cosmetics industries and agrochemistry [4–6], especially owing to their capacity to protect the guest molecules against oxidation, light-induced reaction and loss by evaporation. Additionally, they usually enhance the aqueous solubility of poorly soluble or even insoluble compounds.

Phenols are widely used in the chemical industry as raw material, and therefore often occur in waste waters. Phenol and a number of its chloro- and nitro- derivatives appear as the most highly toxic and commonly occurring pollutants. In a previous paper [7], we reported that the geometrical isomers of substituted phenols were successfully separated by HPLC using a dynamically coated β-CD column. The separation mechanism has often been claimed to depend on the formation of inclusion complexes, where a guest molecule enters the relatively hydrophobic interior of the CD from the larger side of the opening. However, the inclusion formation of geometrical isomers of substituted phenols was not studied. Nitrophenol is a good candidate as a model compound to characterize inclusion formation by FT-Raman spectroscopy, because the stretching mode of the nitro group is easily characterized. The inclusion complexes of 2-, 3-, and 4-chlorostyrene in cyclodextrins were recorded by FT-Raman spectroscopy in the solid state [8]. It was found that the phenyl group of the 2-chlorostyrene was inserted into the hydrophobic cavity of α-CD, glycerol ether α-CD, β-CD, and glycerol ether β-CD, whereas the vinyl group was inserted into the cavity of sulfated β-CD. The phenyl group of the 3-chlorostyrene was inserted into the cavity of glycerol ether α-CD, β-CD, and glycerol ether β-CD, whereas the vinyl group was inserted into the cavity of α-CD and sulfated β-CD. The phenyl group of 4-chlorostyrene was included in the cavity of β-CD, glycerol ether β-CD and sulfated β-CD, whereas the vinyl group of 4-chlorostyrene was inserted into the cavity of α-CD and glycerol ether α-CD, respectively.

In this study, the inclusion complexes of *o*-, *m*-, and *p*-nitrophenol with cyclodextrins were prepared by freeze-drying, and then studied using FT-Raman spectroscopy in the solid state.

Experimental

Materials

α- and β-Cyclodextrin (CD), hydroxypropyl (HP) β-CD, and sulfated β-CD were obtained from Aldrich Co. All the other chemicals were reagent grade and used without further purification. Scheme I shows the structure of the host compounds used in this study.

Preparation of inclusion complexes

The inclusion complexes were prepared by mixing *o*-, *m*-, and *p*-nitrophenol (4.4×10^{-2} mmol) and cyclodextrins (4.4×10^{-2} mmol) in aqueous solution (20 mL) for 24 hr at room temperature. The inclusion complex in the solution state was dried by the freeze-drying method.

FT-Raman spectroscopy experiments

The NIR Fourier transform (FT) Raman spectra were recorded with a Bruker FT-106 Raman module, equipped with a Ge detector cooled by liquid nitrogen, connected to a Bruker

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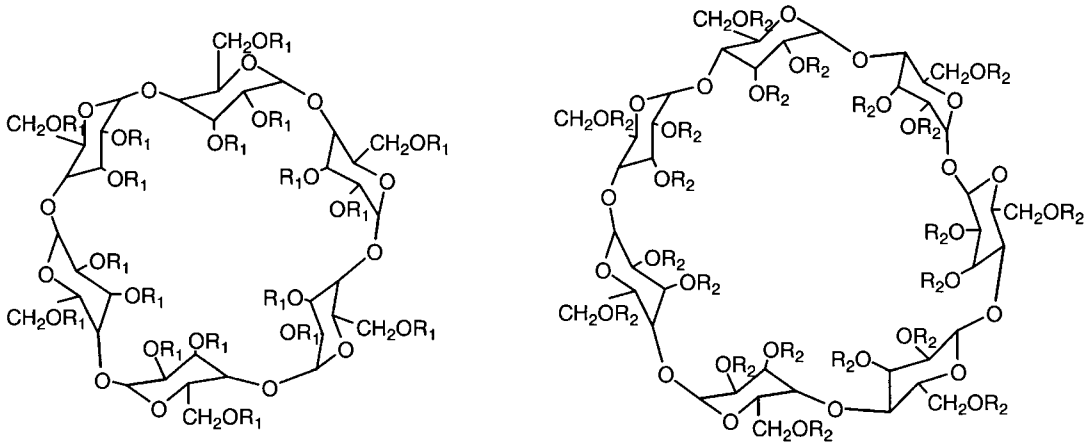

Scheme 1. Structures of the host compounds used in this study.

FT-IR 66 interferometer. For exciting the Raman spectra, a continuous wave diode-pumped Nd:YAG Laser with radiation of wavelength 1064 nm (9398.4 cm^{-1}) was used. In all cases, the laser power was 300 mW and the spectral resolution was 2 cm^{-1}.

Results and discussion

The 1550–1680 cm^{-1} regions of the FT-Raman spectra of the complexes contain the phenyl C=C stretching mode (νC=C) and have no interfering bands of the cyclodextrins. The 2950–3150 cm^{-1} regions of the guest molecules contain νCH bands. In some cases, the νCH region displays band shifts on complexation with cyclodextrins [8]. Therefore, 2 regions, 1550–1680 cm^{-1} and 2950–3150 cm^{-1}, of the nitrophenols included in cyclodextrin were studied.

FT-Raman spectra of o-nitrophenol, in the 1550–1680 cm^{-1} and 2950–3150 cm^{-1} regions

Figure 1 shows the FT-Raman spectra of *o*-nitrophenol, in the 1550–1680 cm^{-1} and 2950–3150 cm^{-1} regions, at room temperature: **1** pure *o*-nitrophenol; **2** α-CD complex; **3** β-CD complex; **4** HP β-CD complex; **5** sulfated β-CD complex. The pure *o*-nitrophenol gives the phenyl ν(C=C) band at 1587 cm^{-1}, whereas in the α-CD complex, the ν(C=C) band was shifted to 1595 cm^{-1} (see Table 1). In the 2950–3150 cm^{-1} region, pure *o*-nitrophenol gives three prominent bands at 3049, 3072, and 3093 cm^{-1} due to νCH=, ring νCH, and asymmetric νCH, respectively. The ring νCH peak in the inclusion complex was shifted to a higher value (3087 cm^{-1}).

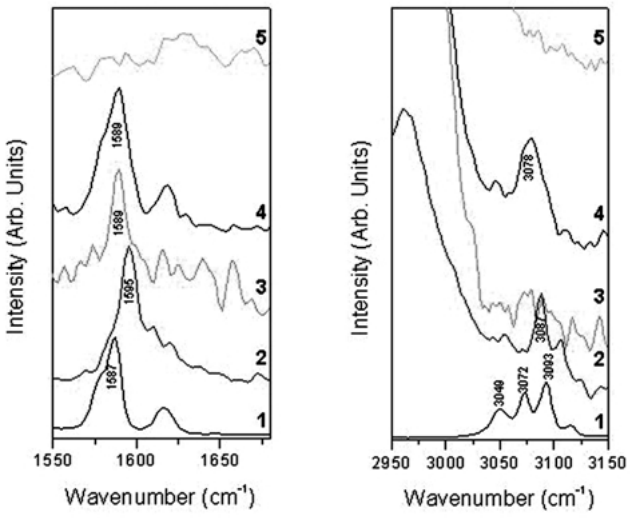

Figure 1. FT-Raman spectra of *o*-nitrophenol, in the 1550–1680 and 2950–3190 cm^{-1} regions. **1** pure *o*-nitrophenol; **2** α-CD inclusion complex; **3** β-CD inclusion complex; **4** HP β-CD inclusion complex; **5** sulfated β-CD inclusion complex.

The phenyl ν(C=C) band of *o*-nitrophenol in the β-CD complexes was shifted to higher wavenumber than that of pure *o*-nitrophenol except for the sulfated β-CD complex where a very poor spectrum was obtained. In the 2950–3150 cm^{-1} region, the ring ν(CH) band of the β-CD complexes was shifted to a higher wavenumber than the 3072 cm^{-1} of pure *o*-nitrophenol (see Table 1).

Table 1 summarizes the ν(C=C) and the ring ν(CH) values of the phenyl group of the *o*-nitrophenol. The phenyl νC=C and ring νCH stretching in *o*-nitrophenol were shifted to a higher wavenumber than that of pure *o*-nitrophenol in the following order:

Table 1. The Raman shifts of the νC=C and νCH stretching bands for the inclusion complexes of *o*-nitrophenol

	Phenyl νC=C stretching (cm^{-1})	Raman shift of the νC=C[a] (cm^{-1})	Ring νCH stretching (cm^{-1})	Raman shift of the ring νCH (cm^{-1})
o-Nitrophenol	1587	0.0	3072	0.0
Inclusion complex of α-CD	1595	8.0	3087	15.0
Inclusion complex of β-CD	1589	2.0	–	–
Inclusion complex of HP β-CD	1589	2.0	3078	5.0
Inclusion complex of sulfated β-CD	_[b]	_[b]	_[b]	_[b]

[a] Raman shift = inclusion complex – pure *o*-nitrophenol.
[b] Spectrum was recorded but no band could be observed.

Table 2. The Raman shifts of the νC=C and νCH stretching bands for the inclusion complexes of *m*-nitrophenol

	Phenyl νC=C stretching (cm^{-1})	Raman shift of the νC=C[a] (cm^{-1})	Ring νCH stretching (cm^{-1})	Raman shift of the ring νCH (cm^{-1})
m-Nitrophenol	1595	0.0	3088	0.0
Inclusion complex of α-CD	1587	−8.0	3078	−10.0
Inclusion complex of β-CD	1593	−2.0	3074	−14.0
Inclusion complex of HP β-CD	1593	−2.0	3078	−10.0
Inclusion complex of sulfated β-CD	1595	0.0	3088	0.0

[a] Raman shift = inclusion complex – pure *m*-nitrophenol.

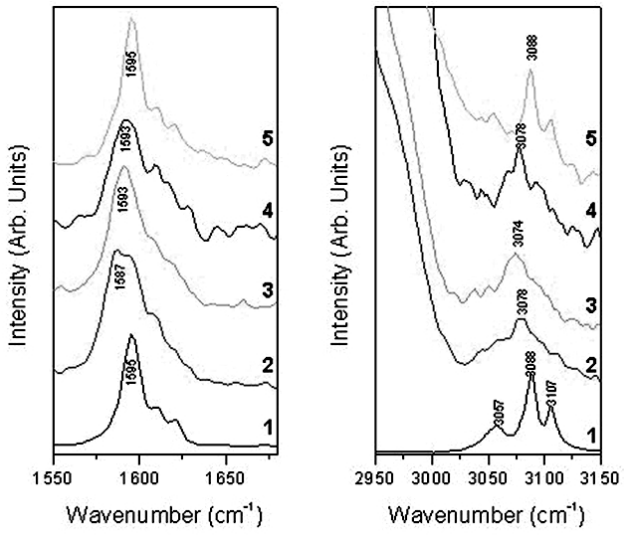

Figure 2. FT-Raman spectra of *m*-nitrophenol, in the 1550–1680 and 2950–3190 cm^{-1} regions. **1** pure *m*-nitrophenol; **2** α-CD inclusion complex; **3** β-CD inclusion complex; **4** HP β-CD inclusion complex; **5** sulfated β-CD inclusion complex.

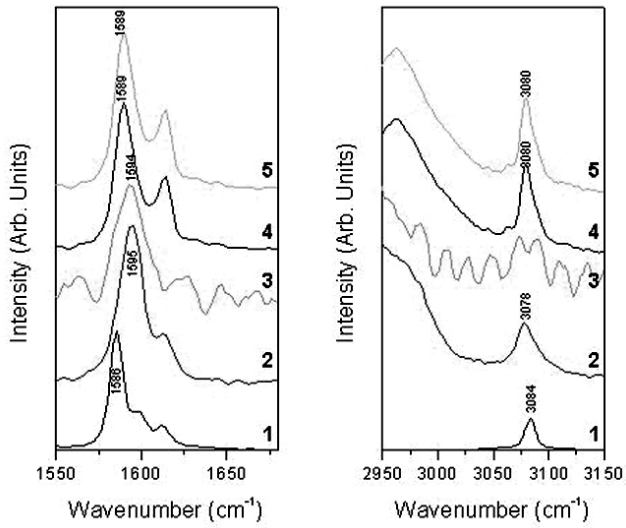

Figure 3. FT-Raman spectra of *p*-nitrophenol, in the 1550–1680 and 2950–3190 cm^{-1} regions. **1** pure *p*-nitrophenol; **2** α-CD inclusion complex; **3** β-CD inclusion complex; **4** HP β-CD inclusion complex; **5** sulfated β-CD inclusion complex.

$$\alpha\text{-CD} > \text{HP } \beta\text{-CD} = \beta\text{-CD}.$$

FT-Raman spectra of m-nitrophenol, in the 1550–1680 and 2950–3150 cm^{-1} regions

Figure 2 shows FT-Raman spectra of *m*-nitrophenol, in the 1550–1680 cm^{-1} and 2950–3150 cm^{-1} regions, at room temperature: **1** pure *m*-nitrophenol; **2** α-CD complex; **3** β-CD complex; **4** HP β-CD complex; **5** sulfated β-CD complex. Pure *m*-nitrophenol gives the phenyl ν(C=C) band at 1595 cm^{-1}, whereas in the α-CD complex, the ν(C=C) band was shifted to a lower wavenumber (1587 cm^{-1}) (see Table 2). In the 2950–3150cm^{-1} region, pure *m*-nitrophenol gave three prominent bands at 3057, 3088, and 3107 cm^{-1} due to νCH=, ring νCH, and asymmetric ν-CH, respectively. The ring νCH peak of the α-CD complex was shifted to a lower wavenumber (3078 cm^{-1}).

The phenyl ν(C=C) band of *m*-nitrophenol in the β-CD complexes was shifted to lower wavenumber than that of pure *m*-nitrophenol. In the 2950–3150 cm^{-1} region, the ring ν(CH) band of the β-CD complexes was shifted to lower wavenumber than that of pure *m*-nitrophenol (see Table 2).

Table 3. The Raman shifts of the νC=C and νCH stretching bands for the inclusion complexes of *p*-nitrophenol

	Phenyl νC=C stretching (cm^{-1})	Raman shift of the νC=C[a] (cm^{-1})	Ring νCH stretching (cm^{-1})	Raman shift of the ring νCH (cm^{-1})
p-Nitrophenol	1586	0.0	3084	0.0
Inclusion complex of α-CD	1595	9.0	3078	−6.0
Inclusion complex of β-CD	1594	8.0	–	–
Inclusion complex of HP β-CD	1589	3.0	3080	−4.0
Inclusion complex of sulfated β-CD	1589	3.0	3080	−4.0

[a] Raman shift = inclusion complex – pure *p*-nitrophenol.

Table 2 summarizes the ν(C=C) and the ring ν(CH) values of *m*-nitrophenol. The phenyl ν(C=C) stretch in *m*-nitrophenol was shifted to lower wavenumber than that of pure *m*-nitrophenol in the following order:

$$\alpha\text{-CD} > \text{HP } \beta\text{-CD} = \beta\text{-CD}.$$

However, the phenyl ν(C=C) and ring νCH stretch of *m*-nitrophenol within sulfated β-CD was not shifted.

FT-Raman spectra of p-nitrophenol, in the 1550–1680 and 2950–3150 cm^{-1} regions

Figure 3 shows the FT-Raman spectra of *p*-nitrophenol, in the 1550–1680 cm^{-1} and 2950–3150 cm^{-1} regions, at room temperature: **1** pure *p*-nitrophenol; **2** α-CD complex; **3** β-CD complex; **4** HP β-CD complex; **5** sulfated β-CD complex. Pure *p*-nitrophenol gives the phenyl ν(C=C) band at 1586 cm^{-1}, whereas in the α-CD complex, the ν(C=C) band was shifted to a higher wavenumber (1595 cm^{-1}) (see Table 3). In the 2950-3150 cm^{-1} region, pure *p*-nitrophenol shows one band at 3084 cm^{-1} due to the ring ν(CH) mode. In the α-CD complex, the band was shifted to a lower wavenumber (3078 cm^{-1}).

The phenyl ν(C=C) band of *p*-nitrophenol in the β-CD complexes was shifted to higher wavenumber than that of pure *p*-nitrophenol. In the 2950–3150 cm^{-1} regions, the ring ν(CH) band of the β-CD complexes was shifted to a lower wavenumber than that of pure *p*-nitrophenol (see Table 3).

Table 3 summarizes the ν(C=C) and the ring ν(CH) values of *p*-nitrophenol. The phenyl ν(C=C) stretch in *p*-nitrophenol was shifted to a higher wavenumber, whereas the ring ν(CH) stretch was shifted to a lower wavenumber than that of pure *p*-nitrophenol in the following order:

$$\alpha\text{-CD} > \text{HP } \beta\text{-CD} > \beta\text{-CD} > \text{sulfated } \beta\text{-CD}.$$

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