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Inclusion complexation and photoprototropic behaviour of 3-amino-5-nitrobenzisothiazole with β-cyclodextrin

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Abstract

The inclusion complexation and photoprototropic behaviour of 3-amino-5-nitrobenzisothiazole (ANBT) in aqueous β-cyclodextrin (β-CDx) solution have been investigated. Absorption and fluorescence intensities of the neutral form of ANBT are enhanced due to the formation of 1:1 complex with β-CDx. The complex formation has been confirmed by IR spectral and SEM studies. In the presence of β-CDx, no change was observed in the ground and excited state acidity constant values when compared with aqueous medium. Based on its inclusion complexation and photoprototropic characteristics of ANBT in β-CDx, the structure of the 1:1 complex is proposed.

Keywords: 3-Amino-5-nitrobenzisothiazole; β-Cyclodextrin; Inclusion complexation; Photoprototropism

1. Introduction

The chemistry of two or more species assembled together without a covalent bond, on the basis for a new type of photoresponse where photochemistry and photophysics of the guest are modified and made unique [1–4] without any change of host is called host–guest chemistry. Cyclodextrins are potential candidates for major role because of their ability to alter physical, chemical and biological properties of guest molecule through the formation of inclusion complexes. The α-, β- and γ-cyclodextrins are widely used natural cyclodextrins consisting of 6-, 7- and 8-D-glycopyranose residues respectively, linked by α-1,4-glycosidic bonds into a macrocycle [5,6]. Each cyclodextrin has its own ability to form inclusion complex with specific guests, and this depends on a proper fit of the guest molecule into the hydrophobic cavity of cyclodextrin.

The derivatives of benzisothiazole are widely used and find application in medical and biomedical fields [7–9]. The photoprototropic behaviour of some amino substituted molecules is well studied in aqueous and β-cyclodextrin medium [10–14]. The photoprototropic behaviour of amino group may be affected by the formation of complex with β-CDx if amino group is inside the cavity of β-CDx [15,16].

Recently, we reported the effect of inclusion complexation on spectral and prototropic behaviour of substituted fluorene and fluorenone compounds with β-CDx [17,18]. The present work reports the inclusion complexation and photoprototropic behaviour of 3-amino-5-nitrobenzisothiazole in β-cyclodextrin medium.

2. Experimental

ANBT was obtained from Aldrich and purified by recrystallisation from aqueous ethanol. β-Cyclodextrin was purchased from S.D. fine chemicals and used as received. Triply distilled water was used for the preparation of experimental solutions. A modified Hammett acidity scale (H_0) [19] was employed for the solutions below pH 1.5 (using a H_2SO_4–H_2O mixture). The concentration of the experimental solutions was 2.7×10^{-4} mol dm^{-3}. To measure the fluorescence intensities for fluorimetric titration, the isosbestic wavelength was used for excitation.

Absorption spectra were recorded with a HITACHI model U-2001 spectrophotometer while fluorescence measurements were made using a JASCO FP-550 recording spectrofluorimeter. pH values in the range of 1–12 were measured using an ELICO

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LI-10T model pH-meter. Fluorescence lifetimes were determined using a time-correlated picosecond photon counting spectrofluorimeter (Tsunami, Spectraphysics, USA). FT-IR spectra were obtained with Avatar-330 FT-IR spectrophotometer using KBr pellet. The range of spectra was from 500 to 4000 cm^{-1}. Microscopic morphological structure measurements were performed with JEOI-JSM 5610 LV scanning electron microscope (SEM).

3. Results and discussion

3.1. Inclusion complexation

The absorption and fluorescence maxima of ANBT at different concentrations of β-CDx at pH 6.8 are given in Table 1. Upon increasing the concentration of β-CDx the absorption maximum at 347 nm was slightly red shifted with a gradual increase in the molar extinction coefficient up to 8.0×10^{-3} M. At concentrations higher than 8×10^{-3} M absorption maxima and absorbance remain unchanged. This behaviour has been attributed to the enhanced dissolution of the guest molecule by inclusion complexation through the hydrophobic interaction between guest molecule and β-CDx.

In this case, the binding constant for the formation of ANBT:β-CDx complex has been determined by analysing the changes in the absorbance with the β-CDx concentration. The binding constant K and stoichiometry of the inclusion complex of ANBT can be determined by the Benesi–Hildebrand [20] equation:

$$\frac{1}{\Delta A} = \frac{1}{\Delta\varepsilon} + \frac{1}{K[\text{ANBT}]_0\,\Delta\varepsilon[\beta\text{-CDx}]_0} \quad (1)$$

where ΔA is the difference between the absorbances of ANBT in the presence and absence of β-CDx, $\Delta\varepsilon$ the difference between the molar extinction coefficients of ANBT in presence and absence of β-CDx, $[\text{ANBT}]_0$ and $[\beta\text{-CDx}]_0$ the initial concentrations of ANBT and β-CDx, respectively and K is the binding constant.

Fig. 1 shows the plot of $1/\Delta A$ versus 1/β-CDx. The linearity of the plot shows the formation of 1:1 complex between ANBT and β-CDx. The binding constant 'K' calculated from the slope of the straight line is found to be $266.67 \pm 10\ M^{-1}$ at 303 K.

Table 1
Absorption and fluorescence spectral data of ANBT

Concentrations of β-CDx (M)	Absorption maxima, λ_{abs} (nm) (log ε)	Fluorescence maxima, λ_{flu} (nm) (excitation wavelength = 350 nm)
0	291.0 (2.68), 347.0 (2.18)	412
1×10^{-3}	291.0 (2.68), 348.5 (2.19)	430, 466
2×10^{-3}	291.0 (2.69), 348.5 (2.20)	431, 468
3×10^{-3}	291.0 (2.70), 348.5 (2.21)	432, 468
4×10^{-3}	291.0 (2.71), 348.5 (2.22)	434, 468
5×10^{-3}	291.0 (2.73), 349.0 (2.24)	434, 469
6×10^{-3}	291.0 (2.74), 349.0 (2.26)	435, 469
7×10^{-3}	291.0 (2.74), 349.0 (2.26)	436, 471
8×10^{-3}	291.0 (2.76), 349.0 (2.29)	436, 471

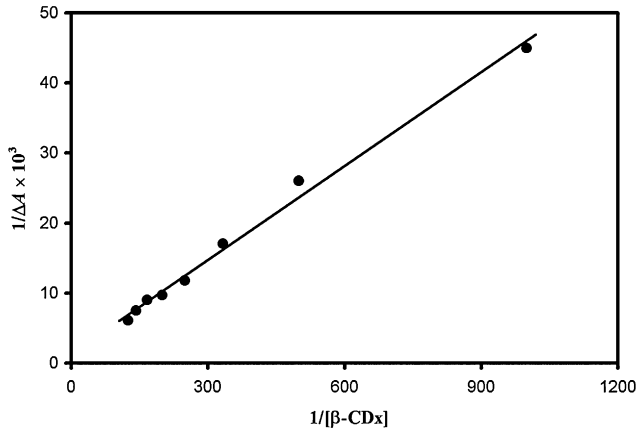

Fig. 1. Benesi–Hildebrand absorption plot for 1:1 complexation of ANBT with β-CDx.

Fig. 2 represents the fluorescence spectra of ANBT without and with β-CDx up to the saturation level of complexation of ANBT in β-CDx (0.008 M). The fluorescence spectrum in aqueous solution gives a single maximum at 412 nm. When β-CDx is added, the band at 412 nm is red shifted to 430 nm with an increase in the intensity of fluorescence. In addition to that, β-CDx addition causes the appearance of maxima at a longer wavelength 471 nm in 0.001 M β-CDx. The intensities of both the maxima increase with increase in the concentration of β-CDx.

The fluorescence excitation spectra of ANBT in 8×10^{-3} M β-CDx are recorded with different emission wavelengths. The excitation spectra recorded with the shorter wavelength and longer wavelength emission bands resemble each other and also the absorption spectrum. Thus, the two fluorescence maxima arise out of the single species of ANBT–β-CDx with the same ground state precursor. It also shows the absence of any red edge effect. Hence, the fluorescence intensity of ANBT–β-CDx complex has two maxima.

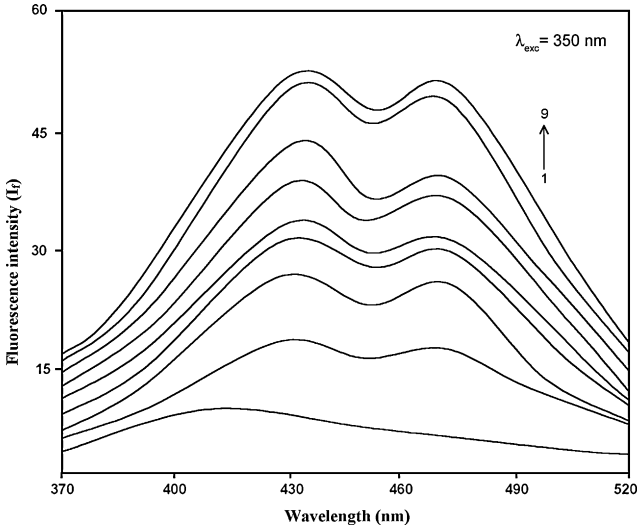

Fig. 2. Fluorescence spectra of ANBT with increasing concentrations of β-CDx (at pH 6.8): (1) 0 M β-CDx; (2) 1.0×10^{-3} M β-CDx; (3) 2.0×10^{-3} M β-CDx; (4) 3.0×10^{-3} M β-CDx; (5) 4.0×10^{-3} M β-CDx; (6) 5.0×10^{-3} M β-CDx; **7**. 6.0×10^{-3} M β-CDx; (8) 7.0×10^{-3} M β-CDx; (9) 8.0×10^{-3} M β-CDx.