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Effect of pH on the encapsulation of the atrazine by β-cyclodextrin at 25°C

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ABSTRACT

The encapsulation of atrazine by β-cyclodextrin has been studied through UV absorption enhancement measurements in aqueous solutions at 25C. This study has been carried out at pH= 0.7, 4, 5,9 and 11. Since the pKa of the atrazine system is 1.68 at 25°C, the protonated (HA) of atrazine should be present at pH less than 1.68. The association constants K of β-CD/atrazine have been determined at different values of pH by using linear and nonlinear regression analysis of the experimental data.The K values obtained were 311 ± 15; 254 ± 15 and 150 ± 15 at the pH 5; 7.3 and 9 respectively.

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KEYWORDS

Cyclodextrin;
UV absorption;
Inclusion complex;
Molecular encapsulation;
pH effect;
Atrazine.

INTRODUCTION

Cyclodextrins are well known as host molecules with an apolar cavity in which different types of guest molecules can be partially or totally included, have been employed in the investigation of photo-physical process[1-5]. Aqueous solutions of cyclodextrins have also been widely used to enhance the luminescence properties of different compounds[6-10].

The intensification of the luminescence of guest in CD cavity is a result of the better protection from quenching and other processes occurring in the bulk solvent. The CD cavity facilitates the inclusion of an apolar and a non-hydrated molecules.

The maximum absorbance or fluorescence intensities are obtained from a molecule which is totally encapsulated inside the cavity.

The observation of steady-state spectroscopic characteristics can be used as an indication of complexation. When the fluorescence or the absorption spectra of a fluorophore in an aqueous environment changes markedly on addition of cyclodextrin to the aqueous solution.A great number of references in the literature[6-16] use this change in the spectroscopic properties of the guest encapsulated by the cyclodextrin (CD) to study the binding process through the association constant K [CD/Guest], and in many of these references the Guest is an acid/base conjugated system[11-16]. The acid/base system is very dependent on the pH of the bulk solution, since this parameter will 'decide' the behavior of the species to be encapsulated by the CD.

Because of the relatively low pKa value of the atrazine group (pKa 1.68) all of the N atoms should be protonated in a pH less than 1.68 which indicates that the N-terminals of the guests should exist as NH_3^+ at pH 1.0. That is to say, in an acidic media (pH 2.0),

TABLE 1 : Composition of the samples used to study the effect of pH on the UV absorption spectra of atrazine in β-cyclodextrin solutions

pH of the sample to be measured	4	6.8	9.5
Volume of atrazine solution (10ppm) mL) prepared in the adequate buffer solution	5	5	5
Volume of β-cyclodextrin solution 0.1mol/L (mL) prepared in the adequate buffer solution	5	5	5

TABLE 2 : The Changes of Ka with the pH values

pH	5	7.3	9
Association constant Ka of atrazine/ β-CD Mol^{-1}	311±10	254 ±10	150 ±10

both host and Guest are positively charged, which will inevitably lead to unfavorable electrostatic repulsions between host and guest. This phenomen indicates that the protonation effect can affects the binding ability of β-cyclodextrin with atrazine[14].

in this work we studied the effect of pH starting from pH= 0.7 to pH= 11, on the encapsulation of atrazine into the cavity of β-cyclodextrin.

EXPERIMENTAL

Instruments

The UV absorption measurements were performed on a Shimadzu UV- 1650 PC. with 10mm quartz cells were used for spectrophotometric measurements.

The pH values are measured using METTLER TOLEDO pH-meter.

Reagents

β-cyclodextrin,hydrochloric acid, mono and dihydrogeno phosphate were purchased from Sigma Aldrich, and used as received. Atrazine was purchased from Rodel-dehein. Distilled water was used to prepare aqueous solutions of β-cyclodextrin and atrazine stock solutions.

Procedures

Preparation of the inclusion complex

Stock standard atrazine solution was freshly prepared by dissolving atrazine crystals in di-ionized water. After stirring for 10 minutes, the solution was filtered to remove any undissolved atrazine crystals. The resulting concentration of the atrazine stock solution was 10ppm (mg/L). Stock solutions of β-CD, (0.01 $mol.L^{-1}$) were freshly prepared in distilled water, and serial dilutions were made from these stock solutions. The different inclusion complexes were prepared by transferring an adequate volume of the atrazine standard solution into a 10ml volumetric flask and completing with the required β-CD. The solutions were then vigorously shaken for 5 minutes before measurements.

Stoichiometry of the inclusion complex

The stoichiometry of [β-CD/atrazine] complex was analyzed by the Scatchard and Benesi-Hildebrand plots[18,19].

According to Scatchard's method (Eq. (1)), we assume that β-CD forms an inclusion complex with atrazin in a 1:1 ratio. For such complex, a plot of $(A-A_0)/[\beta\text{-CD}]$ versus $(A-A_0)$ should give a straight line.

$$\frac{(A-A_0)}{[\beta-CD]_0} = (A_\infty - A_0)K_1 - (A-A_0)K_1 \qquad (1)$$

where A_0 is the absorbance intensity of atrazine in the absence of β-CD; $A\infty$ is the absorbance intensity when all guest molecules are essentially complexed with β-CD; A is the observed absorbance at each β-CD concentration tested; K_1 is the association constant and $[CD]_0$ the β-CD concentration tested.

When a Benesi-Hildebrand plot of $1/(A-A_0)$ versus $1/[\beta\text{-CD}]$ is constructed (Eq. (2)), a straight line is obtained. When the plot of $1/(A-A_0)$ versus $1/\beta\,[\text{-CD}]^2$ is considered, a downward concave curvature is obtained, confirming that the stoichiometry of the[β-CD/atrazine] complex is not 1:2.

$$\frac{1}{(A-A_0)} = \frac{1}{(A_\infty - A_0)K_1[\beta-CD]_0} + \frac{1}{(A_\infty - A_0)} \qquad (2)$$

Association constant of the inclusion complex

Once the stoichiometry of the complex is known, the association constant can be calculated by applying the above described methods. According to the first method, the slope of the straight line gives the association constant. In the Benesi and Hildebrand's method, the association constant is determined by dividing the intercept by the slope of the straight line obtained in the double reciprocal plot.

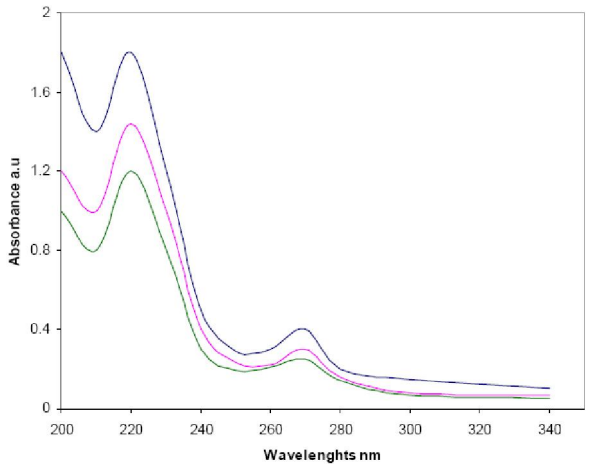

Figure 1 : UV spectra of atrazine aqueous solutions [5ppm] at pH = 4 - 6.8 - 9.5 respectively from top to down

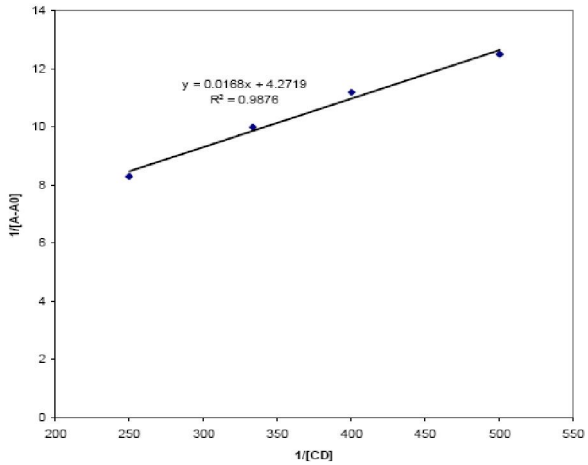

Figure 2 : Atrazine/beta cyclodextrin association constant according to Benesi-Hilderbrand

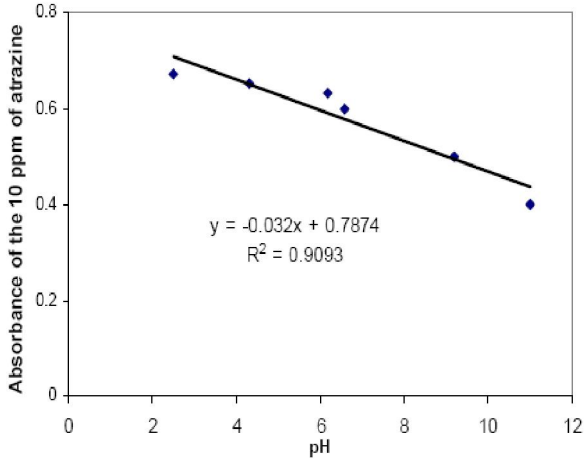

Figure 3 : The plot of the absorbance of at 223 n atrazine/ β-CD at different pH values.versus pH

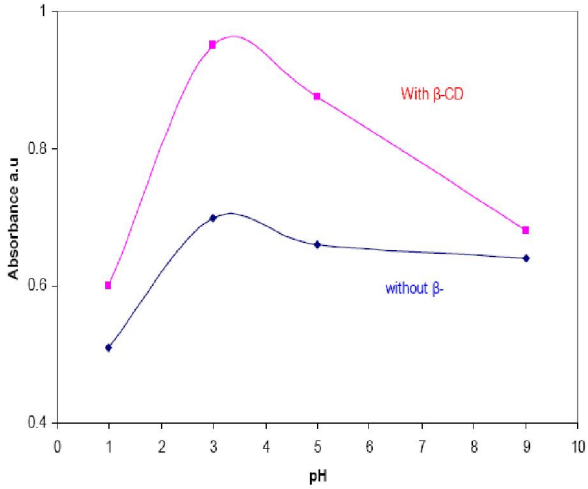

Figure 4 : The plot of absorbance versus pH

Non-linear regression method was also used to confirm the results obtained with the two methods. The non linear regression method is described in equation 3:

$$\Delta I = \frac{K_1 H_0 \Delta I_{max}}{(1 + K_1 H_0)} \quad (3)$$

where $\Delta I = (A\text{-}A_0)$ is the guest-induced absorbance intensity, and is equal to $\Delta_{max} = (A_\infty\text{-}A_0)$ when every host exists as the inclusion complex. Δ_{max} is obtained from the double reciprocal plot (Eq. (1)). H_0 is the initial concentration of host. The association constant (K_1) was estimated by fitting equation (3) to the obtained data.

Solutions

Atrazine standard solution (10ppm) was prepared by dissolving 0.001g of atrazine in 100mL of di-ionized water

A freshly prepared 0.1 M of β-cyclodextrin was used as stock solution.The dilution was carried out by using an adequate phosphate buffer. The pH of the samples were checked before each measurement. The samples used to study the effect of pH on the UV spectra of atrazine dissolved in aqueous solutions were prepared according to the composition described in the TABLE 1.

The solutions used to built the linear and nonlinear regression were prepared as follow:

3mL β-cyclodextrin of atrazine solution (10ppm) were transferred into glass tubes of 20mL. The volumes of β-cyclodextrin (0.01M) solutions which also transferred into the tubes were respectively [0, 0.5, 1, 1.5, 2, 2.5, 3 and 4mL]. An adequate buffer solutions were added to the mixture in order to reach the total volume of 10mL. After shaking UV absorption spectra were recorded for the samples.

RESULTS AND DISCUSSION

Effect of pH on the UV absorption spectra of atrazine/β-cyclodextrin

Ultraviolet (UV)-visible spectra of atrazine in aqueous β-cyclodextrin solutions at different pH were obtained scanning the wavelengths between 200 and 400nm with a Shimadzu UV- 1650 PC (Kyoto, Japan) UV-visible spectrophotometer. Measurements were performed just after preparation and shaking the samples. Atrazine has an absorption maximum at 223nm.

The UV-visible spectra of atrazine,at the same concentration, change with the pH values. It has been observed, as shown in the figure 1, that the absorbance intensity decreases with increasing of pH starting from 4 to reach 9.5.

Determination of the association constant (atrazine/β-CD) at different pH values

UV/VIS spectra were obtained for atrazine and β-CD complex in buffered aqueous solutions at pH 4, 6, 8 and 9, 5 respectively as mentioned above. For each values pH we fixed the concentration of atrazine (5ppm) and the concentrations of β-cyclodextrin were changed from (1×10^{-3}) to (4×10^{-3} M) The absorption intensity of atrazine increased as the concentrations of β-CD increased. The significant changes that were observed suggest an interaction between β-CD and atrazine, with preferential inclusion of atrazine molecules into the non-polar CD cavity.

The calculation based on the Benesi-Hilderbrand and scatchard's methods, showed that atrazine forms a 1:1 inclusion complex with β-CD and the association constant was estimated to be 254 $L.mol^{-1}$ ±10 at pH = 7.3 as shown in figure 2.

Effect of pH on the inclusion of atrazine into β-CD cavities

Effect of pH on the constant association

The association constants of atrazine/beta-cyclodextrin were measured for the same concentration of atrazine [5ppm] with changing the concentration of beta-cyclodextrin from (1×10^{-3}) to (4×10^{-3} M).It has been observed that the value of association constant decreases with the increasing of the pH values.

Effect of pH on the absorbance intensities

UV absorption spectra were registered for atrazine solutions at (3ppm) in different buffer solutions starting from pH = 2.5 to pH = 10. It has been observed that the absorbance decreased 1.7 time when the pH increased from 2.5 to 10.

Protonation effect

The evolution of UV absorbance spectra of atrazine (3ppm) in aqueous solutions at the range of pH between 0.7 and 10 has been studied. A comparison was carried out between the atrazine solutions with β-CD (0.01 M) and without β-CD.

As shown in figure 4, significant changes were observed between pH 5 sand 7 while at low and at high pH no important changes were identified because of the relatively low pKa value of the atrazine (pKa), all of the N atoms should be protonated at pH 0.7-1.68 which indicates that the N-terminals appear as NH_3^+ that is to say, in an acidic media (pH 0.7), both host and atrazine are positively charged, which will inevitably lead to unfavorable electrostatic repulsions between host and guest. However the presence of beta-cyclodextrin offer a partially advantages to the solubility when the beta-cyclodextrin was added to the solution and then a small increasing in the absorbance was detected with the presence of cyclodextrin as shown in figure 4.

At pH more than 1.68 it seems that the protonation of the cavity disappeared and the inclusion of atrazine becomes significantly important due the hydrophobic characteristics of cyclodextrin. The experimental results showed that the constant association of atrazine/cyclodextrin decrease with the increase of pH which can be explained by the decreasing of hydrophobic characteristics of the cyclodextrin cavity at high pH.

CONCLUSION

The encapsulation of atrazine inside the cavity of beta-cyclodextrin was studied in function of pH. It has been demonstrated that the pH values affect dramatically the association constant. At pH=0.7 an important repulsion between the atrazine and the cavity of cyclodextrion which was observed by the small changes of the atrazine absorbance. At pH more than 1.68 the

hydrophobicity characteristics of cyclodextrin became important and then the association constant reached the maximum at pH=5 (311mol^{-1}). At pH more than 7 the hydrophobicity decreased slightly to the reach the constant association 254mol^{-1} and at high pH the association constant became 150mol^{-1}. The results obtained in this work present an important applications in the field of the removal herbicides from the contaminated soil and water or in the pharmaceutical field by controlling the drugs releasing.

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