

Guest-Host Inclusion Complex Formation of 2-, 3-, and 4-Aminobenzoic Acids with Native and Modified Cyclodextrins

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Abstract. The inclusion complexation of 2-aminobenzoic acid (2ABA), 3-aminobenzoic acid (3ABA), and 4-aminobenzoic acid (4ABA) with α -cyclodextrin (α -CD), β -cyclodextrin (β -CD), hydroxypropyl- α -cyclodextrin (HP- α -CD) and hydroxypropyl- β -cyclodextrin (HP- β -CD) were studied in buffer solutions of different pHs (pH~1 and pH~7) and it was carried out using UV-Visible, steady-state and time-resolved fluorescence. Dual fluorescence was observed for all the compounds in aqueous and CD medium. All the ABAs forms 1:1 inclusion complex at pH ~ 1 solution and mixture of 1:1 and 1:2 inclusion complex at pH ~7. With CDs, dual luminescence appeared at pH ~ 1 indicates, both NH₃⁺ and COOH groups are present in the interior of the CDs cavities. FT-IR, ¹H NMR, results suggest ABAs formed a stable inclusion complex with the CDs.

I. Introduction

There have been several studies [1-6] on the electronic spectra of aminobenzoic acids (ABAs). Doub and Vanderbelt recorded the absorption spectra at pH~3 to pH~10. Kopylova *et al* [3] have reported the absorption spectra in aqueous solutions. In 1963, the effect of hydrogen bonding between aminobenzoic acids and the solvent molecules on the spectral shifts has been discussed by Mataga [4]. Tramer [5] has studied the absorption and fluorescence spectra of N-methyl anthranilic acid and N,N-dimethyl anthranilic acid in various solvents. In his work, the problem of the tautomeric equilibria of zwitter ions in the S₁ and T₁ states was discussed. In 1986, Jain *et al* [6] studied the absorption and emission spectra of aminobenzoic acids in methyl cyclohexane, acetonitrile, methanol solvents and at different pH (1N HCl and 1N NaOH). The results have been discussed by the CNDO/S calculation method.

Rajendiran *et al* [7-9] have studied the absorption and fluorescence spectra of the 2ABA, 3ABA and 4ABA in different solvents, pH and β -CD in great detail. Kim *et al*, Jiang *et al* [10] and others [11] demonstrated that the TICT emission of 4-(N,N-diethylamino) and 4-(N,N-dimethylamino)benzoic acid is enhanced on complexation with α -CD. They have attributed this property to the reduced polarity rather than to the restricted molecular motion inside the CD cavity. Furthermore, the restrictive environment of the CD's is known to affect the excited state geometry change [7] which is closely related to the formation of the excited ICT state. Thus, there still remain several arguments on whether the ICT emission is always enhanced upon formation of any CD complexes and to the excited state geometry change is influenced by the CD complex formation. It is necessary, therefore, to study the inclusion interaction of different CDs with 2ABA, 3ABA and 4ABA molecules. From this point of view, it would be interesting to see how the α -CD, β -CD, HP- α -CD and HP- β -CD systems affect the ICT emission and the excited state geometry change of the ICT molecule. The present study reports our extensive measurements on the absorption, emission spectra of 2ABA, 3ABA and 4ABA in different pH with α -CD, β -CD, HP- α -CD and HP- β -CD. This is extension of our earlier work [9-24].

2. Experimental

2.1 Instruments

Absorption spectral measurements were carried out with a Shimadzu UV 1601 PC model UV-Visible spectrophotometer and fluorescence measurements were made with a Shimadzu RF 5301 spectrofluorophotometer. The pH values in the range 2.0-12.0 were measured on an Elico pH meter model LI-120.

2.2 Reagents and materials

2-Aminobenzoic acid (2ABA), 3-aminobenzoic acid (3ABA), 4-aminobenzoic acid (4ABA), α -cyclodextrin, β -cyclodextrin, HP- α -CD, HP- β -CD and all the spectrograde solvents were received from Sigma and Aldrich Chemicals Company and used as such. pH of solutions within the range 2.0-12.0 was adjusted by the addition of phosphate buffers (10^{-3} M) different concentration of NaOH - H_3PO_4 as this amount of buffer do not quench fluorescence of the sample and also do not alter the prototropic equilibrium under study. The solutions were prepared just before each measurement. The concentration of the ABAs solutions was of the order of 2×10^{-4} M to 2×10^{-5} M and the CD solution was varied from 1×10^{-3} M to 1×10^{-2} M.

3. Result and Discussion

3.1. Studies of ABAs with cyclodextrins

Absorption and fluorescence spectra of 2ABA, 3ABA and 4ABA have been analysed and compared in α -CD, β -CD, HP- α -CD and HP- β -CD solutions. Figs. 1 to 6 depict the absorption and emission maxima of the above ABAs (2×10^{-5} M) in pH~1.0 (monocation) and pH~7.0 (monoanion) solutions containing different concentrations of α -CD, β -CD, HP- α -CD and HP- β -CD. In neutral solutions (pH~7), all the ABAs exist as carboxylic anions.

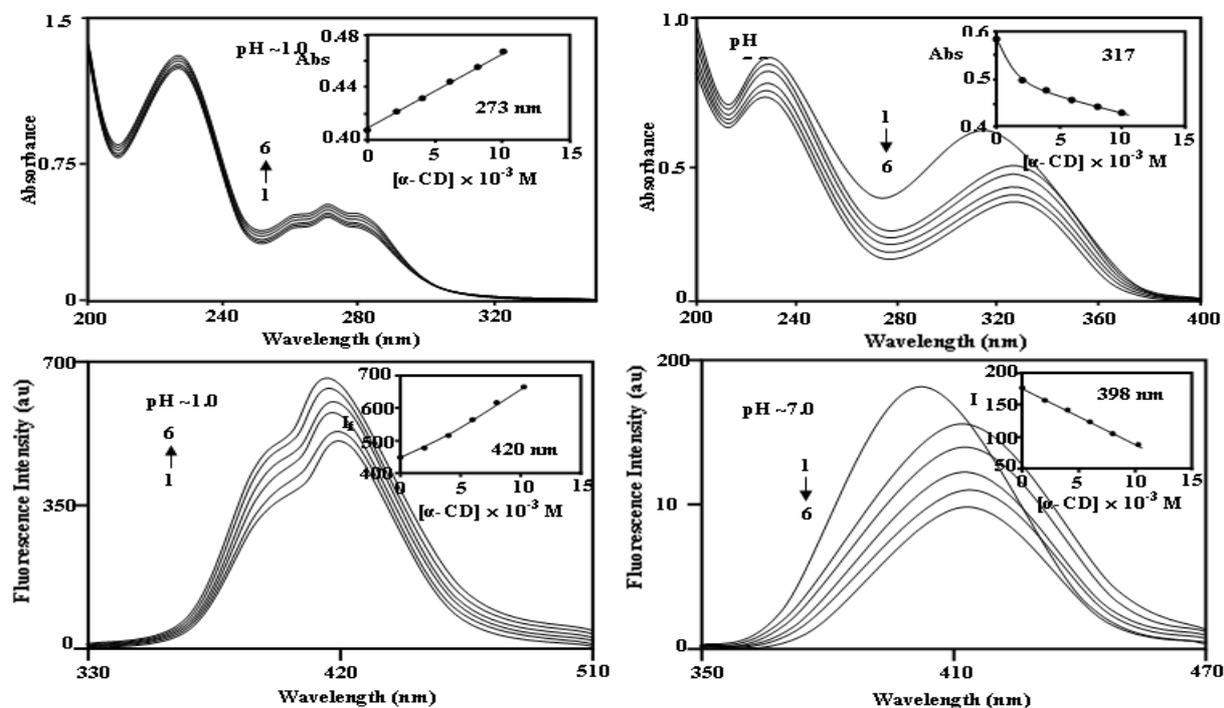


Fig 1. Absorption and fluorescence spectra of 2ABA with various α -CD concentrations (M) at different pH: (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008 and (6). 0.01. Insert Fig.: absorbance/fluorescence intensity vs. $[\alpha\text{-CD}]$.

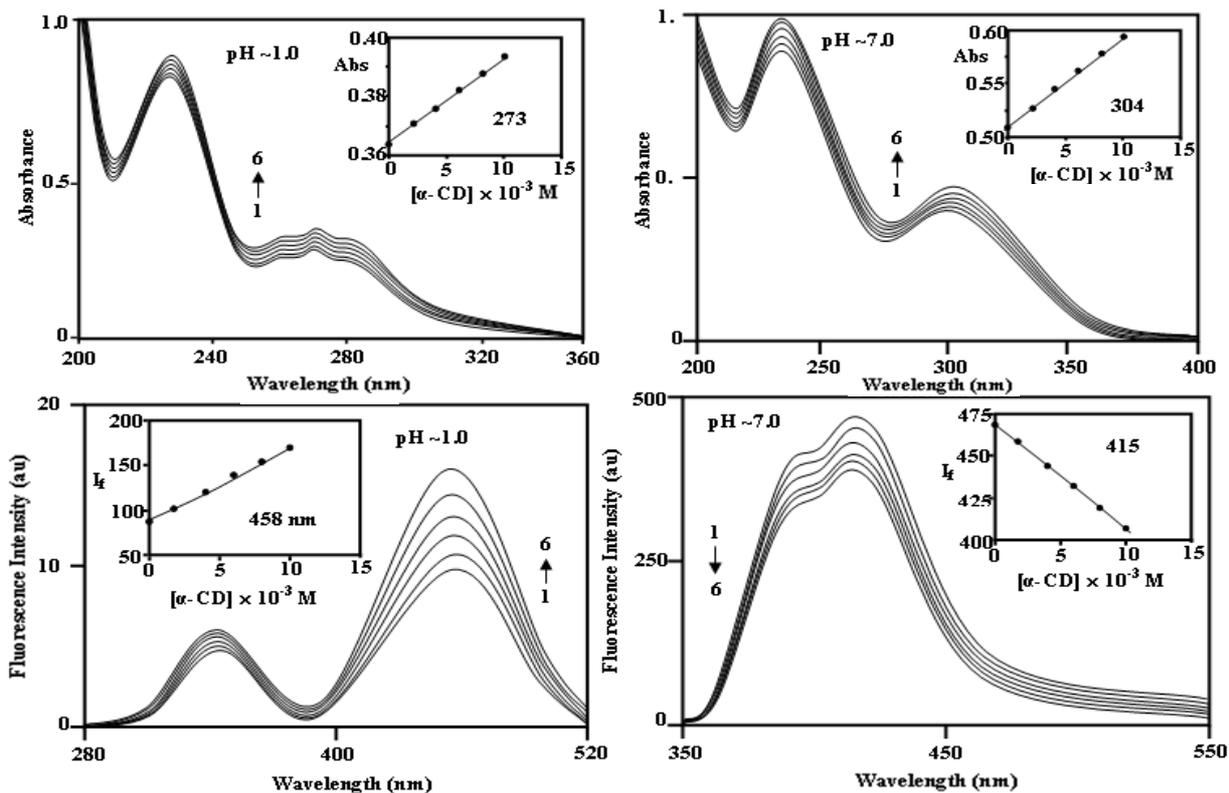


Fig 2. Absorption and fluorescence spectra of 3ABA with various α -CD concentrations (M) at different pH: (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008 and (6). 0.01. Insert Fig.: absorbance/fluorescence intensity vs. $[\alpha\text{-CD}]$.

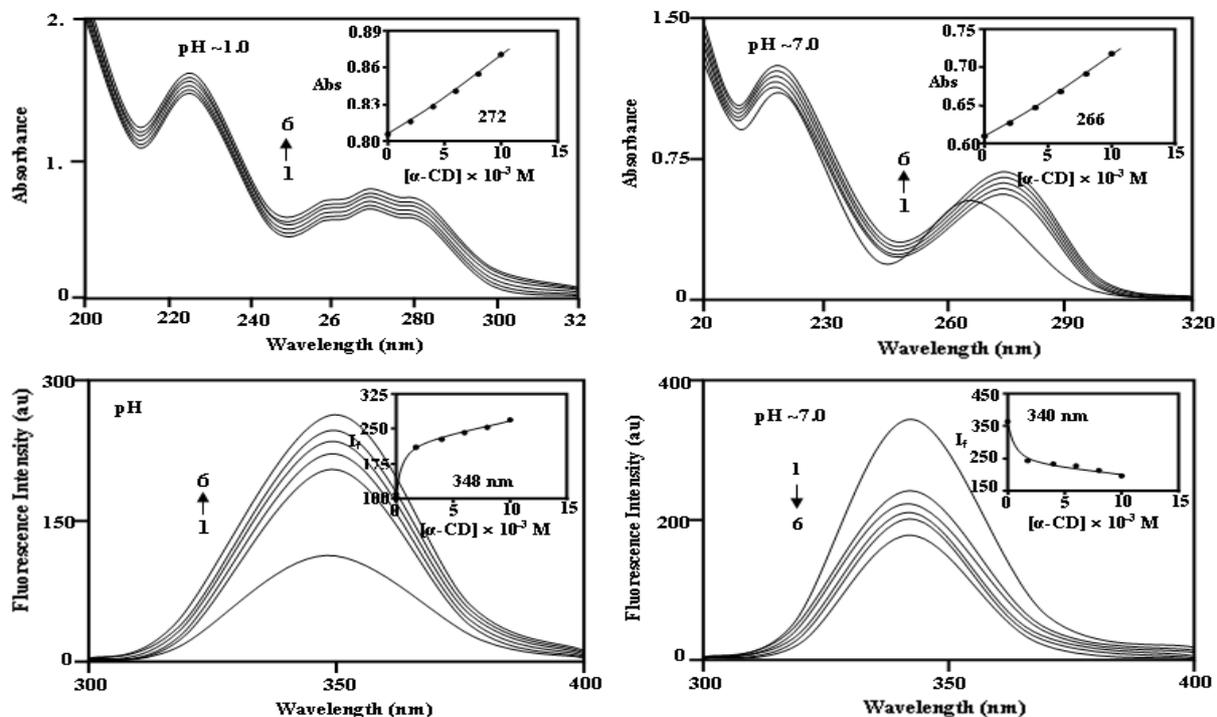


Fig. 3. Absorption and fluorescence spectra of 4ABA with various α -CD concentrations (M) at different pH: (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008 and (6). 0.01. Insert Fig.: absorbance/fluorescence intensity vs. $[\alpha\text{-CD}]$.

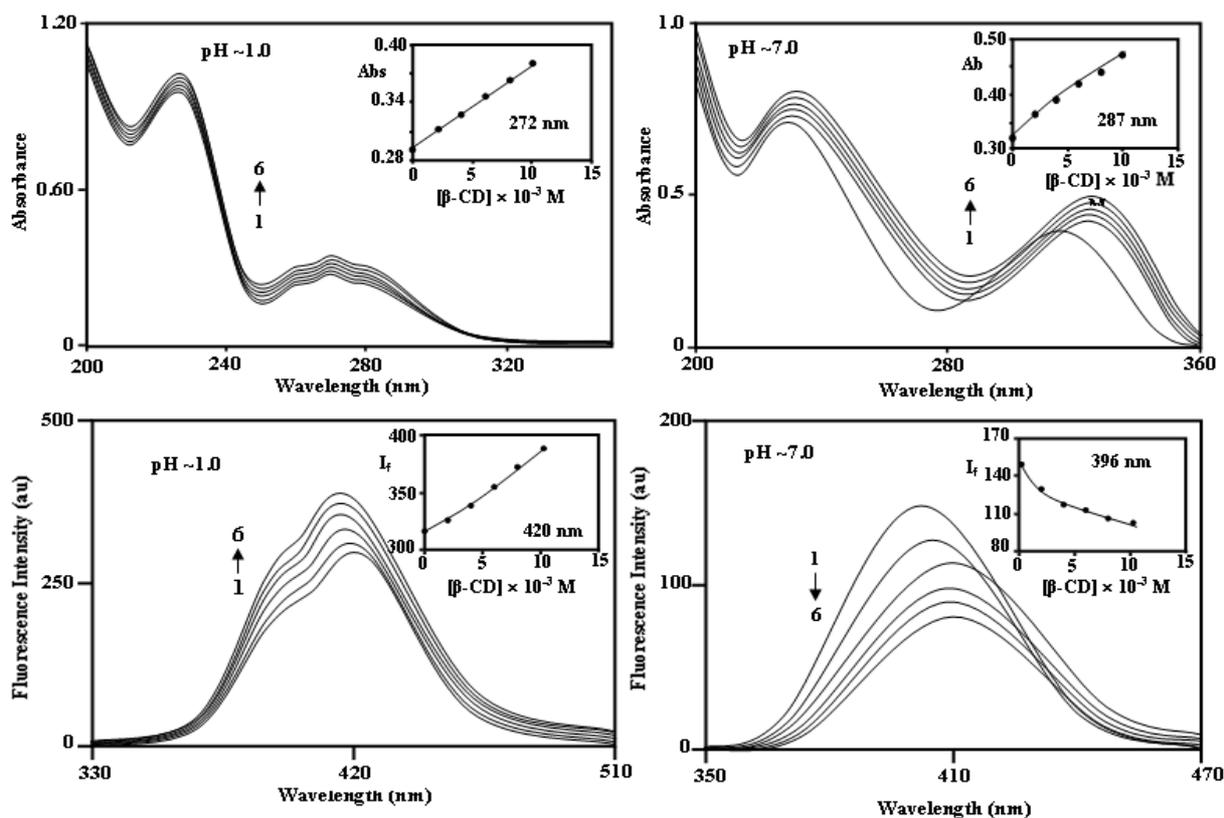


Fig 4. Absorption and fluorescence spectra of 2ABA with various β -CD concentrations (M) at different pH: (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008 and (6). 0.01. Insert Fig.: absorbance/fluorescence intensity vs. $[\beta\text{-CD}]$.

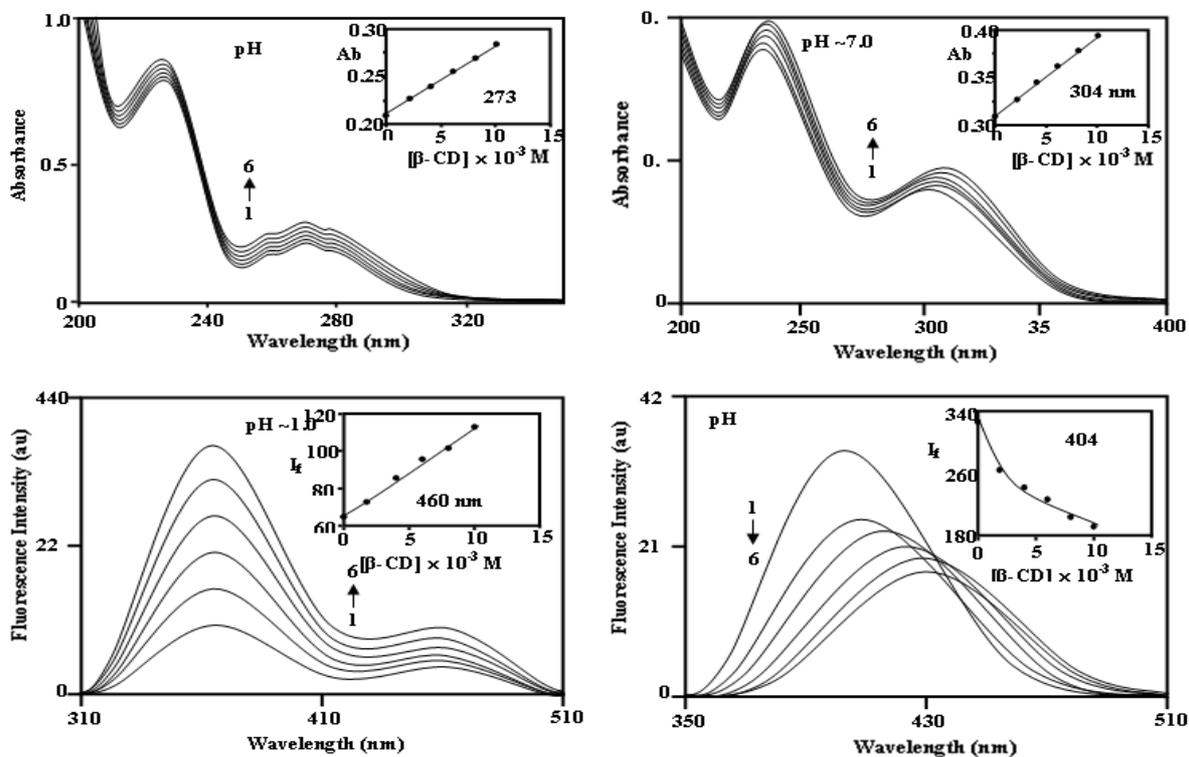


Fig 5. Absorption and fluorescence spectra of 3ABA with various β -CD concentrations (M) at different pH: (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008 and (6). 0.01. Insert Fig.: absorbance/fluorescence intensity vs. $[\beta\text{-CD}]$.

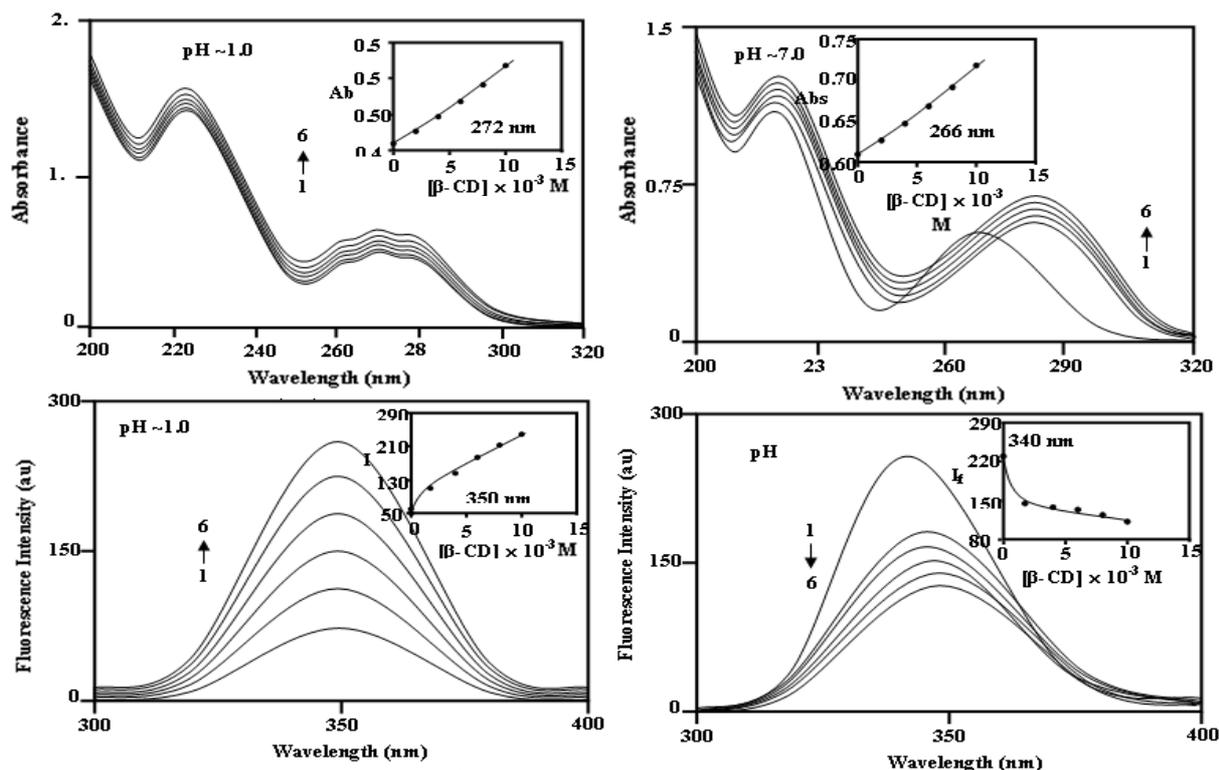


Fig. 6. Absorption and fluorescence spectra of 4ABA with various β -CD concentrations (M) at different pH: (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008 and (6). 0.01. Insert Fig.: absorbance/fluorescence intensity vs. $[\beta\text{-CD}]$.

Hence, we also recorded the absorption and emission spectra at pH~1. In the absorption spectra, the monocation and monoanion maxima of the ABAs are considerably different. The absorption maxima of all the ABAs appear at the same wavelength (at 272 nm) in pH~1 and the shapes of the spectra are also similar to each other. But in pH ~7, the absorption maxima of 2ABA, 3ABA and 4ABA appear at 330 nm, 306 nm and 276 nm respectively. At pH~1, in the presence of CDs, no significant absorption spectral change is observed in all the ABAs, whereas it is seen to undergo a marginal red shift at pH~7.

At pH ~1, the absorption spectra of all the ABAs do not show any change even in the presence of the highest concentrations of CDs used (1×10^{-2} M) whereas a regular red shift observed at pH ~7. Interestingly, in the presence of all the four CDs, at pH~1, the fluorescence characteristics of the three ABAs are seen to undergo drastic change (**Figs. 1 to 6**). In the presence of 4×10^{-3} M CD and above, the fluorescence maxima of the ABAs are red shifted in pH~1, as compared to that pH ~7. In 2ABA and 3ABA, when compared to water, a dual emission is noticed in pH~1. However, in all the CDs and in both pHs, 4ABA gives single emission maximum only. The fluorescence intensities (I_F) of all the ABAs in the CD solutions decreased along with red shift at pH~7, but in pH~1, the I_F values increased at the same wavelength. The emission intensities of 2ABA in pH ~7 initially decreased with increasing β -CD/HP- β -CD concentrations, whereas above 4×10^{-3} M β -CD/HP- β -CD concentrations, the emission intensities increased. However, with α -CD/HP- α -CD solutions, the emission intensities of all the ABAs increased. Further, the absorbance and fluorescence intensity changes were different in α -CDs and β -CDs, which indicate all the CDs form different types of inclusion complexes [9-24].

At pH ~7, the emission maxima of the ABAs in the four CDs solutions were red shifted suggesting that COO⁻ group is located within the non-polar cavity of the CDs, whereas NH₂ group is located in polar medium. This prediction is based on the following reasons: the large rim of the CD contains many secondary hydroxyl groups and thus provides an environment qualitatively similar to polyhydroxyl alcohols. In all the CD medium, no significant spectral shifts observed at pH ~1 clearly establish that carboxyl group is deeply entrapped in the CDs cavities.

The results shown in **Figs. 1 to 6** (pH~1) indicate that the ICT behavior of 2ABA and 3ABA is significantly enhanced by the formation of the inclusion complexes. In pH ~1, above 6×10^{-3} M CDs concentrations, the dual fluorescence typical of intramolecular charge transfer (ICT) can be seen easily. This is because the polarity and viscosity variations may play a more important role in the change in the ICT behavior of 2ABA and 3ABA. This influence could be the result of the altered dissociation of COOH group in both ABAs. In pH ~1 solutions, two bands could be observed at 370 nm (normal emission, LE) and 460 nm (ICT). Upon addition of the CDs in pH ~1, the LE band was strongly enhanced along with a small enhancement of ICT without any spectral shifts whatsoever. Compared to pH~7, in 2ABA and 3ABA, the difference in the spectral change at pH~1 suggests that the structural geometry of the inclusion complexes was different in terms of orientation of guest molecule [6, 7]. Possibly the ICT behavior of 2ABA and 3ABA is dramatically affected by the formation of different types of complexes within the non-polar cavity of CD. It is well known, in CD solution hydrophobicity is the driving force for encapsulation of the molecule inside the cavity and naturally the hydrophobic part (COOH) would like to go inside the deep core of the non-polar cavity and the amino group will be the hydrophilic part of the CD cavity.

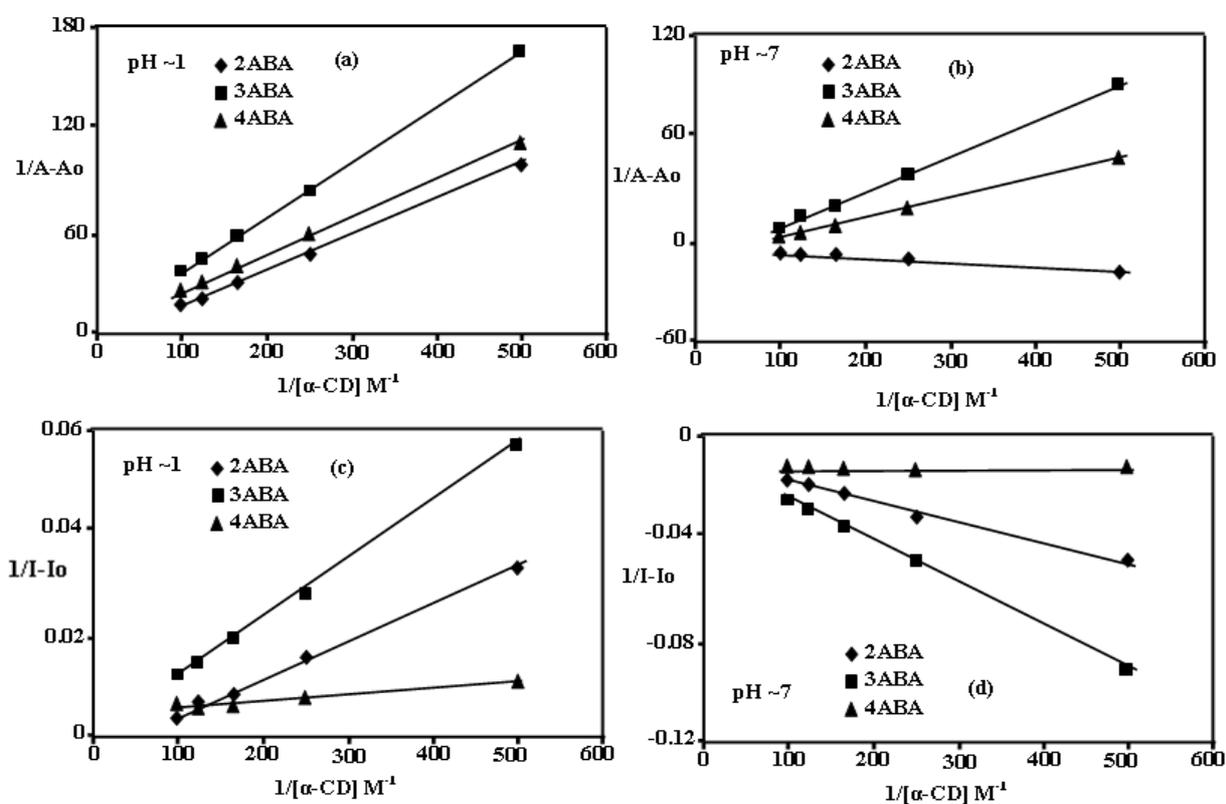
Inside the CD cavities, 2ABA and 3ABA feel much less polar environment and the normal emission (through ICT) is restricted which also causes an enhancement of the normal band. Further, the geometrical restriction of the cavity would restrict the free rotation of the amino or carboxyl group inside the CD cavity and thus hinder the formation of ICT state causing an enhancement of normal LE band. This is reasonable, because at pH~7, amino group is more polar and can form hydrogen bonds with either -OH groups on the CD cavity rim or bulk water molecules or both.

Above 4×10^{-3} M CD concentrations (in pH ~1), the dual fluorescence typical of ICT can be seen easily in 2ABA and 3ABA. Typically, both the LE and the ICT bands were enhanced, and the ICT band was shifted to the blue while the LE band was not shifted. Due to the high polarity of the ICT state, this result should mean that ABA molecules have penetrated into the nonpolar CD cavity and ABA:CD inclusion complexes have been formed. The results shown in **Figs. 1 to 6** (pH~1) indicate that the ICT behavior of the *ortho* and *meta* ABAs in α -CDs solution is higher than β -CDs. Since the cavity size α -CDs is smaller than β -CDs cavity, the *ortho* and *meta* ABA molecules are more tightly encapsulated in the α -CDs; That is why dual emission can easily be formed in the α -CD/HP- α -CD medium. Further, polarity and viscosity variations may play a more important role in the change in the ICT behavior of *ortho* and *meta* isomers at pH ~1. The ICT band of *ortho* and *meta* ABAs was shifted to the red with increasing CD concentration. This provides strong evidence for the protrusion of the COOH group into the hydrophobic phase. This is reasonable, because in *ortho* and *meta* ABAs, the dual luminescence is not observed in the absence of CD medium. Further, the question is why 4ABA molecule does not give ICT emission in both CDs, is because the size of 4ABA molecule is smaller than the CD cavity. Hence 4ABA can freely rotate in the CDs cavities.

The association constant for all the ABA:CD inclusion complexes formation has been determined by analysing the changes in the intensities of absorption and fluorescence maxima with the CDs concentration (**Table 1**). **Figs. 7 to 10** show a plot of $1/I-I_0$ versus $1/[CD]$ and $1/I-I_0$ versus $1/[CD]^2$ change in the fluorescence intensities with increasing concentration of the CDs. It is seen from this plot in pH~1, the fluorescence intensities increased along with CDs concentration. However, in pH~7, the emission intensities of ABAs decreased indicating the incorporation of almost all the ABA molecules in the CD cavity. In the absorption spectra, at pH~1, clear isosbestic points were observed in all the CDs showing well defined 1:1 inclusion complexes were formed between ABAs and CDs.

Table 1. Binding constant and Gibbs free energy of 2ABA, 3ABA and 4ABA with different α -CD and β -CD concentrations

		α -CD/HP α -CD				β -CD/HP β -CD			
		pH~1		pH~7		pH~1		pH~7	
		λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}
2ABA	$K(1:1) M^{-1}$	320	282	289	574	152	378	210	313
	$\Delta G \text{ kJ mol}^{-1}$ (-ve)	14.53	14.21	14.27	16.00	12.65	14.95	10.77	13.76
3ABA	$K(1:1) M^{-1}$	622	2743	47	120	157	129	68	95
	$\Delta G \text{ kJ mol}^{-1}$ (-ve)	16.21	19.93	9.69	12.00	12.34	12.23	10.03	17.26
4ABA	$K(1:1) M^{-1}$	680	745	1933	1866	33	232	89	212
	$\Delta G \text{ kJ mol}^{-1}$ (-ve)	16.43	16.66	19.00	18.87	8.81	13.82	11.31	13.51

**Fig 7.** Benesi-Hildebrand plot for 1:1 inclusion complexation of ABAs with α -CD at different pHs: (a) and (b) Plot of $1/A - A_0$ vs. $1/[\alpha\text{-CD}]$, (c) and (d) Plot of $1/I - I_0$ vs. $1/[\alpha\text{-CD}]$.

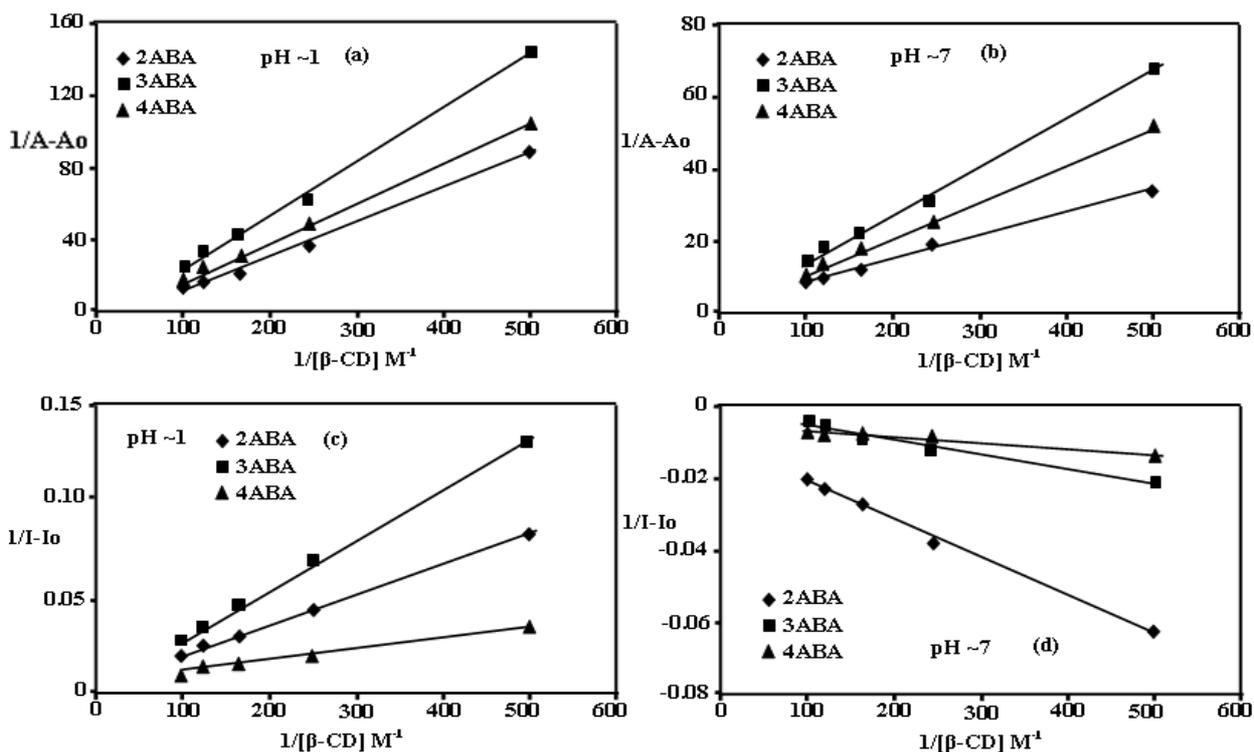


Fig 8. Benesi-Hildebrand plot for 1:1 inclusion complexation of ABAs with β -CD at different pHs: (a) and (b) Plot of $1/A-A_0$ vs. $1/[\beta\text{-CD}]$, (c) and (d) Plot of $1/I-I_0$ vs. $1/[\beta\text{-CD}]$.

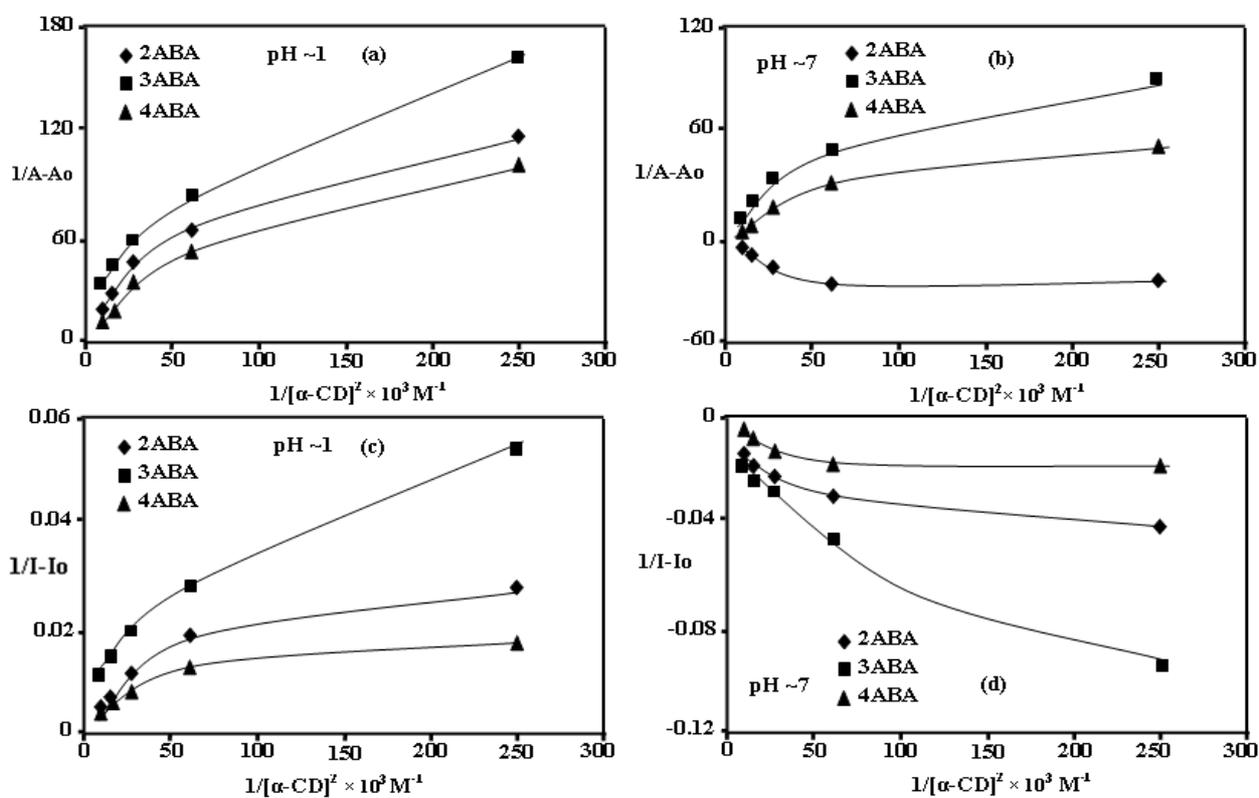


Fig. 9. Benesi-Hildebrand plot for 1:2 inclusion complexation of ABAs with α -CD at different pHs: (a) and (b) Plot of $1/A-A_0$ vs. $1/[\alpha\text{-CD}]^2$, (c) and (d) Plot of $1/I-I_0$ vs. $1/[\alpha\text{-CD}]^2$.

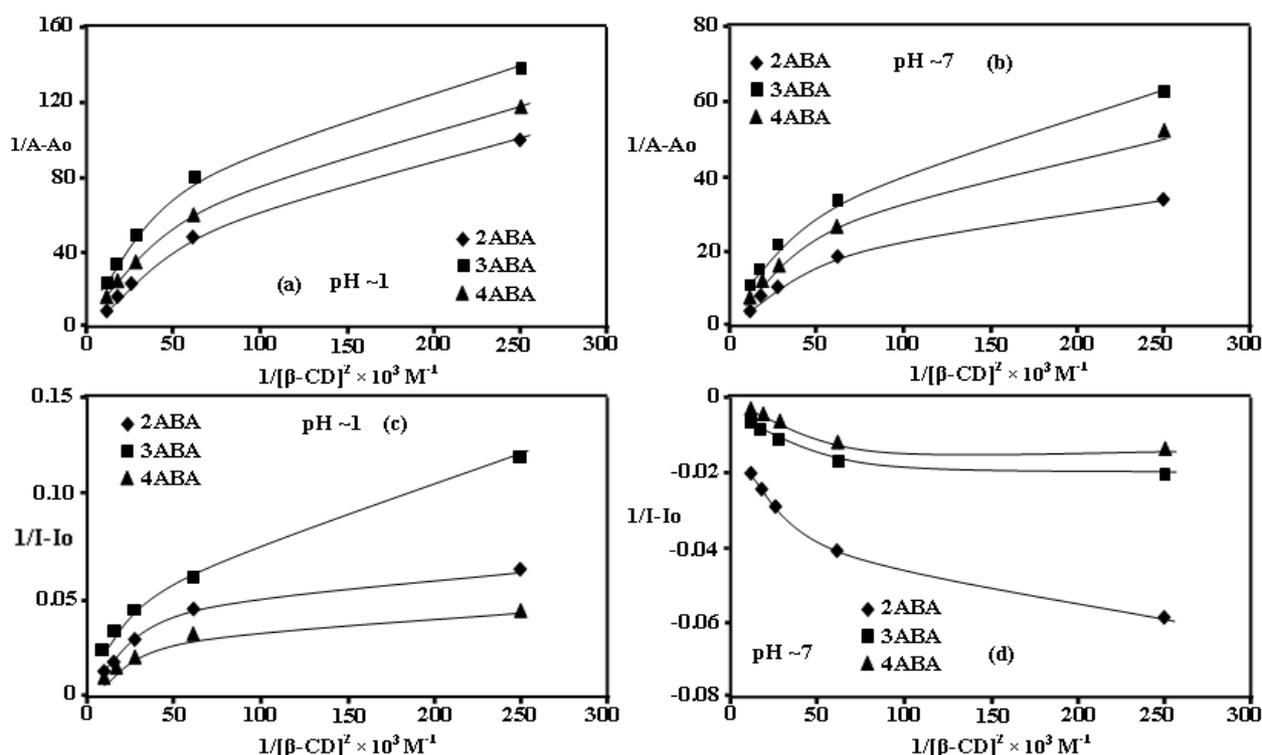


Fig 10. Benesi-Hildebrand plot for 1:2 inclusion complexation of ABAs with β -CD at different pHs: (a) and (b) Plot of $1/A-A_0$ vs $1/[\beta\text{-CD}]^2$, (c) and (d) Plot of $1/I-I_0$ vs $1/[\beta\text{-CD}]^2$

However, at pH~7, in the CDs solutions, no clear isosbestic point was observed in the absorption spectra and thus one can rule out the possibility of the formation of a well-defined 1:1 complex. The absorption and emission spectra of pH ~1 and pH ~7 solutions were different from the other which indicates the existence of at least two kinds of inclusion complexes in this system.

The formation of 1:1 and 1:2 guest: host inclusion complex, the binding constant can be obtained by using the Benesi-Hildebrand equation for the 1:1 complex and the 1:2 complex between ABAs and CD. A plot of $1/I-I_0$ versus $1/[\text{CD}]$ (both absorption and fluorescence) reveals a linear relation at pH ~1 while pH ~7 a plot of $1/I-I_0$ versus $1/[\text{CD}]^2$ gives a straight line as shown in **Figs 7 to 10**. 1:1 inclusion complex gives straight line at pH~1, suggesting that the stoichiometry of the inclusion complex 1:1 is present in the ABA molecules. For pH~1, the Benesi-Hildebrand plot fits a 1:1 model. In the case of pH~7, the results are incompatible with a simple 1:1 association model and the formation of 1:2 complexes must be considered, because the red shift of the spectrum and the increase of absorptivity generally observed for the 1:2 complexes. A comparison of these results suggests the following assignments: (i) linear relation observed in pH ~1 (**Figs. 7 to 10**) indicates 1:1 inclusion complexes were formed in this pH, (ii) a concave curve observed in the Benesi-Hildebrand plot (**Figs.7 to 10**) indicates 1:2 inclusion complexes were formed in pH ~7.

In 1:2 inclusion complexes, the aromatic moieties were partly embedded in the CDs cavity and the amino group forms hydrogen bonding with other CD-OH groups. Such a 1:2 inclusion complex structure gains further stabilization energy by hydrogen bonding between hydroxy groups of the primary and secondary rims of the two different CD molecules; water should be excluded from such a structure, although the small solvent molecule could penetrate the central cavity to interact with the amino group. At high CD concentration, ABAs are bound to two CD molecules. This could explain the different interactions of absorption/ emission spectra observed for pH~1 and pH~7 solutions. The red shifts observed for the 1:2 complexes indicate that the ABAs form strong hydrogen bonds, most likely to oxygen of the glucosidic link of the CDs, but renders hydrogen bonds, where the substrate is the proton acceptor unlikely. This analysis reflects the formation of 1:1 inclusion complex in pH ~1 and mixture of 1:1 and 1:2 inclusion complexes with ABA:2CD in pH ~7 solution. The binding constants obtained from the absorbance and fluorescence intensity are

considerably different from each other again supported the formation for two different complexes between the ABAs and the CDs at pH~1 and pH ~7 solutions. The binding constants were very sensitive to change of pH values, which further supported the selective inclusion associated with the monocation and neutral form of ABAs.

Of the two species (monocation and neutral form), we should note that all the CDs can readily include the protonated species than the anionic species, because in the anionic species amino group can interact with CD-OH groups than protonated NH_3^+ species. It is well known that substituents of aromatic rings capable of H-bonding can bind the OH groups of the CD edges. The energy involved in such H-bond interactions is responsible for the higher binding constants found, when compared to those of the unsubstituted molecule. By assuming this orientation for the ABA molecules in the CDs cavities are easy, because the CDs cavities favour the hydrophobic form of the benzoic acid derivatives [24]. The higher formation constants in pH~1 imply that the NH_3^+ group is more easily embedded in all the CDs cavities than the COOH group of ABAs. This suggests, NH_3^+ group is present in the interior of the CDs cavities, whereas COOH group is present within the upper part of the CDs cavities. The absorption and emission spectral red shifts of ABAs at pH ~7, in all the CDs suggest that amino group is located within the polar cavity, whereas blue shift emission at pH~1 shows COOH group is located in non-polar part of the CDs.

This is further supported by using PM3 calculations. PC-model program was used to find out the geometry of the inclusion complexes. This program helped us to draw the structures of the inclusion complexes. The ground state geometries of all the ABA's and the CDs were optimized using PM3 method. This method provides acceptable approximations to give results, which are quite close to the experimental finding. Considering the shape and dimensions of the CDs, ABAs can completely be encapsulated with the β -CD cavity when compared with than α -CD. The distance between **2ABA** = $\text{H}_5 - \text{H}_8$ is 5.96 Å and $\text{H}_4 - \text{O}_2$ is 6.27 Å and $\text{O}_1 - \text{H}_4$ is 6.04 Å; **3ABA** = $\text{H}_7 - \text{H}_8$ = 5.77, $\text{H}_2 - \text{H}_6$ = 4.32, $\text{H}_7 - \text{H}_9$ = 6.91, $\text{O}_2 - \text{H}_9$ = 5.94, $\text{H}_7 - \text{H}_5$ = 6.53, $\text{O}_1 - \text{H}_8$ = 6.20. These values are less than that the inside β -CD cavity (6.5 Å), but higher than α -CD (5.7Å). Since the length of ABAs is lower than the upper/lower rim value of CD, the amino and carboxylic groups attached benzene ring may be present inside the CD cavity. These findings reveal that ABAs molecules are encapsulated in the β -CD cavity. The thermodynamic parameter ΔG for the association of the guest molecule to CD is given in Tables 6.1.1 to 6.1.3. As can be seen from Tables, ΔG is negative which suggests that the inclusion process proceeded spontaneously at 303 K.

3.2. Fluorescence lifetime

The excited state decay curves for monocation (MC), neutral (N) and monoanion (MA) of 2ABA, 3ABA and 4ABA were measured in water and CD medium. **Table 2** summarizes the lifetime data for the emission of three species in the CD concentrations. Time resolved analyses of the fluorescence decays indicate that all three species are triexponential in water and CD environments, whereas in 4ABA the different type of decay was observed in both mediums. From the observation of absorption and fluorescence data, the intramolecular charge transfer was observed in water and CD for 2ABA and 3ABA. The lifetimes of the ionic species in CD are longer than those observed in aqueous medium. The increase in the value of lifetime with an increase in CD concentration is due to the encapsulation of all species in the CD cavity.

Table 2. Fluorescence lifetime parameters of 2ABA, 3ABA and 4ABA in water and α -, β -cyclodextrins.

Compound	CDs	Lifetime (ns)			Pre-exponential factor			$\langle\tau\rangle$
		τ_1	τ_2	τ_3	a_1	a_2	a_3	
2ABA	pH 1	0.40	2.11	10.21	11.32	15.25	73.43	4.16
	pH 1 – α -CD	0.42	2.15	11.34	17.22	26.16	56.62	4.22
	pH 1 – β -CD	0.45	2.19	15.68	38.08	51.53	10.39	4.38
	pH 7	0.46	2.24	12.33	13.11	17.45	69.44	3.65
	pH 7 – α -CD	0.49	2.28	14.90	19.40	29.32	51.28	3.67
	pH 7 – β -CD	0.52	2.32	17.45	39.23	54.65	6.12	3.72
3ABA	pH 1	0.46	2.61	13.01	2.83	5.76	91.41	4.32
	pH 1 – α -CD	0.29	1.56	14.65	7.10	16.23	76.67	4.39
	pH 1 – β -CD	0.37	1.97	80.90	28.08	41.53	30.38	4.44
	pH 7	0.52	1.98	10.26	5.67	8.32	86.01	3.88
	pH 7 – α -CD	0.55	2.02	12.20	7.10	16.23	76.67	3.93
	pH 7 – β -CD	0.56	2.05	14.27	28.08	41.53	30.38	3.95
4ABA	pH 1	0.06	1.55	8.01	90.72	3.43	5.85	
	pH 1 – α -CD	0.40			100			
	pH 1 – β -CD	0.71			100			
	pH 7	0.08	1.76	8.19	87.56	11.11	1.33	
	pH 7 – α -CD	0.55			100			
	pH 7 – β -CD	0.80	1.69		91.23	8.77		

4. Conclusion

The following conclusions can be arrived at from the above studies: (i) the observation of a large red shifted absorption and emission maxima even in nonpolar solvents indicates that ICT is present along with IHB, (ii) zwitter ion exists only in the ground state, (iii) due to steric effect, the monocation (NH_3^+) and carboxyl groups are twisted in the S1 state, (iv) All the ABAs form 1:1 complex at pH ~ 1 solution and mixture of 1:1 and 1:2 complex at pH ~ 7 with all the four CD, (v) dual luminescence appeared at pH ~ 1 indicates, both NH_3^+ and COOH groups are present in the interior of the CDs cavities, (vi) FT-IR, ^1H NMR, results suggest ABAs formed a stable inclusion complex with the CDs and (vii) the above studies demonstrate that in 2ABA and 3ABA, ICT interactions play a significant role in the inclusion complexes.

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