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Host–guest interaction of L-tyrosine with β-cyclodextrin

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Abstract

The inclusion complexes of β-cyclodextrin (β-CD) with L-tyrosine (L-TYN) were investigated by using spectrophotometers. The absorption and fluorescence enhancement occurs with β-CD and L-TYN forms 1:1 inclusion complex. The unusual blue shift of hydroxyl ion in the β-CD medium confirms OH groups present in the interior part of the β-CD cavity and –COOH group present in the upper part of the β-CD cavity. A mechanism is proposed to explain inclusion process. The inclusion interaction was examined and the thermodynamic parameters of inclusion process ΔG, ΔH and ΔS were determined. The results indicated that the inclusion process was an exergonic and spontaneous process. Stable solid inclusion complexes were established and characterized by FT-IR, scanning electron microscope (SEM) methods.

Keywords: L-Tyrosine; β-Cyclodextrin; Inclusion complex; pH effects

1. Introduction

Cyclodextrins (CDs) have been used to perturb the physical and chemical properties of hydrophobic organic molecules in aqueous solutions. The CDs are capable of incorporating a high range of guest molecules based on hydrophobic and geometrical (Scheme 1) [1]. Generally molecular recognition by native and modified cyclodextrins is currently an interesting in supramolecular chemistry [2], naturally occurring cyclic oligosaccharides composed of six, seven or eight α-(1-4)-linked D-glucosyl residues, generally called, α-, β-, γ-CD, respectively (Scheme 1). They have a toroidal shape with an internal hydrophobic surface and external hydrophilic surface and it is acting as a host molecule. These cyclodextrins are well known as forming stable host–guest inclusion complexes which have the interesting property of including organic, inorganic and biological amino acids (found in proteins) molecules in their cavities [3,4]. The guests have several weak intramolecular forces between host and guest molecules, i.e., dipole–dipole interaction, electrostatic, Vander waals, hydrophobic and hydrogen bonding interactions.

Upon inclusion or partial inclusion of molecules within their hydrophobic interior, CDs can effectively shielded the excited singlet state of molecules from the processes and enhance their fluorescence intensity [5]. The complexed molecules have also been observed to be increased upon formation of inclusion complexes with CDs [6]. Furthermore, these studies seem to indicate differences in the extend of inter- and intra molecular hydrogen bond for the molecules in aqueous solutions of cyclodextrins. Applications of cyclodextrins and their derivatives cover various areas of the chemistry, including the sensing of organic molecules, analytical chemistry, pharmaceuticals, food, encapsulation of drugs and other industrial areas [7–9].

The excited state intramolecular charge transfer (ICT)/ intramolecular hydrogen bond (IHB) process has been attractive topics of investigations as a primary function for basic mechanisms of biological and chemical energy conversion [10–14]. The ICT process of organic molecules containing separating electron donor and electron acceptor moieties has been studied in various homogeneous and heterogeneous media, and many reports revealed that the excited state ICT emission could be maximized by conformation change. The conformational change (such as dimethylaminobenzonitrile derivatives) has been proposed to induce the twist of the whole alkyl amino group with respect to the benzene ring leading to a called

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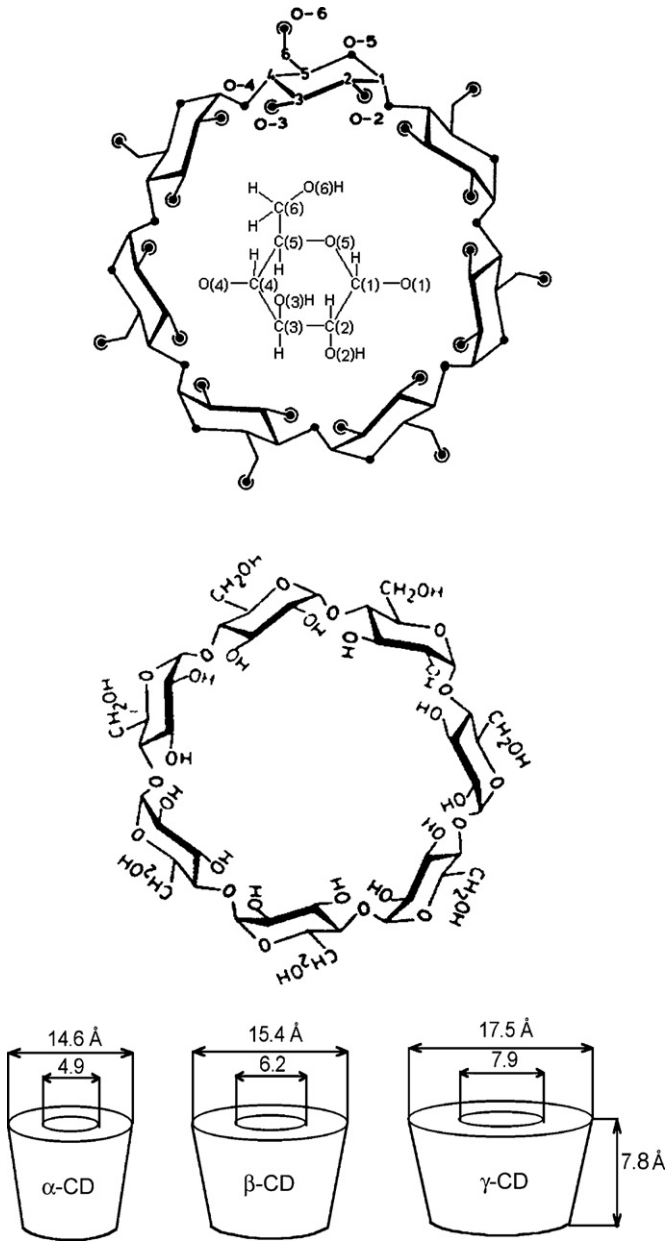


Scheme 1. Chemical structure of β-cyclodextrin, with oxygen• and hydroxyl• groups marked. All glucoses are in C_1 chair form, structure of β-cyclodextrin and molecular dimensions of α-, β- and γ-cyclodextrins.

"twisted intramolecular charge transfer (TICT) state [15,16], respectively.

Also, it has been reported that the intramolecular hydrogen bonding process is an important factor to facilitate the ICT process by maintaining a large twist angle between the electron donor and acceptor groups in the ground states [17]. The reactivity in the excited state, for e.g., proton transfer can also be altered in the presence of cyclodextrine due to interactions of a protonable group with the hydrophilic borders of the cavity [18]. The cyclodextrins have also proven to restrict the twisting of functional groups in molecules that display twisted intramolecular charge transfer (TICT), for example 4-*N*,*N*-dimethyl-amino cinnamic acid [19] or 2-(4′-*N*,*N*-dimethylaminophenyl) bezimidazole [20]. This phase restrictions caused by the inclusion has been used advantageously to probe the dual fluorescence of 9-anthroic acid, controversy such emission spectra [21].

An alternative explanation to TICT has been proposed by Zachariasse et al. [22]. According to the authors the phenomenon is based on a solvent-induced locally excited (LE) and charge transfer (CT) states achieved by a sufficiently small energy gap between the two states. In that respect, CT can be explored by variation of the donor and acceptor groups on either side of the benzene moiety stabilizing the CT transfer state. This property leads to several applications of cyclodextrins in different fields of analytical and synthetic chemistry. The spectroscopic and photochemical behaviors of such complexes are of interest and the changes in fluorescence and electronic absorption properties, excimer and exciplex formation in the excited state protolytic equilibria and photoisomerization have been reviewed [23]. On the other hand, in some molecules having a perpendicular configuration in the ground state (e.g., 9,9′bianthrayl) that visiting relaxation needed to reach the TICT state is not necessary and the overall ICT rate is determined only by the solvent relaxation dynamics [17]. The charge separation in biological molecules is known to be coupled to proton motion which may be proton transfer process [24]. Nevertheless the role of the specific hydrogen bonding in the photo induced TICT (ICT) has not been systematically investigated.

In this study, we report for the absorption and fluorescence characteristics of L-tyrosin (L-TYN) in different β-cyclodextrin concentrations. For the past one decade, the corresponding author has largely been involved in studying photophysical properties [25,26] of various organic fluorophores. This molecule shows intramolecular hydrogen bond/intramolecular charge transfer emission in the excited singlet state. This stimulated us to carry out a study on L-tyrosin.

L-Tyrosin is one of the amino acid, i.e., found in proteins of all life forms. Recently, tyrosin was twisted to see if it could improve the neuropsychological test performances of individuals with phenylketonuria. Pregnant women and nursing mothers should avoid supplementation with L-tyrosin. Ferand et al. [27] were reported the absorption spectra of the amino acids including L-tyrosin horizontal banded structure in their spectra.

The techniques of UV–vis, fluorimetry, FT-IR, Scanning electron microscope and thermodynamic parameters have been used to examine the effects of β-cyclodextrin upon complexation of L-tyrosin. The formation constants of the complexes have been estimated in order to predict and understand the factors affecting complexation between β-cyclodextrin and L-TYN molecules in solution.

2. Experimental

2.1. Instruments

Absorption spectral measurements were carried out with a ELICO BL-198 Bio Spectrophotometer, and fluorescence measurements were made a JASCO FP-550 Spectrofluorimeter. The pH values in the range 2.0–12.0 were measured on ELICO pH meter model LI 120. 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).

2.2. Reagents and materials

L-TYN and β-CD were obtained from E-merck. The purity of the compounds was checked by similar fluorescence spectra when excited with different wave lengths. Triply distilled water used for the preparation of aqueous solutions. Solution in the pH range 2.0–12.0 was prepared by adding the appropriate amount of NaOH and H_3-PO_4. The concentrations of the solutions were of the order 10^{-4} to 10^{-5} mol dm^{-3}. The concentration of β-CD is varied from zero to 1.2×10^{-2} mol dm^{-3}. The stock solution of the L-TYN is 1×10^{-3} mol dm^{-3}.

2.3. Preparation of solid inclusion complex of L-TYN with β-CD

Accurately weighed 1 g of β-CD was placed in to 50 ml conical flask and 30 ml triply distilled water added and then oscillated this solution enough. After that, 0.3 g L-TYN was put in to a 50 ml beaker and 20 ml triply distilled water added and put over electromagnetic stirrer to stir until it was dissolved. Then slowly poured β-CD solutions in to L-TYN solution. The above mixed solution was continuously stirred for 48 h at room temperature. The reaction mixture was put in to refrigerator for 48 h. At this time, we observed that white powder precipitated. The precipitate was filtered by G_4 sand filter funnel and washed with triply distilled water. After dried in oven at 50 °C for 12 h, white powder product was obtained. This is solid inclusion complex of L-TYN with β-CD.

3. Results and discussions

3.1. Effect of β-cyclodextrin

The UV–vis absorption and emission spectral data of L-tyrosine (L-TYN) in different concentrations of β-CD are complied in Table 1. The absorption peaks of L-TYN in pH 7.0 appears (Fig. 1) at 273.5 and 223.7 nm. Upon increasing the concentration of β-CD, the absorption maxima is regularly blue shifted from 273.5 to 264 nm, where as the absorption spectra of L-TYN is seen to undergo a marginal blue shift. However, the absorption intensities of pH 7.0 solutions are regularly increases with increasing concentration of β-CD, no clear isosbestic point is observed in the absorption spectra. The absorption spectra show the marginal change in absorption maxima even in the presence of the highest concentration of β-CD used (1.2×10^{-2} mol dm^{-3}) and there is no change in the absorbance by further addition of β-CD (Fig. 2). Increasing the concentration of β-CD the absorption maximum was slightly blue shifted with a gradual increase in absorbance. This behavior has been attributed to the enhanced dissolution of the guest molecule, through the hydrophobic interaction between guest molecule and non-polar cavity of β-CD [28–30], as observed others also

Table 1
Absorption and fluorescence maxima (nm) of L-tyrosine at different concentrations of β-CD

S. No.	Concentration of β-CD	λ_{abs}	log ε	λ_{flu}
1	Water (without β-CD)	273.5 223.7	4.19 4.50	305 405
2	0.002 M	272.3 223.5	4.29 4.55	306 405
3	0.004 M	271.6	4.45	305 407
4	0.006 M	270.6	4.50	307 403
5	0.008 M	267.8	4.67	307 402
6	0.010 M	265	4.67	308 401
7	0.012 M	263.9	4.78	309 403
Binding constant (M^{-1})		60		119
ΔG (kJ/mole)		−13.45		−14.25
ΔH (kJ/mole)		−69.0		−69.20
ΔS (kJ/mole)		0.19		0.18

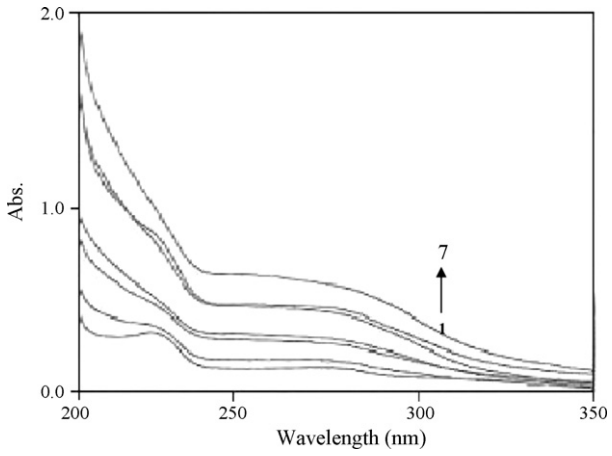


Fig. 1. The absorption spectra of L-tyrosine in different β-CD concentrations (mol dm^{-3}): (1) 0.0 M, (2) 0.002 M, (3) 0.004 M, (4) 0.006 M, (5) 0.008 M, (6) 0.010 M and (7) 0.012 M.

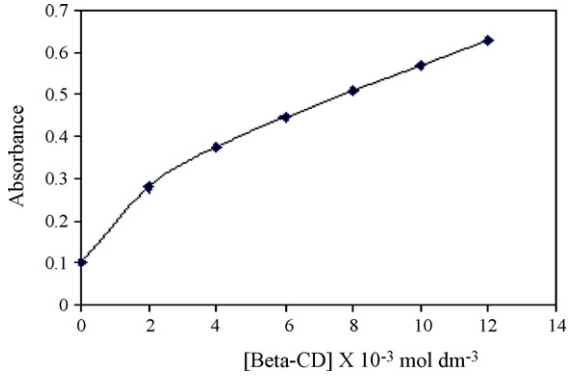


Fig. 2. The absorption intensity of L-TYN changes at 275 nm with different β-CD concentrations.

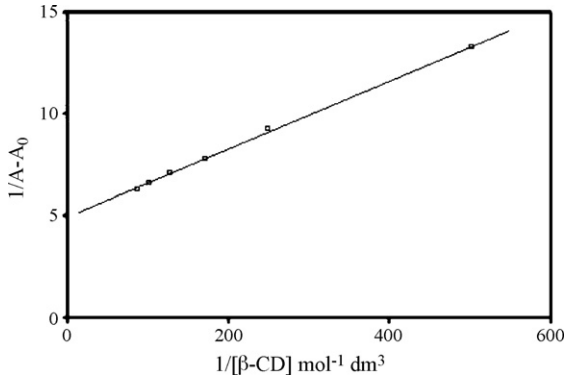


Fig. 3. Benesi–Hildebrand plot of $1/A - A_0$ vs. 1/[β-CD] for L-TYN.

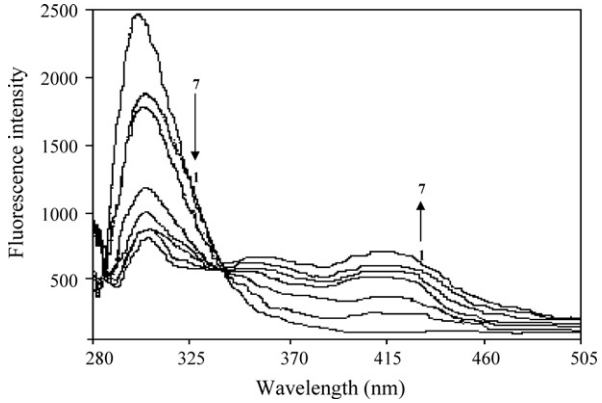


Fig. 4. Fluorescence spectra of L-TYN in different β-CD concentrations (mol dm^{-3}): (1) 0, (2) 0.002, (3) 0.004, (4) 0.006, (5) 0.008, (6) 0.010 and (7) 0.012.

[31,32]. Since, this indicates the formation of 1:1 host–guest type inclusion complex between β-CD and L-TYN molecule. The guest is in a surrounding, i.e., poor in water molecules, and this causes both the blue shift of the absorption and the increase of its absorbance.

For 1:1 inclusion complex between β-CD and L-TYN, the following equilibrium can be written,

$$\text{L-TYN} + \beta\text{-CD} \overset{K}{\rightleftharpoons} \text{L-TYN} : \beta\text{-CD}$$

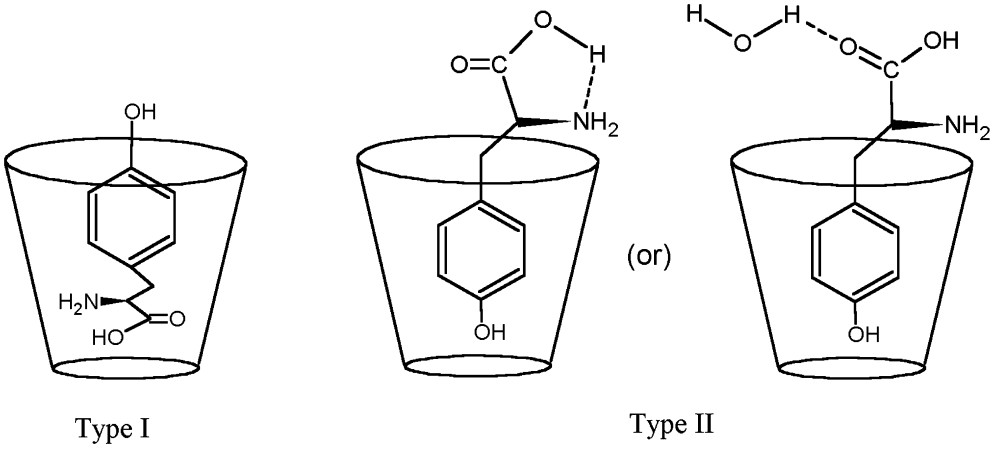
The binding constant '*K*' and stoichiometric ratios of the inclusion complex of L-TYN can be determined according to the Benesi–Hildebrand relation [33] assuming the formation of 1:1 host–guest complex

$$\frac{1}{A - A_0} = \frac{1}{\Delta\varepsilon} + \frac{1}{K[\text{L-TYN}]_0 \Delta\varepsilon[\beta\text{-CD}]_0} \quad (1)$$

Where, A and A_0 is the difference between the absorption of L-TYN in the presence and absence of β-CD, $\Delta\varepsilon$ is the difference between the molar absorption co-efficient of L-TYN and the inclusion complex $[\text{L-TYN}]_0$, $[\beta\text{-CD}]_0$ are the initial concentration of L-TYN and β-CD, respectively. Fig. 3 depicts a plot of $1/A - A_0$ as a function of 1/[β-CD] for L-TYN good linear correlations was obtained, confirming the formation of a 1:1 inclusion complex. From the intercept and slope values of this plot, K is evaluate [$K = 60.25\ M^{-1}$] at 303 K.

The fluorescence spectra of aqueous L-TYN solutions β-CD concentration are presented in Fig. 4. The fluorescence characteristics of L-TYN are entirely different from those compare in absorption spectra. The fluorescence spectra observed two effects; firstly, a dual luminescence is observed at 305 and 405 nm. Secondly, fluorescence intensity is decreases shorter wavelength and increased in longer wavelength along with increasing β-CD concentrations. The positions of the fluorescence maxima and of the isosbestic point located in water and in up to 1.2×10^{-2} M β-CD solution. It was clear isosbestic point observed at 345 nm. From Fig. 4 it is clear that the fluorescence enhancement in β-CD. This suggests the formation of an inclusion complex between L-TYN and β-CD.

Both the emission bands (longer wavelength LW 405 nm, shorter wavelength SW 305 nm) of the full width at half of maximum (FWHM) increases with increase in β-CD concentrations, indicating that intramolecular interactions are greater than intramolecular hydrogen bond (IHB) interaction in β-CD solution. The increase in FWHM observed in both bands clearly establishes that the L-TYN (OH group) present in the interior part, exterior part contain COOH group with water molecule present in intramolecular hydrogen bond (or) 'N' atom lone-pair of electron interact in carboxylic acid H-atom due



Scheme 2. The proposed structure of inclusion complex of L-TYN with β-CD for 1:1 complex.

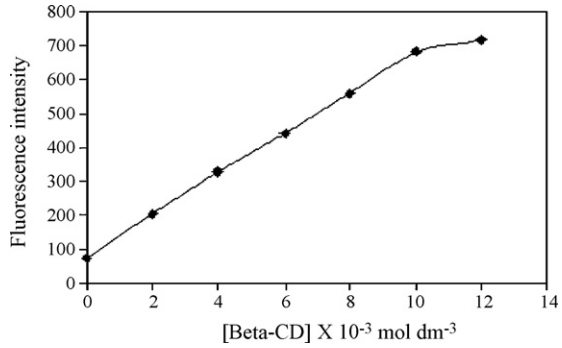


Fig. 5. The Fluorescence intensity of L-TYN changes at 410 nm with different β-CD concentrations.

to β-CD (Scheme 2). The formation of an inclusion complex between L-TYN and β-CD, the complexation is complete at 1.2×10^{-2} mol dm^3, β-CD and there is no change in the fluorescence intensity by β-CD and there is no change in the fluorescence intensity by further addition of β-CD (Fig. 5).

The equilibrium constant 'K' assuming the formation of a 1:1 L-TYN/β-CD can be calculated based on the Benesi–Hildebrand [33] plots using florescence data.

$$\frac{1}{I - I_0} = \frac{1}{I' - I_0} + \frac{1}{K[I' - I_0][\beta\text{-CD}]_0} \quad (2)$$

Where [β-CD] represents the initial concentration of β-CD 'I_0' and 'I' are the florescence intensities in the absence and presence of β-CD, respectively, and I' is the limiting intensity of florescence. The 'K' value where obtained from the slope and the intercept of the plots. The Benesi–Hildebrand plot (Fig. 6) shows excellent regression supporting the assuming 1:1 L-TYN/β-CD inclusion complex. From plot, 'K' is evaluated as 119.94 M^{-1} at 303 K. The binding constant is so small, as compared with other guest molecule β-CD complex as [28–31]. This is probably inter- and intramolecular hydrogen bond present in this molecule.

Naturally, two different types in the inclusion complex formation between L-TYN and β-CD are possible. One is with the –COOH group captured in β-CD cavity and the other is –OH groups captured (Scheme 2). Let us now consider the type-I arrangement, when the carboxyl group of L-TYN is entrapped with in the β-CD cavity, the L-TYN molecule is no longer able to make a H-bonding with the bulk aqueous solution (i.e.) hydrogen bonding interaction inhibited. Thus, if the hydrogen bonding interaction inhibited as in the β-CD inclusion complex the formation of the ICT state by direct excitation at 260 nm also be inhibited [34]. If in the case, L-TYN shows dual emission in β-CD medium. For type-II encapsulation, the cavity will impose a restriction about the free rotation of the CH_2 (alkyl groups) group in its excited state. For this type of complex, making hydrogen bond with the aqueous solution is very much possible as the carboxyl group is available in the bulk solution [35]. Hence, ICT emission intensity remains almost unaltered because the ICT state not depends upon rotation of carboxyl attached alkyl groups, but it depends only on hydrogen bonding between solute and solvents. These features again support the idea that the ICT state in water is further stabilized through exciplex formation between L-TYN and water.

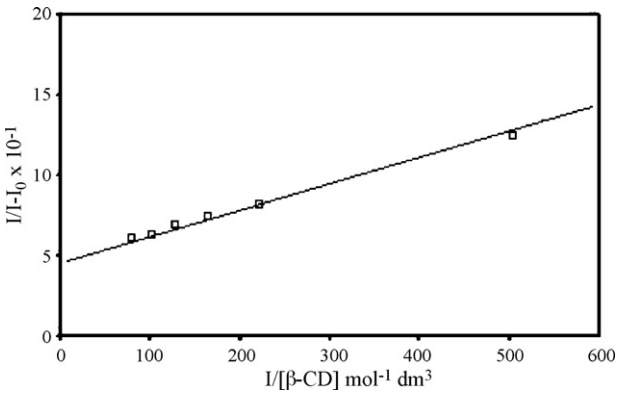


Fig. 6. Benesi–Hildebrand plot of $1/I - I_0$ vs. 1/[β-CD] for L-TYN.

3.2. The thermodynamics of inclusion process

The determination of thermodynamic parameters, here were three parameters in the inclusion process The thermodynamic parameters ΔG, ΔH and ΔS for the association of the guest molecule to β-CD is given in Table 1. The free energy change can be calculated from the formation constant 'K' by Eq. (3).

$$\Delta G = -RT \ln K \quad (3)$$

As can be seen from Table 1, ΔG is negative which suggested that the inclusion process proceeded spontaneously at 303 K. ΔH and ΔS are also negative in the experimental temperature range which indicates that the inclusion process was an exergonic and enthalpy controlled process. The negative enthalpy change arose from the Vander Waal's interaction, while the negative entropy change was 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.

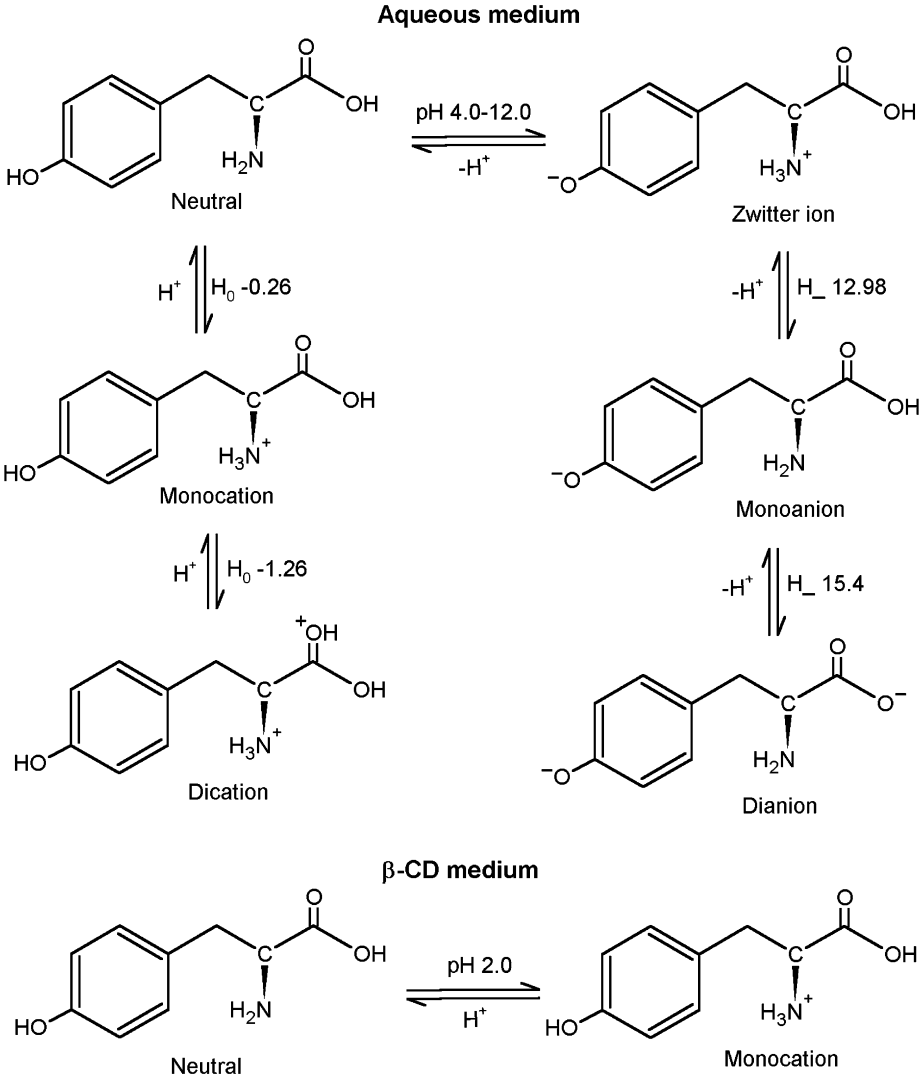
3.3. Effects of pH with β-CD medium

The absorption and fluorescence spectra of L-TYN have been studied in the pH range H_0 −1 to pH ≈ 11 in β-CD medium (Table 2). There are six prototropic species (dication, monocation, Zwitter ion, neutral, monoanion and dianion) present in aqueous medium. But in the case of β-CD medium present only two species (neutral and monocation) in β-CD medium cannot determine pK_a and pK_a^* values for zwitter ion because zwitter ion does not exist consistency pH value (Scheme 3). When compared to aqueous medium some appreciable change in absorption maxima of neutral to monocation.

The pH dependent changes in the absorption and fluorescence spectra of the L-TYN molecule in aqueous solution containing β-CD have been recorded and are shown in Table 2 and Figs. 7 and 8. The equilibrium of L-TYN could be due to the presence of different resonating structure as shown in Scheme 3. The absorption and emission maxima of L-TYN have been in 1.2×10^{-2} M β-CD aqueous solutions in the pH range

Table 2
Various prototropic maxima (absorption and fluorescence) of L-TYN in with and without β-CD medium

Species	With β-CD				Without β-CD			
	λ_{abs}	pK_a	λ_{flu}	pK_a^*	λ_{abs}	pK_a	λ_{flu}	pK_a^*
Dication	266.9 216.0	−1.26	411	−1.15	–	–	–	–
Monocation	274.5 222.5	−0.26	422 302	−0.20	241 218	−1.98	435 325	−2.24
Neutral	266.5 225.6	4.0	408 390	4.0	275 225	4.5	440 336	4.3
Zwitter ion	277.7–267.0 243.2–222.8	4.0–12.0	–	–	–	–	–	–
Monoanion	260 215	12.98	422	14.8	–	–	–	–
Dianion	285	15.40	–	Quench	–	–	–	–



Scheme 3. Various prototropic equilibria of L-TYN in aqueous and β-CD medium.

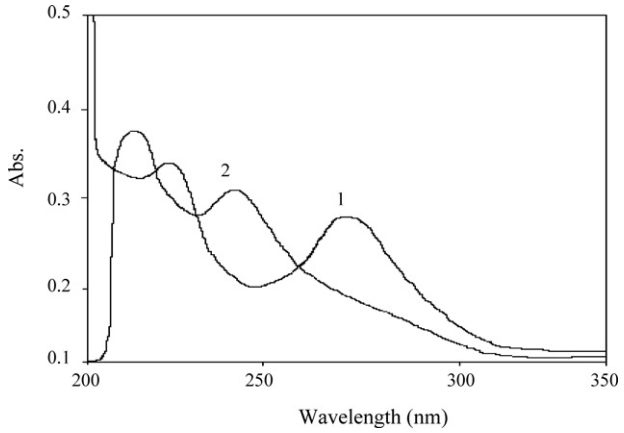


Fig. 7. Absorption spectra of L-TYN in different prototropic species at 303 K: concentration 1×10^{-5} M. (1) Neutral and (2) monocation.

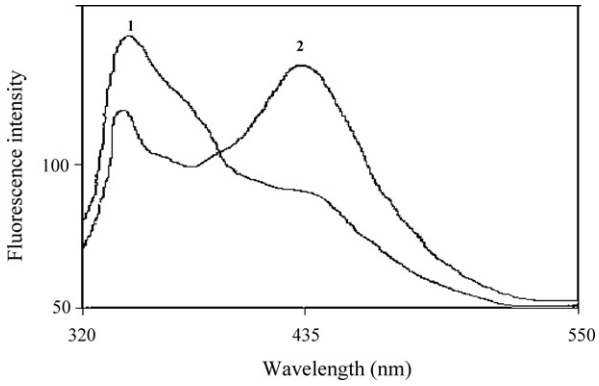


Fig. 8. Fluorescence spectra of L-TYN in different prototropic species at 303 K: concentration 1×10^{-5} M. (1) Neutral and (2) monocation.

pH ≈ 0.1–11. No noticeable change is observed in the absorption maxima of the monocation whereas blue shift is observed in neutral and monocationic of L-TYN in β-CD, then aqueous medium. However, in the excited state, a small blue shift is observed in neutral and monocation, where as the change in emission maxima of monoanion are negligible. This behaviour is different from its ground state, because in the excited state amino group becomes more acidic, where as –COOH group becomes more basic. Further, ICT emission also inhibited in the β-CD medium. Hence a small blue shift emission is observed in neutral and monocation, further the pK_a (pK_a^*) values for the monocation–neutral equilibrium of L-TYN in β-CD is higher than aqueous medium, whereas neutral–monocation equilibrium pK_a (pK_a^*) values is higher than aqueous medium. This finding confirms L-TYN molecule encapsulated in the β-CD cavity.

3.4. FT-IR—spectral studies

The FT-IR spectra of L-TYN, β-CD and the solid inclusion complex. In L-TYN, carboxylic acid OH stretching absorption in the region 2596 cm^{-1} is shifted to 2601 cm^{-1} in the solid inclusion complex. The phenolic OH group appears 1104 cm^{-1} in L-TYN whereas it is shifted 1108 cm^{-1} in solid inclusion complex. Further, the absorption intensity in inclusion complex

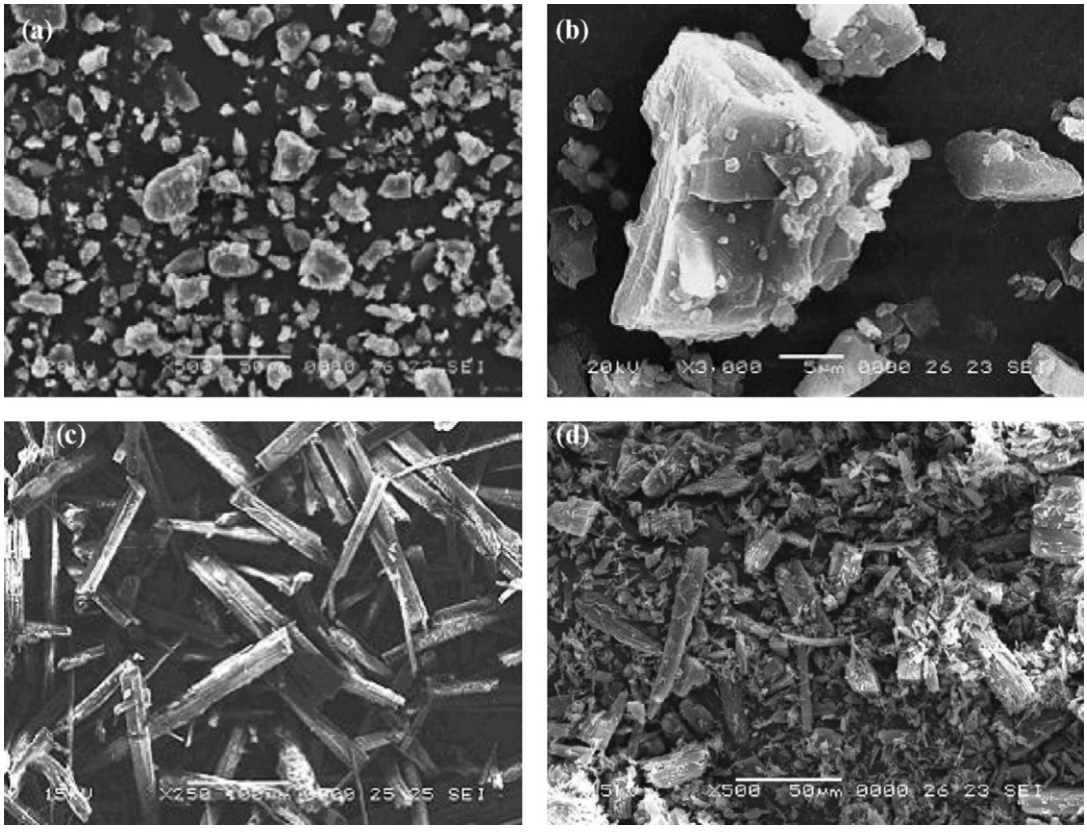


Fig. 9. Scanning electron microscope photographs (Pt coated) of (a) β-CD × 500, (b) β-CD × 3000, (c) L-TYN × 100 and (d) L-TYN–β-CD complex.

was significantly greater than in L-TYN. The inclusion complex FT-IR peaks in the range 1000–2000 cm^{-1} are 30–50% than the free L-TYN molecule. So we can deduce the phenolic group of L-TYN is included into the cavity of β-CD.

3.5. Microscopic morphological observation

First, we observed powdered form of L-TYN and β-CD by scanning electron microscope, then we also observed powered form of inclusion complex (Fig. 8). β-CD shows plated/sheeted structure, L-TYN shows irregular arrangement structure and the solid inclusion complex structure is different from β-CD and L-TYN. Pictures clearly elucidated the difference of powder of each other. Modification of crystal and powder can be assumed as a proof of the formation of new solid inclusion complex (Fig. 9).

4. Conclusion

The following conclusion can be arrived at from the above studies; (i) L-TYN forms 1:1 complex with β-CD; (ii) proton transfer reactions in β-CD medium indicates, OH group present in the interior (non-polar) of the β-CD cavity; (iii) whereas COOH group present in the upper (polar) part of the β-CD cavity; (iv) FT-IR and SEM results suggest L-TYN formed a solid inclusion complex with β-CD; (v) the above studies demonstrate that in L-TYN, ICT/IHB interactions play a significant role in β-CD aqueous/polar medium.

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