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Intramolecular charge transfer associated with hydrogen bonding effects on 2-aminobenzoic acid

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Abstract

Effect of solvents, buffer solutions of different pH and β-cyclodextrin (β-CD) on the absorption and fluorescence spectra of 2-aminobenzoic acid (2ABA) have been investigated. The inclusion complex of 2ABA with β-CD is discussed by semiempirical quantum calculations (AM1), absorption, emission, FT-IR, ^{1}H NMR and scanning electron microscope (SEM). The Stokes shifts in 2ABA is correlated with different polarity scales suggest that 2ABA molecule is more polar in the S_1 state. The increase in the excited state dipole moment values and β-CD studies confirm that the presence of intramolecular charge transfer (ICT) in 2ABA. Acidity constants for different prototropic equilibria of 2ABA in the S_0 and S_1 states are calculated. β-CD studies shows that (i) at pH ∼ 1, 2ABA forms 1:1 inclusion complex with β-CD, whereas at pH ∼ 7, it forms mixture of 1:1 and 1:2 inclusion complex and (ii) at pH ∼ 1, appearance of dual luminescence in higher β-CD solutions indicates carboxyl and amino groups present in the hydrophobic part of the β-CD. A mechanism is proposed to explain the inclusion process.

Keywords: 2-Aminobenzoic acid; β-Cyclodextrin; Inclusion complex; Solvent and pH effects; ICT

1. Introduction

It is well established that electronic charge redistribution does take place at each atom (specially on the acid and basic centres) of the molecule when it is photoexcited [1]. Due to this the acidic and basic properties of these basic centres or groups are quite different in the S_0 and S_1 states [2]. Although it is an elementary, but a very important process, generally described as excited state intramolecular proton transfer (ESIPT) [3–5] is observed in molecules containing both the proton donor (NH_2, OH) groups and the proton acceptor [–N=, carbonyl (C=O)] groups provided the two groups are connected by the intramolecular hydrogen bonding (IHB) in the ground state. This is because, the former becomes stronger acid and the latter becomes stronger base on excitation. Lot of studies [6] have been made to understand the photophysics and dynamics of this process because the systems of this type have been widely used as effective light photodetectors [6] and materials in continuous lasers [7] as well as lot of implications in biology [8].

The position of proton transfer is associated with the change in the charge densities at the respective atom and this is linked to the acid–base properties of the two ionizable groups. Depending upon the positions of these two ionizable groups, the proton transfer may be or may not be solvent-dependent. The detailed studies [9,10] carried out on salicylates and several derivatives of salicylic acid have established that, the proton covalently bonded to hydroxyl oxygen in the S_0 state migrates to the hydrogen bonded carbonyl oxygen to form the phototautomer. Similar kind of phenomenon has also been observed in number of other compounds [11,12] where the basic centre is –N= or  and the acidic centre is either hydroxyl proton or amino proton [12]. Cowgill [13] has studied the spectral behaviour of aminophenols at various pH values to explain the changes in the fluorescence spectrum of 3-aminotyrosin with changing pH. Bridges and Williams [14] have carried out similar studies on various anisidines to correlate the fluorescence spectra observed from the hydroxyindoles. The spectral shifts observed in the absorption and fluorescence spectra of these compounds with changing pH are consistent with the changes observed in the similar compounds [15]. Dogra and coworker [15] has studied the absorption and fluorescence spectra of the aminophenols and

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aminonaphthols in great detail. The acid–base character of these molecules is quite different from the ground and lowest excited singlet states and this is attributed to the relative contributions of the acidity and basicity of these molecules (the neutral and zwitter ions).

There have been several studies [16–20] on the electronic spectra of aminobenzoic acids. Doub and Vanderbelt recorded the absorption spectra at pH ∼ 3–7 and 10.0. Kopylova et al. [17] 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 [18]. Tramer [19] has studied the absorption and fluorescence spectra of *N*-methylanthranilic acid and *N*,*N*-dimethylanthranilic acid in various solvents. In his work, the problem of the tautomeric equilibria molecule ⇌ zwitter ion in the S_1 and T_1 states was discussed. In 1986, Jain et al., studied [20] 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. Further many workers demonstrated the TICT emission of 4-aminobenzoic acid derivatives [21]. The present study reports our extensive measurements on the absorption, emission, FT-IR, ^{1}H NMR, semiempirical calculations and scanning electron microscope of 2ABA in different solvents, pH and β-CD. We present here a somewhat different approach to the earlier work of 2ABA (for example, ICT, Stokes shift correlate with different solvent parameters, calculate ground and excited state dipole moments, prototropic reactions in aqueous medium compared with β-CD medium, etc.). In this regard, the present investigation has been carried out to study the solvatochromic effects of 2ABA. In the last few years, our main emphasis has been to study the effect of solvents of different polarity, acid–base concentrations and β-cyclodextrin on the spectral characteristics of different fluorophores so that they can be used as probe molecules [22–25]. Recently syringaldehyde [23], syringic acid [24], vanillic acid [24], *meta* and *para*-aminobenzoic acids [25] has been studied and this molecules shows intramolecular charge transfer emissions in the excited state. This stimulated us to carry out to the study of the effect of solvents, pH and β-cyclodextrin on spectral characteristics of 2ABA.

2. Experimental

2.1. Instruments

Absorption spectral measurements were carried out with a Hitachi Model U-2001 UV-visible spectrophotometer, and fluorescence measurements were made using a Jasco FP-550 spectrofluorimeter. The pH values in the range 2.0–12.0 were measured on Elico pH meter model LI-10T. FT-IR spectra were obtained with Avatar-330 FT-IR spectroscopy using KBr pelleting. The range of spectra was from 500 to 4000 cm^{-1}. Microscopic morphological structure measurements were performed with JEOL JSM 5610 LV scanning electron microscope (SEM). Bruker Advance DRX 400 MHz super conducting NMR spectrophotometer was used to study ^{1}H NMR spectra (IISc, Bangalore).

2.2. Reagents and materials

2ABA and β-CD were obtained from E-Merck and recrystallized from aqueous ethanol. The purity of the compound was checked by similar fluorescence spectra when excited with different wavelengths. All solvents used were of the highest grade (spectrograde) commercially available. Triply distilled water used for the preparation of aqueous solutions. Solutions in the pH range 2.0–12.0 were prepared by adding the appropriate amount of NaOH and H_3PO_4. A modified Hammett's acidity scale (H_0) [26] for the solutions below pH ∼ 2 (using a H_2SO_4–H_2O mixture) and Yagil's basicity scale (H_-) [27] for solutions above pH ∼ 12 (using a NaOH–H_2O mixture) were employed. The solutions were prepared just before taking measurements. The concentration of the 2ABA solutions were of the order 2×10^{-4} to 2×10^{-5} mol dm^{-3}. The concentration of β-CD solution was varied from 0 to 1×10^{-2} mol dm^{-3}.

2.3. Preparation of solid inclusion complex of 2ABA with β-CD

Accurately weighted 0.6 g β-CD was placed into 50 ml conical flask and 30 ml distilled water was added and then oscillated this solution enough. After that, 0.2 g 2ABA was put into a 250 ml beaker and 20 ml distilled water was added and put over electromagnetic stirrer to stir until it was dissolved. Then slowly poured β-CD solution into 2ABA solution. The above mixed solution was continuously stirred for 48 h at 50 °C. The reaction mixture was put into refrigerator for 48 h. At this time we observed that reddish brown powder precipitated. The precipitate was filtered by G_4 sand filter funnel and washed with distilled water. After dried in oven at 60 °C for 12 h, reddish brown powder product was obtained. This is inclusion complex of 2ABA with β-CD.

3. Results and discussion

3.1. Effect of solvents on the absorption and fluorescence spectra

The absorption and fluorescence spectra of 2ABA have been studied in solvents of various polarities and hydrogen bonding natures. The relevant data are listed in Table 1. When compared to benzoic acid (275 and 234 nm), aniline (281 and 235 nm), 4-aminobenzoic acid (283 nm) [25] and 3-aminobenzoic acid (319 nm) [25], the absorption and fluorescence maxima of 2ABA (333 and 247 nm) is largely red shifted in cyclohexane. This is because intramolecular hydrogen bonding (IHB) present in 2ABA. The red shift increases according to following sequence: benzoic acid < aniline < 4ABA < 3ABA < 2ABA. The above sequence indicates the position of the substituent in the phenyl ring is the key factor for the absorption and emission behaviour, because of the different electronic densities of the HOMO on each atom. Thus in ABA, substitution *ortho* position

Table 1
Absorption, fluorescence spectral data (nm) and Stokes shift (cm^{-1}) of 2ABA in different solvents

S. no.	Solvents	λ_{abs}	log ε	λ_{flu}	Stokes shift
1	Cyclohexane	333.0 247.0	4.16 4.26	380	3715
2	Diethyl ether	338.0 250.5	3.92 4.07	390	3944
3	1,4-Dioxane	338.0 250.5	3.92 4.07	390	3944
4	Ethyl acetate	336.5 251.0	3.97 4.13	396	4465
5	Dichloromethane	336.0 247.5	3.91 4.04	400	4761
6	Acetonitrile	336.0 247.5	3.91 4.04	400	4761
7	*t*-Butyl alcohol	336.5 247.5	3.95 4.12	410	4717
8	2-Propanol	336.5 247.5	3.95 4.12	410	4717
9	2-Butanol	336.5 247.5	4.04 4.22	410	4717
10	1-Butanol	336.5 247.5	4.04 4.22	410	4717
11	Methanol	332.5 247.5	4.02 4.26	410	5075
12	Water	328.8 238.5	4.34 4.13	420	6645

would forms IHB, whereas *meta* position would stabilize the charge transfer (CT) character. Examination of these results reveals that the position and/or the molar extinction coefficient of this band are highly influenced by the nature of the polar substituent in the phenyl ring.

The absorption spectrum of 2ABA in all solvents is characterized by two bands; a longer wavelength band (LW) with a maximum around 336 nm and a shorter wavelength band (SW) at 247 nm. The SW band is ascribed to π–π^* transition of the benzenoid system of the 2ABA, whereas the LW band can be attributed to $\pi \rightarrow \pi^*$ transition within the heterocyclic moiety (i.e., intramolecular hydrogen bonded ring) of the 2ABA molecule. The location of this band at LW, relative to the former one can be ascribed to the higher delocalization of π-electrons of IHB ring. Both the UV bands (π–π^*) suffer a small solvent shifts on changing the polar substituent attached to the phenyl moiety, a behaviour which is characteristic of the type of electronic transition corresponding to these bands. On the other hand, the compound display a broad visible band in emission (within the range 380–420 nm). This band can be assigned to (π–π^*) transition involving the whole electronic system of the compounds with a considerable charge transfer (CT) character. Such a CT originates mainly from the amino group to the carbonyl group which is characterized by a high electron accepting character i.e., this band is due to intramolecular charge transfer (ICT) character.

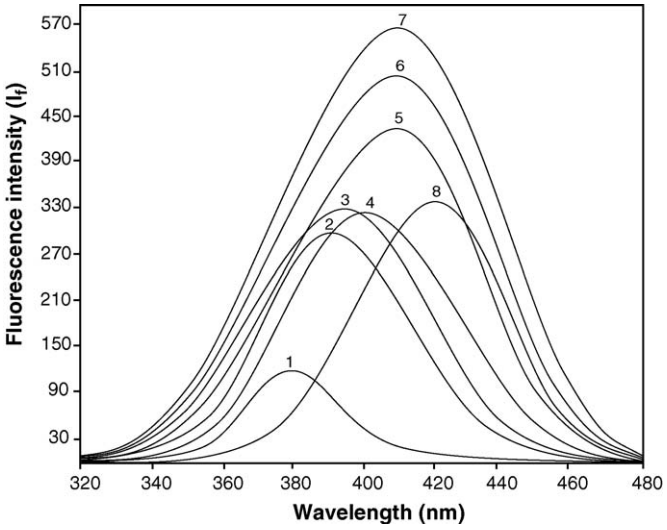
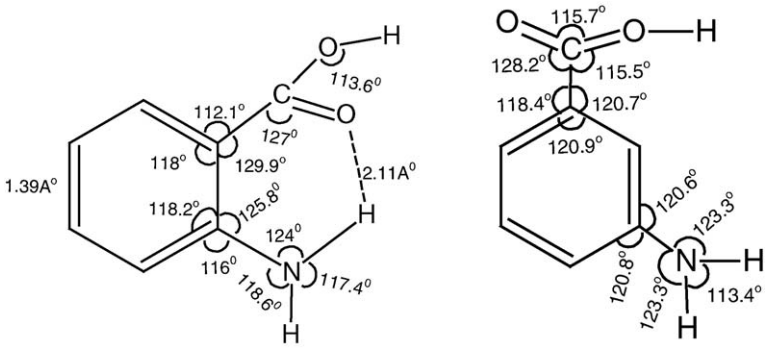


Fig. 1. Fluorescence spectra of 2ABA in selected solvents at 303 K. (1) Cyclohexane; (2) dioxane; (3) ethyl acetate; (4) acetonitrile; (5) 2-propanol; (6) *t*-butyl alcohol; (7) methanol; (8) water.

The absorption spectrum of 2ABA in water at pH $\sim$ 7 is largely blue shifted (310 nm) than other solvents. Acidic pH $\sim$ 1, does not dramatically affect the appearance of the spectrum except for a red shift. This effect of the pH on the absorption spectrum indicates that the carboxyl group is ionized in pH $\sim$ 7, because deprotonation of carboxyl group is blue shifted. The IR absorption spectrum of 2ABA has been recorded in KBr pellet is shown the stretching frequency around 3475–2530 cm^{-1} confirms the presence of zwitter ion in this molecule.

The fluorescence spectra are displayed in Fig. 1. In all solvents 2ABA gives only one broad structureless fluorescence spectra. The emission maxima of 2ABA (380 nm) is also largely red shifted than benzoic acid (302 nm), aniline (320 nm) and 4ABA (325 nm) (all values in nonpolar solvent). Generally, in the first excited singlet state the polarity of the NH_2 or OH bond is increased due to the increased charge transfer interaction from the NH_2 or OH group to the aromatic ring and thus a red shift is observed in water than cyclohexane. Since IHB is play an important role in 2ABA, the emission maxima in cyclohexane is largely red shifted than *meta* and *para* isomers. Larger red shift in the emission band maximum reflects the greater delocalization of the π cloud of the carboxyl group and lone pair of the amino group with the aromatic moiety. Another remarkable aspect of the fluorescence emission of 2ABA is the effect of the solvent polarity. Contrary to the absorption spectra, the emission spectra of 2ABA (410 nm in methanol) are blue shifted relative to those of 3ABA (440 nm in methanol) in hydrogen bonding solvents. This is probably the *meta* directing carbonyl group in 3ABA increase the ICT character in the S_1 state.

In the presence of solvents more polar than cyclohexane, the intensity of the emission spectrum gradually increases from cyclohexane to methanol. The emission in water is strongly pH-dependent, with the Stokes shift reaching its maximum value in acidic aqueous solutions (methanol 5075 cm^{-1}, acidic pH 6645 cm^{-1}). In an acidic medium, the carboxyl group becomes more conjugated with the aromatic π-system, in a situation in



Scheme 1. 2ABA and 3ABA bond angles (AM1 method).

which there is marked charge separation with in the molecule. In the excited state, amino proton and carbonyl group are more acidic and basic, respectively, than in the ground state. Thus, the basic carbonyl atom can accept a proton from the acidic amino group through delocalization of the aromatic ring. The broad and blue shifted emission at pH ∼ 7 is common in molecules having an electron withdrawing group, such as –COOH attached to an aromatic nucleus. However, the nature of such an emission is not always easy to ascertain, since it can be the result of a variety of causes, including dimer formation in the ground state (or other kinds of aggregates), excimer emission, changes in the conformation upon excitation or charge transfer processes [28,29]. Further in 3ABA molecule we observed ICT emission in the S_1 state indicates ICT may also be present in 2ABA molecule [25].

In the case of 2ABA, the fact that the broad band is also appear at alkaline pH could rule out the possibility of 2ABA forming dimers in the ground state (linked by H-bonding) which give rise to excimer emission upon excitation [29]. These dimer cannot form if the carboxylate group is ionized. Further, the presence of amino group in the *ortho* position which strongly forms the six-membered intramolecular H-bonded ring. Moreover, low concentrations currently used, as much as 2×10^{-5} M, rule out this possibility. Even at concentrations as low as 2×10^{-6} to 2×10^{-7} M, the broad emission can be detected. Hence, the most likely reason is, 2ABA is a multimolecular process, the emission of a state with a high intramolecular charge transfer (ICT) character stabilized by the polar and nonpolar solvents. In such a state the donor group is the amino/aromatic moiety of the molecule and the acceptor group is the –COOH. Like absorption spectrum, the fluorescence spectrum in each solvent is broader, that is having broader full width at half the maximum height (FWHM). The FWHM of the fluorescence spectrum increases in polar solvents. This suggests that ICT present in 2ABA molecule and this ICT increases in the protic solvents. This conclusion is based on the following reasons. (i) Two bulkier electron donating and electron withdrawing groups present at *ortho* position, (ii) the large increase in the dipole moment in S_1 state, (iii) in absorption, larger red shifted maxima observed in DMSO (λ_{abs}: 346 and 248 nm; λ_{emi}: 450 nm) which is most hydrogen bond interfering solvent, (iv) effect of trifluoroacetic acid (TFA) to cyclohexane is more pronounced on the absorption and fluorescence spectrum, i.e., with the addition of TFA up to 0.2 M in cyclohexane largely is red shifted (λ_{abs}: ∼347 and 247 nm; λ_{em}: ∼408 nm) than cyclohexane (λ_{abs}: ∼338 and 247 nm; λ_{em}: ∼380 nm). The FWHM of fluorescence spectrum does not change much in this range of TFA used (v) at higher β-CD concentrations (pH ∼ 1) a dual emission is appeared and (vi) the geometry of 2ABA is optimized using the AM1 method, it shows bond angle is deviated from 120° is confirmed 'twisting' of the amino and COOH groups (Scheme 1).

In this molecule, the energy of locally excited state (LE) and charge transfer are equally affected, hence it gives only one emission maxima at longer wavelength. The large red shifted emission maxima in all solvents would indicate a dipolar interaction between the solute and solvent molecules. In nonpolar solvent, the zwitter ionic form is less soluble, hence it gives weakly fluorescent (i.e.) the carboxylate anion already containing a negative charge will not readily accept a second negative charge necessary for the resonance interaction, and consequently the emission is weak in cyclohexane [29].

3.2. Solvatochromism

Few empirical and theoretical solvent polarity scales are in use to explore solvatochromic effects [30]. Empirically or theoretically derived solvent parameters like Lippert $f(D, n)$ [31], Bilot–Kawski (BK) [32] and Reichardt's–Dimroth $E_T(30)$ [33] values as accurate parameters of solvent polarity have been used by several authors to correlate molecular spectroscopic properties [30]. Among these parameters $f(D, n)$ and BK parameters takes into account of solvent polarity alone, whereas $E_T(30)$ incorporate both solvent polarity and hydrogen bonding effects. From the correlation of Stokes shift with any one of these parameters an idea of about the type of interaction between the solute and solvent can be obtained. The solvatochromic shifts reveal that the hydrogen bonding interactions are present along with dipole interactions. In order to confirm this, we used $E_T(30)$, BK and $f(D, n)$ solvent parameters and the values are compared with Stokes shift of 2ABA molecule.

Fig. 2 shows the plots of $\Delta\bar{\nu}_{ss}$ versus the $E_T(30)$, BK and $f(D, n)$ parameters. The increase in Stokes shift from cyclohexane to water in 2ABA is found to be more in accordance with $E_T(30)$ than with BK and $f(D, n)$ values. As mentioned earlier, $E_T(30)$ parameter incorporates both hydrogen bonding and solvent polarity effects whereas the BK and $f(D, n)$ parameters represents only solvent polarity effects. Since hydrogen

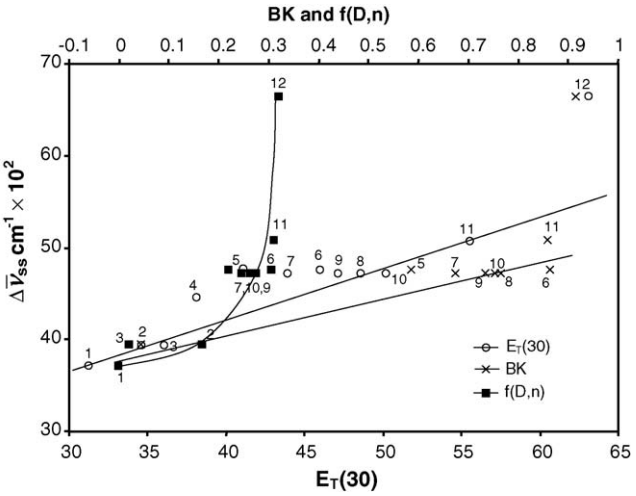


Fig. 2. Plot of Stokes shifts (cm^{-1}) of 2ABA vs. $E_T(30)$, BK and $f(D, n)$ solvent parameters. (1) Cyclohexane; (2) diethyl ether; (3) dioxane; (4) ethylacetate; (5) CH_2Cl_2; (6) CH_3CN; (7) *t*-butyl alcohol; (8) 2-propanol; (9) 2-butanol; (10) 1-butanol; (11) methanol; (12) water.

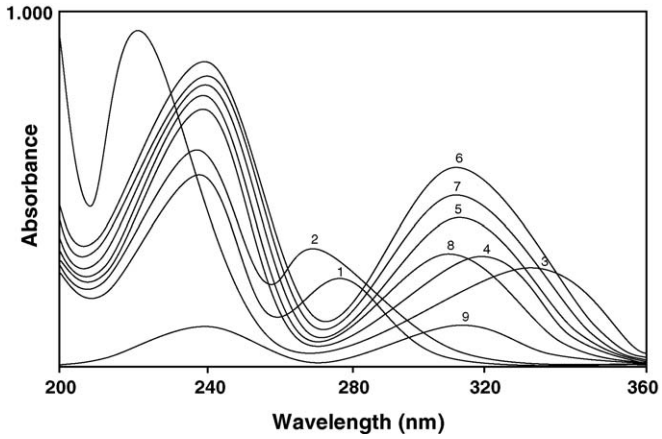


Fig. 3. Absorption spectra of different prototropic species of 2ABA at 303 K: concentration 2×10^{-4} M. (1) Dication; (2) monocation; (3) neutral; (4–7) zwitter ion; (8) monoanion; (9) dianion.

bonding interactions are predominant in the solvatochromic shifts of 2ABA, the Stokes shift versus $E_T(30)$ gives good correlation ($v = 0.9177$) than BK ($v = 0.7630$) and $f(D, n)$ ($v = 0.7512$) parameters. The large deviations in H_2O can be explained as follows. It is well established that the NH_2 group becomes more acidic in the S_1 state and they can donate a proton easily to the solvent and carbonyl group becomes more basic in the S_1 state. In contrast, in the S_0 state, the NH_2 group acts as a proton acceptor. Further zwitter ion is present only in the S_0 state, whereas in the S_1 state ICT emission is present along with IHB in this molecule.

To substantiate this, ground state dipole moments (μ_g) for 2ABA molecule have been calculated using AM1 programme. Many equations are available to determine the excited state dipole moment (μ_e) from absorption and fluorescence data. We shall use the Lippert equation [31] to calculate the excited state dipole moment ($\mu_g = 5.638$ D, $\mu_e = 10.97$ D). The larger dipole moment value is further supported by ICT present in 2ABA molecule. The value of Onsager cavity radius *a* obtained for 2ABA is 3.22 Å. The value of *a* have been obtained by taking the 50% of the maximum length of the molecule. It may be mentioned here, we also calculate *a* from the following equation:

$$a = 3\sqrt{\frac{3M}{4\pi dN}} \quad (1)$$

where *M* is the molecular weight, *N* the Avogadro number *d* the density (1.560). The *a* value obtained by Eq. (1) is (3.24 Å) quite close to the data obtained from the AM1 calculations.

3.3. Effect of pH on absorption spectra

The absorption spectra of various prototropic species of 2ABA was recorded at different acid concentrations and the relevant data are mentioned in Table 2 and Fig. 3. There are six prototropic species (dication, monocation, zwitter ion, neutral, monoanion and dianion in 2ABA. At H_0 −5 value, the maxima (277.5 and 239 nm) present in the dication of 2ABA formed

Table 2
Various prototropic maxima (absorption and fluorescence) and pK_a (pK_a^*) values of 2ABA in without and with β-CD medium

Species	Without β-CD				With β-CD			
	λ_{abs}	pK_a	λ_{flu}	pK_a^*	λ_{abs}	pK_a	λ_{flu}	pK_a^*
Dication	277.5 239.0	>−4.89	420 (wf)	>−2.28	–	–	–	–
Monocation	272.4 238.0	1.8	420	3.4	272.4 229.0	0.8	420	2.0
Neutral	328.5 220.0	3.5	410 (wf)	4.0	330.0 229.0	2.0	410	5.0
Zwitter ion	324.4–315.0 220.0–242.0	3.5–4.8	–	–	–	–	–	–
Monoanion	310.5 240.5	5.0	395	5.5	305.0 247.0	6.0	390	7.0
Dianion	314.0	>16.0	470–480	>14.5	–	–	–	–

wf: weakly fluorescence.

by protonation of the carboxyl group consistent with the results observed by others for the similar protonation [34,35]. Moreover, when the protonation occurred at the hydroxyl or amino groups, these would have been a blue shift in the absorption and emission spectra as noticed in many compounds [12,22]. Hence, the red shift confirms the formation of the dication on protonation of the carbonyl group. The blue shift observed (272.4 and 238 nm) in both the absorption bands, with decrease of hydrogen ion concentration (pH ∼ 1.8) suggest the presence of the monocation, formed by protonating the amino group. The pK_a value of 2ABA is less than aniline (pK_a ∼ 4.0) indicates, 2ABA molecule is more acidic than aniline.

A large red shift is observed in the band maxima 328.4 and 242 nm shows that the neutral species is formed in the range from pH ≈ 2–3.5. In this pH range (pH ≈ 2–3.5) the absorption maxima resemble the spectra observed in non-aqueous solvents and thus can be assigned to be neutral species. The larger red shift 272.4–328.4 nm (difference 56 nm) observed in the absorption maxima, could be due to the formation of neutral species and thereby the formation of a closed ring with the IHB between the amino and carboxyl group. The absorption spectra exhibit a regular blue shift 328.5–315 nm with an increase in the pH 3.5–4.8 indicates that zwitter ion is formed. With an increase on pH from 5, the absorption maxima is again blue shifted (310.5 and 240.5 nm). It is well known fact that deprotonation of carboxyl group gives a blue shifted absorption and emission maxima [24,35]. Above H_ 15, a slight red shift, compared to monoanion (314 nm) is observed, suggesting that the dianion of 2ABA is formed by deprotonating the amino group. The spectral shift observed in the last step is similar to what is normally observed in the deprotonation of an amino group [22]. The pK_a value of the deprotonation of the amino group in 2ABA is consistent with the above explanation. The pK_a values for various equilibria are determined spectrophotometrically and are given in Table 2.

3.4. Effect of pH on fluorescence spectra

The fluorescence spectra of various prototropic forms of 2ABA are shown in Fig. 4. The fluorescence data are given in Table 2 for various hydrogen ion concentrations clearly indicate that the prototropic species of 2ABA formed in the ground state are different from the first excited singlet state. When the acidity is increased from 2 to H_0 −1.0 the fluorescence of 420 nm is quenched due to the formation of dication in carboxyl group. Similar results have also been observed in the case of 3- and 4-aminobenzoic acids [25]. At smaller hydrogen ion concentration (up to pH 3.8) the intensity of fluorescence increases at the same wavelength is due to the monocation of 2ABA, i.e., protonation takes place at the amino group. The blue shift observed in the fluorescence band maximum (410 nm) at pH 4.2 indicates the presence of neutral species. In this pH range, the emission maxima resemble the spectra observed in nonaqueous solvents and thus can be assigned to be neutral species. Usually, the emission band of a corresponding cation in amino group is blue shifted in comparison with the emission band of the normal molecule. Hence, the unusual red shift is observed in 2ABA monocation

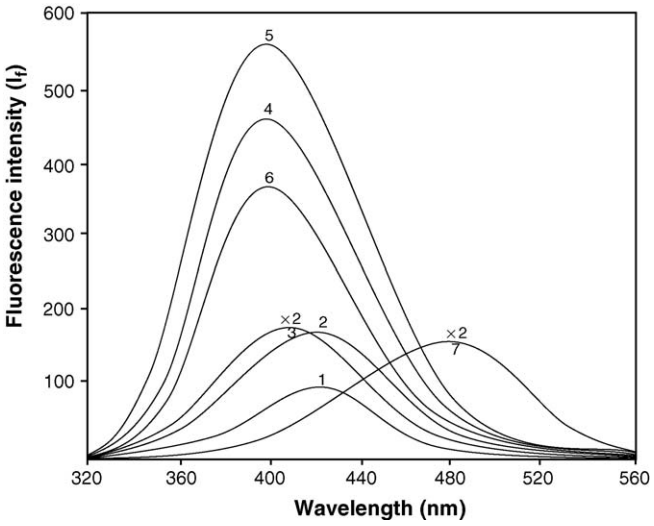


Fig. 4. Fluorescence spectra of different prototropic species of 2ABA at 303 K: concentration 2×10^{-4} M. (1) Dication; (2) monocation; (3) neutral; (4–6) monoanion; (7) dianion.

is due to 'twisting' of the NH_3^+ and COOH groups. This is because two bulkier groups present at *ortho* position [36]. With an increase in pH from 4.5 to 10, 2ABA gives a new blue shifted spectra with the maxima 395 nm suggesting the formation of monoanion in 2ABA. As mentioned earlier, the above result is consistent with the earlier findings that a blue shift is observed in a spectrum when deprotonation takes place at the carboxyl group [35]. Further, increase in pH from 13, a large red shift observed in the emission maxima (470 nm) could be due to the formation of the NH^- ions (dianion) [22]. In 2ABA, the pK_a^* value of neutral-monoanion equilibrium is greater than that in the ground state pK_a value. The tendency for carbonyl and carboxyl aromatic compounds to become more basic in the excited singlet state relative to the ground state is well established [37]. The small differences observed in other equilibria using absorption and fluorescence pK_a (pK_a^*) data could be due to (i) the use of band maxima rather than using 0–0 transitions and the different solvent relaxation for the conjugate species involved in the equilibria in different electronic states and (ii) increase in the acidity and basicity of the amino and carboxyl groups in S_1 state is such that the order of the prototropic reactions in the S_0 state are changed upon excitation. Similar observations are noted in case of molecules containing both the electron-donating and electron-attracting functional groups [37].

3.5. Studies of 2ABA with β-CD

Table 3, Figs. 5 and 6 depict the absorption and emission maxima of 2ABA (2×10^{-5} mol dm^{-3}) in pH ∼ 1.0 (monocation) and pH ∼ 7.0 (monoanion) solutions containing different concentrations of β-CD. At pH ∼ 7, 2ABA exists as a carboxylic anion, hence we also recorded spectrum at pH ∼ 1. The absorption spectra of the two forms (monocation and monoanion) are drastically different. The absorption peaks of 2ABA in pH ∼ 1 appears at 272 nm and in pH ∼ 7, absorption peaks appears around 330 nm. In both cases, no clear isosbestic point

Table 3
Absorption and fluorescence maxima (nm) of 2ABA at different concentration of β-CD

Concentration of β-CD (M)	pH ∼ 1.0			pH ∼ 7.0		
	λ_{abs}	log ε	λ_{flu}	λ_{abs}	log ε	λ_{flu}
0	272.6	3.36	420	317.0	3.83	396
	228.8	4.22		229.0	4.13	
0.002	272.5	3.50	420	326.5	3.85	400
	226.0	4.20		230.0	4.13	
0.012	272.0	3.74	414	330.5	3.96	414
	231.5	4.20	340	246.5	4.13	

is observed in the absorption spectra. In the presence of β-CD, there is no significant change is observed in the absorption maxima at pH ∼ 1, whereas the absorption spectra of 2ABA in pH ∼ 7 is seen to undergo a marginal red shift. It has also been observed that in both solutions, absorption intensities increases with increasing concentration of β-CD. At pH ∼ 1, 2ABA exists in its cationic form and the absorption spectra does not show any change in absorption maxima even in the presence of the highest concentration of β-CD used (1.2×10^{-2} mol dm^{-3}) indicating that, NH_3^+ group present in the hydrophobic part of the β-CD, whereas a regular red shift is observed in pH ∼ 7 indicates, amino group present in the hydrophilic part of the β-CD cavity. Further at pH ∼ 7, the absorption and emission maxima are close to methanol/water substantiate this implication. This may be NH_2 group interact with β-CD–OH groups, hence a regular red shift is observed in pH ∼ 7. The association constant for the β-CD:2ABA complex formation has been determined by analysing the changes in the intensity of absorption and fluorescence maxima with the β-CD concentration.

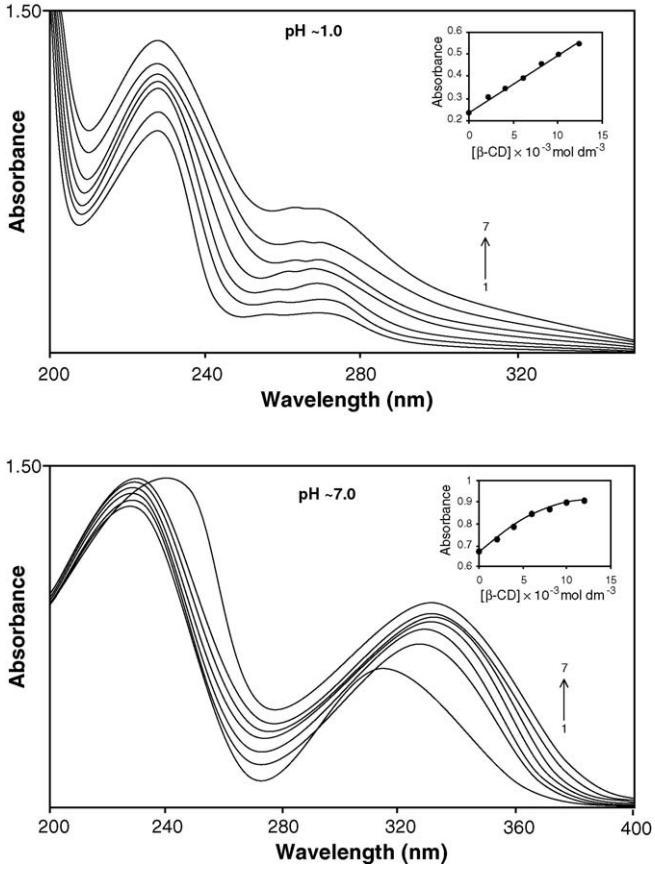


Fig. 5. Absorption spectra of 2ABA in different β-CD concentrations (mol dm^{-3}): (1) 0; (2) 0.002; (3) 0.004; (4) 0.006; (5) 0.008; (6) 0.010; (7) 0.012 (insert figure absorbance vs. β-CD concentration).

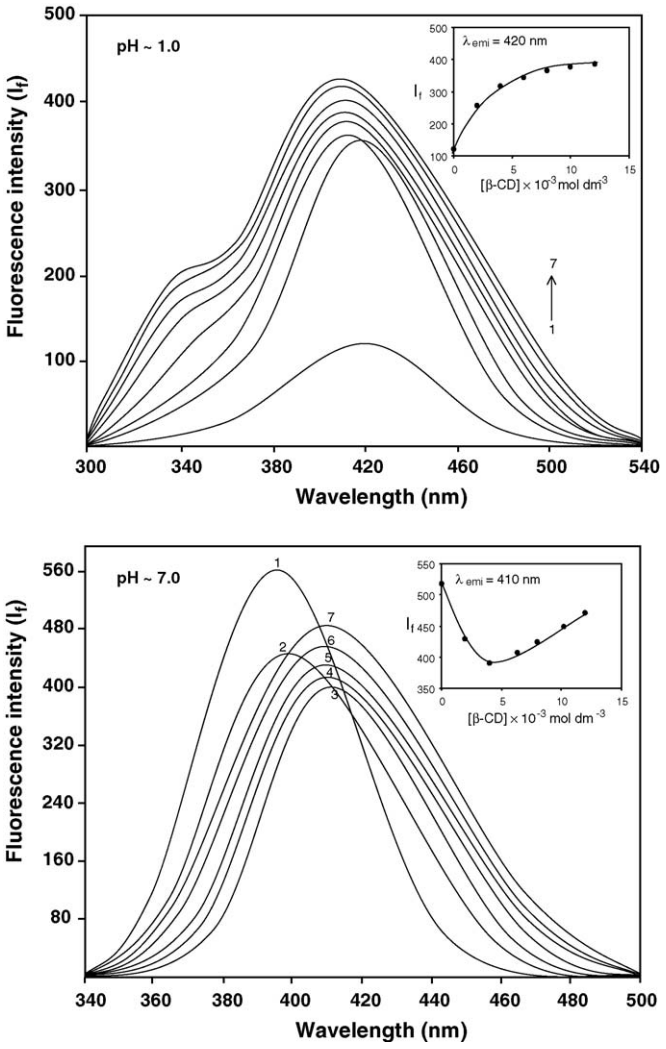


Fig. 6. Fluorescence spectra of 2ABA in different β-CD concentrations (mol dm^{-3}): (1) 0; (2) 0.002; (3) 0.004; (4) 0.006; (5) 0.008; (6) 0.010; (7) 0.012; (insert figure I_f vs. β-CD concentration).

As mentioned earlier, in both solutions, no clear isosbestic point is observed in the absorption spectra and thus one can rule out the possibility of the formation of a well-defined 1:1 complex. But based on the results of *para*-aminobenzoic acid [25], *meta*-aminobenzoic acid [25], *p*-(*N*,*N*-dimethylamino) [21] and *p*-(*N*,*N*-diethylamino)benzoic acid [21], it cannot eliminate completely the possibility that the 1:1 inclusion complex. However, the absorption and emission spectra of pH ∼ 1 and ∼7 solutions are different from each other indicates at least two kinds of inclusion complexes exists in this system.

To determine the stoichiometry of the inclusion complex, a Job's method [38] for the absorption/fluorescence were applied keeping the sum of initial concentration of 2ABA and β-CD

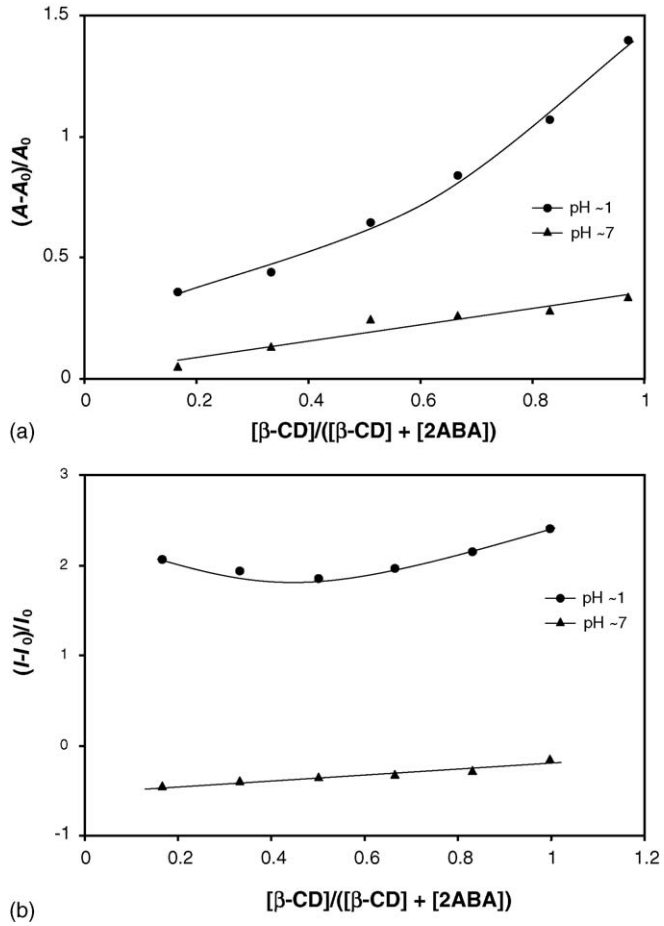


Fig. 7. Job's plot using (a) absorption and (b) fluorescence intensity at pH ∼ 1 and ∼7. The total concentration was 2×10^{-5} mol l^{-1}. Molar fraction is given by [β-CD]/([β-CD] + [2ABA]).

constant and the molar ratio of β-CD changing from 0 to 1. The absorption/fluorescence intensity of 2ABA in the absence of (I_0) and presence of β-CD (I) were determined respectively. A plot of $(A - A_0)/A_0$ and $(I - I_0)/I_0$ versus the molar fraction of β-CD was provided in Fig. 7. It shows that at pH ∼ 7, the $(A - A_0)/A_0$ and $(I - I_0)/I_0$ values versus molar fraction gives the straight line, indicating a 1:2 stoichiometry of the 2ABA with β-CD in the inclusion complex.

In general for a 1:2 stoichiometry of the 2ABA-β-CD inclusion complex, one can describe the equilibrium as follows:

$$\beta\text{-CD} + 2\text{ABA} \overset{K}{\rightleftharpoons} 2\text{ABA} - [\beta\text{-CD}]_2 \tag{2}$$

The corresponding formation constant (K) can be expressed as the following according to the law of mass action:

$$K = \frac{[2\text{ABA} - (\beta\text{-CD})_2]}{[2\text{ABA}][\beta\text{-CD}]^2} \tag{3}$$

where [2ABA − (β-CD)$_2$], [2ABA] and [β-CD] are the concentration of the respective species. The initial concentration of 2ABA and β-CD are respectively represented by the following equations:

$$[2\text{ABA}]_0 = 1 + K[\beta\text{-CD}]^2[2\text{ABA}] \tag{4}$$

$$[\beta\text{-CD}]_0 = 1 + 2K[\beta\text{-CD}][2\text{ABA}][\beta\text{-CD}] \tag{5}$$

To indicate the degree of association between β-CD and 2ABA, it would be useful to introduce the degree of reaction, α, is defined as the ratio between the free 2ABA concentration [2ABA], to the total concentration of the 2ABA, $[2\text{ABA}]_0$. Taking into account that (i) the variations in absorption and fluorescence maxima is proportional to the 2ABA concentration and (ii) the β-CD is in a large excess with respect to 2ABA and at high β-CD concentration essentially all 2ABA molecules are complexed, α is shown to be depend on the initial concentration of β-CD, $[\beta\text{-CD}]_0$ as follows:

$$\frac{\alpha}{1-\alpha} = \frac{1}{K[\beta\text{-CD}]_0^2} \tag{6}$$

The measured absorbance/fluorescence intensity values (I) are directly related to α,

$$a = \frac{[2\text{ABA}]}{[2\text{ABA}]_0} = \frac{I_\infty - I}{I_\infty - I_0} \tag{7}$$

where I is the observed absorbance/fluorescence intensity of 2ABA, actually measured at a defined 2ABA concentration, I_0 is the absorbance/fluorescence intensity of 2ABA in absence of β-CD and I_∞ is the absorbance/fluorescence intensity when the 2ABA is completely complexed by β-CD.

It is apparent from Eq. (6) that the response parameter (α) has a certainly functional relationship with the concentration of β-CD and the inclusion constant (K). Eq. (6) provides the basis for the determination of K value. The experimental data were fitted to Eq. (6) by adjusting K value (Table 4). The fitted results for the inclusion complex of β-CD with 2ABA is shown in Fig. 8. Four curves are calculated (two absorption curves, two fluorescence curves) with Eq. (6) with the different stoichiometric ratio. For a 1:1 and guest:host inclusion complex, plotting $1/(A - A_0)$ versus $1/[\beta\text{-CD}]$ and $1/(I - I_0)$ versus $1/[\beta\text{-CD}]^2$ are given in Fig. 9. 1:1 inclusion complex gives straight line at pH ∼ 1, whereas 1:2 should be linear plot at pH ∼ 7, suggesting that the stoichiometry of the inclusion complex is 1:1 in pH ∼ 1 and 1:2 in pH ∼ 7. Table 4 lists the values of the formation constants for complexes of 2ABA with deduced from the curve fitting data and Benesi–Hildebrand equation.

Further the formation of 1:1 and 1:2 guest:host inclusion complex, the inclusion constant can be obtained by using the modified Benesi–Hildebrand equation [39] for the 1:1 complex (Eq. (8)) and the 1:2 complex (Eq. (9)) between 2ABA and β-CD as shown below:

$$\frac{1}{I - I_0} = \frac{1}{I_\infty - I_0} + \frac{1}{K(I_\infty - I_0)[\beta\text{-CD}]} \tag{8}$$

$$\frac{1}{I - I_0} = \frac{1}{I_\infty - I_0} + \frac{1}{K(I_\infty - I_0)[\beta\text{-CD}]^2} \tag{9}$$

where K is the formation constant, I_0 the initial absorption/fluorescence intensity of free 2ABA, I_∞ the absorption/fluorescence intensity of β-CD inclusion complex and I is the observed absorption or fluorescence intensity. According to Eq. (8), a plot of $1/(I - I_0)$ versus $1/[\beta\text{-CD}]$ (both absorption and fluorescence) reveals a linear relation at pH ∼ 1, as shown

Table 4
Formation constant and ΔG values of 2ABA with β-CD

Inclusion complex	Curve fitting method				Benesi–Hildebrand method			
	pH ∼ 1		pH ∼ 7		pH ∼ 1		pH ∼ 7	
	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}	λ_{abs}	λ_{flu}
Formation constant								
K (1:1) (M^{-1})	191	420	215	343	152	378	210	313
K (1:2) ($\times 10^4\ M^{-2}$)	–	–	39	65	–	–	42	70
ΔG (kJ mol^{-1})								
1:1					−12.67	−14.95	−10.77	−13.76
1:2					–	–	−32.62	−34.76

in Figs. 9a and 10a, whereas at pH ∼ 7 a plot of $1/(I - I_0)$ versus $1/[\beta\text{-CD}]^2$ gives a straight line as shown in Figs. 9b and 10b. Formation constants β-CD:2ABA for the formation of ground state and excited state inclusion complexes were obtained from the β-CD concentration dependence of absorption/emission spectra assuming that the system can be described as a mixture of independently absorbing and reacting species. For pH ∼ 1, the Benesi–Hildebrand plot fit 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 guest:host complexes must be considered, because the red shift of the spectrum and the increase of absorptivity generally observed for the 1:2 complexes [40]. The results are in good agreement with the β-CD complexation effects reported recently on 3ABA/4ABA [25] and 2-naphthol [40]. A comparison of these results suggests the following assignments: (i) linear relation observed in pH ∼ 1 (Figs. 9 and 10) indicates 1:1 inclusion complex is formed in this pH and (ii) a concave curve observed in the Benesi–Hildebrand plot (Figs. 9 and 10) indicates, a mixture of 1:1 and 1:2 inclusion complex is formed in pH ∼ 7.

In 1:2 inclusion complex, the aromatic moiety is partly embedded in the one β-CD cavity and the amino group form

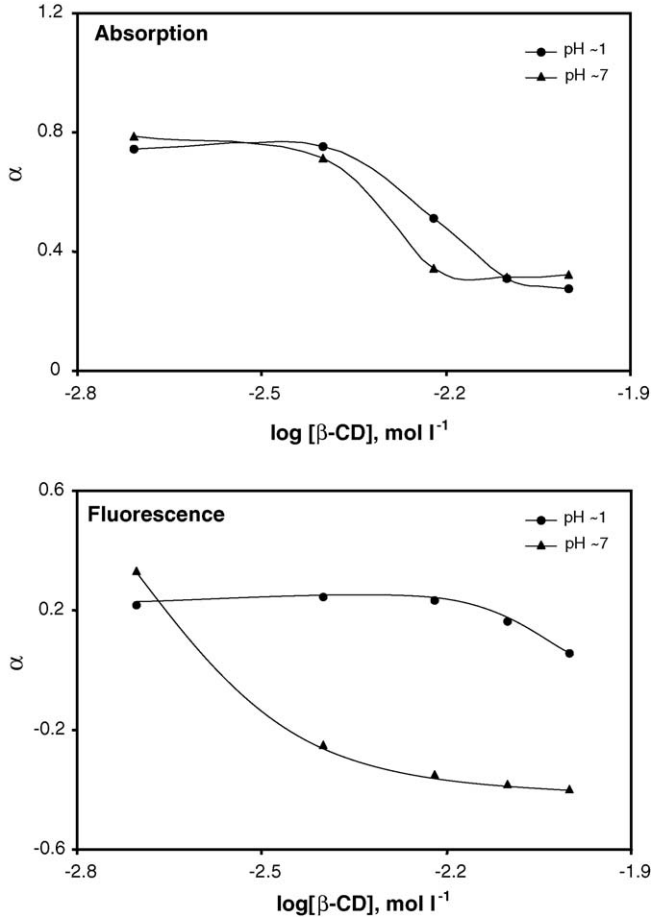


Fig. 8. The response parameter (α) as a function of log[β-CD] at pH ∼ 1 and ∼7. The curve fitting for experimental data were calculated from Eq. (6).

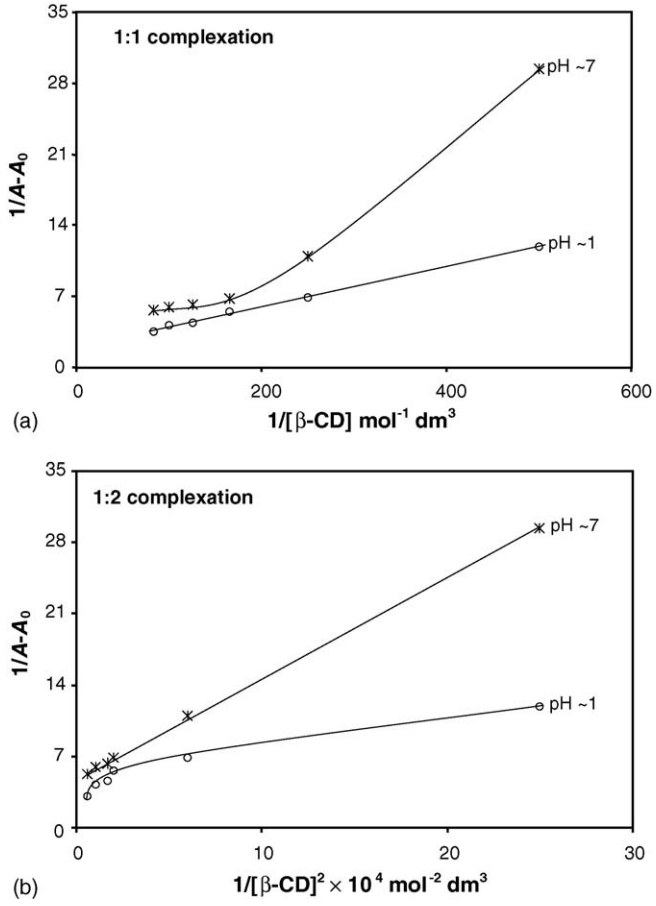


Fig. 9. Benesi–Hildebrand plot of (a) $1/(A - A_0)$ vs. 1/[β-CD] and (b) $1/(A - A_0)$ vs. $1/[\beta\text{-CD}]^2$ for 2ABA.

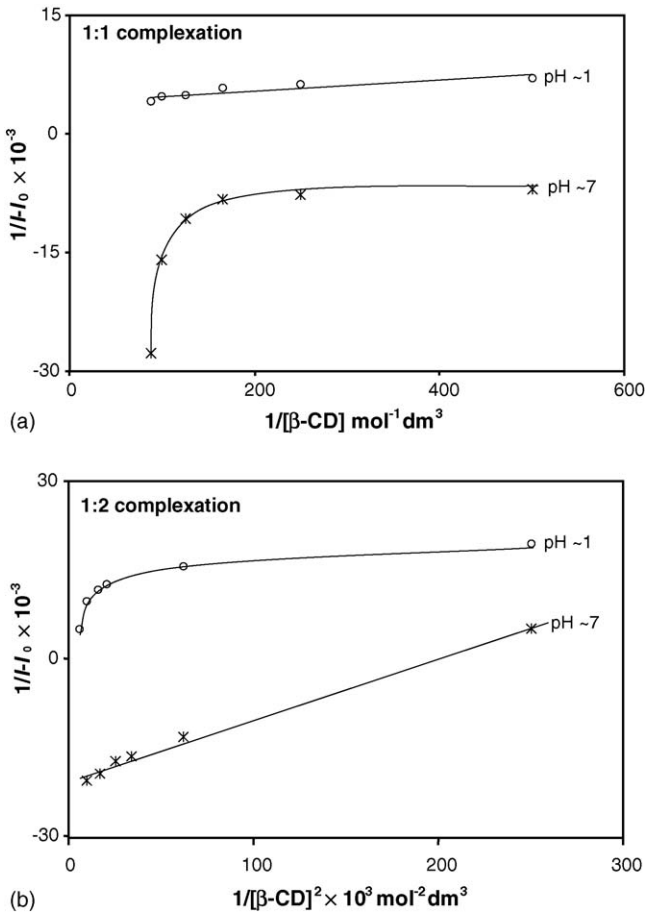
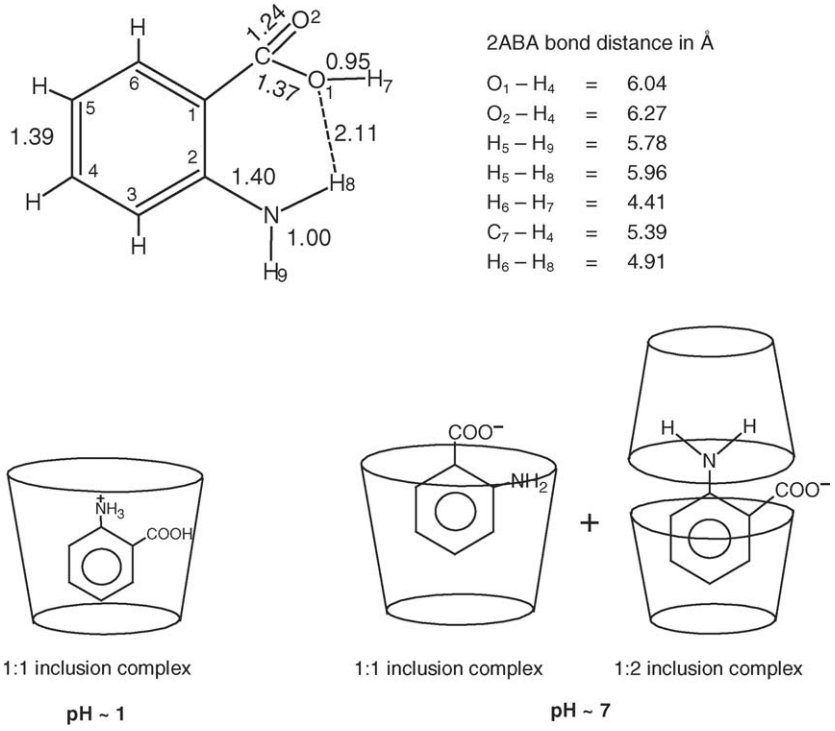


Fig. 10. Benesi–Hildebrand plot for the complexation of 2ABA with β-CD. Plot of (a) $1/(I - I_0)$ vs. 1/[β-CD] and (b) $1/(I - I_0)$ vs. $1/[\beta\text{-CD}]^2$).

hydrogen bonding with other β-CD–OH groups. The formation of the 1:1 and 1:2 guest:host complexes is clearly demonstrated in Scheme 2. 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 β-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. However, most likely this group should bind to the oxygens of the glucosidic bridges as such as interaction is observed for Scheme 2. At high β-CD concentration, 2ABA is bound to two β-CD molecules, this could explain the different interactions of absorption/emission spectra observed for pH ∼ 1 and ∼7 solutions. The large red shift observed for the 1:2 complex indicates that, in this case, 2ABA forms strong hydrogen bonds, most likely to an oxygen of the glucosidic link of the β-CD, 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 2ABA:β-CD in pH ∼ 7 solution. The formation constants obtained from the absorbance and fluorescence intensity are considerably different from each other again supported the formation for two different complexes between 2ABA and β-CD at pH ∼ 1 and ∼7 solutions (Figs. 5 and 6).

In 1:1 complex, the formation constants for protonated 2ABA (pH ∼ 1) is considerably greater than those of its anionic form (pH ∼ 7). The formation constants are very sensitive to change of pH values, which further supported the selective inclusion associated with the species form of 2ABA. Of the two species, we should note that the β-CD can readily include the protonated species than the anionic species, because the former is



Scheme 2. Bond distance (Å) of 2ABA and β-CD (AM1 method).

more hydrophobic than the latter. By assuming this orientation for the 2ABA molecule in the β-CD cavity is easy, because the cyclodextrin cavity favours the hydrophobic form of the benzoic acid derivatives [21]. The higher formation constants in pH ∼ 1 implies that the NH_3^+ group is more easily embedded in the β-CD cavity than the COOH group of 2ABA. This suggests, NH_3^+ group present in the interior of the β-CD cavity, whereas COOH group present within the upper part of the β-CD cavity. It is well known that substituents of aromatic rings capable of H-bonding can bind the OH groups of the β-CD edges. The energy involved in such H-bond interactions are responsible for the higher binding constants found, when compared to those of the unsubstituted molecule. This pattern in the binding has been detected in the complexes between benzene derivatives and β-CD. Thus, benzene [29] has a formation constant of 107 M^{-1}, whereas that for benzoic acid [29] ranges between 126 and 600 M^{-1}. This seems to be the case for 2ABA [pH ∼ 1 ($K \sim 152\,M^{-1}$), pH ∼ 7 ($K \sim 72\,M^{-1}$)].

The fluorescence characteristics of 2ABA in aqueous solutions at pH ∼ 1 are seen to undergo drastic changes in the presence of β-CD (Fig. 6). The fluorescence spectra undergo a gradual blue shift in pH ∼ 1, but it is red shifted in pH ∼ 7 with increasing the β-CD concentrations. In the presence of 4×10^{-3} M β-CD and above, the fluorescence maxima of 2ABA ($\lambda_{em} = 420$ nm) is slightly blue shifted by 6 nm in pH ∼ 1, as compared to that pH ∼ 7 (in this case the difference in red shift is 18 nm). The emission intensity of 2ABA in pH ∼ 7 is initially decreases with increasing the β-CD concentration, whereas above 4×10^{-3} M β-CD concentration, the emission intensity increases along with β-CD concentration. However, in pH ∼ 1 the fluorescence intensity is regularly increased from zero to 1.2×10^{-2} M β-CD concentration. The spectral red shifts of 2ABA emission at pH ∼ 7 in β-CD suggest that, amino group is located within the polar cavity of the β-CD, whereas blue shift emission at pH ∼ 1 shows COOH group is located in non-polar part. This conclusion is based on the following reasons: the large rim of β-CD contains 12 secondary hydroxy groups and thus provides an environment qualitatively similar to polyhydroxyl alcohols. The red shift observed (at pH ∼ 7) in the absorption and emission spectrum of 2ABA in β-CD is consistent with protic solvents. The blue shift observed at pH ∼ 1, in β-CD medium is clearly establish that carboxyl group is entrapped in the non-polar part of the β-CD. Since the dipole–dipole interactions between the β-CD and the carboxyl group is lowered in the less polar environment (hydrophobic part) a blue shift is observed in pH ∼ 1 solutions. Further a dual luminescence maxima appeared at higher β-CD concentration supported this implication. Fig. 10 shows the Benesi–Hildebrand plot of observed changes in the fluorescence intensity with increasing concentration of β-CD. It is seen from insert Fig. 6, that the emission intensity of 2ABA (in pH ∼ 1) initially increases with increasing β-CD concentration and then saturates to a limiting value at 1×10^{-2} M, indicating the incorporation of almost all the 2ABA molecules in the β-CD cavity.

Above 6×10^{-3} M β-CD concentrations (in pH ∼ 1), the dual fluorescence typical of ICT can be seen easily. Typically, both the locally excited state (LE shorter wavelength, 340 nm) and the ICT band (longer wavelength, 414 nm) are enhanced, and the ICT band is shifted to the blue while the LE band is not shifted. Due to the high polarity of the ICT state, this result should mean that the 2ABA molecule has penetrated into the nonpolar β-CD cavity and a 2ABA:β-CD inclusion complex has been formed. The results shown in Fig. 6 (pH ∼ 1) indicate that the ICT behaviour of the 2ABA is dramatically affected by the formation of the inclusion complex; i.e., the polarity and viscosity variations may play a more important role in the change in the ICT behaviour of 2ABA at pH ∼ 1. The ICT band of 2ABA is only slightly shifted to the blue with increasing β-CD concentration. This provides strong evidence for the protrusion of the COOH group into the hydrophobic phase. This is reasonable, because in 2ABA, dual luminescence is not observed in the absence of β-CD medium.

This is further supported by using semiempirical quantum calculations. PC-model program is used to find the initial geometry of the inclusion complex. This program helped us to draw the structure of the inclusion complex. The ground state geometry of 2ABA and β-CD are optimized using AM1 method (MOPAC 6/PC). As suggested and found by others [41] this method provides acceptable approximations to give results, which are quite close to the experimental finding. The internal diameter of the β-CD is approximately 6.5 Å and its height is 7.8 Å. Considering the shape and dimensions of β-CD (Scheme 2), 2ABA can completely encapsulated with the β-CD cavity. Because the distance between H_5–H_8 is 5.96 Å and H_4–O_2 is 6.27 Å and O_1–H_4 is 6.04 Å; these values are less than the inside β-CD cavity value (6.5 Å). Since the length of 2ABA is lower than that of upper/lower rim of β-CD, the amino and carboxylic groups attached benzene ring may be present inside the β-CD cavity. These finding reveals that 2ABA molecule encapsulated in the β-CD cavity.

The free energy change can be calculated from the formation constant K by equation

$$\Delta G = -RT \ln K \tag{10}$$

The thermodynamic parameter ΔG for the association of the guest molecule to β-CD is given in Table 3. As can be seen from Table 3, ΔG is negative which suggests that the inclusion process proceeded simultaneously at 303 K.

The effect of β-CD on the prototropic equilibrium between monocation, neutral and monoanion, the pH-dependent changes in the absorption and fluorescence spectra of the 2ABA molecule in aqueous solution containing β-CD have been recorded and are shown in Table 2. The absorption and emission maxima of 2ABA have been studied in 1×10^{-2} M β-CD aqueous solutions in the pH range pH ∼ 0.1–10. No noticeable change is observed in the absorption and emission band maxima of the monocation, whereas blue shift is observed in monoanion of 2ABA in β-CD than aqueous medium. The pK_a (pK_a^*) values for the monocation-neutral equilibrium of 2ABA in β-CD is lower than in aqueous medium, where as neutral-monoanion equilibrium pK_a (pK_a^*) values is greater than in aqueous medium. These results indicate, 2ABA molecule encapsulated in the β-CD cavity.

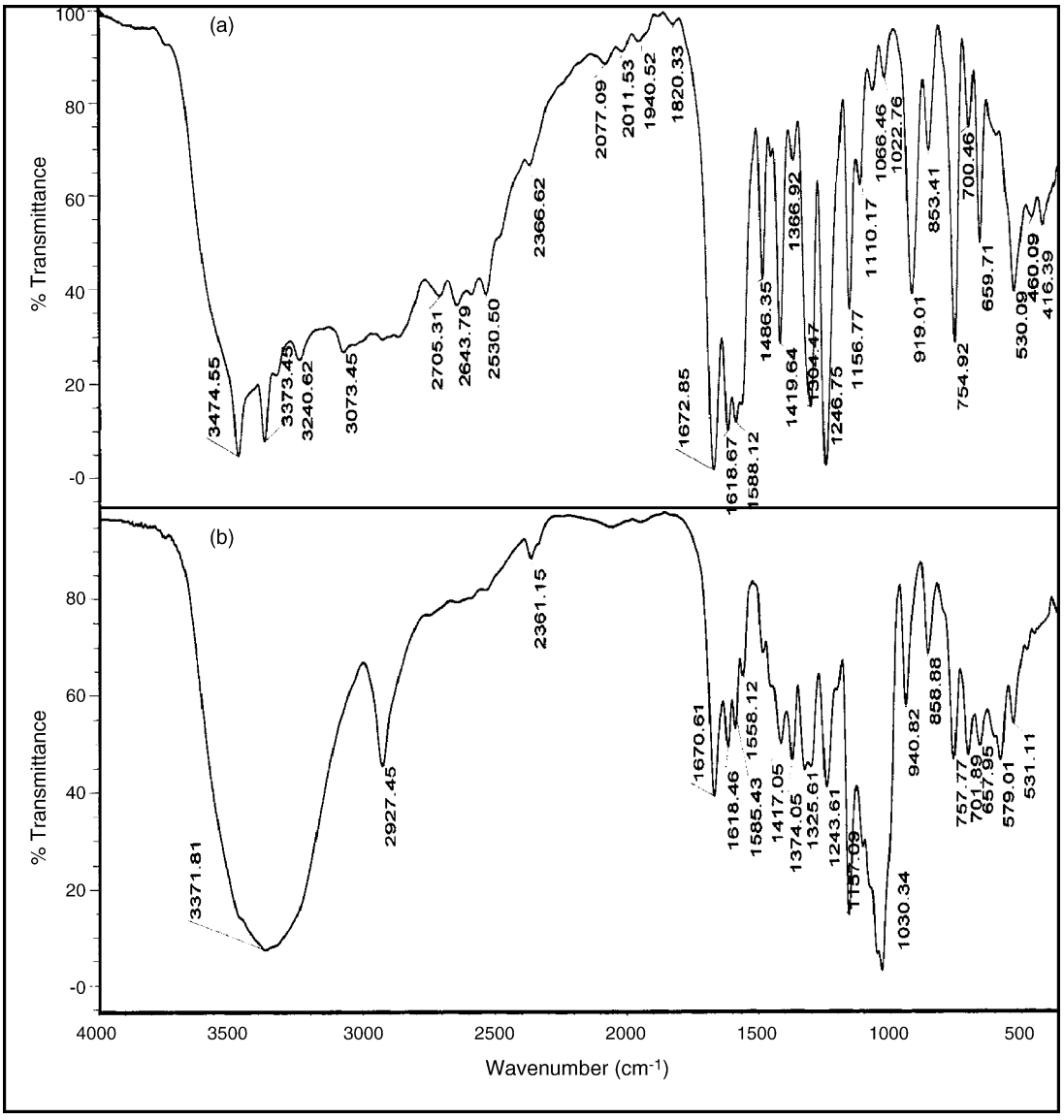


Fig. 11. FT-IR spectra of 2ABA in KBr (a) 2ABA and (b) 2ABA-β-CD complex.

3.6. Infrared spectral studies

Compared FT-IR spectra of 2ABA, β-CD and inclusion complex of 2ABA:β-CD and its shown in Fig. 11. On comparison to 2ABA, the NH_3^+ stretching vibrations are in the region (3073, 3240, 3373 and 3474 cm^{-1}) and symmetrical/asymmetrical NH_3^+ vibrations (2530, 2644 and 2705 cm^{-1}) are largely affected in the inclusion complex 3372 and 2927 cm^{-1}, respectively. Like salicylic acid (1665 cm^{-1}), IHB reduces frequency of the carbonyl stretching absorption to a greater degree 1673 cm^{-1} in 2ABA. In 2ABA the carboxylate ion group (COO^-) absorb strongly near 1419, 1619 and 1673 cm^{-1} are blue shifted in the complex (1417, 1618 and 1670 cm^{-1}), respectively. The N–H bending vibration 1588 cm^{-1} and C–N stretching absorption 1247 cm^{-1} are also blue shifted 1588, 1244 cm^{-1}, respectively. Further, the absorption intensity of the inclusion complex is also significantly weaker (10–50%) than 2ABA molecule. The above finding indicates 2ABA molecule is included to the β-CD cavity.

3.7. Proton magnetic resonance spectral studies

Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy has proved to be a useful tool in the study of β-CD inclusion complexes [42,43]. ^{1}H NMR spectroscopy provides an effective means of assessing the dynamic interaction site of β-CD with that of the guest molecules. The basis of information gained from NMR spectroscopy is located in the shifts, loss of resolution and broadening of signals observed for the host and guest protons [42]. Although, only limited information can be obtained from the ^{1}H NMR data, the observation of slight upfield shifts of the guest protons in the presence of β-CD is consistent with the inclusion of each guest into the cavity.

The resonance assignment of the protons of β-CD are well established [42]. β-CD consistent of six types of protons and the chemical shift of β-CD protons reported by different authors [41,42]. The H-3 and H-5 protons are located in the interior of the β-CD cavity and it is therefore likely that the interaction of the host with the β-CD inside the cavity will affect the chemical shifts of the H-3 and H-5 protons. In order to obtain evidence in support of the structure of the β-CD inclusion complex with 2ABA, we measured ^{1}H NMR spectra of these 2ABA molecules with and without β-CD. Owing to the poor solubility of the guest toward D_2O, we are forced to employ at least 8% volume of DMSO-d_6 as a cosolvent, which made the use of a buffered solution difficult. We define the change in chemical shift ($\Delta\delta$ ppm) as the difference a chemical shifts between proton signals of the guest or β-CD in the presence and absence of β-CD or the guest. Unfortunately, the addition of 8% volume of DMSO-d_6 to a D_2O solution of β-CD caused relatively large upfield shifts of the H-3 ($\Delta\delta = +0.05$) and H-5 ($\Delta\delta = +0.08$) signals, allowing us to expect that the presence of this cosolvent lowers the equilibrium constant for the complexation with β-CD and hence, the guest is merely able to induce the small chemical shift of each proton signals for the host. The addition of 2ABA to the solution of β-CD results in a upfield shift for the 2ABA protons (Table 5). A small upfield shift of (0.12 ppm) in 2ABA was observed for the amino protons. The upfield chemical shift observed for amino protons suggest amino group interact with β-CD–OH groups. Similar results observed earlier by Wang and Eaton [43] an observation from which they concluded the inclusion of *p*-nitroaniline in the cavity and exclude the possibility of complexation to the exterior of the β-CD ring.

Table 5
^{1}H NMR chemical shifts data of 2ABA, inclusion complex and the corresponding complexation shifts in D_2O containing 8% volume DMSO-d_6 at 20 °C

Proton	2ABA	Inclusion complex	$\Delta\delta$
NH_2	7.94	7.82	0.12
H-3	6.67	6.65	0.02
H-4	7.31	7.24	0.07
H-5	6.70	6.62	0.08
H-6	7.92	7.88	0.04

3.8. Microscopic morphological observation

First we observed powdered form of 2ABA and β-CD by scanning electron microscope, then we also observed powdered from of inclusion complex (Fig. 12). Pictures clearly elucidated the difference of powder of each other. β-CD shows sheeted/bladed structure, 2ABA shows flaky structure and the complex present in flaky and irregular aggregately structure. Modification of crystals and powder can be assumed as a proof of the formation of new inclusion complex.

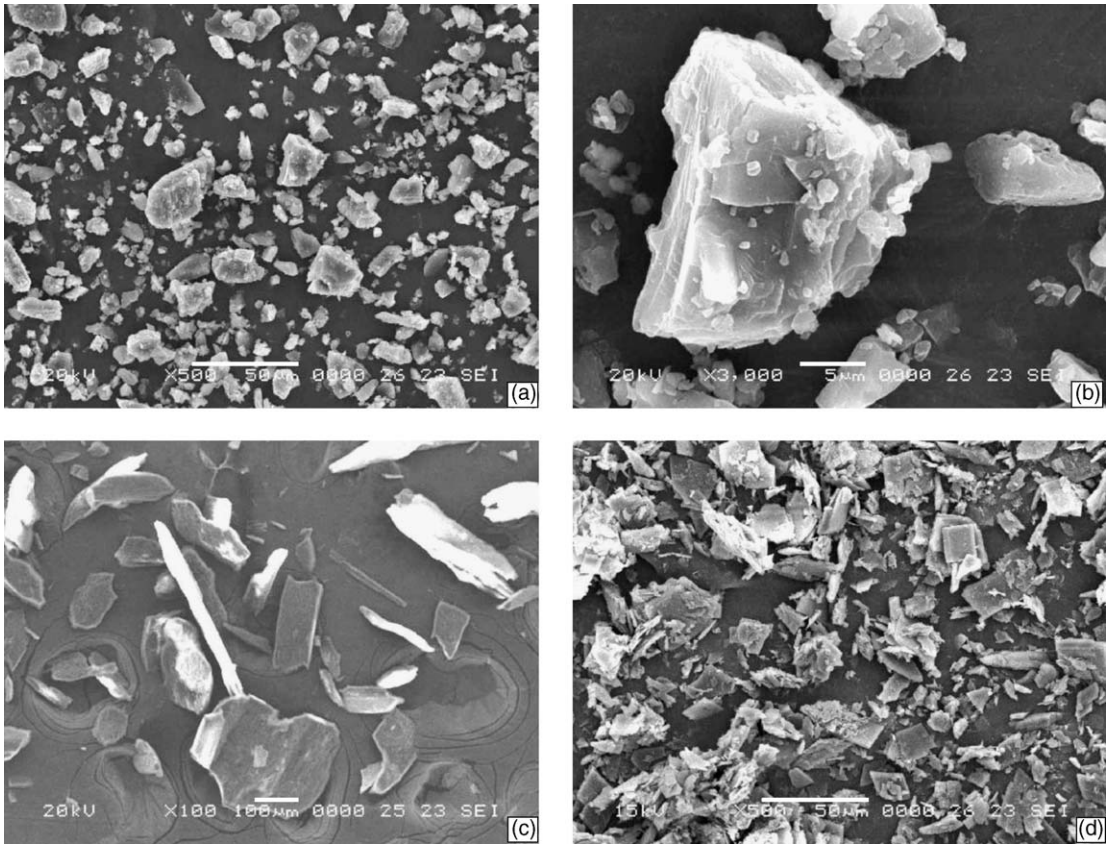


Fig. 12. Scanning electron microscope photographs (Pt coated) of (a) β-CD, (b) β-CD, (c) 2ABA and (d) 2ABA-β-CD complex.

4. Conclusion

The following conclusions can be arrived from the above studies: (i) the observation of a large red shifted absorption and emission maxima even in nonpolar solvents indicates ICT 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 S_1 state, (iv) 2ABA forms 1:1 complex at pH ∼ 1 solution and mixture of 1:1 and 1:2 complex at pH ∼ 7 with β-CD, (v) dual luminescence appeared at pH ∼ 1 indicates, both NH_3^+ and COOH groups present in the interior of the β-CD cavity, (vi) FT-IR, ^{1}H NMR, SEM results suggest 2ABA formed a stable inclusion complex with β-CD and (vii) the above studies demonstrate that in 2ABA, ICT interactions plays a significant role along with IHB.

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