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ORIGINAL PAPER

Stoichiometrically Different Inclusion Complexes of 2-Aminofluorene and 2-Amino-9-Hydroxyfluorene in β-Cyclodextrin: A Spectrofluorimetric Study

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Abstract β-cyclodextrin (β-CDx) forms inclusion complexes with 2-aminofluorene (2AF) and 2-amino-9-hydroxyfluorene (2AHF) in different stoichiometries (Guest-host ratio 1:1 and 1:2 respectively) which is discussed on the basis of study by absorption and fluorescence spectroscopy. The ground and the excited state acidity constants for the neutral–monocation equilibrium of the two fluorophores in aqueous β-CDx medium are determined by spectrophotometric and fluorimetric titration methods respectively. The dual fluorescence observed for 2AHF monocation in aqueous solution is due to the formation of monocation-water exciplex. This monocation-water exciplex formation is hindered in β-CDx solution by the inclusion complexation. Based on the results obtained, the structures of the inclusion complexes are proposed.

Keywords 2-aminofluorene · 2-amino-9-hydroxyfluorene · β-Cyclodextrin · Fluorescence · Fluorimetric titration · Excited state acidity constants

Introduction

β-Cyclodextrin is one of the natural CDx's formed by the enzymatic degradation of starch, and contains seven α-D-glucopyranose rings connected by 1,4′-O-glycosidic bonds. Cyclodextrins have truncated cone geometry with hydrophobic interior lined by C–H hydrogens and ether-like oxygens, and a hydrophilic rim of the cone lined by primary and secondary hydroxyls. This geometry and micro-heterogeneous structure explains their ability to form inclusion complexes with organic molecules [1]. Owing to the formation of inclusion complexes the physical, chemical and biochemical characteristics of guest molecules are modified [2, 3]. CDx's with inclusion properties have been widely used in pharamaceutical [4], food [5], environmental protection analysis [6], and enzyme modeling [7]. Considerable attention has been focused on the luminescence application of cyclodextrin inclusion complexes for analytical purpose [8–10].

Important findings on the spectral characteristics and prototropic reactions of aromatic amines reveal that (i) they become stronger acids in the S_1 state, (ii) they undergo proton–induced fluorescence quenching prior to formation of the monocation (iii) their fluorescence spectra are very sensitive to the environment of the amines [11–19]. The prototropic reactions of 2-aminofluorene (2AF) have been studied by Ritchol and Fitch [20] and reinvestigated by Saha and Dogra [21] in aqueous medium. We have attempted to analyse the inclusion complexation and photoprototropic reactions (neutral–monocation) of 2AF and 2AHF in aqueous β-CDx medium. The OH group at position 9 in the case of 2AHF may have a significant role in deciding the stoichiometry of the 2AHF-β-CDx inclusion complex and in photoprototropic characteristics of 2AHF in β-CDx.

Experimental

2AF and 2AHF were obtained from Aldrich and purified by recrystallisation from 95% (v/v) ethanol-water mixture.

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The purity was checked by thin layer chromatography (single spot) and by the similar fluorescence spectral bands obtained on excitation at different wavelengths. β-CDx was obtained from S.D.Fine chemicals and used as received. Triply distilled water was used to prepare aqueous solutions. Due to the poor solubility of the fluorophores, their stock solutions were made in methanol. Solutions in the pH range 2.5–11 were prepared by adding appropriate amount of NaOH and H_3PO_4. A modified Hammett's acidity scale (H_0) [22] for the solutions below pH 1.5 (using a H_2SO_4–H_2O mixture) was employed. The concentrations of 2AF and 2AFN in experimental solutions were 3.0×10^{-5} M.

The absorption spectra were recorded using a JASCO 7800 spectrophotometer. Steady-state fluorescence measurements were made using a JASCO FP 550 spectrofluorimeter and time-resolved fluorescence data were obtained from a Time–correlated single photon counting picosecond spectrofluorimeter (TSUNAMI, Spectra physics). pH values in the range of 1.5–8.0 were measured on an ELICO LI-1OT pH meter.

Results and discussion

The absorption and fluorescence spectral data of 2-aminofluorene (2AF) and 2-amino-9-hydroxyfluorene (2AHF) as a function of β-CDx concentration are compiled in Table 1 (a) and (b) respectively. Addition of β-CDx (up to 2.4×10^{-3} M in the case of 2AF and 1.0×10^{-2} M in the case of 2AHF) causes a small (1.4 nm) red shift for 2AF and a small (1.2 nm) blue shift for 2AHF. There is no appreciable change in the molar extinction coefficient of 2AF on the β-CDx addition but a small, regular increase in the case of 2AHF. Both of these can be attributed to the inclusion complexation of the fluorenes by β-CDx.

Table 1 Absorption and fluorescence spectral data

Concentration of β-CDx (M)	Absorption maximum (nm) (log ε))	Fluorescence maximum (nm)
(a) 2AF at various concentrations of β-CDx		
0	283.0 (4.75)	373.0
4×10^{-4}	284.0 (4.72)	373.0
8×10^{-4}	284.0 (4.75)	372.0
1.2×10^{-3}	284.0 (4.74)	371.0
1.6×10^{-3}	284.0 (4.74)	371.0
2.0×10^{-3}	284.4 (4.75)	371.0
2.4×10^{-3}	284.4 (4.74)	371.0
(b) 2AHF at various concentrations of β-CDx		
0	296.0 (4.381)	398.0
4×10^{-3}	295.2 (4.392)	370.0
6×10^{-3}	295.2 (4.402)	370.0
8×10^{-3}	295.2 (4.414)	368.0
1×10^{-2}	294.8 (4.422)	368.0

The fluorescence spectra of 2AF and 2AHF with increasing concentration of β-CDx are given in Figs. 1 and 2 respectively. The spectral data are compiled in Table 1 (a) and (b) respectively. Addition of β-CDx causes a small blue shift (2 nm) for 2AF and a large blue shift (30 nm) for 2AHF with increase in fluorescence intensity for both by the addition of β-CDx. The increase in intensity of fluorescence of 2AF and 2AHF with the increase in concentration of β-CDx is shown at the inset of Figs. 1 and 2 respectively. The blue shift in the maxima may be due to the encapsulation of the fluorophores in the non-polar cavity of β-CDx i.e., the guest molecules change their environment from the polar bulk water to the non-polar β-CDx cavity. The larger blue shift in the case of 2AHF may be due to the fact that the guest molecule is encapsulated completely and hidden away from the aqueous environment fully. The complexation in both cases is confirmed by the fluorescence lifetime measurements (Tables 2 (a) and (b)). The lifetimes of the β-CDx-encapsulated forms of 2AF and 2AHF increase on complexation by β-CDx owing to the restricted vibrational relaxation of the guest from the S_1 state. There are single exponential decays for 2AF and 2AHF in aqueous solution and bi exponential decay for the β-CDx-complexed forms of them. The relative amplitudes of the β-CDx-complexed form and the uncomplexed form of the fluorophores also are given in Tables 2 (a) and (b). Above the mentioned maximum concentrations of β-CDx, the amplitudes of the β-CDx-complexed forms do not improve. The χ^2 values of the lifetime measurement are less than 1.23.

The stoichiometry of the inclusion complexes of 2AF and 2AHF in β-CDx and their corresponding binding constants at pH 7 are determined using the Benesi-Hildebrand plot as given by the equations 1 and 2 [23–25].

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{K(I' - I_0)}[\beta\text{-CDx}] \quad (1)$$

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{K(I' - I_0)}[\beta\text{-CDx}]^2 \quad (2)$$

In the above equations, I_0 is the intensity of fluorescence of the fluorophores without β-CDx, I is the intensity with a particular concentration of β-CDx, I' is the intensity at the maximum concentration of β-CDx used and K is the binding constant. There is linearity in the plot of $1/I - I_0$ vs.$1/[\beta\text{-CDx}]$ (Fig. 3) for 2AF and in the plot of $1/I - I_0$ vs.$1/[\beta\text{-CDx}]^2$ (Fig. 4) for 2AHF. Thus the stoichiometry of the 2AF-β-CDx and 2AHF-β-CDx complexes are1:1 and 1:2 respectively. The binding constants, calculated using the slope of the Benesi-Hildebrand plots, are 1.41×10^3 M^{-1} for 2AF-β-CDx and 5.36×10^3 M^{-1} for 2AHF-β-CDx.

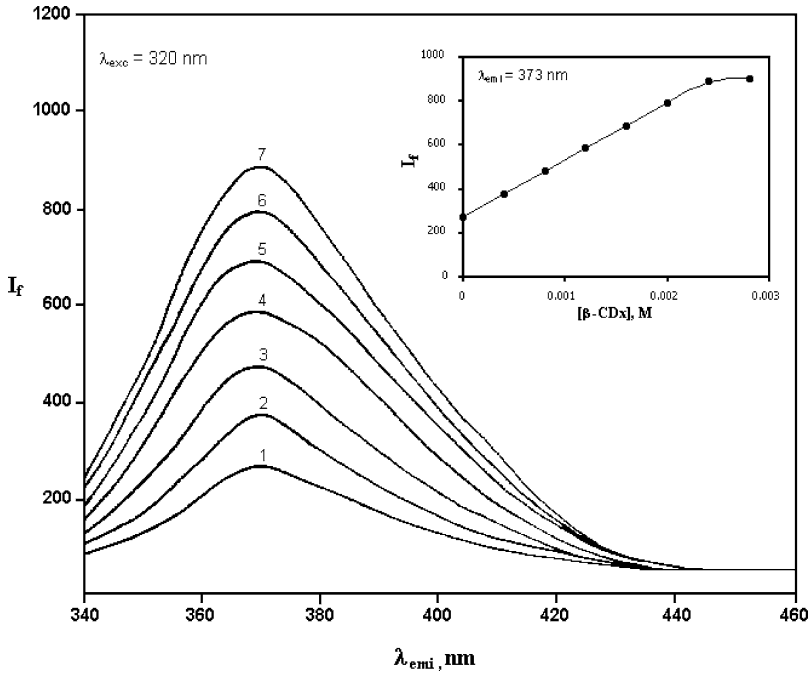

Fig. 1 The fluorescence spectra of 2AF with increasing concentration of β-CDx (Inset: The increase in intensity of fluorescence of 2AF with the increase in concentration of β-CDx) (1. 0 M, 2. 4.0×10^{-4} M, 3. 8.0×10^{-4} M, 4. 1.2×10^{-3} 5. 1.6×10^{-3} M, 6. 2.0×10^{-3} M, 7. 2.4×10^{-3} M)

The free energies of the formation of inclusion complexes of the neutral forms of 2 AF and 2 AHF with β-CDx were determined using the following equation

$$\Delta G = -RT \ln K \tag{3}$$

The ΔG values for 2AF and 2AHF at 303 K are found to be -18.28 and -21.64 KJ/mol respectively. The negative values show that the complex formation is spontaneous in both the compounds.

Effect of acidity

The absorption spectra of 2AF(3.0×10^{-5} M) with 2.4×10^{-3} M β-CDx at various pH values are given in Fig. 5. Decrease of pH from 7.0 causes a gradual blue shift in the maximum from 284.4 nm. At pH 3.4, absorption spectrum is obtained with three maxima at 251.8, 288.4 and 299.6 nm corresponding to the monocation of 2AF molecule bound inside the β-CDx cavity. There is an isosbestic point at 269.2 nm indicating the neutral–monocation equilibrium

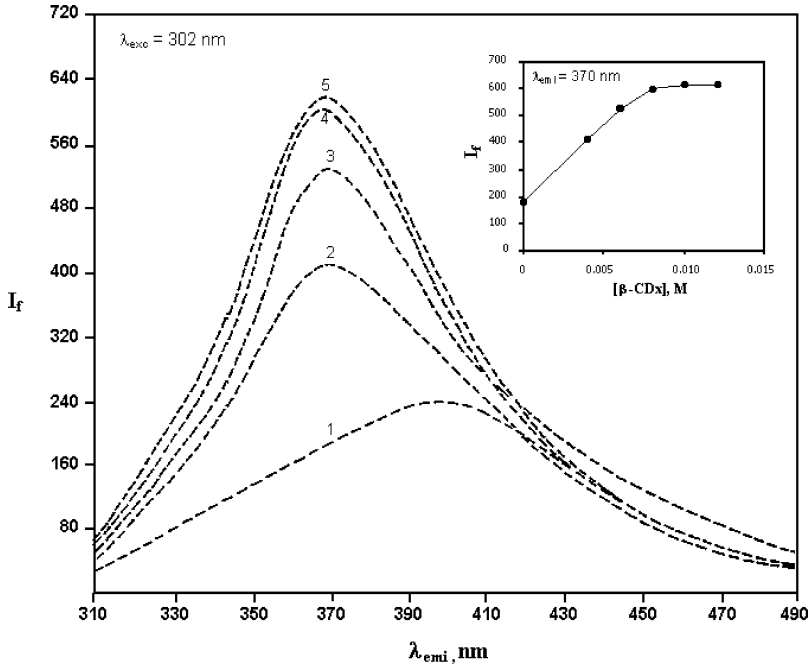

Fig. 2 The fluorescence spectra of 2AHF with increasing concentration of β-CDx (Inset: The increase in intensity of fluorescence of 2AHF with the increase in concentration of β-CDx) (1. 0 M, 2. 4.0×10^{-4} M, 3. 8.0×10^{-4} M, 4. 1.2×10^{-3} M, 5. 1.6×10^{-3} M)

Table 2 Time-resolved fluorescence spectral data

Conc. of β-CDx (M)	Lifetime (s)	Relative amplitudes	χ^2	S. Deviation (s)
(a) 2AF with various β-CDx concentrations				
0	2.25×10^{-9}	100	1.23	5.47×10^{-11}
4×10^{-4}	2.15×10^{-9}	55.76	1.22	1.96×10^{-11}
	6.43×10^{-9}	44.24		4.83×10^{-11}
8×10^{-4}	2.14×10^{-9}	51.98	1.32	2.59×10^{-11}
	6.47×10^{-9}	48.02		3.16×10^{-11}
1.2×10^{-3}	2.23×10^{-9}	51.28	1.26	3.38×10^{-11}
	6.55×10^{-9}	48.02		3.07×10^{-11}
1.6×10^{-3}	2.34×10^{-9}	45.88	1.18	4.25×10^{-11}
	6.62×10^{-9}	54.12		2.86×10^{-11}
2.0×10^{-3}	2.37×10^{-9}	44.72	1.15	4.64×10^{-11}
	6.72×10^{-9}	55.28		2.82×10^{-11}
2.4×10^{-3}	2.15×10^{-9}	37.33	1.27	4.79×10^{-11}
	6.82×10^{-9}	62.67		2.34×10^{-11}
(b) 2AHF with various β-CDx concentrations				
0	2.01×10^{-9}	100	1.16	1.10×10^{-11}
4×10^{-4}	1.78×10^{-9}	17.34	0.96	8.24×10^{-11}
	6.35×10^{-9}	82.66		4.10×10^{-11}
6×10^{-3}	1.53×10^{-9}	10.41	1.14	1.14×10^{-10}
	6.39×10^{-9}	89.59		3.19×10^{-11}
8×10^{-3}	1.55×10^{-9}	7.19	1.15	2.87×10^{-11}
	6.42×10^{-9}	92.81		2.67×10^{-11}
1×10^{-2}	1.56×10^{-9}	4.65	0.99	1.59×10^{-10}
	6.46×10^{-9}	95.35		2.86×10^{-11}

Note. Excitation wavelength = 280 nm; Detection wavelength = 370 nm.

of 2AF in β-CDx. The ground state pK_a of this equilibrium is calculated spectrophotometrically to be 4.23 and it is close to the reported value [21] of 4.5 for the same equilibrium in aqueous solution.

The effect of pH on the absorption spectrum of 2AHF without β-CDx is shown in Fig. 6. With decrease of pH from 6 the absorption maximum of the neutral form at 293.5 nm is blue shifted continuously and becomes constant at pH 2.4 with the maximum at 271.5 nm which corresponds to the

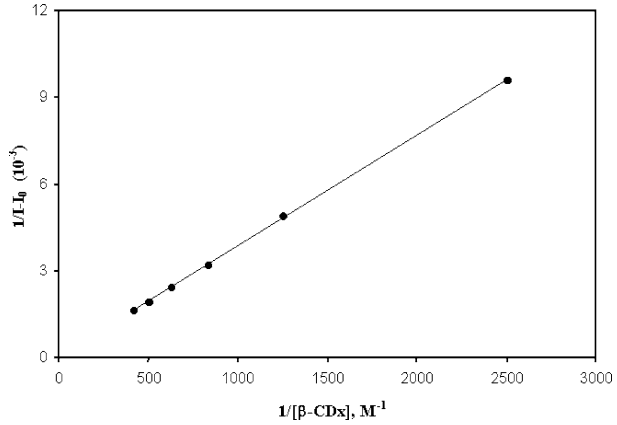

Fig. 3 Benesi-Hildebrand plot for the 1:1 complexation of 2AF in β-CDx

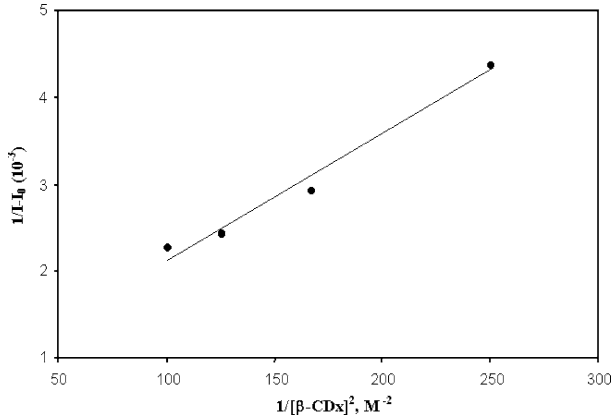

Fig. 4 Benesi-Hildebrand plot for the 1:2 complex of 2AHF in β-CDx

monocation. The presence of clear isosbestic point indicates the equilibrium between the two species viz., neutral and monocation. The ground state pK_a of the neutral–monocation equilibrium determined using absorption spectra is 4.08.

Figure 7 shows the absorption spectra of 2AHF in β-CDx at various pH values. With decrease of pH from 5.0, the absorption maximum at 294.5 nm corresponding to the neutral form of 2AHF is blue shifted. The absorption spectrum with maximum at 272.5 nm corresponds to the monocation of 2AHF formed by the protonation of the amino group. The observation of a clear isosbestic point indicates the equilibrium between the neutral and monocationic forms of 2AHF. The ground state pK_a value, determined from the absorption spectral data for the neutral-monocation equilibrium of 2AHF in β-CDx, is 3.59. This value is less than the pK_a value of 4.08 in aqueous solution.

Between ground state pK_a values of the neutral-monocation equilibrium of 2AF in aqueous and β-CDx media, there is a difference of 0.27 whereas it is 0.49 in the case of the same equilibrium for 2AHF. This shows that the 2AHF molecule in β-CDx requires more acidic condition for protonation than that is required for 2AF molecule. This

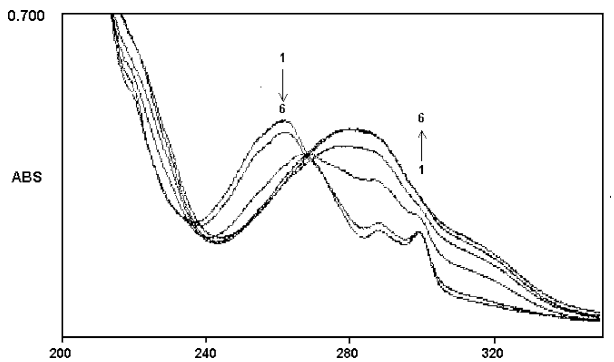

Fig. 5 The absorption spectra of 2AF with 2.4×10^{-3} M β-CDx at various pH values (1. pH 3.4, 2. pH 3.8, 3. pH 4.2, 4. pH 4.6, 5. pH 5.0, 6. pH 5.5)

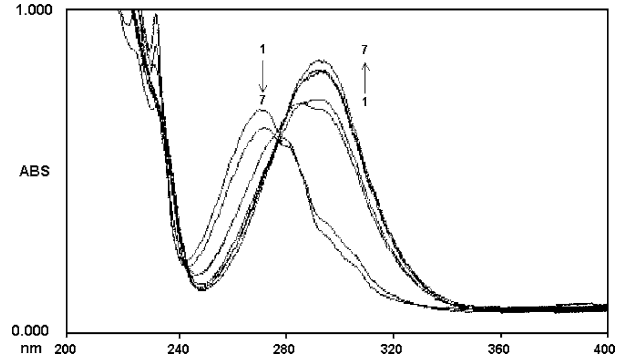

Fig. 6 The effect of pH on the absorption spectrum of 2AHF without β-CDx (1. pH 2.5, 2. pH 3.2, 3. pH 4.0, 4. pH 4.4, 5. pH 4.8, 6. pH 5.3, 7. pH 6.0)

may be due to the difference in the stoichiometry of the two molecules complexed with β-CDx.

The fluorescence spectra of 2AF in β-CDx at various H_0/pH values are given in Fig. 8. Decrease of pH from 7.0 causes the fluorescence band at 372 nm, corresponding to the neutral form of 2AF, to decrease in intensity up to pH 1. At H_0 -0.26, a blue shifted fluorescence band with a maximum at 328 nm starts appearing due to the formation of monocation. The intensity of fluorescence at 328 nm increases up to H_0 -2.76. As seen in Fig. 8, the monocation is found to be less fluorescent when compared to the neutral form of 2AF. A fluorimetric titration (FT) was carried out for the neutral-monocation equilibrium in β-CDx by exciting at isosbestic wavelength (269 nm) and the FT curves are shown in Fig. 9. There is no correspondence between the decrease of the neutral form fluorescence and the increase of monocation fluorescence. This indicates the presence of some process other than proton transfer in the excited state. Initially the decrease in neutral form fluorescence with the increase in acidity is found to be due to the proton induced fluorescence quenching. After this process, monocation starts forming at H_0 -0.26.The proton induced fluorescence quenching has been reported for aromatic amino compounds [12, 14]. In

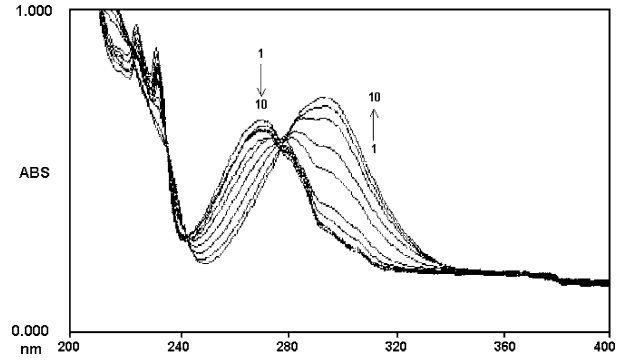

Fig. 7 Absorption spectra of 2AHF in β-CDx at various pH values (1. pH 1.4, 2. pH 1.8, 3. pH 2.2, 4. pH 2.6, 5. pH 3.0, 6. pH 3.5, 7. pH 4.0, 8. pH 4.5, 9. pH 5.0, 10. pH 5.5)

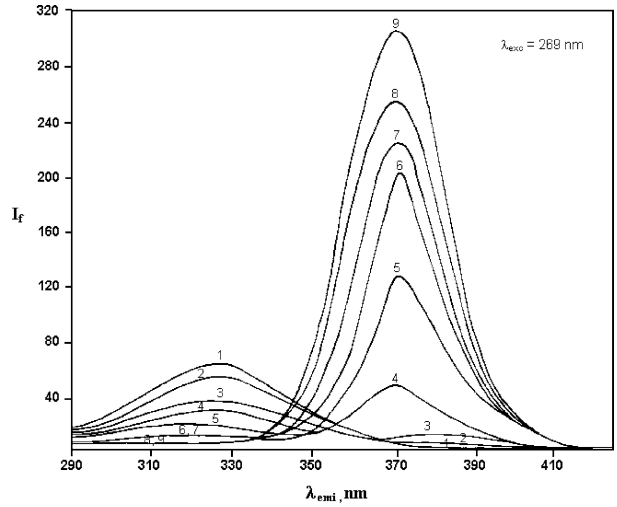

Fig. 8 The fluorescence spectra of 2AF in β-CDx at various H_0/pH values (1. H_0 -3.87, -2.76, 2. H_0 -2.28, 3. H_0 -1.85, 4. H_0 -1.38, 5. H_0 -0.26, 6. pH 1.0, 7. pH 3.0, 8. pH 5.0, 9. pH 7.0)

such cases the excited state acidity constant pK_a* is usually determined from the midpoint of the monocation formation curve and it is found to be -1.8. In aqueous solution the pK_a* value is -1.6. The acidity constants of 2AF in the S_0 and S_1 states without and with β-CDx are given in Table 3.

The fluorescence spectra of 2AHF without β-CDx at various H_0/pH values are displayed in Fig. 10. The spectrum with the maximum at 398 nm at pH 4.0 corresponds to the neutral form of 2AHF. Above this pH there is no change in the fluorescence maximum and its intensity. Decrease of pH from 4.0 causes a decrease in the intensity of fluorescence up to pH 1.0 and then the formation of the monocation is indicated by the shoulder around 324 nm. At pH 0.83 a new red-shifted maximum around 450 nm is formed in addition to the blue-shifted band. Further increase of acidity causes

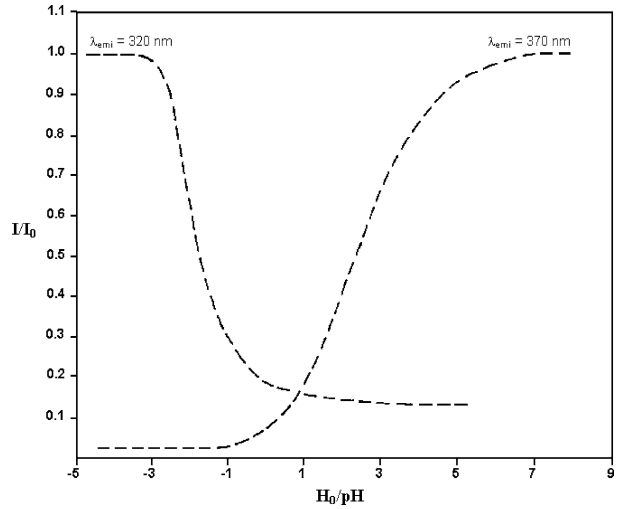

Fig. 9 Fluorimetric titration (FT) curves for the neutral-monocation equilibrium of 2AF in β-CDx

Table 3 Ground and excited state pK_a values for the neutral-monocation equilibrium

Equilibrium (Neutral ⇌ Monocation)	Ground state pK_a	Excited state pK_a
(a) 2AF		
Without CDx	4.50	− 1.6
With β-CDx	4.23	− 1.8
(b) 2AHF		
Without CDx	4.08	0.75
With β-CDx	3.59	—

blue shift in shorter wavelength maximum and at H_0 − 2.76, emission maxima at 318 and 450 nm are observed. The dual fluorescence observed for the monocationic form of 2AHF in aqueous solution could be attributed to the any one of the following causes viz. twisted intramolecular charge transfer (TICT), solvent relaxation and formation of solute-solvent exciplex. This compound will not undergo TICT. To find out the cause for the longerwavelenth maximum, the fluorescence spectrum of monocation produced by trifluoroacetic acid in a non-polar medium cyclohexane was recorded. Only the shorter wavelength maximum at 306 nm was observerd in cyclohexane. Addition of small amounts of water (1–2%) produced the longer wavelength peak. Further addition of water had no effect. If the longer wavelength peak is due to solvent relaxation of the monocation then the addition of small amount of water will not have any effect. The solvent relaxation can occur only due to bulk property of the solvent. The abnormal red shift observed for the monocation of 4,4′-diaminobiphenyl was reported to be due to solvent relaxation [26]. Addition of small amount of water has no effect on the

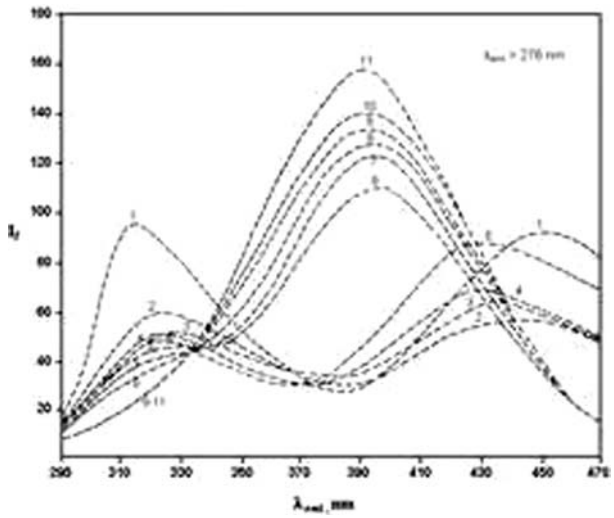

Fig. 10 The fluorescence spectra of 2AHF without β-CDx at various H_0/pH values (1. H_0 − 2.76, 2. H_0 − 1.85, 3. H_0 − 0.26, 4. pH 0.44, 5. pH 0.83, 6. pH 1.0, 7. pH 1.5, 8. pH 2.4, 9. pH 3.3, 10. pH 3.7, 11. pH 4.3)

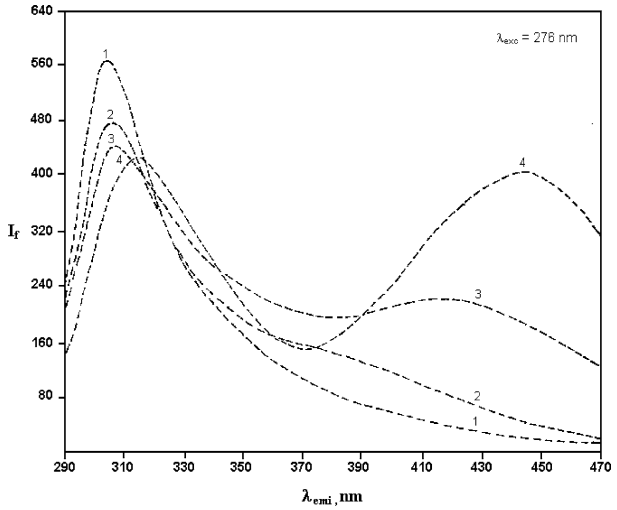

Fig. 11 Fluorescence spectra of 2AHF in cyclohexane/trifluoroacetic acid with different amounts of water (1. Cyclohexane + TFA, 2. Cyclohexane + TFA + water (1%), 3. Cyclohexane + TFA + water (2%), 4. Water (H_0 − 2.76))

absorption spectrum of monocation in cyclohexane. Hence in this case the longer wavelength emission maximum is due to the formation of solute-solvent exciplex. The formation of water exciplex with solute had been reported for several compounds [27, 28]. When the solution is basified then the absorption and fluorescence spectra matches exactly with that of neutral form. This rules out the possibility of a chemical reaction at higher acidic conditions in the excited state.

Fluorimetric titration was carried out by measuring fluorescence intensities at 380 nm and 320 nm. The FT curves are given in inset of Fig. 13. The decrease of fluorescence intensity of neutral form is sharp and sigmoid. But the fluorescence intensity at 320 nm increases slowly and then sharply after H_0 − 1.0. This stretched sigmoid curve may be due to the formation of monocation-water exciplex. In this case the pK_a* value cannot be determined from the meeting point of the two curves. The middle of inflection of fluorimetric titration curve of neutral form may be taken as pK_a* value.

Figure 12 represents the fluorescence spectra of 2AHF in β-CDx at various pH values. With decrease of pH from 7.0, there is a decrease in the intensity of fluorescence of the neutral form (371 nm) with a corresponding increase in the monocation fluorescence intensity at 310 nm. The FT curves for the monocation-neutral equilibrium of 2AHF in β-CDx are shown in Fig. 13. These curves are not sharp as they cover a long range of H_0/pH. This type of curve is obtained when the rates of proton exchange are comparable to the rates of fluorescence. The meeting point may give a value in between pK_a and pK_a* values. Hence pK_a* value cannot be determined accurately from these curves. Absence of longer wavelength emission band shows that the monocation-water

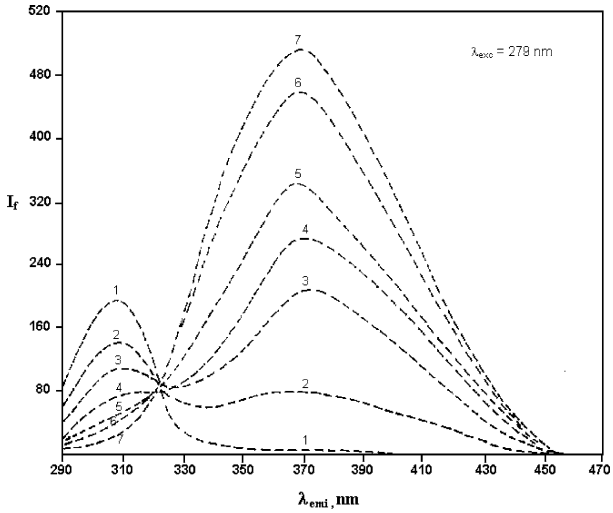

Fig. 12 Fluorescence spectra of 2AHF in β-CDx at various pH values (1. H_0 −2.76, 2. H_0 −0.84, 3. pH 0.44, 4. pH 1.4, 5. pH 2.6, 6. pH 3.6, 7. pH 5)

exciplex is not formed in β-CDx solution. The fluorescence spectrum with only shorter wavelength maximum observed for monocation in Cyclohexane–TFA and β-CDx solution reveals that the monocation in β-CDx solution is in non-polar environment i.e., protonated NH_2 group (NH_3^+) is in the hydrophobic cavity of β-CDx.This again confirms the formation solute-water exciplex in aqueous solution. The ground and the excited state pK_a values for the monocation-neutral equilibrium of 2AHF without and with β-CDx are given in Table 3 (a).

The stoichiometry of the inclusion complex of 2AF in β-CDx is found to be 1:1. There is no significant difference in the ground and the excited state pK_a values of 2AF in aqueous and β-CDx media. This shows that the amino group is in the aqueous environment i.e., outside the β-CDx cavity. Calculations using the software MOPAC/AM1 show that the length of the molecule is 9.538 Å and the other distances are given in Fig. 14a. The length of the β-CDx cavity is 7.8 Å and so the whole molecule cannot be accommodated in the cavity. Based on the observations and the size of the molecule the structure of the inclusion complex of 2AF in β-CDx is proposed as in Fig. 14b.

The stoichiometry of the inclusion complex of 2AHF in β-CDx is 1:2. The length of the 2AHF molecule is 9.685 Å as calculated using MOPAC/AM1 (Fig. 15a). The only difference in the structure of 2AHF from that of 2AF is that it has an OH group at position 9. The OH group has no participation in the delocalisation involved in the molecule and it is not reactive under normal conditions, but it has a major role in deciding the stoichiometry of the 2AHF-β-CDx inclusion complex. Because of the hindrance offered by the OH group to the β-CDx molecule and also by hydrogen bonding interactions of this OH group with OH groups at the rim of β-CDx, the cyclodextrin molecule may be stopping half way down the linear axis of the 2AHF molecule allowing the second β-CDx molecule to enclose the other half. As seen earlier the NH_2 group is inside the β-CDx cavity. Based on these facts, the possible structure of the inclusion complex of 2AHF in β-CDx may be as shown in Fig. 15b.

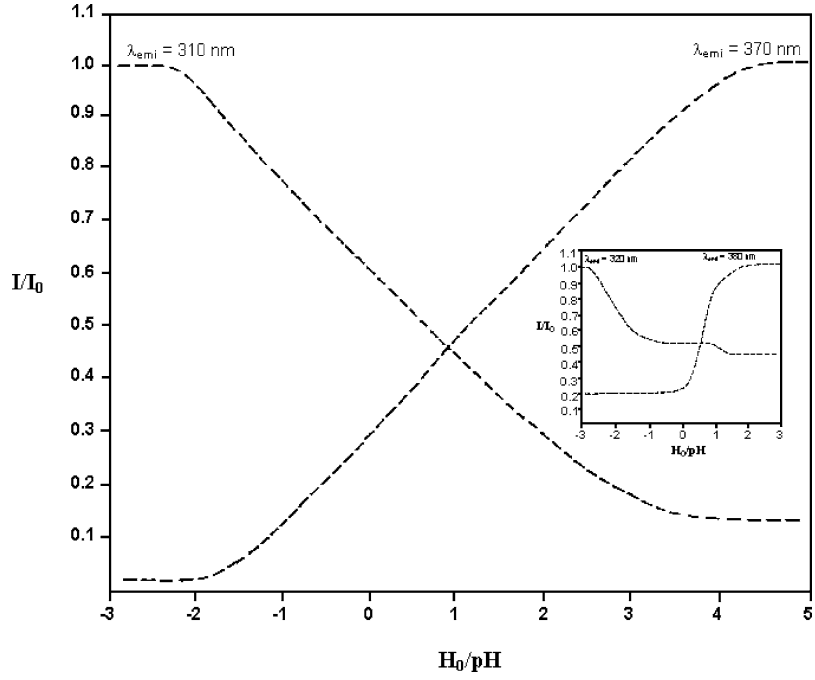

Fig. 13 Fluorimetric titration (FT) curves for the neutral-monocation equilibrium of 2AHF in β-CDx. Inset: Fluorimetric titration curves for the monocation-neutral equilibrium of 2AHF without β-CDx

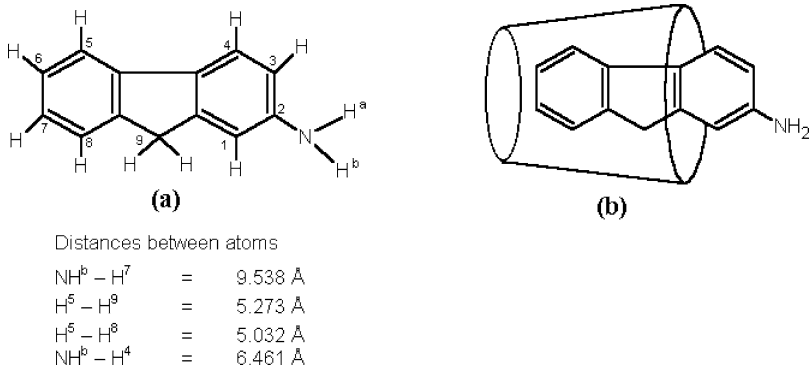

Fig. 14 Schematic diagram of the 1:1 inclusion complex of 2AF in β-CDx

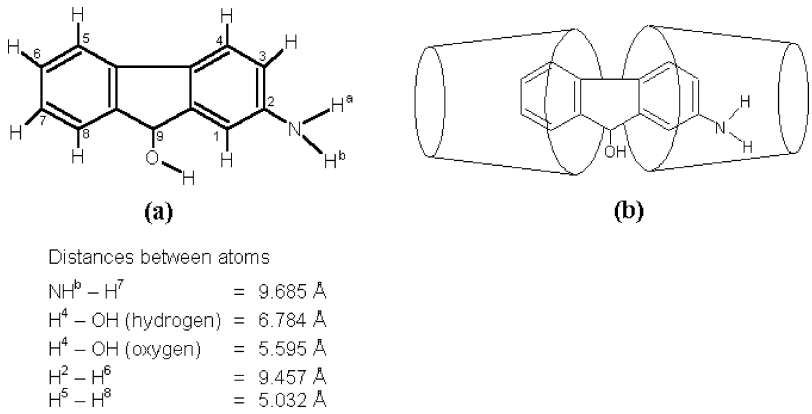

Fig. 15 Schematic diagram of the 1:2 inclusion complex of 2AHF in β-CDx

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References

1. Saenger W (1984) In: Atwood JL, Davies JED, MacNicol DD (eds) Inclusion compounds, vol 2. Academic Press, p 231
2. Bender ML, Komiyama M (1978) Cyclodextrin chemistry. Springer, Berlin
3. Saenger W (1980) Angew Chem Intl Ed Engl 19:334
4. Puglisi G, Sanatagati NA, Pignatello R (1990) Drug Dev Ind Pharm 16:395
5. Matsushima M (1994) Japan Patent 94:343, 419
6. Microgenic Corp (1989) EU Patent 301:847l
7. Sanchez FG, Lopez MH, Gomez JCM (1987) Analyst 112:1037
8. Escander GM (1999) Analyst 124:587–591
9. Escander GM, Munoz de la Pena A (1998) Anal Chim Acta 370:199
10. Araniciba JA, Escander GM (1999) Analyst 124:1833
11. Shizuka H (1985) Acc Chem Res 18:141, and the references therein
12. Swaminathan M, Dogra SK (1983) J Am Chem Soc 105:6223
13. Dey JK, Dogra SK (1990) Chem Phys 143:97
14. Manoharan R, Dogra SK (1987) Can J Chem 65:2013
15. Shizuka H, Ogiwara T, Kimuro E (1985) J Phys Chem 89:4302
16. Manoharan R, Dogra SK (1988) Can J Phys Chem 92:5282
17. Muthu Vijayan Enoch IV, Swaminathan M (2004) Collect Czeck Chem Commun 69:748
18. Muthu Vijayan Enoch IV, Swaminathan M (2004) J Fluorescence 6:751
19. Muthu Vijayan Enoch IV, Swaminathan M (2005) J Inclusion Phenom Macrocyclic Chem 53:149
20. Ritchol H, Fitch BR (1974) Anal Chem 46:1749
21. Saha SK, Dogra SK (1998) J Molec Struc 470:301
22. Jorgenson M, Hartter DR (1963) J Am Chem Soc 85:878
23. Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP (1985) J Am Chem Soc 107:392
24. Szejtli J (1988) Cyclodextrin technology. Kluwer Academic Publishers, Doedrecht, The Netherlands, p 143
25. Cho DW, Kim YH, Kang SK, Yoon M, Kim DJ (1996) J Chem Soc, Faraday Trans 92:29
26. Rajendiran N, Swaminathan M (1995) Bull Chem Soc Jpn 68:2797
27. Kalaiyarasan K, Rajendran N, Swaminathan M (1994) Indian J Chem 33A:335
28. Rajendiran N, Swaminathan M (1995) Bull Chem Soc Jpn 69:2447