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Fluorimetric and prototropic studies on the inclusion complexation of 3,3′-diaminodiphenylsulphone with β-cyclodextrin and its unusual behavior

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ABSTRACT

The photophysical and photoprototropic properties of 3,3′-diaminodiphenylsulphone (3DADPS) in aqueous β-cyclodextrin (β-CDx) solution have been investigated using absorption and fluorescence spectral techniques. β-CDx forms 1:1 inclusion complex with 3DADPS as revealed by steady state and time-resolved fluorescence spectroscopy. This inclusion complex formation was also confirmed by the FT-IR and SEM image analysis of solid complex prepared by co-precipitation method. The existence of twisted intramolecular charge transfer state and the unusual red shift observed during inclusion complexation were analyzed and discussed. The ground and excited state acidity constants in β-CDx are reported. Based on the photophysical and photoprototropic characteristics of 3DADPS in β-CDx, the structure of the 1:1 inclusion complex is proposed.

Molecular recognition is a phenomenon in which a 'receptor' or a 'host' molecule forms a stable complex with one or more 'guest' molecules through weak forces such as hydrogen bonds, van der Waal's and electrostatic interactions. Of many important hosts, cyclodextrins (CDxs) have been widely used over the last decade [1]. Cyclodextrins are cyclic oligosaccharides of six to eight α,D-glucopyranose units (namely α, β and γ-CDx respectively). Significant interest centered on complexation by cyclodextrins is due to their binding ability on several organic molecules of different size and shapes [2].

Numerous studies on the photophysical and photochemical properties of organic guest species complexed with cyclodextrins have been reported [3–7]. Intrinsic, site-specific, fluorescent probes for understanding drug–protein interactions are of current interest [8–12] and the analysis of photophysical behavior of such molecules in cyclodextrin can give information about the correct choice among such probes.

Diphenylsulphones have been reported to be pharmaceutically important as antimalarial and antileprotic drugs [13] and their photophysical and photoprototropic properties have been reported [14]. Absorption and fluorescence spectral techniques serve as tools for studying the effect of acidity on pharmaceutically important compounds. The fluorescence and proton transfer characteristics of some amino substituted diphenyl, diphenylsulphones, diphenylethers, fluorene and thiazole in β-cyclodextrin have been reported from our laboratory [15–20].. Generally organic fluorophores show a blue shift in fluorescence during inclusion complexation with β-CDx. We observed an unusual red shift in both florescence maxima of 3DADPS during inclusion complexation. In this paper, we report the fluorescent and prototropic behaviors of 3,3′-diaminodiphenylsulphone in β-cyclodextrin.

1. Experimental

1.1. Materials and methods

3,3′-Diaminodiphenylsulphone (Aldrich) and β-CDx (S.D. Fine Chemicals) were used as received. The purity of 3DADPS was checked by obtaining identical fluorescence spectra at different excitation wavelengths. The absorption spectra were recorded on a JASCO model 7800 spectrophotometer. Fluorescence spectra were obtained from JASCO FP-770 spectrofluorimeter. Fluorescence lifetimes were determined using a time-correlated picosecond single photon counting spectrofluorimeter (Tsunami, Spectraphysics). pH values in the range of 2–6 were measured on an ELICO pH meter model LI-10T. A modified Hammett's acidity scale (using a H_2SO_4–H_2O mixture) was used for making solutions

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below pH 1.5. FT-IR spectra were obtained with Avatar-330 FT-IR spectrophotometer using KBr pellet. Microscopic morphological structure measurements were performed with JEOL-JSM 5610LV scanning electron microscope (SEM). The isosbestic wavelengths were used for measuring the fluorescence intensities for fluorimetric titration at any analytical wavelength.

1.2. Preparation of solid inclusion complex

The solid 3DADPS–β-CDx complex was prepared using the following method. 3DADPS solution in methanol was added slowly to the saturated solution of β-CDx in water and a suspension was formed. The suspension was stirred at 40 °C for 30 min and stirring continued at room temperature for 24 h. The obtained mass was filtered through 0.45 μm membrane filter and dried at 40 °C in an oven for 24 h. The dried complex was ground to fine powder.

2. Results and discussion

2.1. Inclusion complexation

The absorption spectral data of 3,3′-diaminodiphenylsulphone (3DADPS) with different concentrations of β-CDx at pH 6 is given in Table 1. There is a very small change in the molar extinction coefficient with a slight red shift in longer wavelength absorption at 307 nm. The small red shift may be due to the complexation of 3DADPS by β-CDx.

The fluorescence spectra of 3DADPS at pH 6 with various concentrations of β-CDx are shown in Fig. 1. The fluorescence spectral data is given in Table 1. At pH 6, the 3DADPS molecule exists in the neutral form. A dual emission with two maxima at 333.0 and 411.0 nm was observed for 3DADPS in aqueous solution. It was reported that the shorter (SW) and longer (LW) wavelength bands in water were from the locally excited (LE) and twisted intramolecular charge transfer (TICT) states respectively [14]. These two bands are red shifted with the increase in intensity by the addition of β-CDx and the red shift is more with SW band than with LW band. In general organic fluorophores exhibit a blue shifted fluorescence with increase in intensity. The red shifts reveal that both LE and TICT are stabilized by the addition of β-CDx. The larger red shift in SW band must be due to the hydrogen bonding interaction between the sulphonyl group of 3DADPS and hydroxyl groups present in the outer rim of β-CDx. Formation of TICT state is difficult in β-CDx inclusion complex as the rotation is restricted in the complex. But TICT emission was observed in some of the inclusion complexes formed with β-CDx [21]. In those cases it was found that the half of the molecule was inside the cavity leaving the other half outside the cavity. This structure will not restrict the rotation of the molecule in the excited singlet state. In this case also the inclusion complex may have similar structure. Hence the structure of the complex must be more favorable for both hydrogen bonding interactions and TICT state formation. The complexation seems to be complete at 2.4×10^{-3} M β-CDx concentration as there was no change in fluorescence intensity by further addition of β-CDx.

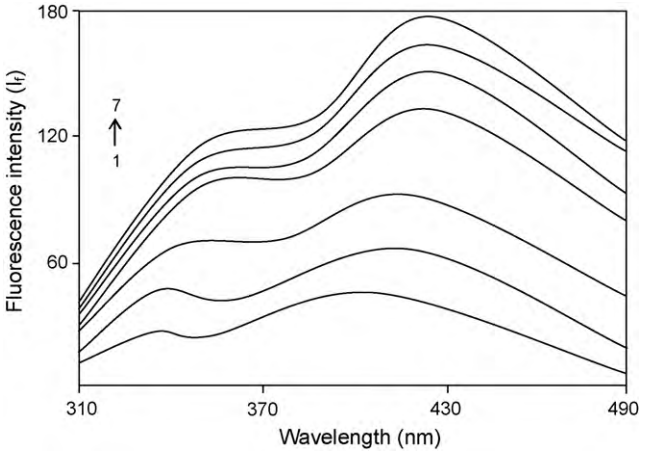

Fig. 1. Fluorescen0ce spectra of 3DADPS with various concentrations of β-CDx: (1) 0 M, (2) 4×10^{-4} M, (3) 8×10^{-4} M, (4) 1.2×10^{-3} M, (5) 1.6×10^{-3} M, (6) 2.0×10^{-3} M and (7) 2.4×10^{-3} M.

Table 1
Absorption and fluorescence spectral data of 3DADPS at different concentrations of β-CDx.

Concentration of β-CDx (M)	Absorption maximum λ_{abs} (nm) (log ε)	Fluorescence maximum λ_{emi} (nm) (excitation 290 nm)
0	228.0 (4.82) 307.0 (3.81)	333 411
4.0×10^{-4}	227.4 (4.83) 307.2 (3.81)	340 420
8.0×10^{-4}	227.6 (4.83) 307.2 (3.82)	355 422
1.2×10^{-3}	227.2 (4.83) 307.2 (3.82)	359 422
1.6×10^{-3}	227.4 (4.84) 307.8 (3.83)	361 424
2.0×10^{-3}	227.4 (4.84) 308.0 (3.83)	362 424
2.4×10^{-3}	227.4 (4.84) 308.0 (3.83)	364 424

The fluorescence excitation spectra of 3DADPS recorded at different emission wavelengths viz., 333 and 412 nm without and with β-CDx are the same and they resemble their absorption spectra. This indicates that the two maxima in the emission spectra are from the same precursor in the ground state.

The formation of inclusion complex was also revealed by the fluorescence decay curves obtained at different concentrations of β-CDx. The fluorescence lifetimes of the 3DADPS molecule in aqueous and in β-CDx were determined from the decay curves

Table 2
Time-resolved fluorescence spectral data of 3DADPS (excitation wavelength = 278 nm; emission wavelength = 432 nm).

Concentration of β-CDx (M)	Lifetime (s)	Relative amplitudes	χ^2	Standard deviation
0	1.08×10^{-9}	100	1.06	1.88×10^{-10}
8.0×10^{-4}	1.04×10^{-9} 2.38×10^{-9}	44.32 55.68	1.05	4.2×10^{-11} 1.38×10^{-10}
1.6×10^{-3}	1.01×10^{-9} 2.69×10^{-9}	21.45 78.55	1.05	4.38×10^{-11} 1.62×10^{-10}
2.4×10^{-3}	1.03×10^{-9} 3.21×10^{-9}	11.87 88.13	1.02	5.01×10^{-11} 1.73×10^{-10}