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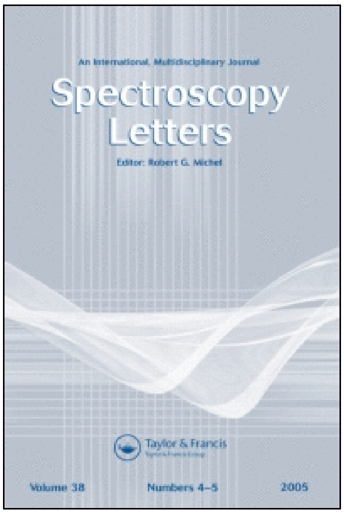

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Infrared Reflection Spectroscopy as a Probe of Interaction and Orientation of the Cyclodextrin Complex at the Surface of Silver

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INFRARED REFLECTION SPECTROSCOPY AS A PROBE OF INTERACTION AND ORIENTATION OF THE CYCLODEXTRIN COMPLEX AT THE SURFACE OF SILVER

Key words: β-Cyclodextrin, Interaction and orientation, Infrared reflection spectroscopy

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ABSTRACT

Preliminary studies concerning the structural characterization of inclusional complexation have been carried out between barbiturate and β-cyclodextrin on silver surface by using infrared reflection absorption spectroscopy (IRRAS). The results not only provide convincing evidence for the complex formation but also reveal special structural features of the supramolecules oriented on Ag surface.

INTRODUCTION

Studies pertaining to explore the complex structure of the supramolecules have been attracting much attention. Cyclodextrins are torus-shaped cyclic oligosaccharides with the hydrophobic central cavities, which have the ability to form inclusion complexes with a variety of inorganic and organic guest molecules[1-3]. This unique ability has led to the widespread utilization of cyclodextrins in many fields; the important examples include the utilization in drugs for complexation and as auxiliary additives to improve the physical and chemical properties[4-10].

Barbitone is a kind of sedative and hyponotic drug which is used for suppression of convulsion, anesthesia and other symptoms. In this study, a solid complex inclusion compound between barbitone and β-cyclodextrin (β-CD) has been prepared and characterized by differential thermal analysis, ^{1}H NMR and infrared reflection absorption spectroscopy. The results indicate that infrared reflection absorption spectroscopy can serve as a novel strategy to sensitively probe the microscopic environment and the structural characterization of the molecular assemly adsorbed on Ag surface.

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EXPERIMENTAL

1. Sample Preparation

The β-CD/barbitone complex was obtained by the coprecipitation method: 93mg of barbitone was mixed with 567mg of β-CD in a 50ml conical flask. 5ml of hot deionized water was added into the flask and the solution was heated over a water bath at 60°C for 2 hours with vigorous stirring. And then the solution was allowed to stand at ambient temperature for two days. A white crystalline material was collected by filtration, washed three times with doubly-distilled deionized water and dried. The yield of the complex was 390mg (59%) (The purity of the complex was confirmed by the elementary analysis.).

2. Instrumentation

The differential thermal analysis were measured using a CDR Differential Thermal Analysis Instrument (China). ^{1}H NMR measurements were recorded with a Bruker AM-500 Nuclear Magnetic Resonance Spectrometer. Deuterium oxide (Beijing, 99.8% atom D) was used as the solvent in the NMR studies. Sample temperature for the NMR experiments was maintained at 20°C.

The infrared reflection absorption spectroscopy was recorded on an IFS 66V Bruker Fourier Transform Infrared Spectrometer. A silver foil was dipped into the adsorbate solution for sample doping. The concentration of doping solution was kept at 0.001M. The limit of resolution for infrared reflectance spectra was 4cm^{-1}.

RESULTS AND DISCUSSION

Originally, the differential thermal analysis were explored to characterize the cyclodextrin complex. The DTA data of the individual components, β-CD, barbitone, the 1:1 physical mixture and the complex obtained are compared, which indicates the clear evidence for complexation. For example, the DTA trace of pure β-CD indicates its melting point at 225°C and desorption of trapped water at 85°C, while the DTA trace of barbitone shows the melting point at 195°C and decomposition peak at 280°C. These melting peaks of barbitone and β-CD are obviously present in the physical mixture but completely disappear in the complex. Moreover, an unknown peak at 145°C which is not appear in any other traces is clearly observed in the scan of the complex, which may be attributed to the complex formation between β-CD and barbitone. On the other hand, the evaporation peak of trapped water in β-CD can be also observed in the physical mixture but entirely disappear in the DTA trace of the complex. This phenomenon may suggest that the trapped water have been completely dispelled by the complexed barbitone, which is also indicated by the conformational analysis of ^{1}H NMR spectroscopy.

Figure 1 is the ^{1}H NMR spectra of β-CD/barbitone complex at 500MHz of D_2O solution. The assignments of β-CD peaks have been previously reported. It can be seen from Figure 1 that in the complex, the H_5 and H_6 resonances appear more resolved with respect to that in pure β-CD, and the chemical shifts of the interior protons, H_3 and H_5, move upfield by ca. 0.05ppm and 0.10ppm, respectively, while the chemical shifts of the outer protons, H_1, H_2, H_4 are relatively unaffected. In comparison, barbitone proton signals are shifted downfield by ca.

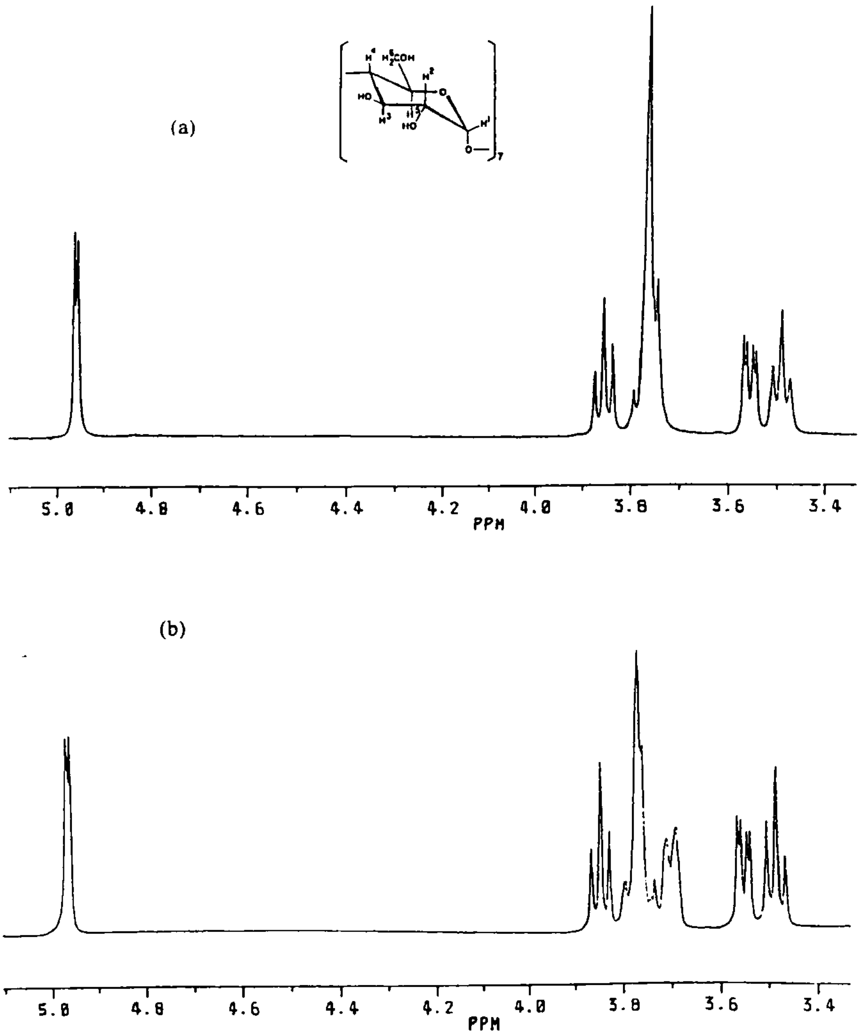

Fig. 1.(a) ^{1}H NMR spectrum of β-cyclodextrin (10^{-3}M) in D_2O
(b) ^{1}H NMR spectrum of β-cyclodextrin/barbitone complex(10^{-3}M) in D_2O

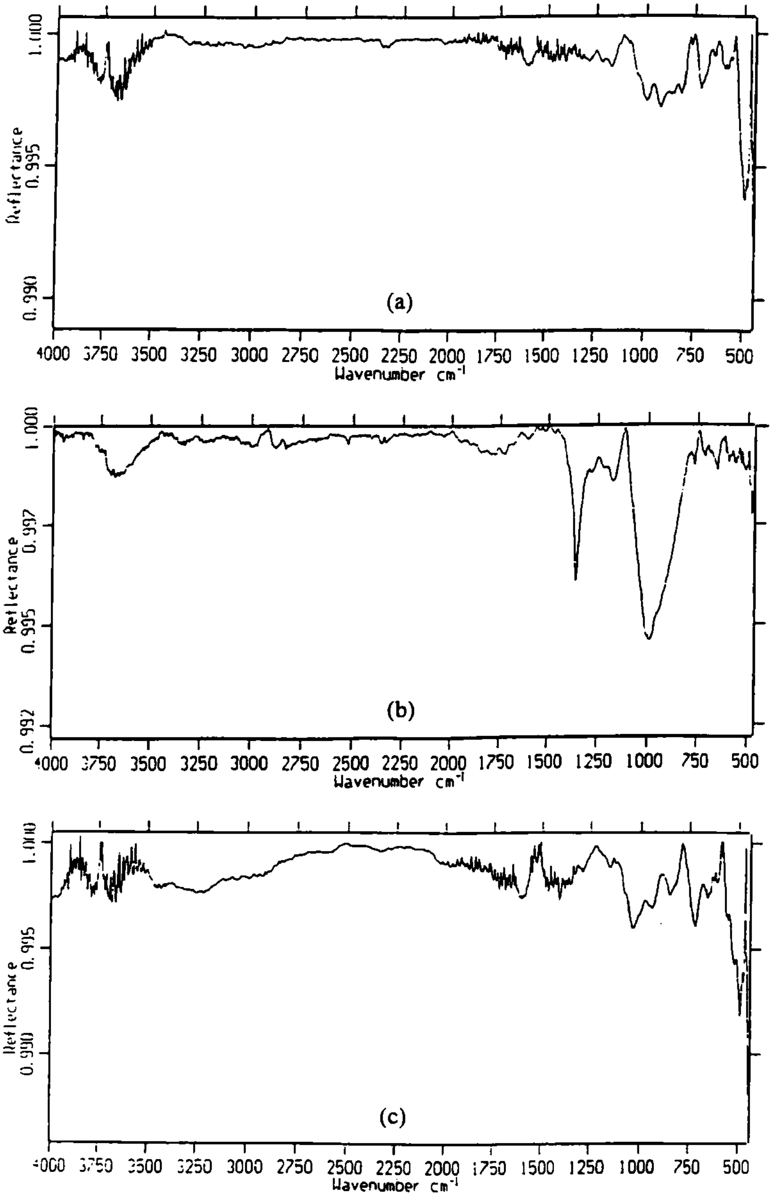

Fig. 2. Reflectance spectra of (a) barbitone, (b) β-cyclodextrin, (c) β-cyclodextrin / barbitone complex on a silver electrode

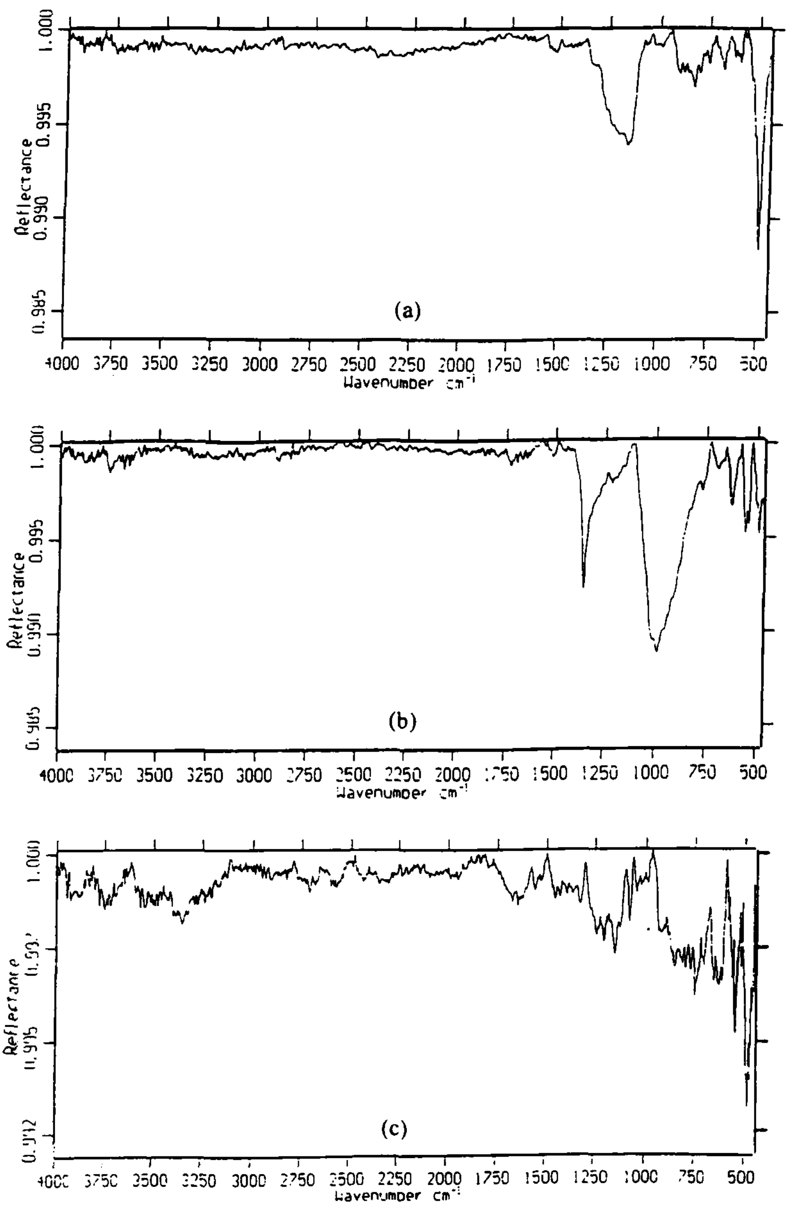

Fig. 3. Reflectance spectra for parallel polarization of (a) barbitone, (b) β-cyclodextrin, (c) β-cyclodextrin / barbitone complex on a silver electrode

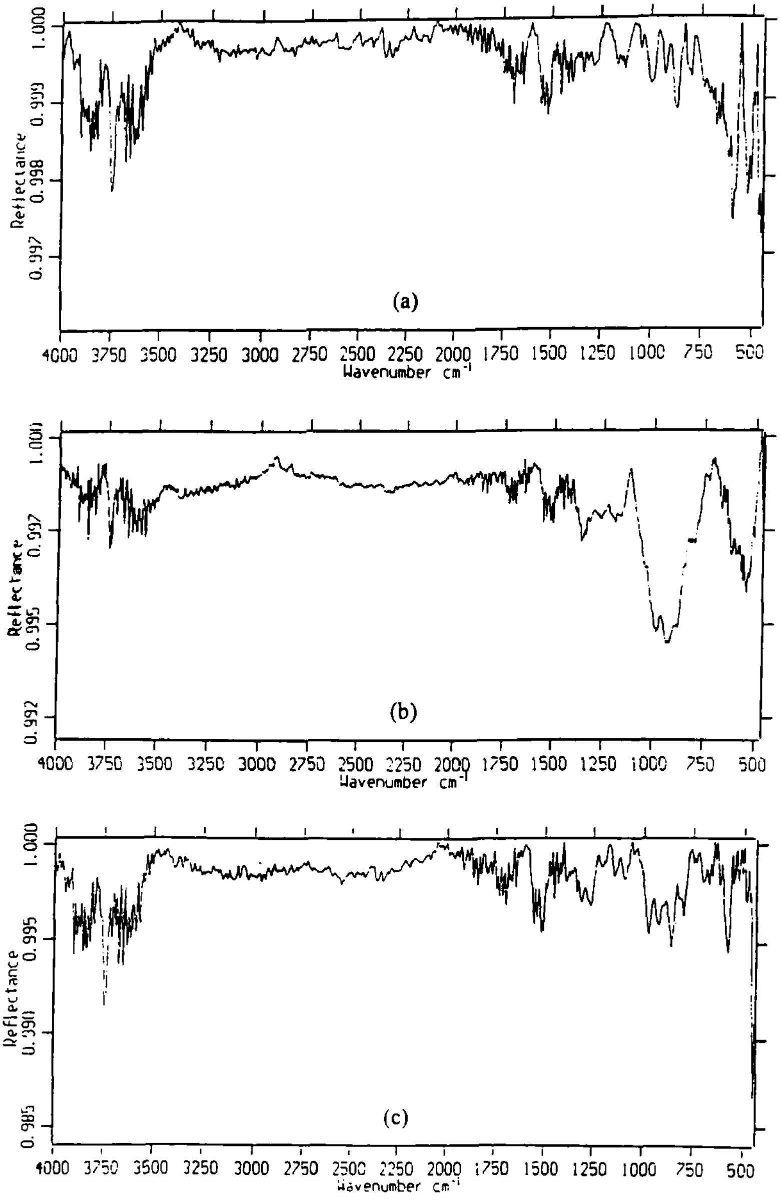

Fig. 4. Reflectance spectra for perpendicular polarization of (a) barbitone, (b) β-cyclodextrin, (c) β-cyclodextrin / barbitone complex on a silver electrode

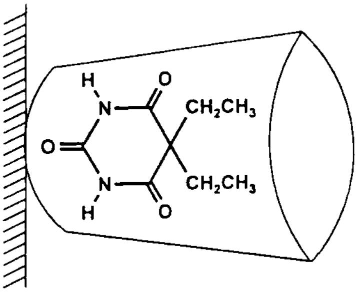

Fig. 5. The orientation of β-cyclodextrin / barbitone complex on a silver surface

0.15ppm upon complexation. Conseqently, it appears clearly that the side-chains of barbitone molecules are also included in the cavity of β-CD.

To further reveal the molecular structural features of the inclusion complexes, we have investigated reflectance spectra of the β-CD/barbitone complex at the Ag surface by using Fourier transform infrared reflection absorption spectrometry. In comparison, the reflectance spectra for parallel and perpendicular polarization of pure barbitone, pure β-CD and the complex are shown in Figure 2, Figure 3 and Figure 4, respectively. The clearest specular reflectance evidence for complexation can be observed from spectra for parallel polarization. In the complex, a new band appears in the 3100cm^{-1}--3600cm^{-1} region, which can be attributed to the N-H stretch mode. The position and breadth of this band may indicate the existence of much stronger hydrogen bonds than in the free barbitone. In addition, the intensity of the 1450cm^{-1} band of barbitone molecule considerably increases upon complexation, also suggesting that the side-chains of barbitone molecule are included in the cavity of β-CD so that they could be oriented on the Ag surface.

On the other hand, it can be found from the specular reflectance spectra for perpendicular polarization that the intensity of the 1700cm^{-1} band in pure barbitone has been markedly decreased in the complex while the 1520cm^{-1} band are slightly affected. Besides, it is obvious in the spectra for parallel polarization that the 1700cm^{-1} band also appears upon complexation. Since the 1700cm^{-1} and 1520cm^{-1} bands are mainly attributed to the C=O groups and C-N bonds respectively, this phenomenon suggests that by the inclusion of barbitone molecule into the cavity of β-CD, these relative groups are all regularly oriented at the surface of Ag.

Consequently, as is mentioned above, it is clear that the β-CD/barbitone complex may be perpendicularly attached to the Ag surface (Figure 5). These findings suggest that the specular reflectance spectroscopy could be utilized to sensitively explore the structural features of the complex supramolecular structures.

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