J Fluoresc (2014) 24:925–931
DOI 10.1007/s10895-014-1373-4

ORIGINAL PAPER

Inclusion Complexation of Phenoxyaliphatic Acid Derivatives of 3,3′-bis(indolyl)methanes with β-Cyclodextrin

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Received: 10 December 2013 / Accepted: 24 February 2014 / Published online: 13 March 2014
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Abstract The inclusion complexation behavior of phenoxyaliphatic acid derivatives of 3,3′-bis(indolyl)methane (BIMs 1–5) with β-cyclodextrin (β-CD) were investigated in both solution and solid state by means of UV-Visible, fluorescence spectroscopy, FT-IR and ^{1}H NMR techniques. The nature of the host–guest inclusion complex between BIMs and β-CD has been elucidated. The experimental results confirmed the existence of 1:1 inclusion complex of BIMs with β-CD. The binding constants describing the extent of formation of the complexes have been determined using Benesi-Hildebrand plots using UV-Vis and fluorescence spectroscopy. BIMs exhibited an affinity for β-CD. The spectral studies suggested the phenyl ring along with alkyl substitutions of BIMs is present inside of β-CD cavity.

Keywords Phenoxyaliphatic acid derivatives of 3,3′-bis(indolyl)methanes · β-cyclodextrin · Inclusion complexes

Introduction

The importance of bis(indolyl)methanes (BIMs) and their derivatives is well recognized by natural as well as synthetic chemists [1]. BIMs exhibit the various applications in pharmaceutical industry [2–4]. Shao et al. reported that bis(3-indolyl)methane skeleton is used as a chemosensor with the anion F^{-} and AcO^{-} in organic aprotic solution [5]. Kim and coworkers studied that bis(3-indolyl)methane skeleton has been demonstrated to be an efficient chromogenic and fluorescent moiety for metal ion sensing [6]. Due to the versatile application possibilities of BIMs, the syntheses of these compounds have become an interesting target for synthetic chemists.

Cyclodextrins (CDs) and their derivatives are as models of biological receptor–substrate interactions is a significant topic in chemistry and biochemistry [7]. CDs can form inclusion complexes with a variety of size suitable organic and inorganic molecules [8]. Therefore, many properties of guest molecules are affected remarkably, such as chemical reactivity [9], volatility [10], absorption spectrum [11], and so on [12]. These changes in chemical and physical properties are of both theoretical and practical interest. CDs and their derivatives have attracted attention as enzyme models [13], chromatographic phases [14], additives for foods [15], pharmaceuticals [16] *etc*. In particular, CD derivatives were applied in drugs to increase the solubility, bio-utility [17], stability [18] *etc*.

In this regard, the present investigation has been carried out the study of the photophysical properties of phenoxyaliphatic acid derivatives of 3,3′-bis(indolyl)methane in its ground and excited states in the presence of β-CD. The solid inclusion complexes of these molecules also were prepared and characterized using FT-IR and ^{1}H NMR techniques. In the last few years, our emphasis has been to study the effect of solvents of different polarity, acid–base concentrations, natural-, and modified α- and β-cyclodextrins on the spectral characteristics of different fluorophores [19–23]. And also we have been synthesized the biologically active phenoxyaliphatic acid and ester derivatives of 3,3′-bis(indolyl)methanes from indole and formylphenoxyaliphatic acids in the presence of potash alum

Electronic supplementary material The online version of this article (doi:10.1007/s10895-014-1373-4) contains supplementary material, which is available to authorized users.

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[24] and potassium titanyl oxalate [25] as a catalyst. This prompted us to study the effect of β-cyclodextrin on phenoxyaliphatic acid derivatives of 3,3′-bis(indolyl)methane using photophysical studies.

Experimental

Materials

Using our previous reported method [24], BIMs (1–5) were synthesized from indole and formylphenoxyaliphatic acid(s) in the presence of potash alum. BIMs (1–5) were isolated using column chromatography. The chemical name of the molecules are given one by one: (i) 2-{2-[bis(1H-indol-3-yl)methyl]}benzene (BIM-1), (ii) 2-{2-[bis(1H-indol-3-yl)methyl]phenoxy}acetic acid (BIM-2), (iii) 2-{2-[bis(1H-indol-3-yl)methyl]-6-methoxyphenoxy}acetic acid (BIM-3), (iv) 4-{2-[bis(1H-indol-3-yl)methyl]phenoxy}acetic acid (BIM-4), and (v) 4-{2-[bis(1H-indol-3-yl)methyl]-6-methoxyphenoxy}acetic acid (BIM-5). The optimized structures of BIMs were shown in Fig. 1 using DFT method. β-Cyclodextrin was purchased from Sigma-Aldrich chemical company and used without further purification. Triply distilled water was used for the preparation of aqueous solutions.

Preparation of Inclusion Complexes in Solution

A stock solution of BIMs was prepared in methanol and the concentration of stock solution was 2×10^{-3} M. Exactly 0.2 ml of this stock solution was transferred into each 10 ml volumetric flask. To this, varying concentrations of β-CD solution (range from 1.0×10^{-3} to 1.0×10^{-2} M) was added. The mixed solution was diluted to 10 ml with triply distilled water and shaken thoroughly. The final concentration of BIMs in all the flasks was 4×10^{-5} M.

Preparation of Inclusion Complexes in Solid State

The inclusion complexes of the BIMs with β-cyclodextrin were prepared as per co-precipitation method [26]. The solution of these molecules in required concentrations were added drop by drop to β-cyclodextrin solution of the required concentration. The mixtures were stirred for a period of 48 h and filtered. The filtrate was cooled for 24 h in refrigerators. The precipitate obtained was filtered through G-4 crucible, washed with water and dried in air for 24 h. After drying in an oven at 60 °C for 24 h, a pale pink colour solid was obtained.

Instruments

Absorption spectral measurements were carried out with a Systronics-double beam UV-visible spectrophotometer 2203 smart and fluorescence measurements were made by using a Elico sl 170 spectrofluorimeter. Infrared spectra were recorded on a JASCO FT-IR Model 410 spectrophotometer (in KBr pellet). Band positions are reported in reciprocal centimetres (cm^{-1}). ^1H NMR spectra were recorded on a Bruker (Avance) 300 MHz NMR instrument using TMS as internal standard and $CDCl_3$ as solvent.

Results and Discussion

Effect of β-Cyclodextrin

Table 1 summarizes the absorption maxima, molar extinction coefficient and fluorescence maxima of BIMs and β-CD inclusion complexes in aqueous solution. Figure 2 depicts the absorption and fluorescence spectra of BIM1 in aqueous solution containing various concentrations of β-CD (vide Absorption and fluorescence spectra of BIM 2–5 are given in the supporting information—Fig. S1 and S2). The insert Fig. 2 show the changes of both absorbance and fluorescence intensity was observed as a function of the concentration of β-CD. The absorption spectrum of BIMs in aqueous solution (2×10^{-5} M) exhibited λ_{max} around 290 nm for π–π* transition with less or more molar absorptivity of 35.1570×10^3 M^{-1} cm^{-1} for all molecules. Upon increasing the β-CD concentrations, the absorbance of BIMs are increased at the same wavelength without the shift of the absorption maximum. The increase in absorbance is due to the detergent action of β-CD and is attributed to the additional dissolution of the guest adsorbed on the surface of the walls of the container [27–29]. The above interesting results are due to all molecules are transferred from more protic environment (bulk aqueous phase) to less protic β-CD cavity environment.

No clear isosbestic point was observed in the absorption spectra and the absorbance changes are very small. In general, the existence of an isosbestic point in the absorption spectra is an indication to the formation of well defined 1:1 complexes [27–29]. The possibilities proposed for this deviation are (i) more than one guest molecule could have got accommodated within a single β-CD cavity, (ii) due to the space restriction of β-CD cavity, more than one type of complex each having 1:1 stoichiometry might have been formed, (iii) the solution containing methanol (1 %) could have made some interaction between these components, and (iv) the strong detergent action of β-CD could have prevented the formation of isosbestic point [30–33]. In β-CD solutions, increase in the absorbance indicates that the aromatic ring is encapsulated in the non-polar β-CD cavity.

Fluorescence spectra of BIMs with β-CD were measured in aqueous solution at pH 7.2. The maximum absorption wavelength of BIMs was chosen for excitation. The excitation and emission maxima of BIMs are presented in Table 1. With

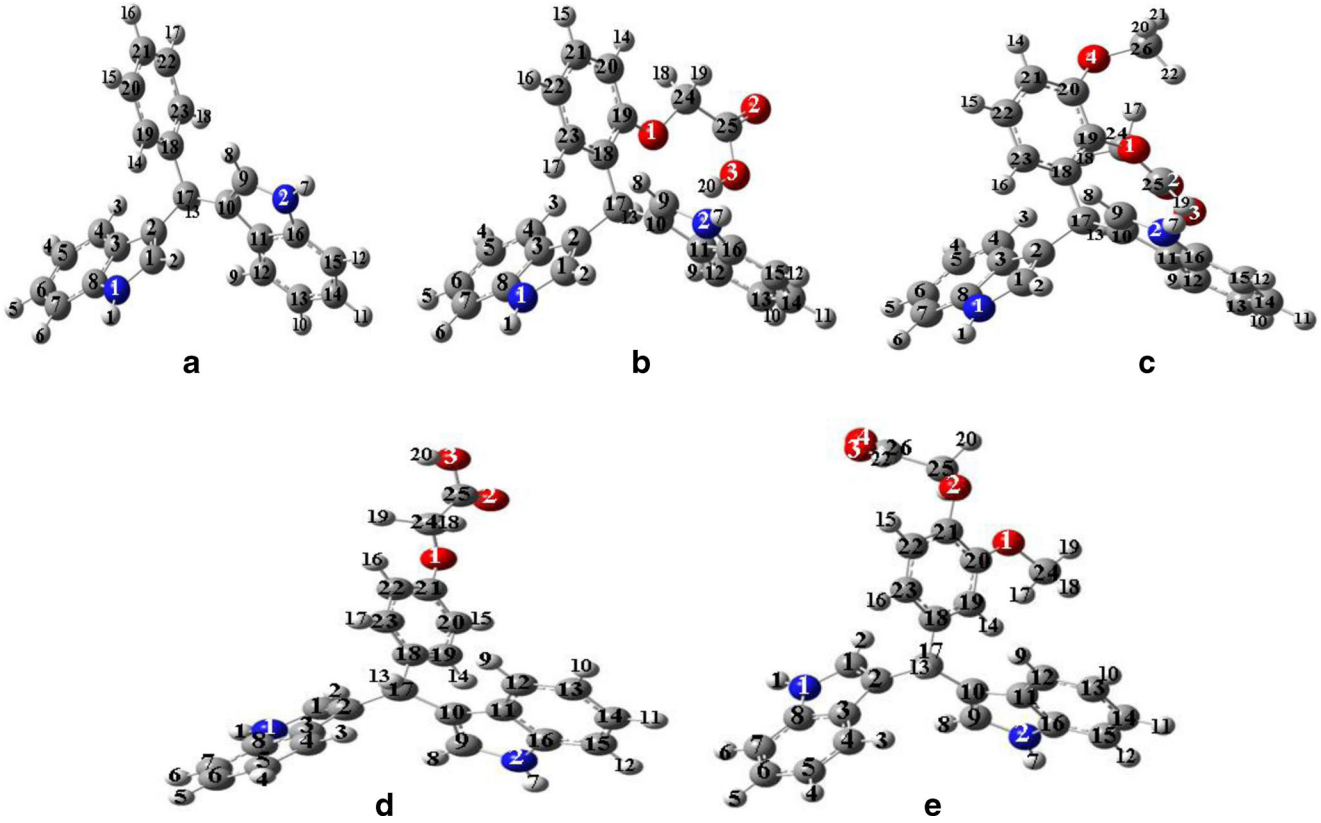

Fig. 1 The optimized structures of **a** BIM 1, **b** BIM 2, **c** BIM 3, **d** BIM 4 and **e** BIM 5 using DFT method

the addition of β-CD to the solution of BIMs, the fluorescence intensity was markedly enhanced (Fig. 2). The increase of fluorescence intensity is due to the formation of complexes of β-CD with BIMs could be explained as the guest molecules were entrapped in the cavity of β-CD. The microenvironment around β-CD with smaller polarity and stronger rigidity would restrict the freedom of guest molecules inside the cavity and increase the fluorescence intensity. Furthermore, the steric hindrance of β-CD torus can protect the excited states from non-radiative and quenching process that normally occur in bulk buffer solution and enhance the fluorescence efficiencies of guest molecules [34]. The fluorescence intensity of BIMs gradually increased with increasing the concentration of β-CD and finally reached a saturation point (Fig. 2).

Table 1 Absorption and emission spectral studies of BIM 1–5 in different concentrations of β-cyclodextrin

Concentration of β-CD M	BIM 1			BIM 2			BIM 3			BIM 4			BIM 5		
	λ_{abs}	log ε	λ_{flu}	λ_{abs}	log ε	λ_{flu}	λ_{abs}	log ε	λ_{flu}	λ_{abs}	log ε	λ_{flu}	λ_{abs}	log ε	λ_{flu}
Water	290	3.11	350	290	3.38	350	290	3.40	350	290	3.65	350	290	3.68	350
	230	4.01		230	4.21		230	4.25		230	4.38		230	4.40	
0.002	290	3.14	350	290	3.40	350	290	3.42	350	290	3.68	350	290	3.71	350
	230	4.03		230	4.23		230	4.28		230	4.40		230	4.43	
0.004	290	3.16	350	290	3.43	350	290	3.45	350	290	3.70	350	290	3.73	350
	230	4.07		230	4.25		230	4.30		230	4.43		230	4.46	
0.006	290	3.19	350	290	3.47	350	290	3.48	350	290	3.72	350	290	3.76	350
	230	4.11		230	4.28		230	4.33		230	4.46		230	4.48	
0.008	290	3.23	350	290	3.51	350	290	3.51	350	290	3.75	350	290	3.79	350
	230	4.15		230	4.30		230	4.36		230	4.49		230	4.51	
0.01	290	3.26	350	290	3.54	350	290	3.54	350	290	3.78	350	290	3.82	350
	230	4.18		230	4.33		230	4.39		230	4.52		230	4.54	
Excitation wavelength	290			290			290			290			290		
Binding constant (M^{-1})	322		410	386		457	408		502	448		557	531		635
ΔG KJ / mole (−ve)	14.54		15.15	15.00		15.42	15.14		15.66	15.37		15.92	15.80		16.25

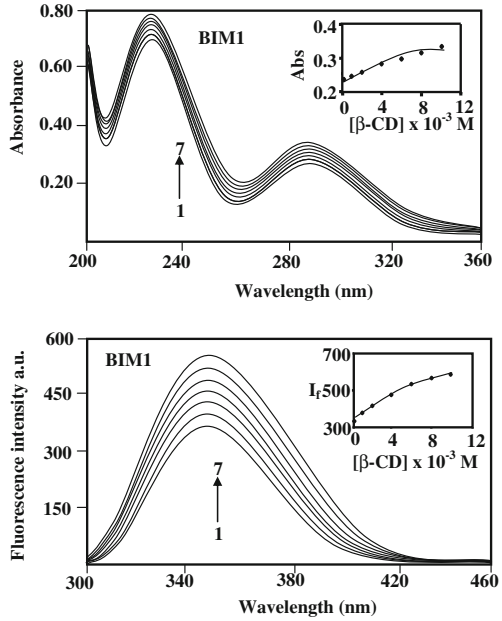

Fig. 2 Absorption and fluorescence spectra of BIM1 in different β-cyclodextrin concentrations (M): (*1*) 0, (*2*) 0.002, (*3*) 0.004, (*4*) 0.006, (*5*) 0.008 and (*6*) 0.01. *Insert fig*.: absorbance and fluorescence intensity vs. β-CD concentrations

Interestingly, at higher β-CD concentrations, the absorption and emission spectral shape of all molecules are same indicating the formation of similar type of inclusion complexes.

Determination of Binding Constant

The binding constant for all the inclusion complexes has been determined by analyzing the changes in the intensity of absorption and fluorescence maxima with β-CD concentration. In order to determine the stoichiometry of the inclusion complexes, the dependence on β-CD of the BIMs absorbance and fluorescence were analyzed by using the Benesi-Hildebrand equation [35]. 1:1 (Eq. 1) complexes from BIMs and β-CD are as shown below:

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

Where K is the binding constant, I_0 is the initial absorption/fluorescence intensity of free guest molecules, I′ is the absorption/fluorescence intensity of β-CD inclusion complex and I is the observed absorption/fluorescence intensity. According to Eq. 1, a plot of $1/I-I_0$ *versus* 1/[β-CD] (both absorption and fluorescence) gives a straight line (Fig. 3). This analysis reflects the formation of 1:1 inclusion complex between BIMs and β-CD [36]. The binding constant (K) for the inclusion complexes were determined from the slope and intercept of the B-H plots (Table 1). The binding constant value depends on several parameters like weak forces (H-bonding, hydrophobic and van der Waals forces), size and shape of the guest molecules relative to the host cavity.

Solvatochromic Studies

To deduce the polarity effect on the microenvironment of BIMs within the β-CD cavity, we have studied a solvatochromic study by comparing the absorption and the fluorescence of BIMs in solvents with increasing polarity [24]. The spectral properties of BIMs in different solvents are compared with that of the inclusion complexes (BIMs–β-CD). With comparison of these results of BIMs, the absorption maximum is slightly red shifted from cyclohexane to water and in inclusion complexes. No significant change was observed in the absorption maxima in β-CD compared to water except the increase in absorbance. The emission spectra of inclusion complexes closely resemble to BIMs spectra in alcohol, suggesting that the inclusion complexes formed is in an alcohol-like environment provided by the rings of hydroxyl groups at each end of β-CD cavity. The solvatochromic shifts reveal that the hydrogen bonding is present along with dipole interactions.

The free energy change was calculated from the binding constant (K):

$$\Delta G = -RT\ln K \quad (2)$$

The value of thermodynamic parameter ΔG for the formation of the guest molecules to β-CD is given in Table 1. Change in Gibbs free energy (ΔG) associated with various BIMs–β-CD complexations was evaluated from their respective K values. Table 1 reveals that there is a strong host–guest binding ability between β-CD and BIMs quantitatively. It can be concluded that these complexation process is highly feasible, which is evident from the negative value of ΔG for BIMs–β-CD inclusion complexes.

Further, the calculated parameter show negative values of ΔG, suggesting that the formation of inclusion complexes between BIMs and β-CD were an entropy driven process in which the key role is played by van der Waals forces [37]. In this mechanism, when water molecules bind inside the β-CD cavity they are replaced by the guest molecules during complexation; due to the above process entropy is released with consequent reduction of the energy of the system. The negative free energy change can be attributed to the reduced configurational freedom of the entrapped guest molecules. The fluorescence enhancement in the inclusion complexes indicated that BIMs were interactive within the less protic interior of the β-CD cavity than in the aqueous phase.

Considering the above discussions, the possible inclusion mechanism is proposed as follows. Generally different types of inclusion complexes may be formed with BIMs and β-CD

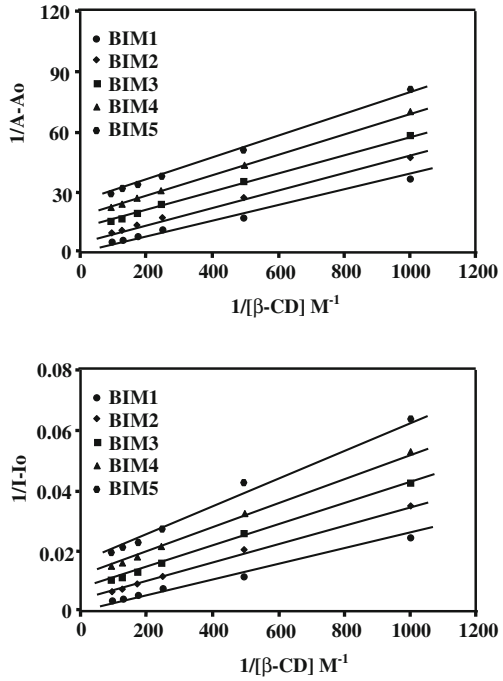

Fig. 3 The Benesi-Hildebrand plot of absorption and fluorescence spectra of BIM 1–5. Plot of $1/A-A_0$ vs. 1/[β-CD] and Plot of $1/I-I_0$vs. 1/[β-CD]

(Fig. 4) (vide supporting information, BIMs 3–5–β-CD Fig. S3). In 1:1 inclusion complexes, one of the indole rings is captured or the benzene ring is captured whereas in 1:2 inclusion complex both indole and aromatic rings may be captured by the β-CD cavity. In 1:1 inclusion complexes, the indole ring is embedded in the β-CD environment and the –NH group could form a hydrogen bond with the secondary hydroxyl group of the bigger cyclodextrin side, whereas the phenyl ring is included in the β-CD environment and not possible to form a hydrogen bond with the secondary or primary hydroxyl group of β-CD cavity. We may expect the dual emission in the β-CD environment for the 1:2 inclusion complexes between BIMs and β-CD. N. Rajendiran et al. [38, 39], reported that the tricylic compounds was formed different types of inclusion complexes with β-CD. In these molecules, the two emission wavelengths were observed in the presence of β-CD due to the formation of different types of inclusion complexes. Further, the Benesi–Hildebrand analysis reflects that one type of inclusion complex is formed between BIMs and β-CD.

This is further supported by density functional theory calculation (DFT). The internal diameter of the β-CD is approximately 6.5 Å and its height is 7.8 Å. To determine the dimensions of BIMs geometry of the ground state was optimized by DFT. Based on single crystal XRD data [24] and DFT for BIM-2, the vertical distance between H1–H15 is 8.58 Å whereas the horizontal distance between H5–H11 is

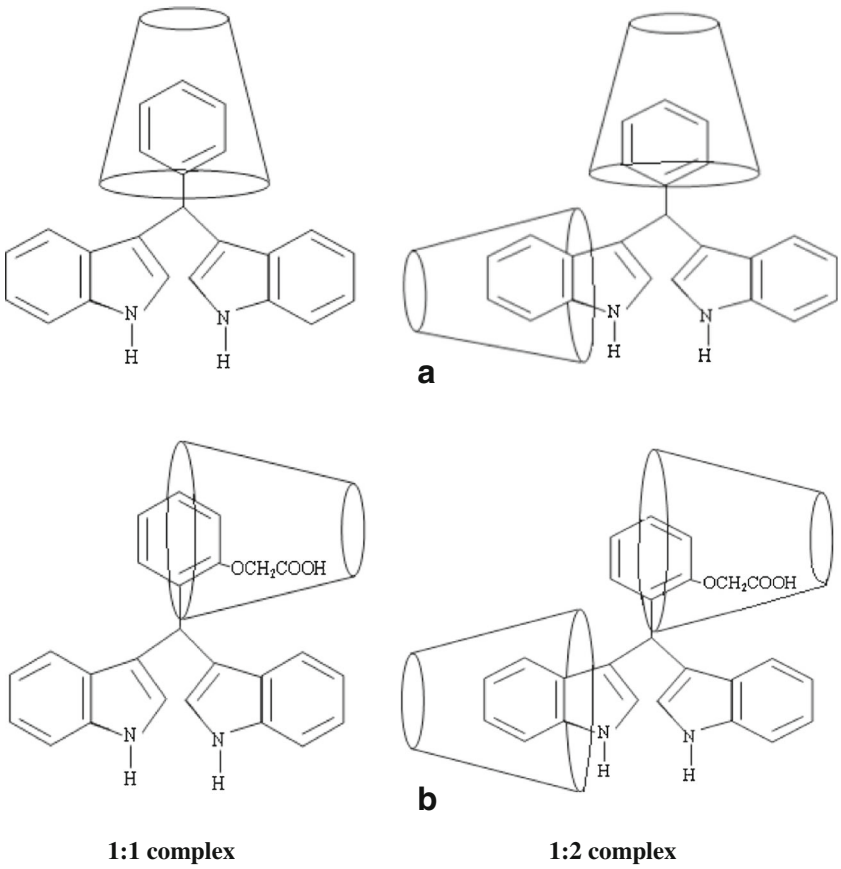

Fig. 4 The proposed models of inclusion complex of **a** BIM1, **b** BIM2 with β-CD for 1:1 and 1:2 inclusion complex

11.45 Å. The vertical and horizontal distance of the particular bond lengths for the other four molecules was calculated using DFT method only. This calculation revealed that the length between the aromatic and indole rings in BIMs are greater than that of β-CD cavity, they cannot be encapsulated completely within the β-CD cavity. Therefore we concluded that BIMs formed 1:1 inclusion complex with β-CD. The phenyl ring with alkyl substitutions of BIMs is embedded in the β-CD cavity and two indole rings are present in the aqueous phase.

From the above findings, it is clear that in β-CD solutions, hydrophobicity is the driving force for encapsulation of the molecules inside the β-CD cavity. Generally the hydrophobic part likes to go inside the deep core of the non-polar β-CD cavity [40–42].

Solid Inclusion Complexes Studies

FT-IR Spectral Studies

The formation of inclusion complexes was confirmed by FT-IR spectroscopy because bands resulting from the included part of the guest molecules are generally shifted or their intensities altered [43]. If β-CD and BIMs form inclusion complexes, the non-covalent interactions between them such as hydrophobic interactions, van der Waals interactions, and hydrogen bonds are lowered the energy of the inclusion part of BIMs which reduce the absorption intensities of the corresponding bands. We can see that there are apparent differences between the spectra of BIMs–β-CD and that some characteristic IR peaks of BIMs change obviously by comparison of the FI-IR spectrograms of BIMs and the inclusion complex of β-CD (vide supporting information, Fig. S4).

The −NH stretching frequency for BIMs appears around 3,419–3,368 cm^{-1} and is slightly moved in the inclusion complexes spectra to a shorter wave number. The –C=O stretching frequency is present at 1,725 cm^{-1} and is largely red shifted in the inclusion complexes to 1,742 cm^{-1}. The observed changes in the FT-IR spectra of BIMs–β-CD inclusion complexes are due to the restriction of the vibration of free BIMs upon encapsulation into β-CD cavity, indicating the formation of inclusion complexes from BIMs and β-CD. The phenyl ring with alkyl substitutions in BIMs was inserted into the cavity of β-CD.

^{1}H NMR Spectral Studies

NMR spectroscopy is the most powerful tool for the study of formation of inclusion complexes from CDs and a variety of guest molecules [44, 45]. The ^{1}HNMR spectra of the inclusion complex of between these molecules and β-CD (vide supporting information, Fig. S5). In the present work, ^{1}H NMR measurement was performed to elucidate the structure of BIMs–β-CD complexes. In general, the resonances of the protons of β-CD located within or near the cavity (H-3, 5, 6) shows remarkably large shifts in the mixture. A minor shift is observed for the resonance of H-1, 2, 4 located on the exterior of β-CD [46]. In particular, the resonance of the protons of β-CD, located within or near the cavity showed remarkably large up-field shift (−0.20, −0.19 ppm) in the complex, which suggested that the resonance of H-3 and H-5 are shielded largely in the complex, the phenyl ring with alkyl substitution must penetrate deeply into the cavity. A minor shift (−0.04, −0.07 ppm) was observed for the resonance of H-atoms located on the exteriorof β-CD.

Since BIMs contain three parts, two indole rings and one phenyl ring with substitution, this may lead to two isomeric 1:1 complex and 1:2 complex. To ascertain the structure of the inclusion complexes, ^{1}H NMR spectroscopy studies of BIMs were therefore under taken. The proton signals of BIMs phenyl ring with substitutions showed up or down-field shifts between the free and complex form, indicating that they are affected as a result of complexation. It can be deduced from this information that phenyl ring with substitution probably entered the inner cavity of β-CD. These observations proved the reality of the inclusion complexation and showed that the driving forces for the formation of the inclusion complexes are hydrophobic interactions [47].

Conclusion

The present work demonstrated that the aqueous solubility of BIMs was enhanced considerably by formation of an inclusion complex with β-CD. Thus, the β-CD may be useful in improving the dissolution and the bioavailability of BIMs in pharmaceutical formulation. The spectral data suggested that the formation of a stable 1:1 stoichiometric complex of β-CD–BIMs. The spectral studies suggested that the phenyl ring along with alkyl substitutions of BIMs is present inside of β-CD cavity. FT-IR and ^{1}H NMR spectra strongly confirmed that the inclusion complexes are formed between BIM 1–5 and β-CD.

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