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ORIGINAL ARTICLE

Spectroscopic studies on the inclusion complex formation between 7-iodo-8-hyroxyquinoline-5-sulfonic acid and β-cyclodextrin

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Abstract Formation of an inclusion complex between 7-iodo-8-hyroxyquinoline-5-sulfonic acid (IHQS) and β-cyclodextrin is studied by spectrophotometry and ^{1}H NMR techniques. Spectral changes in the emission spectra upon the addition of β-cyclodextrin to IHQS in aqueous media were too small to allow for the determination of the binding constant. On the other hand; absorption spectra show a pronounced changes upon the addition of β-cyclodextrin that allowed for the determination of the binding constant. Absorption measurements show 1:1 inclusion of IHQS in the β-cyclodextrin cavity with an association constant of 135 ± 25 M^{-1}. ^{1}H-NMR studies are used to confirm the inclusion and to provide information about the geometry of IHQS inclusion in the cavity of β-cyclodextrin.

Keywords Inclusion complexes · β-cyclodextrin · Spectrophotometry · 8-hydroxyquinoline · Benesi–Hildebrand · ^{1}H-NMR

Introduction

Proton transfer reactions play a fundamental role in a variety of chemical and biological processes [1–9]. A comprehensive understanding of the mechanisms and dynamics of these reactions is, therefore, of great importance. Photoacids undergo an acidity enhancement upon photo-excitation and have a relevant role in technological applications, as well as in many biological processes [10]. The study of photoacidity phenomenon is of great interest both from basic science perspective, because it allows the investigation of fast proton-transfer reactions and, from a practical point of view, as a means of generating protons at a specified instant of time [11].

Cyclodextrins (CDs) are shaped like a truncated cone polysaccharides made up of six to eight D-(+) glucopyranose monomers connected at the 1 and 4 carbon atoms. The cavities of CDs are relatively hydrophobic and have an internal diameter of 4.7–8.3 A^o [12]. This difference in cavity size allows binding specificity to be tailored based on substrate size and geometry. It is known that cyclodextrins (CDs) have the property of forming inclusion complexes with guest molecules with suitable characteristics of polarity and dimension [13]. This ability has been widely used in studies of general inclusion phenomena and enzyme–substrate interactions [14], applied in food and pharmaceutical industries, [14–16], and has also been used for analytical purposes [17–21].

The behavior of bifunctional molecules, which can serve as prototypes for structurally related subunits in many important biomolecules, has attracted the attention recently. In these bifunctional molecules, proton transfer from a hydroxyl or amino proton to an acceptor such as a carbonyl oxygen or a nitrogen atom is a fundamentally important reaction playing a crucial role in many biological and photochemical processes [22–24].

8-Hydroxyquinoline and its derivatives have found extensive applications as analytical reagent in absorption spectrophotometry and fluorometry because of their ability to form complexes with many metal ions [25–35].

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It has been experimentally found that the hydroxyquinoline derivatives have an intense fluorescence in concentrated acids, lack of fluorescence in water or alkanes, formation of the H-bonded complexes with water or alcohol molecules and very low quantum efficiency for singlet–triplet intersystem crossing [36]. The donor acidic and acceptor basic groups are in close proximity and hydrogen-bonded to each other in 8-HQ. The intramolecular proton-transfer process could occur in the ground and excited states.

Although a large number of systems are capable of forming inclusion complexes with CDs, the changes in the photophysical properties on encapsulation are, in many cases too small to provide any meaningful and reliable information on the micro-heterogeneity of the CD or the location of the probe. This necessitates further studies of the complexation processes involving probes whose photophysical properties are sensitive to any change in the environment. In the majority of inclusion complexes with β-cyclodextrin changes in the fluorescence of the guest compounds were used to study the formation constants while changes in the ground state were minimal. We have previously [37–40] examined the effect of inclusion on the intramolecular excited state proton transfer for different 1-naphthol and 2-naphthol derivatives and found that changing the substituent position has clearly affected the emission characteristics of the host. Fluorescence emission measurements were used to determine the association while the changes in the absorption spectra were too weak to follow the inclusion process.

In contrast to the previously studied systems [36–39] 7-iodo-8-hyroxyquinoline-5-sulfonic acid has very weak fluorescence in neutral solution, however changes in the absorption spectra upon inclusion inside β-cyclodextrins are very pronounced. An explanation for such behaviour is given and ^{1}H NMR technique is used to confirm the inclusion processes and to give an idea about the geometry of inclusion. Such an inclusion would improve the sensitivity of the fluorescence methods used for the determination of metal cations upon their complexation with 8-hydroxyquinoline derivatives.

Experimental

7-iodo-8-hyroxyquinoline-5-sulfonic acid (IHSQ) was obtained from Aldrich and recrystallized from ethanol. β-Cyclodextrin was obtained from Aldrich and used as received. Doubly distilled water was used. Concentrations of IHSQ were 2×10^{-5} M, while those of β-cyclodextrin were around 0.1 mM to maximum solubility.

Absorption spectra were recorded on an Agilent diode array 8453 spectrophotometer. Steady state fluorescence measurements were obtained using a Shimadzu 5301 spectrofluorophotometer. NMR spectra were recorded in D_2O on a Varian Mercury VX-300 spectrometer. ^{1}HNMR data analysis was carried out using MestReC 4.9.9 software. Chemical shifts have been expressed in parts per million (ppm) relative to HDO signal as a reference at 4.80 ppm. For ^{1}H NMR measurements, the concentrations of IHSQ and β-CD were about 2×10^{-3} M and 0.02 M respectively. All measurements were carried out at 25 °C.

Results and discussion

Figure 1 shows the absorption spectra of IHSQ in aqueous solution containing various concentrations of β-CD. When β-cyclodextrin is added to IHSQ, the absorbance at 250 nm is increased while that at 285 nm decreases with an enhancement of the absorbance in the range of 326 nm with two isosbestic points at 264 and 300 nm. The absorption spectral changes indicate the formation of inclusion complex between IHSQ and β-cyclodextrin.

For 1:1 inclusion complex formed between IHSQ and β-CD, the equilibrium can be written as:

$$\mathrm{IHSQ} + \beta\mathrm{-CD} \leftrightharpoons \mathrm{IHSQ} - \beta\mathrm{-CD} \quad (1)$$

The association constant can be determined according to the Benesi–Hildbrand relation [41] for a 1:1 host–guest complex:

$$\frac{1}{\Delta A} = \frac{1}{\Delta\varepsilon} + \frac{1}{K\,\Delta\varepsilon\,\beta\mathrm{-CD}} \quad (2)$$

where ΔA is the difference between the absorbance of IHSQ in the presence and absence of β-CD, $\Delta\varepsilon$ is the difference between the molar absorption coefficient of IHSQ and the inclusion complex and K is the association constant.

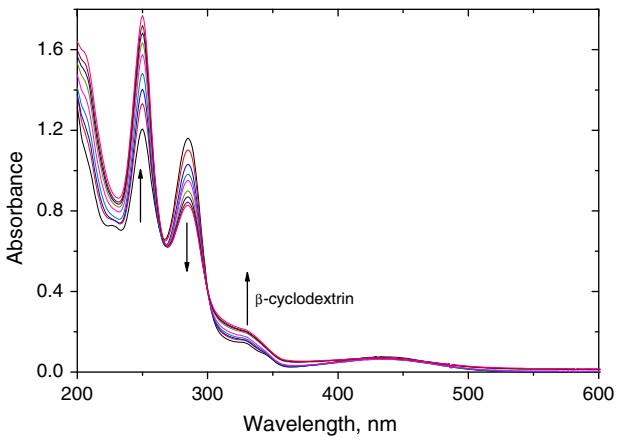

Fig. 1 The absorption spectra of IHSQ in aqueous solution and different concentrations of β-cyclodextrin (from 0 to 8 mM β-CD)

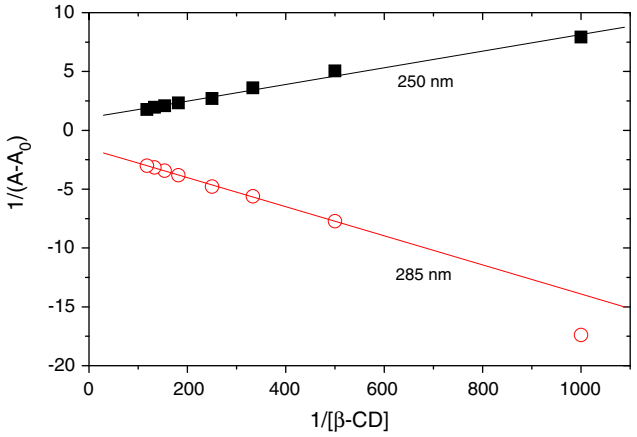

Fig. 2 The Benesi–Hildbrand plot of $1/(A - A_0)$ versus $1/[\beta\text{-CD}]$

A linear plot (Fig. 2) is obtained according to Eq. 2 which suggests that IHSQ-β-CD inclusion complex has a 1:1 stoichiometry. The association constant, K, for the formation of the inclusion complex is determined from the ratio of intercept to slope in the linear Benesi–Hildbrand plot and found to be $135 \pm 25\ M^{-1}$.

It has been reported that the poor fluorescence emission from 8-hydroxyquinolines results from a photoinduced tautomerization reaction followed by deexcitation of the tautomer which occurs via a nonradiative route especially in aqueous medium [42]. Even though, the weak emission of IHQS shows an enhancement upon the addition of β-cyclodextrin, the changes were too small to allow for the determination of the association constant.

Further support for the inclusion of IHQS inside β-CD cavity was obtained using proton nuclear magnetic resonance (^{1}H NMR) measurements, which has been proved to be useful tool in the study of cyclodextrin inclusion complexes [37–40, 42–52]. The information gained from NMR spectroscopy relies on the observation of selective line broadening and/or chemical shift displacement of ^{1}H NMR spectral signals of the guest and host protons [37–40, 42–58].

The chemical shift of β-CD protons (Fig. 3a, solid lines) reported by different authors were very close to those in this work $\pm$ 0.05 ppm [37–40, 44, 46, 56, 57]. It is well known that H-3 and H-5 protons are located in the interior of the β-CD cavity; therefore, it would be expected that the inclusion of IHQS with β-CD will specifically affect the chemical shifts of these two protons.

Addition of IHQS to β-CD causes an upfield shift of β-CD spectrum (Fig. 3a, dotted lines). The ^{1}H NMR spectrum of IHQS-β-CD show that the signal due to H-4 is the least affected and upfield shifted by about 0.004 ppm. H-1 and H-2 show also an upfield shift by 0.008 and 0.001 ppm respectively. The signal due to H-3 is upfield

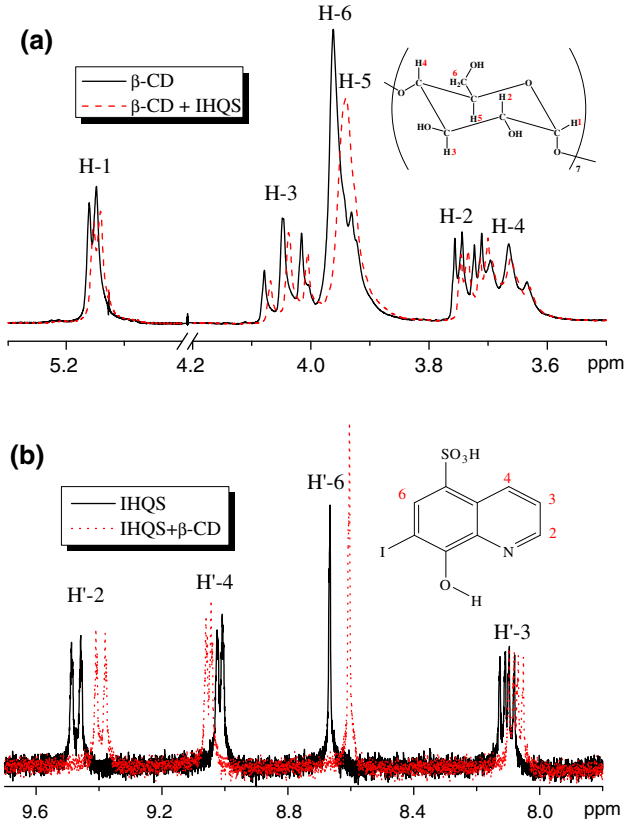

Fig. 3 **a** 300 MHz ^{1}H NMR spectra of β-cyclodextrin in the presence and absence of IHQS in D_2O. **b** 300 MHz ^{1}H NMR spectra of IHQS in the presence and absence of β-cyclodextrin in D_2O

shifted by about 0.012 ppm, while the unresolved band due to H-5 and H-6 protons shows an upfield shifted with difficulty assigning the value of chemical shift for each proton. Even though the chemical shifts observed for β-CD ^{1}H NMR spectrum are not as strong as observed previously for naphthol derivatives [37–40]; the observed chemical shifts suggest that IHQS interacts with the internal protons of β-CD.

Further confirmation is obtained by following the changes in the chemical shifts of IHQS. The ^{1}H NMR spectrum of IHQS is shown in Fig. 3b and reveals that IHQS has three types of protons. Two doublets centred at 9.017 and 9.473 ppm for H′-4, H′-2 respectively, one singlet for H′-6 at 8.666 ppm and multiplet for H′-3 centred at 8.103 ppm. The chemical shift values given by the ChemDraw version 8 NMR calculations are in accordance with these assignments. Addition of IHQS to the solution of β-CD results in much pronounced changes in the ^{1}H NMR spectrum of the guest than observed previously for naphthol derivatives [37–40]. The signals of H′-2 and H′-6 show the highest observed shifts as 0.077 and 0.062 ppm respectively. The multiplet due to H′-3 shows an upfield shift of about 0.029 ppm. H′-4 signal shows a downfield shift of about 0.034 ppm.

In other words, the signals due to H′-2 and H′-6 protons are the most affected upon inclusion; therefore, it can be concluded that IHQS is inserted inside the cavity with these protons closer to the interior protons of β-CD (H-3 and H-5) than the other IHQS protons.

The observed upfield shift of β-CD protons together with the fact that IHQS protons are shifted unequally gives the conjecture that the insertion of IHQS inside β-CD cavity is asymmetrical.

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