



## Study of $\beta$ -Cyclodextrin Effect on Acidity Constant of 2-(2*H*-Benzo(d)(1,2,3)triazol-2-yl)- phenol by Spectrophotometry

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**Abstract:** The interaction of solutes with  $\beta$ -cyclodextrin leads to apparent changes in their chemical properties, such as shifts in their absorption spectra and acid-base equilibrium. Formation of inclusion complexes between acid and/or base forms of a compound with  $\beta$ -CD can change the amount of conditional acidity constant. The acidity constants of 2-(2*H*-benzo(d)(1,2,3)triazol-2-yl)phenol ( $C_F$ ) in water and in the presence of varying amounts of  $\beta$ -cyclodextrin at 25 °C and an ionic strength of 0.1 M have been determined spectrophotometrically. To evaluate the pH-absorbance data, a resolution method based on the combination of soft- and hard-modeling is applied. The acidity constant of all related equilibria are estimated using the whole spectral fitting of the collected data to an established factor analysis model. DATAN program was applied for determination of acidity constant. The  $pK_a$  value of  $C_F$  is  $8.50 \pm 0.10$ . The  $pK_a$  value is decreased by increasing  $\beta$ -CD concentration.

**Keywords:** 2-(2*H*-benzo(d)(1,2,3) triazol-2-yl) phenol,  $\beta$ -cyclodextrin, Acidity constant, DATAN.

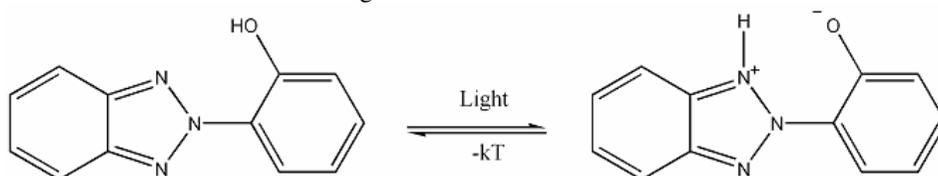
### Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides composed of D(+) glucopyranose units with the shape of a torus. To a first approximation they can be regarded as cylinders with a hydrophilic exterior and a hydrophobic interior. In aqueous solutions, the insertion of a hydrophobic guest in to the cyclodextrin molecule results complexation in which no covalent bonds are broken or formed. During formation of the inclusion complex the main driving force of complex formation is release of enthalpy-rich water molecules from the cavity. Water molecules are displaced by more hydrophobic guest molecules present in the solution to attain an apolar–apolar association and decrease of cyclodextrin ring strain resulting in a more stable lower energy state<sup>1</sup>. Due to their unique ability to form inclusion

complexes with numerous compounds CDs are frequently applied in various fields of chemistry<sup>2</sup>. As a result of this inclusion a change of the chemical or physical properties of the guest molecule is generally observed opening a wide field of applications in areas such as organic and analytical chemistry<sup>3</sup>.

The interaction of solutes (small and medium-sized organic molecules) with  $\beta$ -cyclodextrin leads to apparent changes in their chemical properties, such as shifts in their absorption spectra and acid–base equilibrium. Formation of inclusion complexes between acid and/or base forms of a compound with  $\beta$ -CD can change the amount of conditional acidity constant,  $k' A, C$ , *i.e.* the  $\beta$ -CD concentration dependent acidity constant. The change in acidity constant depends on the relative stability of the inclusion complexes of acidic and basic forms of the compound with  $\beta$ -CD. Preferential inclusion of acid form causes a decrease in conditional acidity constant and preferential inclusion of basic form causes an increase in it.

2-(2*H*-Benzotriazol-2-yl)phenolic compounds are useful as ultraviolet absorbers, as well as their utilization in polymers, dyes and cosmetics. When 2-(2*H*-benzotriazol-2-yl)phenolic ultraviolet absorbers are mixed with polymers or the other substances, the weight of formers are usually <1% of that of the latter's. The function of these compounds is to change the energy of ultraviolet light to heat energy and it differs from that of hindered phenols or hindered amines to make the chain reaction of generated active radicals impossible. UV absorption causes the electron density to move from the phenolic oxygen to the nitrogen atom. The nitrogen becomes more alkaline than the oxygen as a result and a proton transfer occurs. This mesomeric form represents an excited state, which stabilizes as a result of a radiationless transition to the ground state. The typical protection mechanism of benzotriazole is illustrated in the Figure 1<sup>4</sup>.



**Figure 1.** The typical protection mechanism of benzotriazole

Dissociation constants can be a key parameter for understanding and quantifying chemical phenomena reaction rates, biological activity, biological uptake, biological transport and environmental fate<sup>5</sup>. Several methods for the determination of dissociation constants, such as potentiometric titration, spectrophotometric determination and conductometry, have been reported<sup>6,7</sup>.

Spectrophotometric methods are in general highly sensitive and as such are suitable for studying chemical equilibria in solution. When the components involved in the chemical equilibrium have distinct spectral responses, their concentrations can be measured directly, and the determination of equilibrium constant is trivial. Several spectrophotometric methods have been developed to determine the equilibrium constants of chemical processes. Occasionally, problems arise because of strong overlapping of chemical components involved in equilibrium and some uncertainties from using some complex mathematical algorithms, to solve such problems<sup>8-10</sup>. However, much more information can be extracted if multivariate spectroscopic data are analyzed by means of an appropriate multivariate data analysis method.

Data analysis was carried out by DATAN package that developed by Kubista group<sup>10-12</sup>, called the physical constraints approach, which provides a unique solution by requiring that the calculated concentrations obey an assumed equilibrium expression and demonstrates its applicability by determining the acidity constants of two and four protolytic forms of fluorescein. A possible advantage of the Kubista *et al.* method is that it mixes a soft-modeling approach with a hard-modeling approach. This might be best and more general strategy, since it can handle different situations, with only a partial knowledge of the chemistry of the system. The physical constraints method calculates spectral profiles, concentrations and equilibrium constants by utilizing equilibrium expressions that related the components. The theory and application of physical constraints method were discussed by Kubista *et al.* in several papers<sup>13-17</sup>.

In this work, we applied the physical constraints approach to determine the acidity constants of 2-(2*H*-benzo[d][1,2,3]triazol-2-yl)phenol ( $C_F$ ) in pure water, water-cyclodextrin media solutions at  $25 \pm 0.5$  °C and an ionic strength of 0.1 M spectrophotometrically.

## Experimental

2-(2*H*-benzo(d)(1,2,3)triazol-2-yl)phenol ( $C_F$ ),  $\beta$ -cyclodextrin, hydrochloric acid, sodium hydroxide and potassium nitrate were analytical grade commercial and products from Merck. These reagents were used without further purification. Standard stock solution of  $1 \times 10^{-3}$  M of  $C_F$  was prepared by dissolving appropriate amounts of  $C_F$  in water. The stock solution of  $\beta$ -cyclodextrin was prepared by dissolving weighted amounts of substances in appropriate amounts of water. All of the solutions were prepared in deionized water.

### Instrumentation

A Jasco (V-530) spectrophotometer controlled by a computer and equipped with a 1 cm path length quartz cell was used for UV-vis spectra acquisition. Spectra were acquired between 300 and 600 nm. A Denver ub-10 pH-meter furnished with a combined glass-saturated calomel electrode was calibrated with at least two buffer solutions at pH 4.01 and 9.21 (which pH adjustment contains error with respect to the direct use of the buffer solutions).

### Computer hardware and software

All absorption spectra were digitized at five data points per nanometer in the wavelength 300-600 nm and transferred (in ASCII format) to a 2006 XP (1.00 GB RAM) computer for subsequent analysis by MATLAB software, version 6.5 (The Math Works) or for processing by using DATAN package.

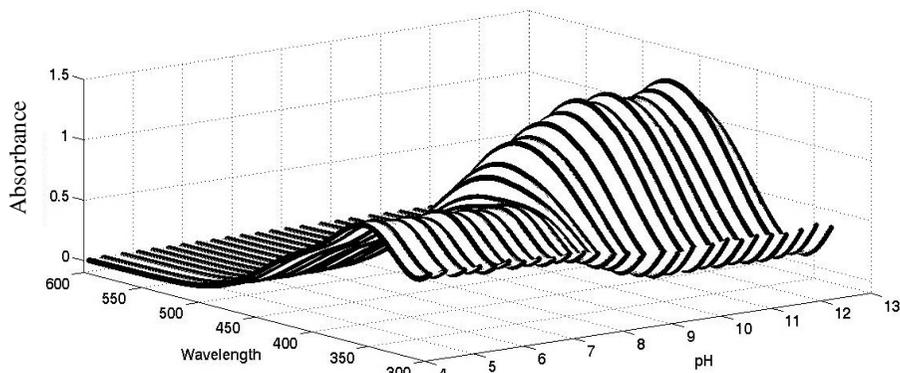
### Spectrophotometric titrations

For the  $C_F$  ( $1 \times 10^{-3}$  M) in pure water, water-cyclodextrin mixtures titration, absorption spectra were measured with a titration set-up consisting of a computer interfaced to a spectrophotometer. After each pH adjustment, solution is transferred into the cuvette and the absorption spectra are recorded. Ionic strength was maintained at 0.1M by adding appropriate amounts of  $KNO_3$ . All measurements were carried out at the temperature ( $25 \pm 0.5$  °C).

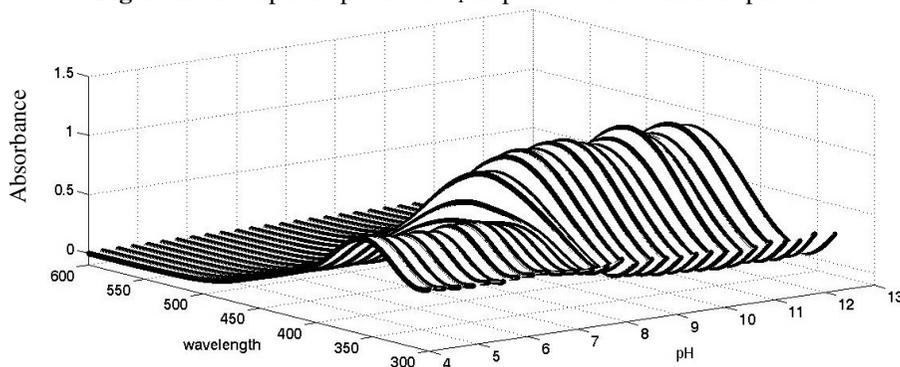
## Results and Discussion

The UV-Vis spectra of 2-(2*H*-benzo(d)(1,2,3)triazol-2-yl)phenol in pure water at various pH values at 300-600 nm were recorded. In order to determine the influence of the in  $\beta$ - cyclodextrin acidity constants, a series of experiments were run at different  $\beta$ -cyclodextrin concentration. To neglect the effect of variations in the ionic strength during titration, the ionic strengths of the solutions used were kept constant at 0.1 M using potassium nitrate as a supporting

electrolyte. Three-dimensional electronic absorption spectra of 2-(2*H*-benzo[d][1,2,3]triazol-2-yl)phenol in pure water water-cyclodextrin are shown in Figures 2&3.



**Figure 2.** Absorption spectra of  $C_F$  in pure water at different pH values



**Figure 3.** Absorption spectra of  $C_F$  in water- $\beta$ -CD ( $6 \times 10^{-3}$  mol  $L^{-1}$ ) solutions at different pH values

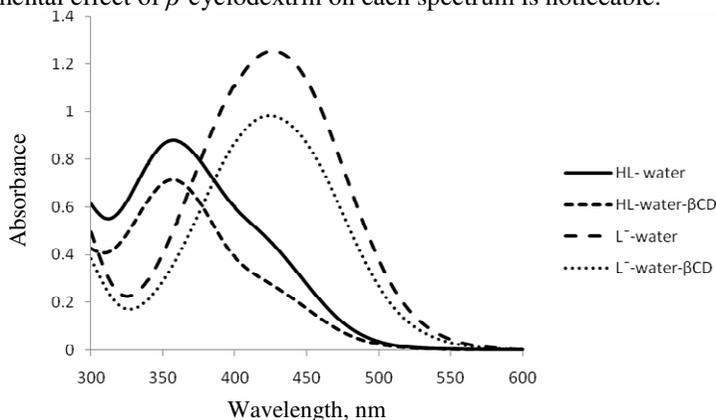
The principal component analysis (PCA) of all spectra data matrices shows at least two significant factors. These two factors are attributed to the protonated and deprotonated forms of the mono-protic dye. From inspection of the experimental spectra it is hard to guess even the number of protolytic species involved. For determination of acidity constant of 2-(2*H*-benzo(d)(1,2,3)triazol-2-yl)phenol in several mixtures DATAN 3.1 was used. Output of DATAN program is pKa values, number of principal components, concentration distribution diagrams and pure spectrum of each assumed species. The pKa values of 2-(2*H*-benzo(d)(1,2,3)triazol-2-yl)phenol are listed in Table 1.

**Table 1.** Acidity constants of  $C_F$  in pure water and at different concentrations of  $\beta$ -cyclodextrin at 25 °C and constant ionic strength (0.1 M  $KNO_3$ )

$\beta$ -Cyclodextrin Conc., M	pKa <sub>1</sub>
0.0000	8.50±0.10
0.0008	8.29±0.11
0.0016	8.10±0.11
0.0032	7.91±0.13
0.0040	7.88±0.10
0.0060	7.88±0.12

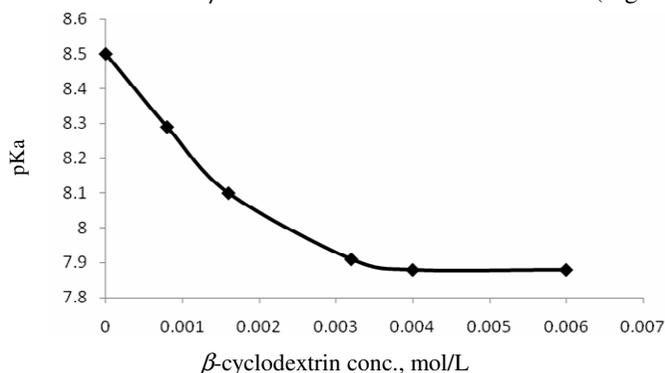
As Table 1 shows, the acidity constant of  $C_F$  decreases by increasing concentration of  $\beta$ -CD. As mentioned above the decrease in the acidity constants as a function of  $\beta$ -CD is due to more stabilization of basic form of  $C_F$  in the presence of  $\beta$ -CD, as a result of formation of a more stable inclusion complex than its acidic form, and driving the equilibrium to producing basic form.

DATAN program was used to obtain pure spectrum of 2-(2*H*-benzo(d)(1,2,3)triazol-2-yl)phenol in different  $\beta$ -cyclodextrin media. Sample spectrum of the calculated pure spectra of all species in pure water and water-cyclodextrin ( $6 \times 10^{-3}$  mol L<sup>-1</sup>) are shown in Figure 4. The fundamental effect of  $\beta$ -cyclodextrin on each spectrum is noticeable.



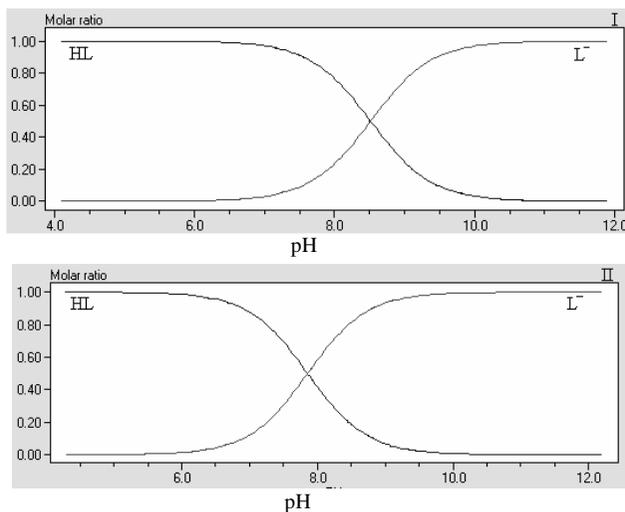
**Figure 4.** Sample spectrum of the calculated pure spectra of all species in pure water and water-cyclodextrin ( $6 \times 10^{-3}$  mol L<sup>-1</sup>)

Many papers and reviews have discussed the effect of  $\beta$ -cyclodextrin on the apparent pKa values<sup>18-20</sup>. In this work we observed the shift of spectrum in  $\beta$ -cyclodextrin media and then we calculated the pKa values of 2-(2*H*-benzo(d)(1,2,3)triazol-2-yl)phenol in this media system. The pKa value is changed in different concentrations of cyclodextrin. The pKa values are decreased with increase of cyclodextrin concentration. The changes in conditional acidity constant as a function of  $\beta$ -CD concentration were not linear (Figure 5).



**Figure 5.** The plot of pKa as a function of concentrations of  $\beta$ -CD

The most important features of distribution diagrams are the pH limit of evolving and disappearance of components. So, according to distribution diagrams it is concluded that the spectra at pH < 6.5 were assigned to HL form because this form is dominated at this pH range. At pH > 10.5 the L<sup>-</sup> form is dominated and hence the spectra mostly attributed to this form. Samples of obtained distribution diagrams are shown in Figure 6.



**Figure 6.** Distribution of major species of  $C_F$  as a function of pH for the spectral data of Figures 1-2, in (I) pure water and (II) water- $\beta$ -CD ( $6 \times 10^{-3}$  mol  $L^{-1}$ ) solution

### Conclusion

In this work, we distinguish the behavior of acidity constants of  $C_F$  in pure water and water- $\beta$ -cyclodextrin systems at  $25 \pm 0.5$  °C and ionic strength of 0.1 M that are studied by multi-wavelength spectrophotometric method. Results show that the  $pK_a$  values of  $C_F$  are influenced as the concentration of  $\beta$ -cyclodextrin added to the solution. DATAN is a useful tool for resolution of the different species present in equilibria systems. By using this method and without any prior knowledge about the system, we can obtain concentration profiles and pure spectra from the experimental data.

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