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Electrostatic Effects on the Inclusion Process of Sodium p-(3-t-Butyl-4-Hydroxyphenylazo)Benzene Sulfonate with Modified Cyclodextrin and Its Metal Complex

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ELECTROSTATIC EFFECTS ON THE INCLUSION PROCESS OF SODIUM
p-(3-t-BUTYL-4-HYDROXYPHENYLAZO)BENZENE SULFONATE WITH
MODIFIED CYCLODEXTRIN AND ITS METAL COMPLEX

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Abstract The electrostatic interaction between charged β -cyclodextrin having ethylenediamine group and the title azo compound was investigated by $^1\text{H-NMR}$ spectroscopy.

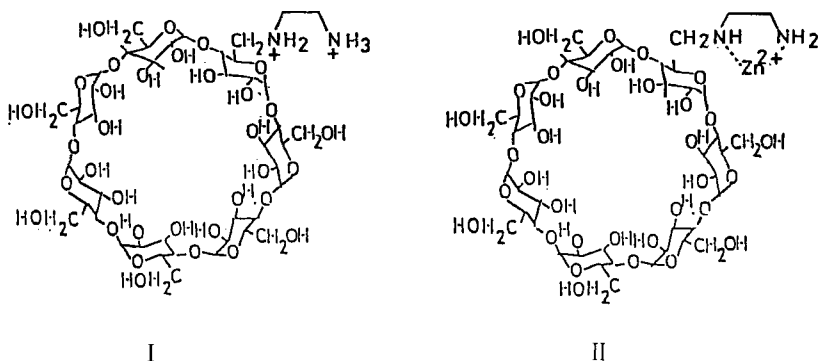
Keywords: β -cyclodextrin, $^1\text{H-N.M.R.}$ spectroscopy, ethylenediamine group

INTRODUCTION

Enzyme such as carboxypeptidase A exhibits regiospecific and/or regioselective molecular recognitions in various modes of interactions with substrate.¹ In order to elucidate such excellent higher-order functions of the enzyme, one should investigate the molecular recognition using simple model compounds. Cyclodextrins (CD_x) are known to be one of the available biomimetic model compounds which form inclusion complexes with various guest molecules by van der Waals force, hydrophobic interaction, etc.² We have examined electrostatic effects on the inclusion process of charged CD_x . In this paper, the molecular inclusion reaction between charged $\beta\text{-CD}_x$ having ethylenediamine group ($\beta\text{-CD}_x\text{en}$; I) or its zinc complex ($\beta\text{-CD}_x\text{en-Zn}^{2+}$; II) and sodium p-(3-t-butyl-4-hydroxyphenylazo)-benzene sulfonate (3-tBu-HAB) were studied by uv-vis and NMR spectroscopy.

EXPERIMENTAL

$\beta\text{-CD}_x\text{en}$ was prepared according to the literature.³ 3-tBu-HAB was synthesized by azo coupling method and purified by cellulose column chromatography. $^1\text{H-NMR}$ spectra were measured at pH 4.0.



RESULTS AND DISCUSSION

The dissociation constants, K_a , for each inclusion complex at pH 4.0 were determined by visible absorption spectroscopy. The values of K_a for the inclusion complexes of modified CD_x with 3-tBu-HAB (4.3×10^{-4} for β - CD_x en, 4.5×10^{-4} for β - CD_x en- Zn^{2+}) were found to be about 1.6 times larger than that of the inclusion complex of the parent CD_x ($K_a = 2.7 \times 10^{-4} \text{ mol dm}^{-3}$). This indicates that the inclusion complexes of two modified host molecules are slightly unstable than that of the parent β - CD_x . This difference in stability of each complex would be attributable to the difference in the interaction site between host molecule and 3-tBu-HAB. The interaction sites in these inclusion complexes were determined by 1H -NMR measurements. In general, the proton of the guest molecule is shifted downfield by van der Waals shifts or steric perturbation caused by intimate interaction with the inner proton of the host molecule (Figure 1).^{4,5} The signals of all protons in 3-tBu-HAB exhibit downfield shift by the formation of inclusion complex with β - CD_x . Whereas, in charged CD_x system, the magnitudes in shift are subtly different from those of parent CD_x system. From the comparison of the magnitude of downfield shift, the interaction sites between the host molecules and 3-tBu-HAB were determined. Two doublet peaks from four protons $H_{\theta,12}$ and $H_{\theta,11}$ of sulfanilate moiety in 3-tBu-HAB were observed in β - CD_x system. More interestingly, the signals of these protons become a singlet peak in charged CD_x system. This unusual phenomenon is caused by the electrostatic interaction between the positive charge of modified CD_x and the negative charge of sulfonate

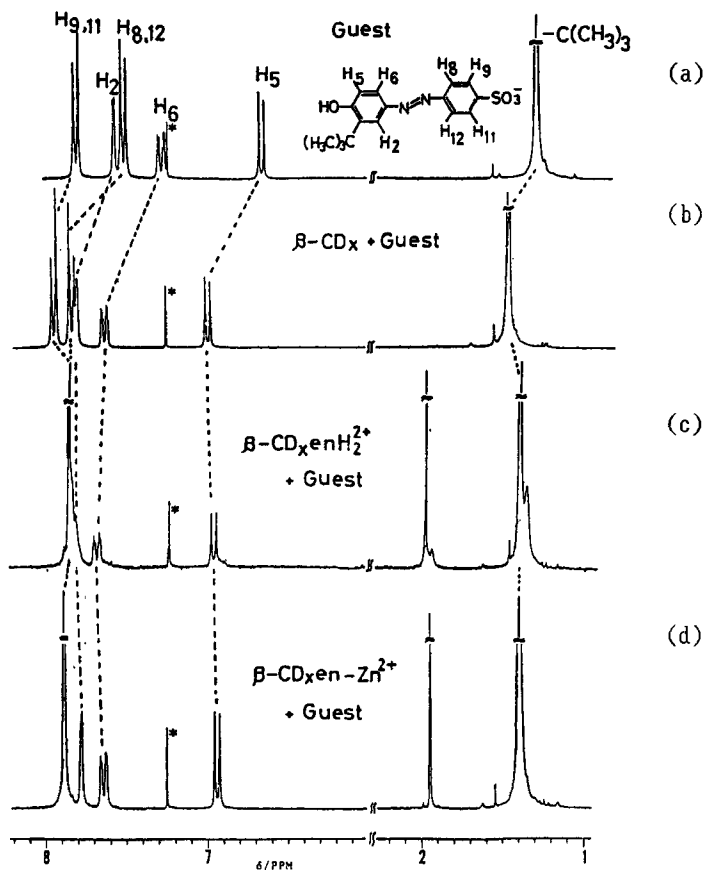


FIGURE 1. ^1H -NMR spectra (270 MHz) of 3-tBu-HAB(a) and the $\beta\text{-CD}_x$ (b), $\beta\text{-CD}_x\text{en}$ (c), $\beta\text{-CD}_x\text{en-Zn}^{2+}$ (d) inclusion complexes of 3-tBu-HAB in D_2O .

group ($-\text{SO}_3^-$) in 3-tBu-HAB. The mechanism of inclusion reaction in both systems is proposed as shown in Figure 2. A series of azo compounds having a long axis ($15\sim 17\text{\AA}$) are well known to form regio-specifically inclusion complexes with CD_x .⁶⁻¹⁰ Since the internal diameter of the cavity of $\beta\text{-CD}_x$ is considerably larger than the size of the plane of the aromatic ring, 3-tBu-HAB penetrates into the cavity of $\beta\text{-CD}_x$ in such a way that phenol moiety with a bulky t-butyl group locates regio-specifically with $\beta\text{-CD}_x$ by van der Waals force. In the modified CD_x system, 3-tBu-HAB can not penetrate deeply into the cavity owing to the electrostatic interaction between the positive

charge on ethylenediamine group of charged CD_x and the negative charge of 3-tBu-HAB. Consequently, the charged CD_x 's interact preferentially with the sulfanilate moiety of 3-tBu-HAB. Therefore the stability of these inclusion complexes decreases because of these specific interaction. From these studies, it turned out that the electrostatic interaction between host and guest operates in the inclusion complexes of charged CD_x 's and plays an important role in the inclusion process of charged CD_x with substrate.

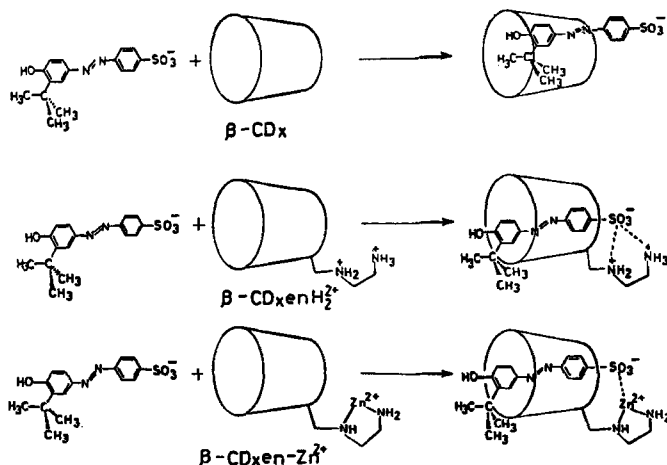


FIGURE 2. Proposed mechanism for the inclusion reaction of 3-tBu-HAB with β - or charged β - CD_x 's.

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