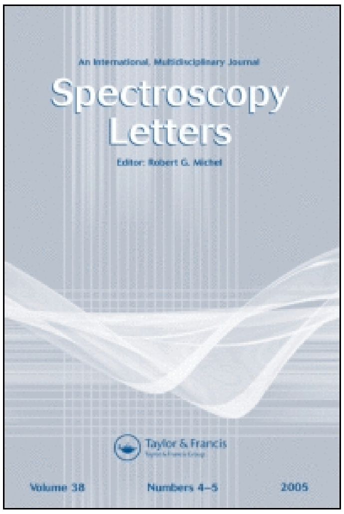

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Infrared Studies of the Weak Complex of Thiamine with β-Cyclodextrin in Aqueous Media

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INFRARED STUDIES OF THE WEAK COMPLEX OF THIAMINE WITH β–CYCLODEXTRIN IN AQUEOUS MEDIA

Key words: Inclusion complex, β–cyclodextrin, Thiamine hydrochloride, Fourier transform infrared spectroscopy.

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ABSTRACT

The spectral characteristics of thiamine hydrochloride in the absence and presence of β–cyclodextrin (β–CD) have been investigated to reveal the nature of the noncovalent interaction of the cyclodextrin system. It is indicated that Fourier transform infrared (FTIR) spectrometry could provide a unique and sensitive technique for the detection of microenvironment changes in solutions of the guest, which is especially important in the cases like the weak interaction between thiamine hydrochloride and β–CD, where other spectroscopic data lack of distinct changes.

INTRODUCTION

Interactions of cyclodextrins (CDs) with various kinds of organic or inorganic species have attracted a continuing interest. Cyclodextrins possess hydrophobic cavities owing to the high electron density provided by the glycosidic oxygens or the hydroxyl groups within the inner surface of the cavity[1], and thus in aqueous solution any geometric fit of hydrophobic molecules can be readily included into the cyclodextrin cavities which would effectively exclude water inside the cavities[2,3]. The minor structural variations induced by complexation could produce remarkably different behavior, resulting in some important changes in the physical and chemical properties[4-10]. Recently, we have studied the quenching of barbiturate fluorescence by β–cyclodextrin through spectroscopic and electrochemical methods[11,12]. Owing to the advantages of the spectral range and versatility, Fourier transform infrared (FTIR) spectrometry can afford detailed information about the molecular structure of the complex to further reveal the mechanism of the relative molecular interactions[12]. Particularly, if the complex is very weak or lacking the distinct changes of other spectroscopic data, FTIR studies could then afford a unique mode to sensitively detect the environmental changes in solutions of the guest molecules.

Fundamentally, thiamine is pertaining to carbohydrate metabolism. If complexed with CDs, it may make an appropriate model for studies of the biologically active molecule structures and molecular interactions. In this study, we have investigated the effect of β–CD on spectral properties of thiamine hydrochloride in aqueous solutions, and the results show that when the changes of fluorescence or absorption induced by the relatively weak complex are small, FTIR studies can provide important information pertaining to the complexation of cyclodextrin models.

EXPERIMENTAL

The absorption and fluorescence measurements were performed on a UV–240 spectrophotometer (Shimadzu, Japan) and a Model 204–A spectrofluorimeter Hitachi, respectively. Infrared spectra were recorded on a Nicolet 170RS Fourier transform infrared (FTIR) spectrometer equipped with a liquid nitrogen–cooled MCT detector and continuously purged with high pure dry nitrogen. The samples were placed in a 15 μm pathlength cell of Si. Infrared measurements were made with 200 times accumulation of interferograms and then Fourier transformed to acquire spectra with a 4 cm^{-1} resolution. The reference spectra including the water spectrum were recorded under similar conditions so that they could be subtracted from those of sample spectrum.

Thiamine hydrochloride was of analytical reagent grade (China) and used as supplied. The β–cyclodextrin (China) was twice recrystallized before use. Doubly–distilled deionized water was used throughout. All measurements were carried out at 20 ± 0.1 ℃.

RESULTS AND DISCUSSION

The absorption and steady–state fluorescence emission spectra of aqueous thiamine hydrochloride with and without β–CD indicate the formation of the weak complexes. Small but significant changes in the absorption spectra occur upon addition of β–CD (See Fig. 1.). The absorption band of thiamine hydrochloride located at ca. 242 nm experiences a distinct blue shift with a slight increase in absorbance in the presence of β–CD. On the other hand, with a decrease in absorbance, the weaker band centered at ca. 262 nm is red–shifted relative to that in aqueous thiamine hydrochloride alone. These spectral changes are similar to those observed when thiamine hydrochloride is transferred from water to ethanol (not shown), indicating that bound thiamine hydrochloride is in an alcohol–like environment provided by the rings of hydroxyl groups at each end of the β–CD cavity. In the meantime, it is observed that thiamine hydrochloride could be converted into a highly fluorescent compound in basic solutions in the presence or absence of an oxidant, and the excitation and emission spectra indicated an excitation maximum at 370 nm and an emission maximum at 440 nm. The fluorescence emission has been found to exhibit a little enhancement by addition of β–CD, suggesting the weak complex formed between the fluorophore and β–CD.

To obtain the information pertaining to the molecular structure of the complex and further reveal the nature of the host–guest system, we have successfully investigated the infrared (IR) spectra of this model by using Fourier transform infrared (FTIR) spectrometry. Figure 2 illustrates the infrared spectra of aqueous thiamine hydrochloride in the absence and presence of the β–CD. Some distinct changes appear in the corresponding IR spectra, indicating the presence of the inclusion complexes in solution upon addition of β–CD.

With addition of β–CD, the ca. 1560 cm^{-1}band arises from the ca. 1750 cm^{-1}band of aqueous thiamine hydrochloride alone, suggesting the diminution of the solvent effect on the vibration of the 1560 cm^{-1}band. Since the location of this band is almost identical with the position of the $C=C$, $C=N$, or NH bands in pure thiamine hydrochloride spectrum, this significant change also indicates that the breakdown of the water structure inside β–CD as well as the elimination of water molecules surrounding these functional groups of thiamine hydrochloride molecules occur by inclusion. The result is consistent with that obtained by fluorescence / absorption mode, suggesting that the nitrogen heterocycle possessing the side–chain NH_2 may be included in the hydrophobic cavity of β–CD.

In addition, another remarkable change of vibration feature is also observed by addition of β–CD. The position of the CH_3 band of aqueous thiamine hydrochloride (ca. 1360 cm^{-1}) slight shifts to lower frequency with the marked decrease of the band intensity in the presence of β–CD. This phenomenon could be also likely attributed to the inclusion of the side–chain CH_3 with the

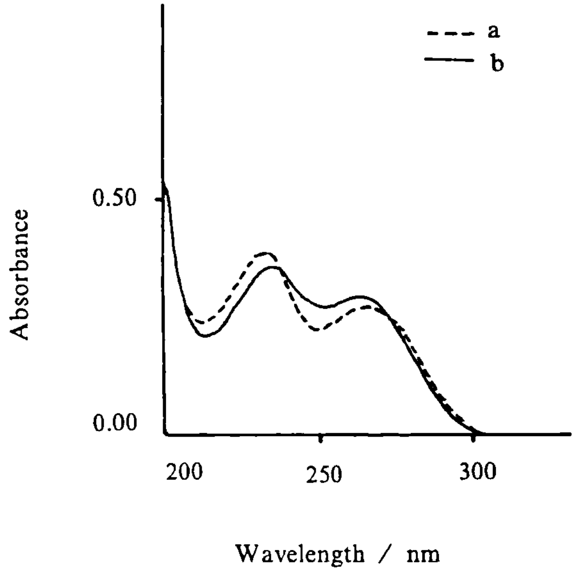

Fig. 1. Absorbance spectra of aqueous thiamine hydrochloride (3.0×10^{-5}M) (a) with β–CD (1.0×10^{-3}M) and (b) without β–CD.

elimination of water molecules upon complexation which would lead to the considerable decrease of relaxation of the solvent molecules. Consequently, from the especially striking feature of the corresponding IR spectra, it appears that the nitrogen heterocyclic moiety having the side–chains CH_3 and NH_2 is likely included by β–CD, and the microenvironment changes would be induced by forming the inclusion complexes.

As a complementary way, we have investigated the nuclear magnetic resonance (NMR) of this model to further confirm the specific host–guest interaction sites. As expected, the NMR spectrum of β–CD / thiamine hydrochloride shows no distinct changes, suggesting that the presence of the second heterocyclic moiety possessing the positively charged nitrogen within thiamine hydrochloride molecule may prevent deep penetration of the guest into the host. Therefore, in view of our findings above, it is apparent that the inclusion of the nitrogen heterocyclic moiety having the side–chains CH_3 and NH_2 and the exclusion of the second heterocyclic moiety possessing the positively charged nitrogen result in the weak complex formed between β–CD and thiamine hydrochloride.

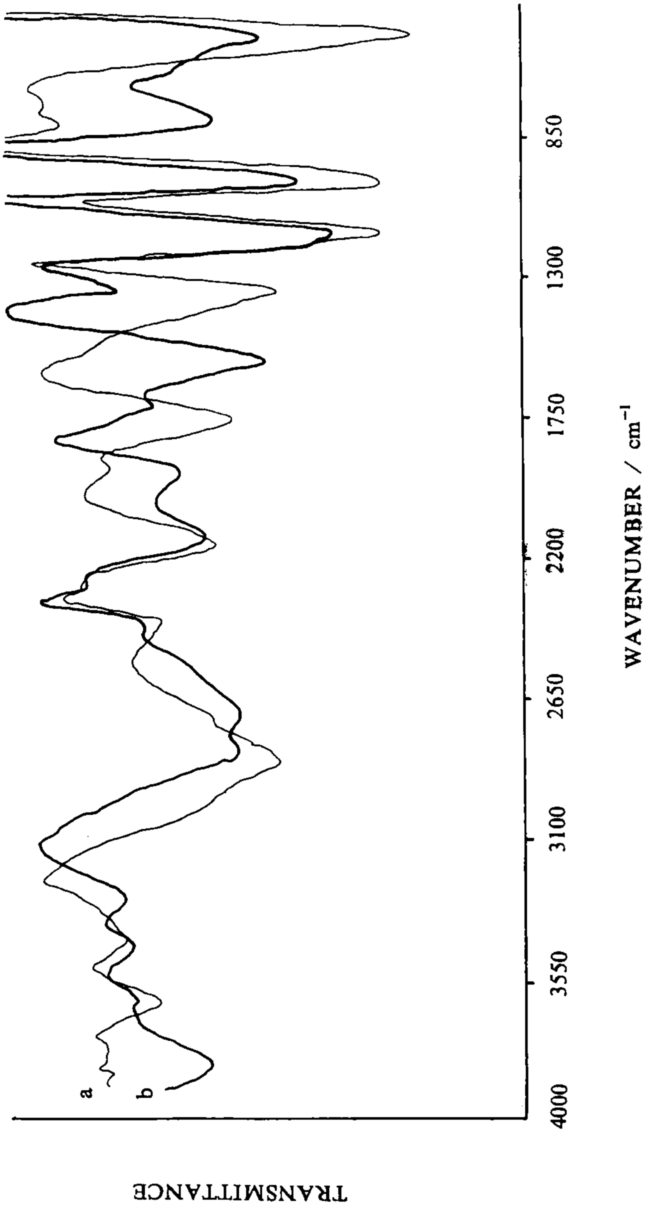

Fig. 2. FTIR spectra of aqueous thiamine hydrochloride (a) in the absence and (b) presence of β-CD.

CONCLUSION

Fourier transform infrared (FTIR) studies of the aqueous inclusion complex can provide fresh insight into the molecule structure and reveal important information in relation to the molecular interactions of the cyclodextrin complex system. Besides, the effects of cyclodextrins on the infrared spectra of the guest molecules can also be utilized to sensitively detect the environment changes in solutions of the guest. Especially, when the complex is rather weak and its other spectral characteristics show no significant changes, FTIR spectrometry can play an important role to study the mechanism of the complexation.

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