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Photophysical behaviour of 4-hydroxy-3,5-dimethoxybenzoic acid in different solvents, pH and β-cyclodextrin

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Abstract

Effect of solvents, buffer solutions of different pH and β-cyclodextrin on the absorption and fluorescence spectra of 4-hydroxy-3,5-dimethoxybenzoic acid [HDMB] have been investigated. The inclusion complex of β-CD with HDMB is investigated by UV–vis, fluorometry, FTIR, ^{1}H NMR, scanning electron microscope (SEM) and semiempirical methods. The thermodynamic parameters (ΔG, ΔH and ΔS) of inclusion process are also determined. The Stokes shifts of HDMB correlated with various solvent polarity scales, suggest that the HDMB molecule is more polar and the change in dipole moment is large in the S_1 state. The pK_a and pK_a^* values of neutral-monoanion and monoanion–dianion equilibria have been determined with fluorimetric titrations and Förster cycle methods and compared. β-Cyclodextrin studies shows that HDMB forms a 1:1 inclusion complex with β-CD. A mechanism is proposed to explain the inclusion process.

Keywords: 4-Hydroxy-3,5-dimethoxybenzoic acid; Solvent effects; pH effects; β-Cyclodextrin; Inclusion complex

1. Introduction

The spectral characteristics (absorption and fluorescence spectra and their intensities) of an aromatic molecule are dependent on the nature as well as on the position of the substituent in the aromatic ring [1]. Therefore, the fluorescence and absorption spectra of an aromatic molecule may different significantly from isomer to isomer [2]. For example, the carboxylic group becomes more basic if $\pi \rightarrow \pi^*$ is the lowest energy transition and thus leads to red and blue shifts in the spectral characteristics on protonation and deprotonation, respectively. Similarly, the OH group and NH_2 group become stronger acids on excitation and thus lead to red shifts and blue shifts on deprotonation and protonation. Although the spectral behaviour of the molecules containing both electron donating and electron withdrawing groups remains qualitatively the same in the ground and the excited states. There are certain molecules that contain the above kind of functional groups where the excited state reactions are quite different from those in the ground state [3–5]. The gain in acidity of the electron donating group and the gain in basicity of the electron withdrawing group in the same electronically excited molecule is so great that the order of dissociation of the two groups is reversed with respect to the normal order observed in the ground state.

The proton transfer processes of intramolecularly hydrogen-bonded molecules are topics of current research activity [6–8]. The process of excited state intramolecular proton transfer which typically shows a largely Stokes shifted fluorescence band has become a field of active research due to its widespread implications as uv stabilization, stimulated radiation production, information storage, fluorescent solar concentrator as well as environmental probes in biomolecules [9]. Solvent effects on proton transfer to solvent raise interesting problems concerning static and dynamic processes,

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particularly intriguing is the question, when the solvent which is also the proton acceptor, behaves as a continuous medium or whether its molecular properties indispensable in understanding proton transfer and proton solvation dynamics. Several spectroscopic studies support the hypothesis that compounds like *ortho*-hydroxybenzaldehyde, methyl salicylate derivatives and related compounds are hydrogen bonded to the solvent in hydrogen bonding solvents [10]. The proton transfer of aromatic molecules, which are hydrogen bonded in the ground state undergoes changes markedly depending on the kind of substitution on the aromatic ring or carbonyl group.

Mukherjee et al. have been also noted that both the absorption and emission spectra of 4-methyl-2,6-diacetylphenol (MAOH) are considerably different from that of 4-methyl-2,6-diformylphenol (MFOH) despite the similarity in the molecular structure [6,11]. Replacement of the hydrogen atoms of the formyl group in MFOH by methyl groups seems to change the nature and position of the absorption and emission spectra [6,11]. Ware et al. [12] studied 3,7-dihydroxy-2-naphthoic acid (DNA) and 3-hydroxy-2-naphthoic acid (HNA) in great detail. They described a fluorescence quenching reaction via an intramolecular proton transfer for HNA. It has been shown that bases, which promote the proton transfer function parallely by static and dynamic quenching mechanisms. Catalan et al. [13] studied some esters of *o*-hydroxynaphthoic acids. They suggested that the photostability of such compounds does not rely on the photophysics of their proton transferred tautomer but on the nonradiative dynamics of their respective normal tautomers. All the molecules studies exhibit a great photostability to uv radiation compared to those of methyl salicylate [14].

In this regard, the present investigation has been carried out to study the solvatochromic effects of hydroxy, carbonyl and methoxy groups in aromatic ring. This is an extension of our earlier work [15–18]. 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 [15–18]. Recently, 4-hydroxy-3,5-dimethoxybenzaldehyde has been studied and this molecule shows intramolecular charge transfer emission in the excited state [18]. This stimulated us to carry out a study on HDMB. In this paper we are reporting the effects of solvents, pH and β-cyclodextrin on spectral characteristics of 4-hydroxy-3,5-dimethoxybenzoic acid.

2. Experimental

2.1. Instruments

Absorption spectral measurements were carried out with a Hitachi Model U-2001 UV–vis 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-10 T. FTIR spectra were obtained with Avatar-330 FTIR spectroscopy using KBr pelleting. The range of spectra was from 500 to 4000 cm^{-1}. Bruker Advance DRX 400 MHz super conducting NMR spectrophotometer was used to study ^1H NMR spectra. Microscopic morphological structure measurements were performed with JEOL TSM 5610 LV scanning electron microscope (SEM).

2.2. Reagents and materials

HDMB and β-CD were obtained from E-merck and recrystallized from aqueous ethanol [19]. 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 or AnalaR) 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) [20] for the solutions below pH ∼ 2 (using a H_2SO_4–H_2O mixture) and Yagil's basicity scale (H_-) [21] for solutions above pH ∼ 12 (using a NaOH–H_2O mixture) were employed. The solutions were prepared just before taking measurements. The concentrations of the solutions were of the order (10^{-4} to 10^{-5} mol dm^{-3}). All experiments were carried out at 30 °C.

2.3. β-Cyclodextrin solution preparation

The concentration of stock solution of HDMB was 2×10^{-3}. Transferred these stock solution into 10 ml volumetric flasks which containing 0.2 ml of this solution. Following this added 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2×10^{-2} mol dm^{-3} β-CD solution into volumetric flasks. The mixed solution was diluted to 10 ml with triply distilled water (or) appropriate buffer solution and shaken thoroughly. So that the final concentration of HDMB in each flask is 4×10^{-5} mol dm^{-3}. The absorption and fluorescence spectra were recorded or intensities were measured at 30 ± 1 °C using 1 cm quartz cell.

2.4. Preparation of solid complex of HDMB 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 HDMB was put into a 50 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 HDMB solution. The above mixed solutions was continuously stirred for 48 h at room temperature. The reaction mixture was put into refrigerator for 48 h. At this time we observed that white crystal 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 white powder product was obtained. This is inclusion complex of HDMB with β-CD.

3. Results and discussion

3.1. Effect of solvents

The absorption maxima, $\log \varepsilon$ and fluorescence maxima of syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid, HDMB) is obtained in solvents with various polarities and hydrogen bonding abilities. The relevant data are complied in Tables 1 and 2 along with the spectral data of vanillic acid (4-hydroxy-3-methoxybenzoic acid, HMB) [22] and 4-hydroxybenzoic acid (HB) [23]. When compared to HB the absorption maxima of HDMB is red shifted in any one solvent. This shows that intramolecular hydrogen bonding present in HDMB. Due to steric effect of methoxy groups in HDMB, the absorption maxima of HDMB is blue shifted to HMB i.e., presence of two methoxy groups at *ortho* position (with respect to OH group) decrease the OH group interactions with aromatic ring.

Solvents can interact with methoxy (OCH_3), carbonyl (C=O) and hydroxyl (OH) groups. The interaction of solvents with the lone pair of above groups will lead to a blue shift and the solvent interaction with the hydrogen atom of the OH group will lead to a red shift both in absorption and fluorescence spectra. An analysis of solvatochromic shifts of HDMB reveals that the absorption maxima are red shifted from cyclohexane to water. HDMB show absorption maxima around 269 nm in non-polar solvents. The molar extinction coefficient is very high ($\sim 10^{-4}$ cm^{-1}). These results imply that this band is attributed to the (π, π^*) transition of benzene ring and not to the (n, π^*) transition of the carbonyl group [24,25]. The fluorescence spectra of HDMB is regularly red shifted as the polarity and proton donor capacities of the solvent increases. Moreover, the spectral shifts observed in the absorption spectrum of HDMB in protic and aprotic solvents are consistent with the characteristic behaviour of amino [15] and hydroxyl groups [16–18].

In all solvents HDMB gives only one broad structureless fluorescence maxima. The fluorescence spectra are displayed in Fig. 1. The results of fluorescence maxima can be explained on the ground state that charge migration from the hydroxyl group towards the benzene ring increases on excitation. Generally, in the first excited singlet state, the polarity of the OH

Table 1
Absorption maxima (nm) and $\log \varepsilon$ of HDMB, HMB and HB in different solvents and pH

No.	Solvents	HDMB		HMB		HB	
		λ_{abs}	$\log \varepsilon$	λ_{abs}	$\log \varepsilon$	λ_{abs}	$\log \varepsilon$
1	Cyclohexane	269.0	(sat)			251.0	4.18
2	Diethyl ether	274.0	4.59				
3	Dioxane	274.5	4.67	290.0	3.70	252.0	4.25
				259.0	4.00		
4	Ethyl acetate	274.2	4.60				
5	Dichloromethane	273.0	4.50				
6	Acetonitrile	274.0	4.59				
7	*t*-Pentyl alcohol	271.5	4.52				
8	*t*-Butyl alcohol	272.0	4.53				
9	2-Butanol	270.4					
10	2-Propanol	271.0	4.51				
11	1-Butanol	271.0					
12	Ethanol	271.2	4.51	286.0	3.16	255.0	4.20
				255.0	3.92		
13	Methanol	271.6	4.56				
14	Water	273.0	4.65	290.0	3.76	255.0	4.14
				260.0	4.05		
		217.0	4.09	217.5	4.30		
15	Monocation	277.0	4.05	293.0	3.70	250.0	4.10
		210.0	4.35				
16	Monoanion	261.0	4.21	286.0	3.64	245.0	4.07
		215.0	4.30	251.0	4.00		
17	Dianion	303.0	4.35	298.0	4.17	281.0	4.13
		232.5	4.09	280.0	4.11		
		213.5	4.03	225.0	4.08		

Table 2
Fluorescence maxima (nm) and Stokes shift (cm^{-1}) observed for HDMB in different solvents with $E_T(30)$, BK and $f(D,n)$ values

No.	Solvents	λ_{flu}	$\Delta\bar{\nu}_{ss}$ cm^{-1}	$E_T(30)$	BK	$f(D,n)$
1	Cyclochexane	322	6119	30.9	−0.001	−0.001
2.	Diethyl ether	328	6009	34.6	0.397	0.167
3	Dioxane	330	6129	36.0	0.043	0.02
4	Ethylacetate	332	6350	38.1	0.488	0.201
5	Dichloromethane	330	6327	41.1	0.586	0.218
6	Acetonitrile	332	6376	46.0	0.864	0.305
7	*t*-Pentyl alcohol	338	7247	41.9		
8	*t*-Butyl alcohol	340	7353	43.9	0.673	0.245
9	2-Butanol	340	7571	47.1	0.734	
10	2-Propanol	340	7489	48.6	0.766	0.274
11	1-Butanol	340	7516	50.2	0.754	0.263
12	Ethanol	345	7877	53.7	0.812	
13	Methanol	348	8083	55.5	0.858	0.309
14	Water	352	8670	63.1	0.913	0.320
15	Monocation ($H_0 - 2.0$)	360	8323			
16	Monoanion (pH ~ 6)	340	8902			
17	Dianion	370	5976			
18	Correlation co-efficient			0.8793	0.6584	0.6750

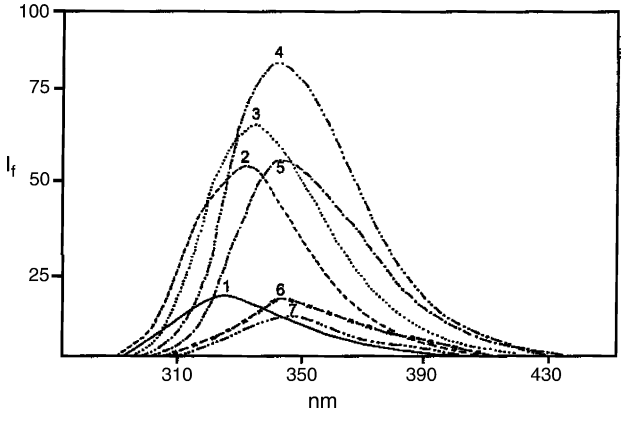
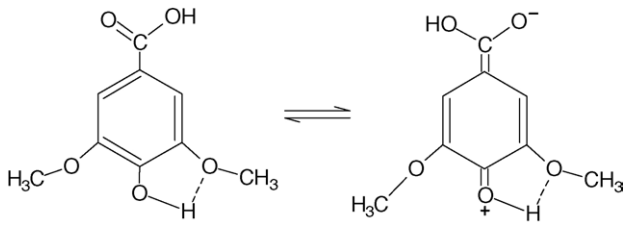


Fig. 1. Fluorescence spectra of HDMB in selected solvents at 303 K, concentration $\approx 4 \times 10^{-5}$ mol dm^{-3}: (1) cylohexane, (2) dioxane, (3) acetonitrile, (4) *t*-butyl alcohol, (5) 2-propanol, (6) methanol, (7) water.



Scheme 1.

bond is increased due to the increased charge transfer interaction from the hydroxy group to the aromatic ring and thus a red shift is observed in water than cyclohexane.

Another remarkable aspect of the fluorescence emission of HDMB is the effect of solvent polarity. In the presence of solvents more polar (H_2O) the emission spectrum widens, losing gradually its emission intensities. This is due to presence of dipolar structure of this molecule (Scheme 1). The emission in water is strongly pH dependent (discussed in latter) with the Stokes shift reaching its maximum value in acidic aqueous solutions (8670 cm^{-1}). The broad Stokes shifted emission at acidic pH is common in molecules having an electron withdrawing group such as COOH, attached to an aromatic nucleus [25]. 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 states (or other kinds of aggregates) excimer formation (or) charge transfer processes. An example of this is 9-anthroic acid [25b], which has been the subject of a number of studies in the past providing different interpretations of its fluorescence emission [25b].

In the case of HDMB, the fact that the broad band does appear at alkaline pH could ruled out the possibility of HDMB forming dimers in the ground state (linked by H-bonding). This is because dimers cannot form if the carboxylate group is ionized and if dimer is formed the emission should be structured. Further, the low concentrations currently used, as much as 2×10^{-5} M, ruled out this possibility. Even at concentrations as low as 2×10^{-6} M, the broad emission can be detected. In HDMB, the donor group is the hydroxyl group and the acceptor group is the –COOH. In an acidic medium, the carboxyl group becomes more conjugated with the aromatic π-system, in a situation in which these is a marked charge separation within the molecule (Scheme 1). The large Stokes shift in polar and non polar solvents would indicate a primarily dipolar interaction between the solute and the solvent molecules.

3.2. Correlation of solvatochromic shift with the solvent polarity

When a solute is placed in a solvent, one observes the combined effects of general and specific interactions. The separation of these interactions is often difficult. Empirically or theoretically derived solvent parameters like Reichardt's–Dimroth, $E_T(30)$ [26], Bilot–Kawski, BK [27] and Lippert, $f(D,n)$ [28] values as accurate registers of solvent polarity have been used by several authors to correlate molecular spectroscopic properties [29]. Among these parameters BK and $f(D,n)$ 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 HDMB molecule (Table 2). The Stokes shift ($\Delta\bar{\nu}_{ss} = \bar{\nu}_{abs}\,\max - \bar{\nu}_{flu}\,\max$), can be related to solvent polarity by the Lippert equation [28]

$$\Delta\bar{\nu}_{ss} = \frac{2\,(\mu_e - \mu_g)^2}{hca^3} f(D,n) + K \tag{1}$$

where

$$f(D,n) = \frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1} \tag{2}$$

$$f(D,n) = \frac{(D-1)/(2D+1) - (n^2-1)/(2n^2+1)}{\{1-\beta(n^2-1)/(2n^2+2)^2\}\{1-\beta(D-1)/(2D+2)\}} \tag{3}$$

$\Delta\bar{\nu}_{ss}$ is the Stokes shift (cm^{-1}), μ_g and μ_e are the dipole moments of the HDMB molecule in the ground and excited states, respectively, 'c' is the velocity of light, 'h' is the Planck constant, 'K' is the constant, 'D' and 'n' are static dielectric constant and refractive index of the solvent, respectively, 'β' is a constant factor (in most cases, approximately unity). The $f(D,n)$ and BK parameters defined by Eqs. (2) and (3), respectively and $E_T(30)$ is an empirical scale based on the spectral shifts of *N*-phenolbetaine dye in solvents of varying polarity [26].

The Stokes shift of HDMB measured in different solvents are correlated with $E_T(30)$, BK and $f(D,n)$ parameters (Table 2). The Stokes shift observed in HDMB is larger than those observed in other hydroxy molecules [16–18]. These results indicate that the increase in the dipole moment of HDMB is greater than those observed in other hydroxy molecules. Fig. 2a–c 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 HDMB 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 bonding interactions are predominant in the solvatochromic shifts of HDMB, the Stokes shift versus $E_T(30)$ gives good correlation than the other two parameters. The Fig. 2b and c shows dramatic change in the slope in an intermediate polarity region (i.e.) the plots are non-linear. The large deviations in hydroxylic solvents can be explained

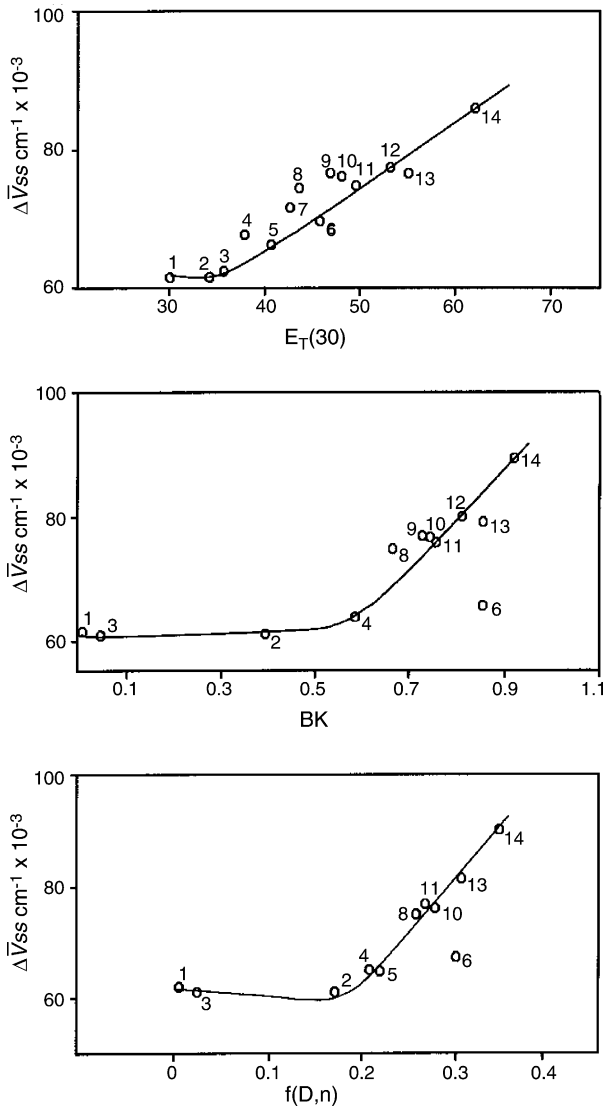


Fig. 2. Plot of Stokes shift (cm^{-1}) of HDMB vs. $E_T(30)$, BK and $f(D,n)$ solvent parameters (numbers refer to Table 2).

as follows [29]. It is well established that the –OH group becomes more acidic in the S_1 state and they can donate a proton easily to the solvent. In contrast, in the S_0 state, the –OH group acts as a proton acceptor. This means that the hydrogen bond between the solvent molecule and the lone pair of the –OH group in the S_0 state is broken on excitation and a hydrogen bond is formed between the proton of the –OH group and the lone pair of the solvent molecule. Upon excitation the dipolar structure (Scheme 1) is stabilised in the S_1 state resulting in a highly Stokes shifted fluorescence emission in HDMB. Furthermore, intramolecular hydrogen bond is also present in this molecule. As a result, large Stokes shifts is observed in HDMB both in polar and non polar solvents.

3.3. Effect of pH

The absorption and fluorescence spectra of HDMB have been studied in the H_0/pH/H_- range of −10 to 17.0. The

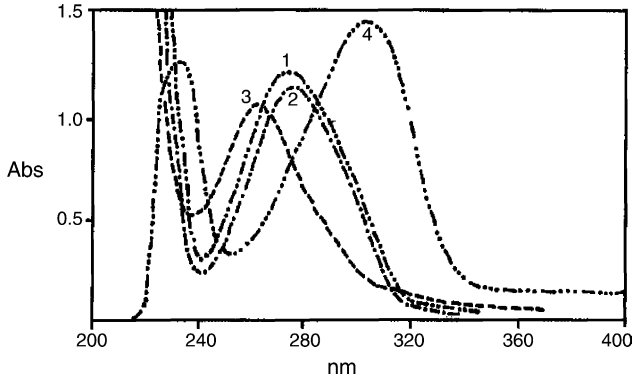


Fig. 3. Absorption spectra of HDMB in different acid concentrations: (1) neutral, (2) monocation, (3) monoanion, (4) dianion.

relevant data are given in Tables 1 and 2. Absorption and fluorescence spectra of various prototropic species are shown in Figs. 3 and 4, respectively. In the pH range 2–3 absorption spectra resemble the spectra observed in non-aqueous solvents and thus can be assigned to be neutral species [16]. The absorption spectra exhibit a progressive red shift with an increase in the concentration of acid and at H_0 −1.0 a highly red shifted broad band appears. If π–π^* transition is the lowest energy transition, protonation of carbonyls results in a red shift of the electronic spectrum [24,25]. As mentioned earlier, π–π^* is the lowest energy transition in HDMB. The red shift confirms the formation of the cation on protonation of the carbonyl group. The formation of cation in carbonyl group is already reported [22,24,25]. With an increase in pH from 3.0, around pH 4.0 the absorption maxima is blue shifted. The blue shift in the absorption spectra below pH 5 confirms that deprotonation takes place at the carboxyl group. Further increase on pH from 5, HDMB gives a newly red shifted spectrum with the maxima (303.0, 232.5 and 213.5 nm). This clearly suggest that formation of a dianion obtained by the deprotonation of the OH group. It is well known fact that deprotonation of COOH group gives blue shifted absorption and emission maxima [24,25] whereas deprotonation of hydroxyl group gives red shifted absorption and emission maxima [16–18]. Furthermore, it can be seen that in absorption, the dianion of

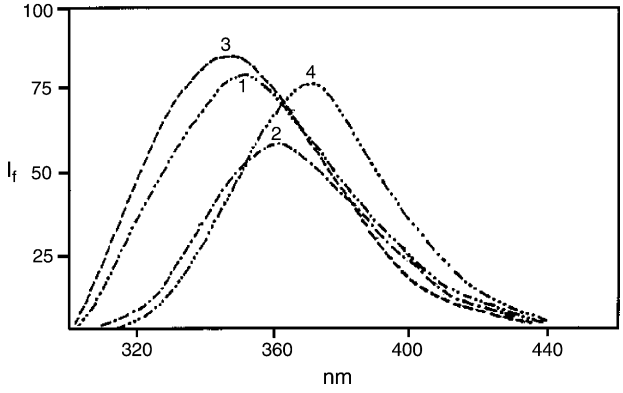


Fig. 4. Fluorescence spectra of HDMB in different acid concentrations: (1) neutral, (2) monocation, (3) monoanion, (4) dianion.

Table 3
pK_a values of different prototropic equilibria of HDMB in the lowest excited singlet and ground states

Equilibria	pK_a abs	pK_a^* FT	Förster cycle method		
			pK_a^* abs	pK_a^* flu	pK_a^* ave
Without β-CD					
Neutral ⇌ Monoanion	4.30	6.90	7.74	8.47	8.11
Monoanion ⇌ Dianion	8.90	8.60	−2.35	3.59	0.62
With β-CD					
Neutral ⇌ Monoanion	4.22	6.80	7.45	10.13	8.79
Monoanion ⇌ Dianion	8.60	8.50	2.83	5.09	3.95

FT: fluorimetric titration, abs: absorption data, flu: fluorescence data, ave: average of absorption and fluorescence data.

HDMB gives a larger red shift, indicating a greater degree of interaction between the ionic substituent and the aromatic ring.

The fluorescence spectra of various prototropic species of HDMB are shown in Fig. 4. In pH 3–4 the emission spectra resemble the spectra observed in non-aqueous solvents and thus can be assigned to the molecular forms of HDMB [16]. When acid concentration is increased from pH 3.5, the fluorescence maxima of HDMB is red shifted and give maximum of 360 nm. This red shift spectra indicates that protonation should occur at the carbonyl group, because protonation at the phenolate ion leads to a blue shift [16]. As mentioned earlier, protonation of carbonyl groups leads to red shifted absorption and fluorescence maxima [24,25].

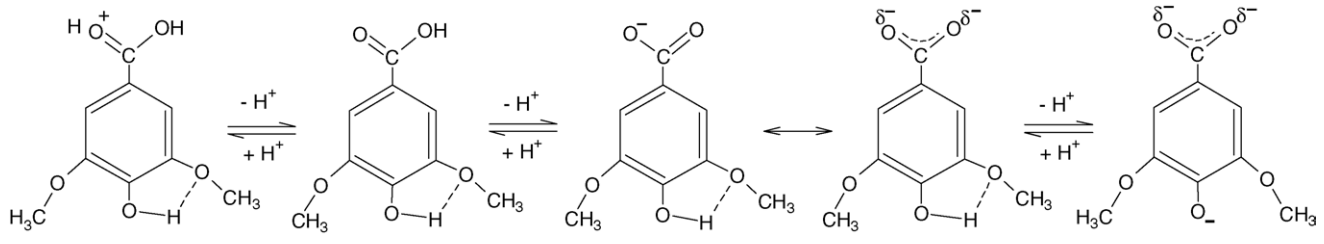
The neutral species of HDMB is weakly fluorescent. When the pH is increased from 4, around pH 7 the weakly fluorescent band of HDMB molecule is blue shifted and the intensity of the newly formed fluorescent band increases. The above results clearly suggests that in HDMB deprotonation takes place at the carboxyl group (i.e., monoanion is formed in the carboxyl group). Further increase in pH from 7.0, around pH 9 the fluorescence spectrum of HDMB is red shifted and give maxima of 370 nm. This red shifted maximum is due to the formation of a dianion obtained by the deprotonation of OH group.

3.4. Acidity constants

The ground state acidity constants of both equilibria are calculated spectrophotometrically and are given in Table 3. The difference in ground state pK_a values of neutral-monoanion equilibrium of HDMB (p$K_a \approx 4.30$), HMB (p$K_a \approx 4.38$) [22], *p*-hydroxybenzoic acid (p$K_a \approx 4.58$) [23] and benzoic acid (p$K_a \approx 4.4$) are small [30]. It can be explained as follows: The negative charge of the carboxylate ion is shared by the two carboxylate oxygen atoms but cannot be effectively delocalized by the aromatic ring. This is because the oxygens of the carboxylate anion are not directly adjacent to the aromatic ring. Since the benzene ring does not effectively participate in resonance stabilization of the carboxylate anion, substituents on a benzene ring does not vary the acidity. This is confirmed by a small red shift observed with on increase in λ_{exc} could be due to the presence of different resonating structures as shown in Scheme 2.

The pK_a value of HDMB monoanion–dianion equilibrium (p$K_a \approx 8.8$) is close to HMB (p$K_a \approx 8.9$) [22], *p*-hydroxybenzoic acid (p$K_a \approx 9.13$) [23] but less than phenol (p$K_a \sim 10$) [16]. This suggests that the molecule becomes more acidic. This is due to the presence of carbonyl group *para* to –OH group (i.e.) an electron withdrawing carbonyl group on the aromatic ring is acid strengthening. It enables the ring to withdraw more electrons from the phenoxy oxygen. This stabilizes the phenoxide ion still further and results in a stronger acid.

The pK_a^* value for both equilibria in the S_1 state was determined by fluorimetric titrations (FT) (Fig. 5) as well as with the help of the Förster cycle methods [31] using absorption, fluorescence and the average of the absorption and fluorescence maxima. The data are compiled in Table 3. In HDMB, 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 [32,33]. The pK_a^* (FT) value for monoanion–dianion equilibrium of HDMB is smaller than the ground state pK_a values. The pK_a^* values obtained by FT and Förster cycle methods are different from each other and



Scheme 2. Various prototropic equilibria of HDMB.

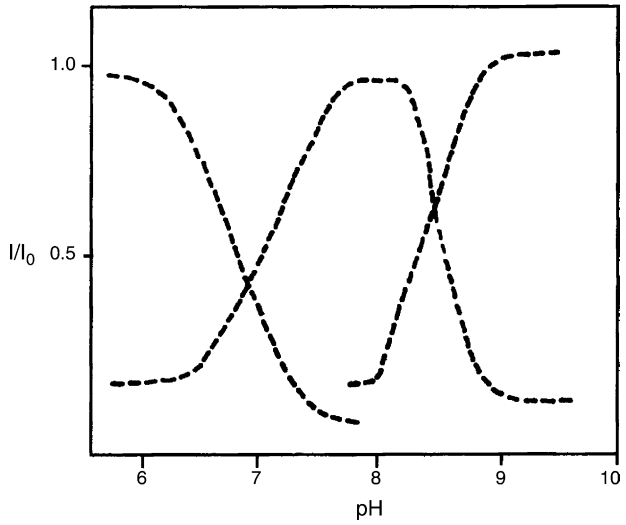


Fig. 5. A plot of I/I_0 vs. pH of the various prototropic species of HDMB.

this is due to difference in the solvent relaxation of the species in this equilibrium.

3.5. β-Cyclodextrin effects

Table 4 shows the absorption and fluorescence maxima of HDMB (4×10^{-5} mol dm^{-3}) in pH ∼ 1.0 and 7.0 solutions containing various concentrations of β-CD. At pH ∼ 7 HDMB exists as a anion hence we also recorded spectrum at pH ∼ 1. However, in pH ∼ 1.0 there is no significant change in the absorption spectra of HDMB. In both cases, no clear isosbestic point is observed in the absorption spectra. In the presence of β-CD, there is a slight red shift is observed in the absorption maxima at pH ∼1 (268–270 nm), whereas in pH ∼ 7 is seen to undergo a marginal red shift (262–273 nm). It has also been observed that both absorption intensities slightly decreases with increasing β-CD concentration. β-CD concentrations higher than 8×10^{-3} mol dm^{-3} the band maxima and the absorbance remain unchanged. This

Table 4
Absorption and fluorescence maxima (nm) of HDMB at different concentrations of β-CD

No.	Concentration of β-CD	pH ∼ 1.0			pH ∼ 7.0		
		λ_{abs}	log ε	λ_{flu}	λ_{abs}	log ε	λ_{flu}
1	Water (without β-CD)	268.0	4.50	350	262.0	4.60	350
2	0.002 M	268.4	4.46	350	268.5	3.24	350
3	0.004 M	268.6	4.44	350	271.5	3.22	360
4	0.006 M	269.0	4.44	350	272.0	3.20	360
5	0.008 M	270.2	4.40	350	272.5	3.17	360
6	0.010 M	270.2	4.40	350	273.0	3.17	360
7	0.012 M	270.2	4.40	350	273.0	3.17	360
Formation constant (M^{-1})		190		105	203		109
ΔG (kJ mol^{-1})		−13.2		−11.7	−13.4		−11.8
ΔH (kJ mol^{-1})		−184.6			−184.6		
ΔS (J mol^{-1} k^{-1})		−0.566		−0.570	−0.565		−0.570

Formation constant, ΔG, ΔH and ΔS values present in bottom of the table.

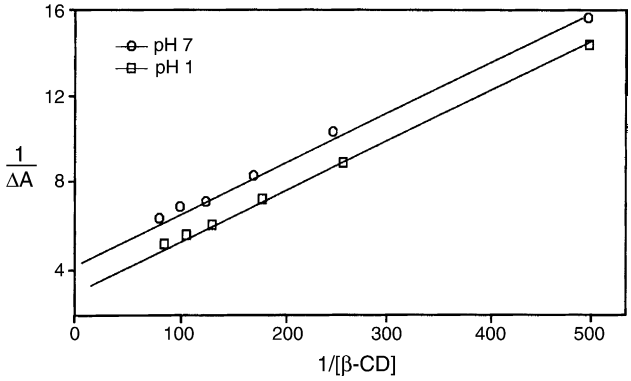


Fig. 6. Plot of $1/\Delta A$ vs. 1/[β-CD] for HDMB.

behaviour has been attributed to the enhanced dissolution of the HDMB molecule through the hydrophobic interaction between HDMB and β-CD. These results indicate that HDMB molecule is entrapped in the β-CD to form inclusion complex. In both cases, the association constant for the formation HDMB:β-CD complex has been determined by analyzing the changes in the intensity of absorption and fluorescence maxima with the β-CD concentration. In the case of inclusion complex formed between HDMB and β-CD the equilibrium can be written as

$$\text{HDMB} + \beta\text{-CD} \rightleftharpoons \text{HDMB}\ldots\beta\text{-CD}$$

The formation constant K_b and stoichiometric ratios of the inclusion complex of HDMB can be determined according to the Benesi–Hildebrand [34] relation assuming the formation of a 1:1 host–guest complex.

$$\frac{1}{\Delta A} = \frac{1}{\Delta\varepsilon} + \frac{1}{K_b[\text{HDMB}]_0 \Delta\varepsilon[\beta\text{-CD}]_0} \quad (4)$$

where ΔA is the difference between the absorbance of HDMB in the presence and absence of β-CD, $\Delta\varepsilon$ is the difference between the molar absorption coefficient of HDMB and the inclusion complex $[\text{HDMB}]_0$ and $[\beta\text{-CD}]_0$ are the initial concentration of HDMB and β-CD, respectively. Fig. 6 depicts a plot of $1/\Delta A$ as a function of 1/[β-CD] for HDMB. Good linear correlations was obtained, confirming the formation of a 1:1 inclusion complex. From the intercept and slope values of this plot K_b is evaluated [pH ∼ 1 = 190 M^{-1} and pH ∼ 7 = 203] at 303 K (Table 4).

Fig. 7 depicts the emission spectra of HDMB (excited at 270 nm) with varying concentration of β-CD. The effect of β-CD on the fluorescence spectra of HDMB is more pronounced than the corresponding effect on the absorption spectra. At pH 1.0 the intensity of fluorescence maximum only increases whereas in pH ∼ 7 two main effects are observed a red shift and an increase in the fluorescence intensity on the addition of β-CD upto a concentration of 12×10^{-3} mol dm^{-3}. It is clear that the fluorescence enhancement in pH ∼ 7 is stronger than that in pH ∼ 1. The fluorescence intensity is larger in β-CD than in aqueous solution. The red shift of the fluorescence maximum and the enhancement of the

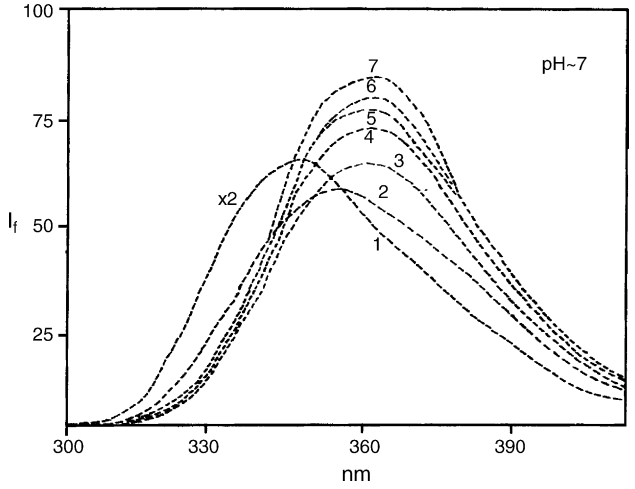


Fig. 7. Fluorescence spectra of HDMB in different β-CD concentrations (mol dm^{-3}): 1.0, 2.0.002, 3.0.004, 4.0.006, 5.0 008, 6.0.010, 7.0.012.

fluorescence intensity suggest the formation of an inclusion complex between HDMB and β-CD. An increase in the fluorescence intensity for the formation of an inclusion complex was observed earlier [34–37]. The complexation is complete at 8×10^{-3} mol dm^{-3} β-CD and there is no change in the fluorescence by further addition of β-CD.

The β-CD dependence of HDMB fluorescence can be analysed by the Benesi–Hildebrand [32] plot as given by the following equation

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{K_b(I' - I_0)[\beta\text{-CD}]_0} \quad (5)$$

where $[\beta\text{-CD}]_0$ represents the initial concentration of β-CD, I_0 and I are the fluorescence intensities in the absence and presence of β-CD, respectively and I' is the limiting intensity of fluorescence. The K_b values were obtained from the slope and the intercept of the plots. The Benesi–Hildebrand plots (Fig. 8) show excellent linear regression ($r \approx 0.9670$) supporting the 1:1 HDMB/β-CD inclusion complex. From the plot K_b is evaluated as 105 M^{-1} at pH ∼ 1 and 109 M^{-1} at pH ∼ 7 and ΔG value is −11.8 kJ mol^{-1}. The formation constant is also

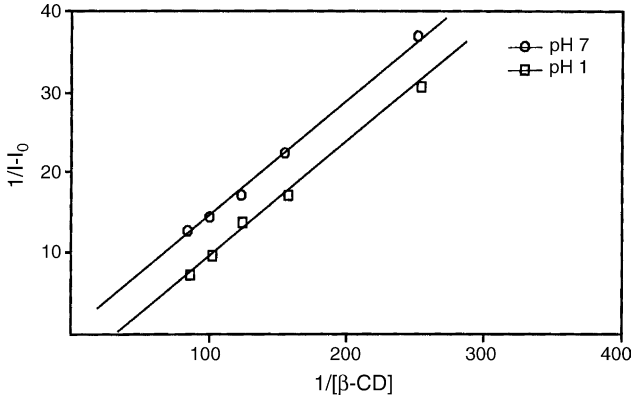


Fig. 8. Benesi–Hildebrand plot for the complexation of HDMB with β-CD.

small like 4-hydroxy-3,5-dimethoxybenzaldehyde (93 M^{-1}) [18], 1,2,3-trihydroxybenzene (148 M^{-1}) [17] and 1,2-dihydroxybenzene (200 M^{-1}) [18]. This again confirm hydrogen bonding interaction present in this molecule [38,39].

There are three important thermodynamic parameters in the inclusion process [35]. The free energy change can be calculated from the formation constant 'K' by the following equation

$$\Delta G = -RT \ln K \quad (6)$$

At constant temperature

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (7)$$

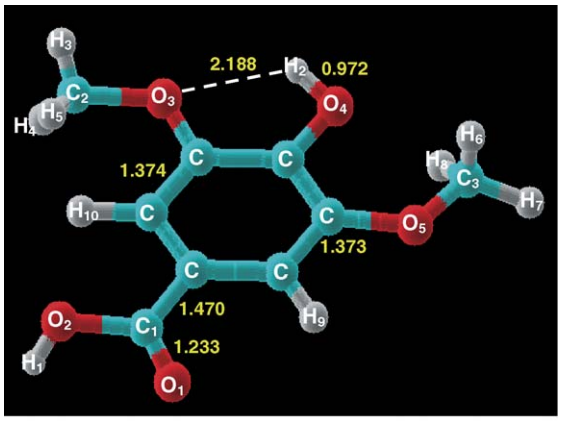
The thermodynamic parameters ΔG, ΔH and ΔS for the binding of the guest molecule to β-CD is given in Table 4. As can be seen from Table 4, ΔG is negative which suggests that the inclusion process proceeded simultaneously at 303 K. ΔH and ΔS are also negative in the experimental temperature range, which indicates that the inclusion process is an exothermic and enthalpy controlled process. The negative enthalpy change (ΔH) arose from the van der Waal's interaction, while the negative entropy change (ΔS) is the steric barrier caused by molecular geometrical shape and the limit of β-CD cavity to the freedom of shift and rotation of guest molecule. The experimental results indicate that the inclusion reaction of β-CD with guest was an exothermic reaction accompanied with negative ΔS. In this case, the actions that enthalpy and entropy change played were on the contrary. The conclusion of this study is that changes in ΔH are largely compensated for by changes in ΔS.

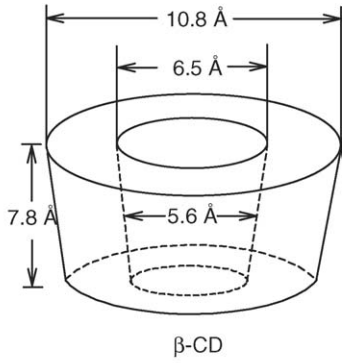
3.6. Possible inclusion complex of HDMB

The absorbance and fluorescence spectra of HDMB have been studied in the pH range H_0 −1 to pH ∼ 10 in β-CD (Table 5). When compared to aqueous medium no appreciable change is observed in β-CD in absorption maxima of neutral and monoanion, whereas dianion gives blue shifted maximum. The ground and excited pK_a (pK_a^*) values for the neutral-monoanion equilibrium are also same. Considering the above discussions, the possible inclusion mechanism is proposed as follows. Naturally, two different types

Table 5
Various prototropic maxima (absorption and fluorescence) of HDMB in with and without β-CD medium

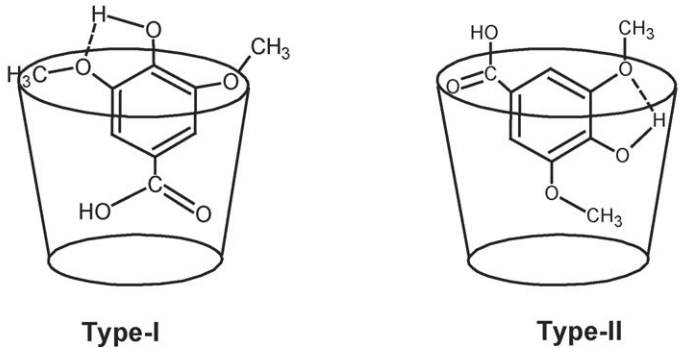
Species	With β-CD			Without β-CD		
	λ_{abs}	λ_{flu}	$\Delta\bar{\nu}_{ss}$	λ_{abs}	λ_{flu}	$\Delta\bar{\nu}_{ss}$
Neutral	272 217	360	8987	273 218	355	8060
Monoanion	260 215	350	8902	261 215	350	8902
Dianion	285	360	7300	303 232	370	5976





HDMB bond distance in Å

$O_1 - H_2$	=	6.930	$O_1 - H_1$	=	2.232	$O_1 - O_2$	=	2.212
$O_1 - H_7$	=	6.875	$O_5 - H_4$	=	6.216	$O_1 - O_4$	=	6.412
$O_3 - H_7$	=	6.216	$H_4 - H_7$	=	8.165	$O_2 - O_4$	=	6.490
$O_3 - O_5$	=	4.826	$H_5 - H_7$	=	7.847	$O_2 - H_2$	=	7.023
$O_4 - H_1$	=	6.984	$H_1 - H_2$	=	7.545			
$O_2 - H_3$	=	6.101	$H_9 - H_{10}$	=	4.333			



Scheme 3. Bond distance (Å) of HDMB and β-CD by AM1 method (MOPAC-6.0 version, PC model).

of inclusion complex formation between HDMB and β-CD are possible. One is with the carboxyl group captured and the other is $-OCH_3$ and OH groups captured in the β-CD cavity (Scheme 3). In type-I arrangement, the carboxyl group of HDMB is entrapped with in the β-CD cavity. If COOH group encapsulated in the β-CD cavity the dianion maxima (i.e., deprotonation of hydroxyl group in absorption) should be similar to aqueous medium. Our results indicate dianion maxima of HDMB is blue shifted in β-CD (285 nm) than aqueous medium (303 nm) and monoanion maxima is follow the same trend both in aqueous and β-CD medium. The ground and excited state pK_a (pK_a^*) values for the neutral-monoanion equilibrium is also same (Table 3). For type-II arrangement $-OCH_3$ and OH groups of HDMB is entrapped with in the cavity. The dianion maxima of HDMB (deprotonation of hydroxyl group) is also blue shifted in β-CD than aqueous medium [17,18]. It is already reported when the OH group is entrapped in the β-CD cavity, the anions in β-CD medium are blue shifted than aqueous medium. Furthermore, the results observed in HDMB is similar to 4-hydroxy-3,5-dimethoxybenzaldehyde [18], 1,2,3-trihydroxybenzene [18] and naphthols [41,42]. This confirms that the environments around the $-COOH$ in β-CD are same in the bulk aqueous medium and $-OH$ group present in the β-CD cavity. These features indicate that in Scheme 3, type-II complex is favoured than type-I.

This is further supported by using semiempirical quantum mechanical calculations. The internal diameter of the β-CD is approximately 6.65 Å and its height is 7.8 Å (Scheme 3). To determine the dimensions of HDMB geometry of the ground state was optimized by using AM1 (MOPAC 6.0 version using PC model). The vertical distance between H_1 and H_2 is 7.545 Å whereas the horizontal distances between H_3 and H_7 and H_4–H_7 is 8.165 and 7.847 Å, respectively. This calculation revealed that the length of the two methoxy groups are higher than β-CD. Since the length between two methoxy groups in HDMB is larger than that of the upper rim of β-CD and one of the methoxy group attached at C_3 or C_5 should be

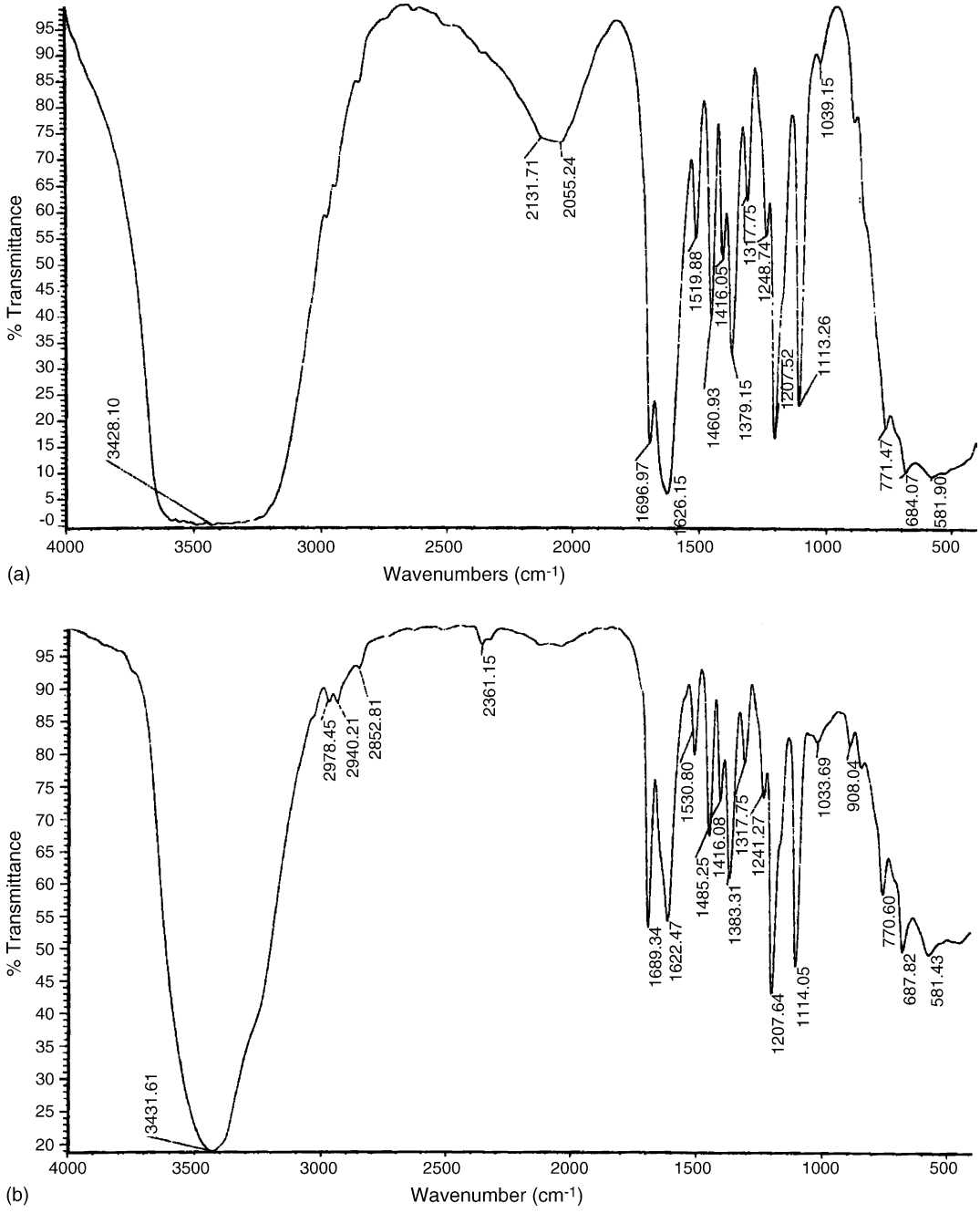


Fig. 9. FTIR spectra of HDMB in KBr (a) HDMB, (b) HDMB-β-CD inclusion complex.

projected outside the cavity and will be available in the bulk solution due to the size restriction in the β-CD cavity. In this case, the possibility of 1:2 complex will be excluded, due to the size restriction inside the cavity.

3.7. Infrared spectral studies

Compared FTIR spectra of HDMB, β-CD and the solid inclusion complex of HDMB with β-CD just as shown in Fig. 9 and Table 6. Absorption peaks of COOH group appearing 1697–1698 cm^{-1} are the vibrational absorption of carbonyl group of HDMB. The phenolic OH group appears

Table 6
Difference in FTIR absorption peak intensities of HDMB before and after formation inclusion complex

	HDMB (cm^{-1})	Inclusion complex (cm^{-1})	Difference in AI (%)
$\nu_{C=O}$	1697	1699	20
Bending vibration of OH in ν_{COOH}	1416	1416	30
ν_{OH} of phenolic group	1378	1384	40
ν_{C-O} of phenolic	1207	1207	30
$\nu_{C-O-CH3}$ group	1113	1114	30

AI: absorption intensities.

1375 cm^{-1} in HDMB whereas it is red shifted 1383 cm^{-1} in inclusion complex. Further, the absorption intensity in inclusion complex was significantly weaker than in HDMB. The inclusion complex IR peaks in the range from 1000 to 2000 cm^{-1} are 30–50% weaker than the free HDMB molecule. So we can deduce the phenolic OH group of HDMB is included into the cavity of β-CD.

3.8. ^1H NMR spectral studies

Proton nuclear magnetic resonance (^1H NMR) spectroscopy has proved to be a powerful tool in the study of inclusion complexes [40–42]. ^1H 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 this shifts, loss of resolution and broadening of signals observed for the host and guest protons [40–42]. Although, only limited information can be obtained from the ^1H 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 [40–42] and consists of six types of protons. The chemical shift of β-CD protons reported by different authors are very close to those reported in this work. The H-3 and H-5 protons are located in the interior of the β-CDs 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. A minor shift is observed for the resonance of H-1, H-2 and H-4 located on the exterior of 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 in the presence and absence of β-CD. 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 ($\Delta\delta = +0.18$) 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. As can be seen from Table 7, the chemical shifts data for the inclusion complex

Table 7
^1H NMR chemical shifts data of HDMB, inclusion complex and the corresponding complexation shifts in D_2O containing 8% volume DMSO-d_6 at 20 °C

Proton	HDMB	Complex	$\Delta\delta$
H-2	7.34	7.26	+0.12
H-3	3.90	3.96	−0.06
H-4	7.25	7.37	−0.12
H-5	3.90	3.96	−0.06
H-6	7.34	7.26	+0.12

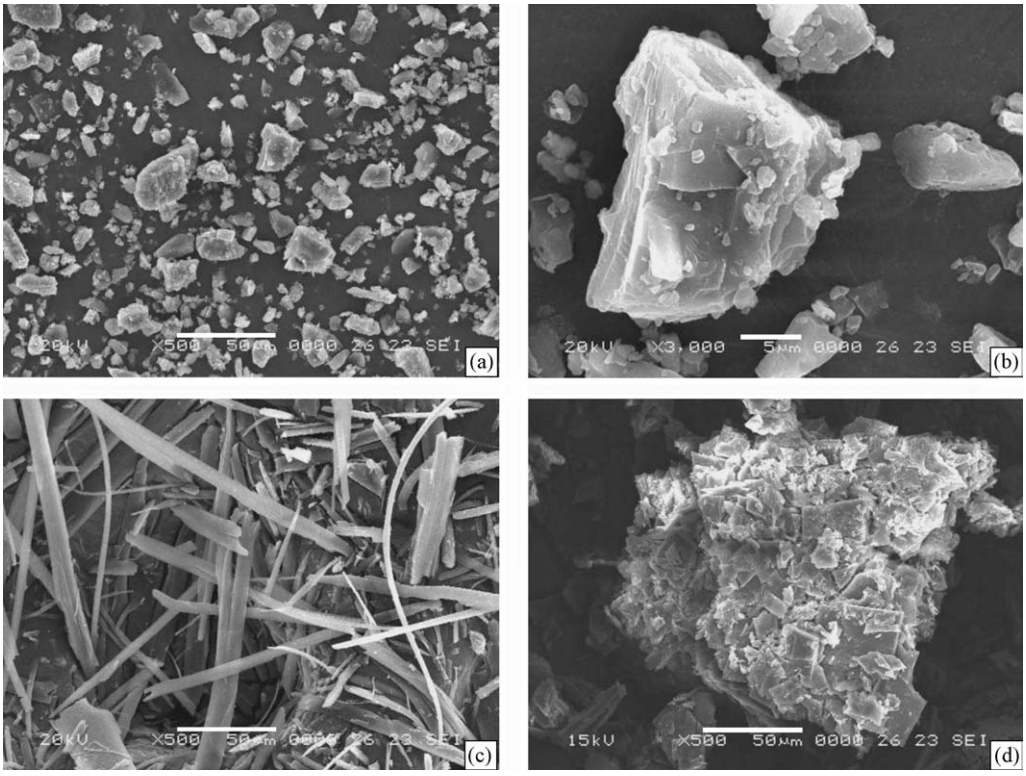


Fig. 10. Scanning electron microscope photographs of (Pt. coated) (a) β-CD-500 μm, (b) β-CD-3000 μm, (c) HDMB-500 μm, (d) HDMB-β-CD inclusion complex, 500 μm.

was different from the free compound. In HDMB, the phenolic OH (H-4, −0.12 ppm) and methoxy (H-3, −0.06 ppm) are downfield shift in the complex, which suggested that phenolic OH group is shielded largely in the complex and it must be penetrate deeply into the cavity. Further, as can be seen from Table 7, the resonance of HDMB protons with in theβ-CD cavity were shifted downfield when the inclusion complex was formed, which provided that the HDMB has preferred fixed orientation within the β-CD cavity.

3.9. Microscopic morphological observations

First we observed powdered form of HDMB and β-CD by scanning electron microscope, then we also observed powdered from of inclusion complex (Fig. 10). Pictures clearly elucidated the difference of powder of each other. Modification of crystals and powder can be assumed as a proof of the formation of a inclusion complex.

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